Magnetic Nanoparticle Assemblies

edited by Kalliopi N. Trohidou



Magnetic Nanoparticle Assemblies

Magnetic Nanoparticle Assemblies

edited by Kalliopi N. Trohidou CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL 33487-2742

© 2015 by Taylor & Francis Group, LLC CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works Version Date: 20140814

International Standard Book Number-13: 978-981-4411-97-4 (eBook - PDF)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www. copyright.com (http://www.copyright.com/) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at http://www.taylorandfrancis.com

and the CRC Press Web site at http://www.crcpress.com

Contents

Prefc	Preface				
1.	Biogen and Th	ic and B eir Asse	iomimetic Magnetic Nanoparticles mblies	1	
	Georgia C. Papaefthymiou				
	1.1	1.1 Introduction			
	1.2 Biomineralization of Iron				
	1.3 Bacterial Magnetomes			4	
		1.3.1	Synthetic vs. Biogenic Nanomagnetite	9	
		1.3.2	Microarraying of Magnetosomes	12	
	1.4	Ferritin			
		1.4.1	Nature of the Ferrihydrite Core	15	
		1.4.2	Magnetic Properties of Ferritin	18	
	1.5	Biomir	netics	23	
		1.5.1	Magnetoferritin	25	
		1.5.2	Beyond Iron Oxides	29	
		1.5.3	Metal and Metal Alloy Nanoparticles	31	
	1.6	Nanoparticle Superstructures			
		1.6.1	Magnetoferritin Arrays	35	
			1.6.1.1 3D arrays	35	
			1.6.1.2 2D arrays	39	
	1.7	Conclu	sion	41	
2.	Contro	lling the	Structure and Properties of		
	Nanost	tructure	d Magnetic Materials Produced		
	by Dep	ositing	Gas-Phase Nanoparticles	45	
	Chris Binns				
	2.1 Introduction				
	2.2	Pure M	Magnetic Nanoparticle Films		
		2.2.1	Morphology of Pure Deposited		
			Nanoparticle Films	48	
		2.2.2	Magnetic Behavior of Pure Deposited		
			Nanoparticle Films	49	
	2.3	Magne	tic Nanoparticles in Matrices	57	
		2.3.1	Controlling the Atomic Structure of		
			Nanoparticles in Matrices	57	
			A		

vi Contents

		2.3.2	Controlling the Magnetic Properties of		
			Isolated Nanoparticles in Matrices	62	
		2.3.3	Controlling the Magnetic Properties by		
		0.0.4	Nanoparticle Volume Fraction	70	
		2.3.4	Producing Nanoparticle Hydrosols by		
			Deposition of Gas-Phase Particles into	0.4	
			Liquid Matrices	81	
3.	Time	-Depende	ent Phenomena in Nanoparticle		
	Asser	nblies		91	
	Òscar	r Iglesias			
	3.1	Magne	tic Relaxation in Noninteracting		
		Nanop	article Ensembles	95	
	3.2	Model	s of Interacting 1D Chains of		
		Nanop	articles	100	
	3.3	Compu	utational Details	103	
		3.3.1	Calculation of Dipolar Energies	103	
		3.3.2	The Monte Carlo Algorithm	105	
		3.3.3	Dipolar Fields in 1D	106	
	3.4	Effecti	ve Energy Barrier Distributions	107	
	3.5	Relaxa	tion Curves: $T \ln(t/\tau_0)$ Scaling with		
		Intera	ctions	109	
		3.5.1	Simulations of the Time Dependence		
			of Magnetization	110	
		3.5.2	$T \ln(t/\tau_0)$ Scaling in the Presence of		
			Interactions	112	
	3.6	Evolut	ion of $f_{\rm eff}(E_{\rm b})$ and of Dipolar Fields	114	
	3.7	Effecti	ve Energy Barrier Distributions from		
		$T\ln(t)$	(au_0) Scaling	117	
	3.8	Hyster	esis Loops	122	
	3.9	Conclu	isions	124	
4.	Elem	entary Ex	citations in Magnetic Nanoparticles		
	Probed with ⁵⁷ Fe Nuclear Magnetic Resonance and				
	Mössbauer Spectroscopy				
	Michael Fardis, Alexios P. Douvalis,				
	George Diamantopoulos, Ioannis Rabias,				
	Thomas Bakas, Hae Jin Kim, and				
	Georg	gios Papa	vassiliou	105	
	4.1	Introd	uction	129	

	4.2	Magnetization Dynamics in Magnetic					
		Nanoparticles					
		4.2.1	Superparamagnetic and Blocking				
			States	132			
		4.2.2	Uniform Mode in Mössbauer and				
			Nuclear Magnetic Resonance				
			Spectroscopies	135			
			4.2.2.1 Hyperfine magnetic field in				
			Mössbauer spectroscopy	135			
			4.2.2.2 Nuclear relaxation in nuclear				
			magnetic resonance				
			spectroscopy	137			
	4.3	⁵⁷ Fe M	össbauer Spectroscopy Experiments	140			
	4.4	⁵⁷ Fe N	uclear Magnetic Resonance				
		Spectr	oscopy Experiments	143			
		4.4.1	Nuclear Magnetic Resonance Line				
			Shapes	143			
		4.4.2	Nuclear T_2 Transverse Relaxation	147			
	4.5	Conclu	iding Remarks	154			
5.	Magne	tic Prop	erties of Spinel Ferrite Nanoparticles:				
5.	Magne Influer	tic Prop ice of th	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure	159			
5.	Magne Influen Davide	tic Prop ice of th Peddis	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure	159			
5.	Magne Influen Davide 5.1	tic Prop ice of th <i>Peddis</i> Introd	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction	159 159			
5.	Magne Influen Davide 5.1 5.2	e tic Prop ace of th e <i>Peddis</i> Introd Magne	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles:	159 159			
5.	Magne Influen Davide 5.1 5.2	etic Prop ace of th Peddis Introd Magne An Intr	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction	159 159 161			
5.	Magne Influen Davide 5.1 5.2	tic Prop ce of th Peddis Introd Magne An Intr 5.2.1	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction itism in Nanoparticles: roduction Magnetism in Condensed Matter	159 159 161 161			
5.	Magne Influen Davide 5.1 5.2	tic Prop ce of th Peddis Introd Magne An Intr 5.2.1 5.2.2	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles	159 159 161 161 163			
5.	Magne Influen Davide 5.1 5.2	tic Prop ce of th Peddis Introd Magne An Intr 5.2.1 5.2.2 5.2.3	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles Magnetic Anisotropy	159 159 161 161 163 165			
5.	Magne Influen Davide 5.1 5.2	Properties Properties Produces Preddise Preddise Introduces An Intro 5.2.1 5.2.2 5.2.3	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles Magnetic Anisotropy 5.2.3.1 Magnetocrystalline	159 159 161 161 163 165			
5.	Magne Influen Davide 5.1 5.2	etic Prop ce of th Peddis Introd Magne An Intr 5.2.1 5.2.2 5.2.3	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles Magnetic Anisotropy 5.2.3.1 Magnetocrystalline anisotropy	159 159 161 161 163 165 166			
5.	Magne Influen Davide 5.1 5.2	etic Prop nee of th Peddis Introd Magne An Intr 5.2.1 5.2.2 5.2.3	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles Magnetic Anisotropy 5.2.3.1 Magnetocrystalline anisotropy 5.2.3.2 Magnetostatic anisotropy	 159 159 161 161 163 165 166 			
5.	Magne Influen Davide 5.1 5.2	etic Prop nee of th Peddis Introd Magne An Intr 5.2.1 5.2.2 5.2.3	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles Magnetic Anisotropy 5.2.3.1 Magnetocrystalline anisotropy 5.2.3.2 Magnetostatic anisotropy (shape anisotropy)	159 159 161 161 163 165 166			
5.	Magne Influen Davide 5.1 5.2	etic Prop ce of th Peddis Introd Magne An Intr 5.2.1 5.2.2 5.2.3	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles Magnetic Anisotropy 5.2.3.1 Magnetocrystalline anisotropy 5.2.3.2 Magnetostatic anisotropy (shape anisotropy) 5.2.3.3 Surface anisotropy	 159 159 161 161 163 165 166 166 166 166 			
5.	Magne Influen <i>Davide</i> 5.1 5.2 5.3	etic Prop nee of th Peddis Introd Magne An Intr 5.2.1 5.2.2 5.2.3	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles Magnetic Anisotropy 5.2.3.1 Magnetocrystalline anisotropy 5.2.3.2 Magnetostatic anisotropy (shape anisotropy) 5.2.3.3 Surface anisotropy tic Structure of Nanoparticles	159 159 161 161 163 165 166 166 166 166			
5.	Magne Influen <i>Davide</i> 5.1 5.2 5.3	Magne 5.3.1	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles Magnetic Anisotropy 5.2.3.1 Magnetocrystalline anisotropy 5.2.3.2 Magnetostatic anisotropy (shape anisotropy) 5.2.3.3 Surface anisotropy tic Structure of Nanoparticles Spin Canting	159 159 161 161 163 165 166 166 166 168 168			
5.	Magne Influen 5.1 5.2 5.3	An Introduction of the Peddis Introduction of the Peddis Introduction of the Peddis An Introduct	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles Magnetic Anisotropy 5.2.3.1 Magnetocrystalline anisotropy 5.2.3.2 Magnetostatic anisotropy (shape anisotropy) 5.2.3.3 Surface anisotropy tic Structure of Nanoparticles Spin Canting 5.3.1.1 Temperature dependence	 159 159 161 163 165 166 166 166 168 168 			
5.	Magne Influen 5.1 5.2 5.3	An Introd 5.2.1 5.2.2 5.2.3 Magne 5.3.1	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles Magnetic Anisotropy 5.2.3.1 Magnetocrystalline anisotropy 5.2.3.2 Magnetostatic anisotropy (shape anisotropy) 5.2.3.3 Surface anisotropy tic Structure of Nanoparticles Spin Canting 5.3.1.1 Temperature dependence of spin canting	 159 159 161 161 163 165 166 166 166 168 168 171 			
5.	Magne Influen <i>Davide</i> 5.1 5.2	Magne 5.3.1 5.3.2 5.3.2	erties of Spinel Ferrite Nanoparticles: e Magnetic Structure uction tism in Nanoparticles: roduction Magnetism in Condensed Matter Magnetic Single-Domain Particles Magnetic Anisotropy 5.2.3.1 Magnetocrystalline anisotropy 5.2.3.2 Magnetostatic anisotropy (shape anisotropy) 5.2.3.3 Surface anisotropy tic Structure of Nanoparticles Spin Canting 5.3.1.1 Temperature dependence of spin canting Iron Oxides with a Spinel Structure	159 159 161 161 163 165 166 166 166 168 168 168 168 171 172			

viii Contents

	5.3.3	Spin Canting and Cationic Distribution:			
		Magnetic Structure of Spinel Ferrite			
		Nanoparticles	174		
5.4	Magnetic Properties of Spinel Ferrite				
	Nanop	articles: Influence of the Magnetic			
	Struct	ure			
	5.4.1	Surface Magnetism	181		
	5.4.2	Magnetic Anisotropy	186		
		5.4.2.1 Influence of the cationic			
		distribution	187		
	5.4.3	Saturation Magnetization	188		
FePt Fi	lms wit	h Graded Anisotropy for Magnetic			
Record	ling		199		
Th. Speliotis and D. Niarchos					
6.1	Short l	History of Magnetic Recording	199		
6.2	Perper	Perpendicular Recording Media for			
	1 Tb/i	n ² and beyond	201		
6.3	High <i>K</i> _u Materials				
6.4	Fabrication Methods				
	6.4.1	Sputtering	207		
	6.4.2	Thermal Evaporation	208		
	6.4.3	Thin-Film Growth	208		
6.5	Technologies for Future Recording Media				
6.6	FePt G	raded Media for Perpendicular			
	Magne	tic Recording	211		
6.7	Funda	mental Properties of L1 ₀ FePt	211		
	6.7.1	Optimization of FePt Single Layers			
		on MgO	211		
	6.7.2	L1 ₀ FePt on Amorphous Substrates	214		
		6.7.2.1 Texture control and seed layer	214		
	6.7.3	L1 ₀ FePt Based Exchange-Spring			
		Phenomenon	217		
	6.7.4	Production of Prototype L1 ₀ /A1 FePt			
		Nanostructures	217		
		6.7.4.1 L1 ₀ /A1 FePt semicore-shell			
		nanocomposites	218		
	6.7.5	Hard/Graded FePt Granular Layers	219		
	5.4 FePt Fi Record <i>Th. Spe</i> 6.1 6.2 6.3 6.4 6.5 6.6 6.7	5.3.3 5.4 Magner Nanop Structu 5.4.1 5.4.2 5.4.3 FePt Films witt Recording Th. Speliotis au6.1 Short 16.2 Perper1 Tb/i6.3 High K6.4 Fabric6.4 Fabric6.4 Fabric6.4 Fabric6.4 Fabric6.4.16.4.26.4.36.5 Techno6.6 FePt GMagner6.7 Funda6.7.16.7.26.7.36.7.4	5.3.3 Spin Canting and Cationic Distribution: Magnetic Structure of Spinel Ferrite Nanoparticles 5.4 Magnetic Properties of Spinel Ferrite Nanoparticles: Influence of the Magnetic Structure 5.4.1 Surface Magnetism 5.4.2 Magnetic Anisotropy 5.4.2.1 Influence of the cationic distribution 5.4.3 Saturation Magnetization FePt Films with Graded Anisotropy for Magnetic Recording Th. Speliotis and D. Niarchos 6.1 Short History of Magnetic Recording 6.2 Perpendicular Recording Media for 1 Tb/in ² and beyond 6.3 High K_u Materials 6.4 Fabrication Methods 6.4.1 Sputtering 6.4.2 Thermal Evaporation 6.4.3 Thin-Film Growth 6.5 Technologies for Future Recording Media 6.6 FePt Graded Media for Perpendicular Magnetic Recording 6.7 Fundamental Properties of L1 ₀ FePt 6.7.1 Optimization of FePt Single Layers on MgO 6.7.2 L1 ₀ FePt on Amorphous Substrates 6.7.3 L1 ₀ FePt Based Exchange-Spring Phenomenon 6.7.4 Production of Prototype L1 ₀ /A1 FePt Nanostructures 6.7.4.1 L1 ₀ /A1 FePt semicore-shell nanocomposites 6.7.5 Hard/Graded FePt Granular Layers		

			6.7.5.1	Growth of $L1_0$ FePt/graded		
				FePt nanocomposites		
				prepared using UHV		
				sputtering on MgO(002)	220	
				substrates	220	
7.	Fabrica	tion of	Patterned	Nanoparticle Assemblies		
	via Lith	ography	/		227	
	Gang C	Chen				
	7.1	Introdu	uction		227	
	7.2	Fabrica	ation Tech	niques	229	
		7.2.1	Direct Pa	itterning Assembly	229	
		7.2.2	Fabricati	on of NP Assemblies on		
			Patterne	d Templates	231	
	7.3	Summa	ary and Pe	erspective	246	
8.	Magne	tic Beha	vior of Co	mposite Nanoparticle		
•	Assem	blies			253	
	Marianna Vasilakaki. Georae Maraaris.					
	and Ka	lliopi N.	Trohidou			
	8.1	Introdu	uction		253	
	8.2	The Mo	odel and S	imulation Method	260	
		8.2.1	Simulatio	ons of the Magnetic Behavior		
			of Nonin	teracting Core/Shell		
			Nanopar	ticles in the Atomic Scale	262	
		8.2.2	Simulati	ons of the Magnetic Behavior		
			of Intera	cting Core/Shell		
			Nanopar	ticles in the Mesoscopic Scale	265	
	8.3	Magnetic Behavior of Noninteracting				
		Core/S	hell Nano	particles: Study of		
		Intrapa	aracteristics	269		
	8.4	Magnetic Behavior of Interacting Core/Shell				
		Nanop	articles: Iı	nterparticle Interactions		
		Effects			273	
		8.4.1	Random	Assemblies	273	
		8.4.2	Ordered	Arrays of Core/Shell		
			Nanopar	ticles	278	
	8.5	Conclu	ding Rem	arks	280	

Preface

Magnetic nanoparticles with diameters in the range of a few nanometers are today at the cutting edge of the modern technology and innovation due to their use in numerous applications ranging from engineering to biomedicine. Their unique magnetic properties emerge because their size becomes comparable to various characteristic physical lengths (correlation length, domain wall width) and also the number of the surface spins with reduced coordination becomes comparable to that of the core spinsinfluencing the overall magnetic behavior. In the case of composite nanoparticles, core/shell interface acts as an additional source of diverse magnetic effects which can be studied and exploited for specific applications. Nanoparticles in the materials exist in assemblies. They are either dispersed or inserted in host materials or even combined with them resulting in random or self-organized nanostructures. The process of synthesis and dispersion of the magnetic nanoparticles in a host is a crucial point in nanotechnology, as the performance of final products is profoundly affected by the state of dispersion of embedded nanoparticles. Above all these, the understanding of the interparticle interactions is necessary to clarify the physics of these assemblies and their use in the development of high-performance magnetic materials.

This book reviews prominent research studies on the static and dynamic magnetic properties of nanoparticle assemblies gathering together experimental and computational techniques in an effort to reveal their optimimum magnetic properties for biomedical use, nanoelectronics, catalysis and as ultra-high magnetic recording media. The selected collection of articles includes studies on: biogenic and biomimetic magnetic nanoparticle formation and their self-assembly for nanoelectronics, biosensors, and heterogeneous catalysis, nanostructured magnetic materials produced by Gas-Phase nanoparticles, spinel ferrite nanoparticles, FePt films with graded anisotropy for ultra-high magnetic recording media, patterned nanoparticle assemblies via Lithography, Monte Carlo simulations for the study of dynamic magnetic behavior of nanoparticles and their assemblies and static magnetic behavior of core/shell nanoparticles and their assemblies, combined NMR and Mössbauer techniques as probes for the microscopic investigation of the electronic fluctuations of magnetic nanoparticles.

In this book, PhD students and researchers in materials science can find current detailed computational and experimental investigations regarding magnetic nanoparticle assemblies and their intraparticle and interparticle interactions in order to understand the underlying physics and to visualize the future applications of them.

I would like to thank all the authors for their efforts which made it possible to provide this book to the scientific community.

> Kalliopi N. Trohidou Athens, Greece April 2014

Chapter 1

Biogenic and Biomimetic Magnetic Nanoparticles and Their Assemblies

Georgia C. Papaefthymiou

Department of Physics, Villanova University, Villanova, PA 19085, USA gcp@villanova.edu

1.1 Introduction

Living organisms produce magnetic nanoparticles of well-defined size and crystallinity under mild physiological conditions through the process of biomineralization, that is, the biological regulation of crystal growth, particle size, morphology, and organization [1, 2]. Biomineralization results in the production of a variety of complex composite materials, ranging from the nano- to the macroscopic, by integrating inorganic matter within the organic world of biology for structural support, magnetoreception, and iron storage. The resulting biominerals may be amorphous or crystalline, forming structures of varying degrees of complexity from a single unit to numerous individual units or aggregates. The aggregated units are usually arranged in an orderly fashion, and when crystalline the crystallographic axes are often aligned. The resulting highly organized bioinorganic structures exhibit excellent physical and chemical properties that often surpass those of artificial materials produced by usual synthetic methods employed in the laboratory, which most often require harsh conditions of high temperature, pressure, or pH values [3]. Among the various biomineralization products found in nature, iron biominerals are magnetic. The bestknown biogenic magnetic nanoparticles are the ferrimagnetic nanostructures formed by magnetotactic bacteria [4–6] and the antiferromagnetic nanoparticles formed by the iron storage protein ferritin [7–9]. In the first part of this chapter we explore biogenic nanoparticles to gain an appreciation of the controlled formation of magnetic nanoparticles in vivo and learn from the chemistry of life how to perfect laboratory synthesis and assembly of highquality, monodispersed magnetic nanocrystals through biomimetic processes.

Early efforts to biomimicry, that is, to integrate the organic and inorganic world in the assembly of magnetic nanoparticles, addressed the encapsulation of various ferrite nanoparticles within block copolymer supports [10, 11]. However, the resulting nanocomposites were often inhomogeneous and exhibited nanoparticle polvdispersity. There has also been extensive effort in the synthesis of magnetic nanoparticles using microemulsions where the nanoparticles are synthesized within the confined spaces of micelles or reverse micelles. The resulting nanoparticles are monodispersed, each encapsulated within a shell of surfactant molecules [12, 13]. Many investigators extend the definition of biomimetic systems to include other core/shell nanostructures, where the shell consists of a biocompatible inorganic rather than organic substance, such as magnetic core/silica shell nanocomposite nanoparticles, as well as of magnetic/quantum dot/silica shell heterostructured nanoparticles [14, 15]. Presently, the forefront of exploration in the biomimetic synthesis and assembly of magnetic nanoparticles lies in nanotemplating using protein cages and viral capsids [16]. These organic shells are used to coordinate the nucleation and growth of magnetic nanoparticles and their subsequent assembly into arrayed mesostructures. In the second part of this chapter we present an introductory discussion of the advantages afforded by biological templates in facilitating the assembly and organization of magnetic nanostructures over multiple length scales. These advantages stem from the ability to genetically modify the interior and exterior surfaces of biological templates in order to initiate the nucleation of a variety of magnetic nanophases and impart surface site recognition properties for nanoparticles arraying on solid substrates. The chapter does not intend to give a comprehensive review of the literature but rather to exemplify the concept of the hierarchical assembly, aggregation, and superlattice formation of magnetic nanoparticles derived from bioinspired routes.

1.2 Biomineralization of Iron

The biomineralization of iron hydroxides is widespread among organisms due to the utilization of iron atoms by proteins for oxygen and electron transport in metabolic processes. The most widely studied biomineralization product occurs in the iron storage protein ferritin. Ferritins represent a superfamily of proteins that are ubiquitous in biological systems [17]. They are large, multicomponent proteins that self-assemble to form molecular cages within which a hydrated ferric oxide is mineralized. Mammalian ferritin forms a 7 nm micellar core of hydrated iron (III) oxide (ferrihydrite). It was first described by V. Laufberger in 1937 [18] as a protein isolated from horse spleen containing about 20% iron. An iron-rich mineral deposit similar in composition to that of ferritin is found in the dermal granules of Molpadia intermedia, a species of marine invertebrates [19]. These dermal granules, ranging in size from 10 µm to 350 μm, serve as strengthening agents in the connective tissues of the dermis; they contain inclusions of iron hydroxide deposits seen as electron dense subunits of 9 nm to 14 nm diameter in transmission electron micrographs.

Magnetite is the most common of the known iron oxide biominerals. It was first identified by H. Lowenstam in 1962 [20] in the denticle capping of chitons (primitive marine mollusks). Magnetite precipitation and tooth formation in chitons proceed through the biochemically controlled reduction of ferrihydrite [21]. Unlike ferrihydrite, which is a common product of both biological and inorganic processes, inorganically magnetite is formed only at elevated temperatures and pressures in igneous and metamorphic rocks. Yet, chitons are capable of forming magnetite under ambient conditions. By natural selection, the chitons somehow biochemically mediate the transformation of ferrihydrite to magnetite in order to perform a biological function, even at atmospheric temperature and pressure. In an entirely different biological function magnetite deposits have been identified with "magnetoreception," the ability of living organisms to sense the polarity or the inclination of the earth's magnetic field [22]. Some bacteria, honeybees, homing pigeons, and migratory fish are known to possess such sense.

1.3 Bacterial Magnetomes

Magnetotactic bacteria synthesize membrane-enclosed intracellular crystalline magnetic particles, called magnetosomes, comprising primarily iron oxides or, in rare cases, iron sulfides. Magnetosomes are nanometer-sized, magnetic mineral crystal deposits enveloped by a stable lipid membrane, which contains some lipids and proteins, often referred to as membrane vesicles. They are aligned to form chains within the bacterium, thus creating a biomagnetic compass that enables the bacterium to orient in the earth's magnetic field. a phenomenon known as "magnetotaxis." These are microaerobic bacteria endowed with flagella, which allow them to swim and migrate along oxygen gradients in aquatic environments. They were first reported in 1975 by microbiologist R. Blakemore [23]. Studies have revealed that magnetic bacteria tightly control the synthesis of their own magnetite mediated by the magnetosome membrane (MM), which has a distinct biochemical composition and contains specific magnetosome membrane proteins (MMPs) [24]. Since 1975, a variety of strains have been found to exist in marine and freshwater habitats [6, 25-27]. Figure 1.1 shows electron micrographs of bacteria and magnetosomes from three different strains of typical magnetotactic bacteria. Magnetosomes can be isolated from bacteria with intact MMs surrounding the magnetic particles, as indicated in Fig. 1.1c, where the MMs, indicated by the arrow, are clearly visible [6].

Magnetotactic bacteria living in marine, sulfidic environments grow magnetosome crystals of the iron sulfide mineral greigite (Fe₃S₄), which is isostructural with magnetite and is also ferrimagnetically ordered at room temperature [28]. Bacterial Fe₃O₄ appears to persist in sediments after death and lysis of cells, contributing to fossil and paleomagnetic records.





Figure 1.1 Transmission electron micrographs of typical magnetotactic bacteria and magnetosomes: (a) Magnetotactic Spirillum (MV-4) with a flagellum at each end of the cell and a chain of electron-dense, magnetite containing magnetosomes along the long axis of the cell (reproduced with permission from D. A. Bazylinski and R. B. Frankel, (2004) Magnetosome formation in prokaryotes, Nat. Rev. Microbiol., 2, 217-230) [4], (b) transmission electron micrograph of thin-sectioned magnetic cells of Magnetotactic Spirillum (MS-1). The chains of crystals within the cell are clearly visible. (Reproduced with permission from Richard B. Frankel, Richard P. Blakemore and Ralph S. Wolfe, (1979) Magnetite in freshwater magnetotactic bacteria, Science, 203, 1355) [5], (c) isolated magnetosomes from Magnetospirillum Gryphiswaldense. Arrow indicates the magnetosome membrane (MM). (Reproduced with permission from D. Schüler, (2004) Molecular analysis of a subcellular compartment: the magnetosome membrane in magnetospirillum gryphiswaldense, Arch. Microbiol., 181, 1 [6]).

The magnetite particles in magnetosomes are of single-domain size and have a stable magnetic moment aligned along the {111}

6 Biogenic and Biomimetic Magnetic Nanoparticles and Their Assemblies

crystallographic axis, the easy direction of magnetization for magnetite. This maximizes the magnetic moment per particle, as the {111} direction yields approximately 3% higher saturation magnetization than do other directions. The organic supporting matrix and magnetic interactions between magnetosomes keep the magnetic moment of the individual magnetite crystals parallel to the chain axis. Along the chain, the individual magnetosome moments simply add up vectorially to maximize the total magnetic moment and, therefore, the torque exerted on the resulting "biological bar magnet" by an external magnetic field. Figure 1.2 shows an electron holography micrograph of a section of the chain in *Magnetospirillum magnetotacticum*, along with the magnetic field lines derived from electron interference patterns superimposed on the positions of the magnetosomes [4]. The confinement of the magnetic field lines within the magnetosomes is indicative of perfectly aligned single magnetic domains and shows that the chain of magnetosomes acts as a single magnetic dipole. Using this extraordinary design of magnetic engineering the bacterium builds a strong enough magnetic moment to passively orient, at ambient temperatures, in the direction of the weak terrestrial field of only ~0.5 gauss (0.5×10^{-4} T) [5].



Figure 1.2 (a) Electron holography of single-domain magnetite particles in a region of the magnetosome chain in *Magnetospirillum magnetotacticum*. (b) Magnetic field lines. (Reproduced with permission from D. A. Bazylinski and R. B. Frankel (2004) Magnetosome formation in prokaryotes, *Nat. Rev. Microbiol.*, 2, 217–230 [4]).

Detailed studies of the crystal structure of the magnetite particles within magnetosomes indicate that they contain highly crystalline magnetite of cubo-octahedral shape, vielding superior magnetic properties. Overall, magnetosome crystals have high chemical purity, narrow size distribution, and species-specific morphologies, unattainable in inorganically precipitated magnetite. These features point to magnetosome formation under strict biological control, a process known as "biologically controlled mineralization." Magnetosomes extracted from cells can easily disperse in aqueous solutions because of the presence of the enveloping organic membrane [6]. Thus, they do not suffer from particle agglomeration as purely inorganically grown nanocrystals do. Figure 1.3 shows electron micrographs of magnetosomes extracted from magnetotactic bacterial cells, together with bare or oleic acid-coated inorganically prepared magnetite nanoparticles. The biogenic magnetites do not agglomerate because of their membrane, whereas inorganic particles need further treatment to prevent them from agglomerating. In dispersing the nanoparticles. the biological membrane is seen to play a role similar to that of surfactants in the bottom-up synthesis of magnetic nanoparticles by chemical methods; in vivo, however, the biological membrane of magnetosomes has a far more active role to play in controlling and guiding magnetosome nanocrystal growth [24].



Figure 1.3 TEM images of (a) isolated magnetosome particles, (b) purely inorganic magnetite nanocrystals, and (c) inorganic magnetite crystals encapsulated in oleic acid. (Reproduced with permission from C. Lang, D. Schüler, D. Faivre (2007) Synthesis of magnetite nanoparticles for bio- and nanotechnology: genetic engineering and biomimetics of bacterial magnetosomes, *Macromol. Biosci.*, **7**, 144–151 [27]).

8 Biogenic and Biomimetic Magnetic Nanoparticles and Their Assemblies

Magnetosomes from *Aquaspirillum magnetotacticum* have been studied by Mössbauer spectroscopy [29]. The spectra indicate the presence of stoichiometric magnetite and small amounts of paramagnetic Fe^{3+} and Fe^{2+} species, as shown in Fig. 1.4. The additional Fe^{3+} appeared to be associated with the magnetosomes, and the Fe^{2+} with the magnetosome membrane, suggesting a strong interaction between membrane-bound proteins and the crystalline biominerals.



Figure 1.4 Mössbauer spectra of *Aquaspirillum magnetotacticum* bacteria at T = 200 K. (a) The spectrum of a sample frozen immediately after harvesting the cells. (b) The spectrum obtained in a sample which was held at 285 K for a few days before freezing. Lines at position c correspond to an Fe³⁺ quadrupole doublet; lines at positions d correspond to an Fe²⁺ doublet. The remaining spectral features are those of stoichiometric magnetite. The solid lines are theoretical fits to the data. (Reproduced with permission from S. Ofer, I. Nowik, E. R. Bauminger, G. C. Papaefthymiou, R. B. Frankel and R. P. Blakemore (1984) Magnetosome dynamics in magnetotactic bacteria, *Biophys. J.*, **46**, 57–64 [29]).

1.3.1 Synthetic vs. Biogenic Nanomagnetite

Magnetite nanocrystals can be formed readily by coprecipitation reactions of ferrous and ferric salts in the mole ratio of Fe^{3+}/Fe^{2+} = 2:1 in aqueous solutions by the addition of alkalis at elevated temperatures. A comparison of the crystalline and magnetic properties of magnetite nanocrystals formed by biomineralization with those of chemically synthesized magnetite nanoparticles demonstrates the superior quality of magnetic nanocrystals assembled by the process of biomineralization in magnetotactic bacteria.

In a study by Han et al. [30] magnetite nanoparticles were synthesized by the coprecipitation method. Specifically, 0.5 M FeCl₃ solution (300 mL) and 0.5 M FeSO₄ solution (150 mL) were mixed and stirred at 55°C under a N₂ atmosphere, and then 3 M NaOH solution (250 mL) was added and the temperature was raised to 65° C and the chemicals were allowed to react for one hour. Subsequently, a 100 mL water solution with 0.03 mol of dissolved sodium dodecylsulfonate as surfactant was added. The temperature was raised at 90°C, and the reaction was allowed to continue for an additional 30 minutes before it was stopped by cooling down the solution. The resulting magnetite nanoparticles of about 10 nm average diameter were compared to those grown by *Magnetospirillum gryphiswaldense* MSR-1, isolated from the bacterial cells with the magnetosome membrane intact, enveloping the magnetosomes.

Figure 1.5 compares the X-ray diffraction (XRD) patterns of magnetosomes with those of chemically derived magnetite particles. The powder diffraction peaks observed matched well with the standard Fe_3O_4 reflections for both magnetosomes and nanoparticles. Both systems show high crystallinity, with the magnetosomes exhibiting superior crystallinity, as indicated by the sharpness of the reflection peaks, even though some of the broadening of the peaks associated with the synthetic Fe_3O_4 nanoparticles is due to their smaller size. Figure 1.6 presents transmission electron microscopy (TEM) micrographs of the samples. It is observed, as shown in Fig. 1.6a, that the magnetosomes tend to form bent chains, often forming closed loops. This configuration minimizes magnetostatic energy by concentrating the magnetic field lines within the magnetosome chain loops, whereby the magnetic field lines close upon themselves,

minimizing any stray magnetic fields. In contrast, the synthetic magnetite particles cluster together in a random fashion.



Figure 1.5 XRD diffraction patterns of (a) magnetosomes and (b) synthetic magnetite. (Reproduced with permission from L. Han, S. Li, Y. Yang, F. Zhao, J. Huang, J. Chang, (2007) Comparison of magnetite nanocrystal formed by biomineralization and chemosynthesis, *J. Magn. Magn. Mater.*, **313**, 236 [30]).



Figure 1.6 (a) TEM micrographs of magnetosomes and (b) synthetic magnetite particles. (Reproduced with permission from L. Han, S. Li, Y. Yang, F. Zhao, J. Huang, J. Chang, (2007) Comparison of magnetite nanocrystal formed by biomineralization and chemosynthesis, *J. Magn. Magn. Mater.*, 313, 236 [30]).

The particle size distributions obtained from measuring the diameters of 100 nanoparticles of synthetic Fe_3O_4 and magnetosomes are shown in Figs. 1.7a and 1.7b, respectively. The particle size of the synthetic magnetite varied from 7 nm to 18 nm, with the maximum of the size distribution at 9–12 nm. The particle size of the magnetomes varied from 10 nm to 60 nm, with the maximum of the size distribution at 40–50 nm. The crystal size distribution of the magnetosomes is asymmetric with a sharp cutoff toward larger particles, while that of the synthetic particles exhibits a log-normal distribution with a sharp cutoff toward smaller particles. It is well known that crystal growth resulting from particle nucleation under supersaturation conditions results in lognormal particle size distributions. In contrast, the controlled crystal growth of magnetosomes within membrane vesicles results in the characteristic particle size distribution observed in Fig. 1.7b.



Figure 1.7 Particle size distributions of synthetic magnetite particles (a) and magnetosomes (b). (Reproduced with permission from L. Han, S. Li, Y. Yang, F. Zhao, J. Huang, J. Chang, (2007) Comparison of magnetite nanocrystal formed by biomineralization and chemosynthesis, *J. Magn. Magn. Mater.*, **313**, 236 [30]).

The authors compared the magnetization curves obtained at 300 K for the samples of magnetosomes and synthetic magnetite. The synthetic magnetite particles showed no hysteresis due to their smaller mean size (~ 10 nm) that puts them in the superparamagnetic regime; that is, their blocking temperature (for thermally driven spin reversals), $T_{\rm B}$, for the characteristic measuring time of the magnetometer is below room temperature. In contrast, the magnetosomes show hysteresis with a coercivity of 75 Oe, indicating

that at room temperature they are stable single-magnetic-domain particles due to their larger mean diameter (~45 nm) and possibly higher magnetocrystalline anisotropy.

The observation that biogenic magnetites in bacteria have dimensions that fall in the relatively narrow single-domain stability range of magnetite particles has important implications in the fields of rock magnetism and paleomagnetism because these singledomain magnetite particles are among the most stable carriers of "natural remnant magnetization" in many marine sediments and sedimentary rocks. This average grain size has been interpreted as a result of natural selection on the magnetic crystals formed by organisms that use their internally formed magnetite for geomagnetic sensitivity of some sort. Thus, these biogenic magnetite particles are often appropriately termed "magnetofossils." The search for magnetofossils in Martian meteorites and on the surface of Mars constitutes the basis of explorations for extraterrestrial life in our planetary system. Furthermore, an in-depth understanding of how MMPs exert physicochemical control over crystal growth in magnetotactic bacteria has immediate relevance to biotechnology with respect to the tailoring of magnetic nanoparticles with desired magnetic characteristics using biomimetic approaches.

1.3.2 Microarraying of Magnetosomes

Investigators have demonstrated the controlled assembly of magnetosomes by guiding the motion of magnetotactic bacteria with microelectromagnets, which produced various magnetic field patterns on micrometer-length scales, by controlling the motion of the bacteria inside a microfluidic chamber [31]. The microelectromagnets consisted of lithographically patterned conductors that generated versatile magnetic fields, allowing sophisticated control of magnetotactic bacteria inside the microfluidic chamber. The bacteria were stained with fluorescent dye, and the electromagnetic manipulation process was monitored with a fluorescent microscope. After assembly the cellular membranes of the bacteria were removed by cell lysis to leave the biogenic magnetic nanoparticles at desired locations. Figure 1.8 shows some typical assemblies obtained. These ordered magnetic structures can

serve as a system to study the magnetostatic interactions between closely spaced nanoparticles. This experiment indicates how one may combine biomineralization and micromanipulation to develop a new method for growing and assembling nanoparticles into customized structures.



Figure 1.8 1D magnetosome arrays produced by the micromanipulation of *Magnetospirillum magnetotacticum* (MS-1) with microelectromagnets. (Reproduced with permission from H. Lee, A. M. Purdon, V. Chu and R. M. Westervelt (2004) Controlled assembly of magnetic nanoparticles from magnetotactic bacteria using micro-electromagnet arrays, *Nano Lett.*, 4(5), 995–998 [31]).

1.4 Ferritin

Ferritin is a ubiquitous intracellular protein that is produced by almost all living organisms, including bacteria, algae, higher plants, and animals. It is a large globular protein, whose unique molecular structure allows it to play a very important role in cellular chemistry. Vertebrate ferritins are composed of 24 amino-acid chains of two types, known as light (L) and heavy (H), which coassemble to form a hollow protein shell, as determined from X-ray crystallography, creating an interior cavity within which iron is sequestered. The de-mineralized protein, consisting of a protein shell void of iron, is known as apoferritin; it has an exterior diameter of 12 nm and an interior diameter of 7 nm. Within the protein cavity each ferritin molecule can store up to 4500 iron (Fe³⁺, S = 5/2) ions in the form of a solid mineral, hydrous ferric oxide, or ferrihydrite. Smaller, ferritinlike shells have been identified in bacteria, known as Dps proteins, which are composed of only 12 subunits and likewise form mineral cores, albeit of much smaller size, ~500 Fe/shell versus ~4500 Fe/ shell for canonical ferritins.

The most important difference between the H and L chains lies in the fact that H chains contain a catalytic site known as the "ferroxidase center." The center reacts with iron in its ferrous state and induces its oxidation to its ferric state, using either O_2 or H_2O_2 as the oxidant. The oxidized iron is then released from the ferroxidase center and ushered into the interior cavity of the apoferritin molecule. The center's binding sites thus become available for additional iron oxidation reactions. L subunits lack such a catalytic center but provide a higher density of negatively charged carboxyl groups from glutamic acid residues on the interior cavity surface of the protein that function as multiple nucleation sites for the controlled hydrolytic polymerization of Fe³⁺ ions, leading to the formation of the ferrihvdrite biomineral core of ferritin. Thus, the L and H chains play cooperative roles in the iron uptake and deposition mechanism. By their high capacity to promote efficient iron core nucleation and growth the L chains contribute to the avoidance of the nonspecific hydrolysis of iron outside the protein shell and result in all iron being hydrolyzed and stored within the ferritin cage.

X-ray crystal structure determination of ferritin by Lawson et al. in 1991 [32] indicated that between subunits there are small pores, or channels, of about 0.3 nm diameter, through which ions or small molecules can travel. These channels play a crucial role in ferritin's ability to uptake and release iron in a controlled fashion. Fourfold channels are formed at the intersection of four subunits, while threefold channels are formed at the intersection of three subunits. The two types of channels have different properties and thus perform different functions. The walls of a threefold channel are lined with charged, polar (hydrophilic) amino acids such as aspartate (Asp) and glutamate (Glu), while the walls of a fourfold channel are lined with nonpolar (hydrophobic) amino acids, such as alanine and leucine. Schematic representations of a ferritin molecule viewed down the fourfold axis and canonical and Dps protein shells are shown in Fig. 1.9 [33, 34]. The polarity of the threefold channels facilitates interaction with the Fe²⁺ ions, enabling their entrance and exit from the protein cage. In contrast, the nonpolar nature of the fourfold channels cannot facilitate such ion passage. It is believed that the function of the fourfold channels is the transport of electrons into and out of the cavity, which allows oxidation or reduction of iron on the surface of the mineral core. The details of the mechanism responsible for electron transport are not, as yet, well understood.



Figure 1.9 Schematic representation of (a) horse spleen ferritin viewed down the 4-fold axis, (b) protein shell of mammalian ferritin, and (c) protein shell of Dps protein from *Listeria innocua*. The diameters of the biomineral core and outer protein surface are in indicated in each case. ((a) Adapted from (a) Yamashita, I. (2001) Fabrication of two-dimensional array of nanoparticles using ferritin molecules. *Thin Solid Films*, **393**, 12–18, [33]; (b) and (c) Yamashita, I. (2008) Biosupramolecules for nano devices: biomineralization of nanoparticles and their applications, *J. Mater. Chem.*, **18**, 3813–3820 [34]).

1.4.1 Nature of the Ferrihydrite Core

Ferrihydrite, or hydrous ferric oxide, can be precipitated directly from oxygenated iron-rich aqueous solutions as a fine-grained, defective nanomaterial of various degrees of crystallinity. Its powder XRD pattern can vary from that of two broad scattering bands in its most disordered state to a maximum of six strong lines in its most crystalline state [35], as shown in Fig. 1.10. The six-line form corresponds to the nominal chemical formula FeOOH- $0.4H_2O$; however, the exact structure is fundamentally indeterminate as the water content is variable.

One of the most readily (commercially) available sources of ferritin for experimentation is extracted from equine spleen, or horse spleen ferritin (HoSF). Figure 1.11 gives the TEM micrograph of a sample of HoSF ferritin. The iron core is seen to have a diameter of up to \sim 7 nm, consistent with the interior cavity size of the protein shell. The protein shell around each core keeps the hydrous iron oxide particles isolated from each other, preventing coagulation.



Figure 1.10 X-ray diffraction patterns for six-line (top) and two-line (bottom) ferrihydrite, Cu Kα radiation. (Reproduced with permission from V. A. Drits, B. A. Sakharov, A. L. Salyn, A. Manceau, (1993) Structural model for ferrihydrite, *Clay Miner.*, 28, 185 [35]).



Figure 1.11 TEM micrograph of native, in vivo produced HoSF ferritin. (Sample purchased from Sigma-Aldrich).

The in vivo produced biomineral core may be removed from the protein to obtain apoferritin, allowing subsequent in vitro reconstitution of the core under controlled laboratory conditions. Through this process "reconstituted ferritins" with various degrees of iron loading can be prepared, as shown in Figs. 1.12a and 1.12b, which present TEM micrographs of reconstituted HoSF with 500 and 3,000 Fe atoms/protein shell, respectively [36]. Through



Figure 1.12 (a) TEM micrograph of in vitro reconstituted HoSF with 500Fe/protein, (b) TEM micrograph of reconstituted horse HoSF with 3,000Fe/protein and (c) variation of XRD spectra of the reconstituted HoSF mineral core with increasing iron loading (core size). (Reproduced with permission from F. M. Michel, H.-A. Hosein, D. B. Hausner, S. Debnath, J. B. Parise, D. R. Strongin, (2010) Reactivity of ferritin and the structure of ferritin-derived ferrihydrite, *Biochim. Biophys. Acta*, 1800, 871 [36]).

terminal ligation the protein sheath provides surface passivation to the nascent ferrihydrite nanoparticles and keeps the cores sterically separated from each other. The XRD spectra of the derived cores indicate the formation of ferrihydrite, with the degree of crystallinity increasing with particle size, as shown in Fig. 1.12c. In vitro studies using reconstituted ferritins have greatly contributed to the elucidation of the mechanism by which ferritin stores and releases iron. Furthermore, using recombinant DNA technology, recombinant ferritin molecules not found in biological organisms have been produced in the laboratory.

1.4.2 Magnetic Properties of Ferritin

Extensive investigations of the magnetic and Mössbauer properties of ferritin have been reviewed recently by the author [37]. Ferritin has been coined an ideal superparamagnet due to the fact that the organic apoprotein shell surrounding the iron biomineral keeps the magnetic cores separated from each other, ensuring the absence of interparticle magnetic interactions between ferritin molecules [38]. Figure 1.11 gives a TEM micrograph of HoSF. The dark magnetic cores are seen to be clearly separated by the protein shell. This allows the cores to respond as isolated magnetic particles to thermal excitation or to the application of external magnetic fields. This behavior is confirmed in zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements shown in Fig. 1.13 [42]. A sharp peak is observed in the ZFC curve, with its maximum indicating a blocking temperature $T_{\rm B}$ = 13 K for ferritin. The overall shape of the ZFC/FC magnetization curves is characteristic of a magnetically isolated, noninteracting magnetic core.

The antiferromagnetically ordered ferritin core possesses a net magnetic moment due to spin noncompensation at the surface and the possible presence of defects within the interior of the core, as originally proposed by Néel for single-magnetic-domain antiferromagnetic particles [39–41]. This makes the ferritin core a two-phase magnetic nanoparticle, as has been observed in detailed magnetic and Mössbauer studies. By definition a superparamagnet behaves as a paramagnet above its blocking temperature and shows hysteresis below its blocking temperature. Thus, magnetization curves of ferritin taken above $T_{\rm B}$ must follow Langevin behavior,

and those taken below $T_{\rm B}$ must show a hysteresis loop. Figure 1.14 shows typical initial magnetic isotherms for ferritin at $T > T_{\rm B}$, reproduced from the work of Kilcoyne and Cywinski [43], while Fig. 1.15, reproduced from the same publication, shows the hysteretic behavior of ferritin at T = 5 K, and the temperature dependence of the coercivity, below the blocking temperature.



Figure 1.13 ZFC/FC magnetization curves of HoSF in 50 Oe applied field, showing characteristic signature of noninteracting, superparamagnetic nanoparticles. Inset: expanded scale around the ZFC and FC bifurcation point. (Reproduced with permission from Makhlouf, S. A., Parker, F. T. and Berkowitz, A. E. (1997) Magnetic hysteresis anomalies in ferritin, *Phys. Rev. B*, 55, R14717 [42]).

The isothermal magnetization curves of Fig. 1.14 do not follow simple Langevin behavior, however—an indication that ferritin is not a simple superparamagnet. Specifically, the isothermal magnetization was best fit to Eq. 1.1, where an additional linear term had to be added to the Langevin function in order to obtain a satisfactory fit [43].

J

$$M(x) = M_{s}(\cot h(x) - 1/x) + \chi H$$
(1.1)



Figure 1.14 Typical initial magnetic isotherms obtained from DC magnetization measurements of HoSF at different temperatures. (Reproduced with permission from Kilcoyne, S. H. and Cywinski, R. (1995) Ferritin: a model superparamagnet, *J. Magn. Magn. Mater.*, 140–144, 1466–11467 [43]).

In the above equation M_s is the saturation magnetization, $L(x) = (\cot h(x) - 1/x)$ is the Langevin function, H is the applied magnetic field, $x = \mu_c H/kT$, where μ_c is the magnetic moment of the ferritin core due to spin noncompensation, and χ is a constant. The authors indicate that best fits were obtained with a value of $\mu_c \approx 300 \ \mu_B$. The additional linear contribution to the magnetization changes little with temperature and is proposed to arise from the superantiferromagnetic behavior of the core. The non-Langevin behavior of the ferritin core has been observed by other investigators as well [44, 45].

A close examination of the dynamic Mössbauer magnetic properties of the ferritin core also indicates a two-phase spin system, of interior versus surface spins. Figure 1.16 gives the Mössbauer temperature profiles of in vitro–reconstituted (1,500 Fe/protein) and in vivo–produced HoSF [46]. At 4.2 K a superposition of the two magnetic subspectra is observed, the inner one corresponding to surface spins and the outer one corresponding to interior or core spins. As temperature increases the two subcomponents enter independently into increasingly faster relaxation regimes, with the surface spins fluctuating faster than the interior spins at a given temperature, as indicated by the superimposed simulated spectra for the two subcomponents. At *T* = 80 K, both subcomponents collapse to quadrupolar spectra. The overall temperature profile indicates a blocking temperature *T*_B = 40 K.



Figure 1.15 Temperature dependence of the coercive field of HoSF. Inset: Hysteresis loop at 5 K. (Reproduced with permission from Kilcoyne, S. H. and Cywinski, R. (1995) Ferritin: a model superparamagnet, *J. Magn. Magn. Mater.*, 140–144, 1466–11467 [43]).

The splitting between the two outer absorption lines of a magnetic sextet gives a measure of the strength of the internal hyperfine magnetic field, *H*, experienced by the ⁵⁷Fe nucleus. The decrease of the hyperfine magnetic field with increasing temperature prior to quadrupolar collapse is due to collective magnetic excitations [47], according to which the observed hyperfine field follows Eq. 1.2:

$$H = H_0 \left(1 - \frac{kT}{2KV} \right) \tag{1.2}$$



Figure 1.16 Mössbauer spectra of lyophilized, in vitro reconstituted HoSF (a), and in vivo produced HoSF (b) as extracted from horse spleen. Solid lines through the experimental points are least square fits, including hyperfine field distributions, to a superposition of iron subsites as indicated (Reproduced with permission from Papaefthymiou, G. C. Arthur J. Viescas, Eamonn Devlin and Athanassios Simopoulos, Electronic and Magnetic Characterization of in vivo Produced vs. in vitro Reconstituted Horse Spleen Ferritin (2007) in Nanophase and Nanocomposite Materials V, edited by S. Komarneni, K. Kaneko, J. C. Parker, and P. O'Brien (Mater. Res. Soc. Symp. Proc. Volume 1056E, Warrendale, PA), HH03-27, [46]).

In the above equation H_0 is the saturation hyperfine field at $T \rightarrow 0$, k is Boltzmann's constant, *T* is the temperature, *K* is the magnetic anisotropy density, and *V* is the volume of the particle. According to this model the hyperfine field is reduced by a maximum of 15% from its saturated value before the spectrum collapses to a quadrupole doublet. Figure 1.17 plots the reduced values of the average magnetic hyperfine fields at the inner (circles) and surface (triangles) sites as a function of sample temperature. For the interior sites, H/H_0 follows Eq. 1.2, corresponding to a superparamagnetic core undergoing collective magnetic excitations. In contrast, H/H_0
for the surface sites shows a precipitous collapse, inconsistent with superpamagnetism.



Figure 1.17 Temperature dependence of the reduced hyperfine magnetic fields at interior and surface sites. (Reproduced with permission from Papaefthymiou, G. C. Arthur J. Viescas, Eamonn Devlin and Athanassios Simopoulos, Electronic and Magnetic Characterization of in vivo Produced vs. in vitro Reconstituted Horse Spleen Ferritin (2007) in *Nanophase and Nanocomposite Materials V*, edited by S. Komarneni, K. Kaneko, J. C. Parker, and P. O'Brien (*Mater. Res. Soc. Symp. Proc.* Volume 1056E, Warrendale, PA), HH03-27, [46]).

1.5 Biomimetics

The exquisite control in crystallinity, shape, and form exercised in the formation of biogenic magnetic nanoparticles through the process of biomineralization has given birth to bioinspired or biomimetic synthetic approaches, which explore the possibility of preparing manmade materials by mimicking biological processes in nature [48]. Bacterial magnetosomes and the biomineral core of ferritin are examples of nature's incorporation of hard, inorganic matter within soft, organic templates, endowed with designed, end-use functionalities. It is these hard/soft interface processes, the crystallization of inorganic materials at organic interfaces, that biomimetic materials synthesis attempts to profitably utilize for the synthesis of functional hierarchical structures. Understanding the biomolecular construction routes that give rise to the incorporation of well-controlled inorganic structures within biological entities should allow for the development of biomimetic chemistry in the laboratory, where synthesis and self-assembly processes on organic templates could be coupled to produce the designer's materials with controlled properties [3].

The negatively charged glutamate residues lining the inner surface of the ferritin protein shell with COO⁻ groups play a crucial role in nucleation-driven crystallization of the ferrihydrite core due to their electrostatic attraction of the positively charged iron ions. This Coulombic attraction is not specific to iron alone; it would act on any other positively charged ions, enabling nucleationdriven mineralization within the ferritin cage to occur for a range of transition metal ions. Once an ionic species enters the interior of the protein cage nucleation and hydrolytic polymerization leading to mineralization can be driven by purely electrostatic effects. Under reducing conditions and in the presence of iron chelators ferritin can be depleted of its ferrihvdrite biomineral core and reconstituted under conditions favoring the synthesis of ferrimagnetic iron oxide phases, magnetite and maghemite, as schematically depicted in Fig. 1.18. This electrostatically driven molecular control of mineral precipitation exercised by ferritin within the confined space of the protein cage is, therefore, of interest in the synthesis of biomimetic magnetic nanoparticles.



Figure 1.18 Schematic depicting the synthesis route to the formation of magnetoferritin.

1.5.1 Magnetoferritin

In 1992 Mann et al. [49] demonstrated the synthesis of such ferrimagnetic phases within ferritin. In their experiment the iron was removed from native HoSF by dialysis, under a nitrogen atmosphere, against thioglycolic acid (HSCH₂COOH) in a sodium acetate (CH₃COONa) buffer at pH 4.5. The resulting apoferritin solution was buffered at pH 8.5 and maintained at a temperature of 55°C to 60°C under argon in a water bath. Fe(II) solution (prepared by the dissolution of ferrous ammonium sulfate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O_1$, in de-aerated water) was added slowly in small increments along with small amounts of air to produce slow oxidation. Parallel control experiments in the absence of apoferritin in the solution were also performed. Remarkably, different products were observed under TEM analysis, in size and morphology, as shown in Fig. 1.19. Most particles derived from the ferritin-reconstituted experiments were discrete and spherical and exhibited a narrow size distribution with a mean particle diameter of (6 ± 1.2) nm, as seen in Fig. 1.19A. The data confirmed that the protein cage remained intact and that the magnetic particles were formed within the protein shell, as seen in Fig. 1.19B, where the stained protein forms bright, white crowns around the magnetic nanoparticles. In contrast, the control reaction, without apoferritin templates produced a mixture of spherical magnetite and elongated goethite nanoparticles (Fig. 1.19C). The single-crystal nature of the particles is demonstrated in Fig. 1.19D. However, the data could not unequivocally distinguish between maghemite, v-Fe₂O₃, and magnetite, Fe₂O₄,

This seminal experiment established the use of apoferritin as a confined reaction vehicle, or nanoreactor, for the production of iron oxide nanoparticles. The process takes advantage of the unusual stability of the apoferritin shell at elevated temperatures (60° C) and pH (8.5) needed for the synthesis of magnetite, as low-temperature methods failed to produce magnetite in the presence of the protein shell. It is believed that magnetite/maghemite production within the ferritin cage proceeds in a way analogous to that of ferrihydrite—through the controlled oxidation of Fe²⁺ ions at the ferroxidase center and subsequent migration and nucleation at the COO⁻-lined interior surface of the protein cage. Just like in the case of ferritin biomineralization in vivo, this process is presumably favored over the competing reaction in bulk solution because of the catalytic oxidation of Fe²⁺ ions at the ferroxidase center and the surface of

26 Biogenic and Biomimetic Magnetic Nanoparticles and Their Assemblies

the developing mineral core. This differentiation between "inside" and "outside" is essential to the effective in vivo functioning of the protein and is also central to the ferritin-nanotemplating approach for the synthesis of nanophase materials within the apoferritin shell.



TEM micrographs of (A) an unstained sample of reconstituted Figure 1.19 ferritin showing distinct magnetite particles (scale bar = 50 nm); (B) a stained sample of (A) showing an intact protein shell surrounding the magnetite cores (scale bar = 50 nm); (C) magnetite crystals formed in the control reaction (scale bar = 100 nm); the needle-shaped crystals were identified as the mineral goethite (α -FeOOH); and (D) a high resolution lattice image of an individual reconstituted ferritin core showing the single-crystal nature of the particle. Two sets of lattice fringes are observed corresponding to the {111} (interatomic spacing d = 0.465 nm) and {002} (d = 0.4198 nm) planes of magnetite. The angle between these planes is 54°, consistent with a cubic lattice symmetry (scale bar = 5 nm). (Reproduced with permission from F. C. Meldrum, B. R. Heywood and S. Mann, (1992) Magnetoferritin: in vitro synthesis of a novel magnetic protein, Science, 257, 522, [49]; corrected figure on p. 729).

The synthesis of magnetoferritin is now well established, having been reproduced by other investigators, at various degrees of iron loading, and its magnetic properties have been widely studied. Figure 1.20 shows TEM and high-resolution TEM (HRTEM) micrographs of 7.3 nm magnetoferritin particles, along with magnetization data. Superparamagnetic behavior is observed with a blocking temperature $T_{\rm B} = 30$ K; the magnetization versus applied magnetic field data shows no hysteresis at T = 300 K, but it becomes hysteretic at T = 4 K with a coercive field of $H_c = 1200$ Oe. Fitting of the superparamagnetic data to a Langevin function indicates roughly



Figure 1.20 (A) TEM micrographs of magnetoferritin (bar 40 nm). (B) High resolution TEM micrograph of a single magnetoferritin core with the {111} lattice fringes indicated (bar 4 nm). (C) Magnetic moment *vs.* field of magnetoferritin at T = 300 K. (D) Hysteresis loop of magnetoferritin at T = 4 K. (Reproduced with permission from M. T. Klem, M. Young and T. Douglas, (2005) Biomimetic magnetic nanoparticles, *Mater. Today*, **8**, 28–37 [50]).

a core magnetic moment $\mu_c = 13,100 \,\mu_{\rm B}$, corresponding to a particle core containing to the order of 12,000 Fe atoms [50]. The small magnetic moment of the native ferritin core of μ_c = 300 $\mu_{\rm B}$, due to its predominately antiferromagnetic nature, limits its value in practical applications. The increased moment on magnetoferritin makes it a favorable candidate for practical applications. In addition to HoSFderived magnetoferritin molecules, magnetoferritins formed in Dps ferritin from *Listeria innocua* and in cowpea chlorotic mottle virus (CCMV) have also been reported. This Dps protein has an interior diameter of 6 nm, while the CCMV viral capsid has an interior cavity of 24 nm, producing magnetite nanoparticles with $T_{\rm B}$ = 5 K and 200 K, respectively [50]. The viral capsids, once depleted of their genomic content, can be engineered to possess negatively charged interior walls and, thus, electrostatically attract Fe²⁺ ions and induce hydrolytic iron polymerization within their interior cavities in a wav analogous to that of the ferritin protein cages.

As discussed earlier, XRD characterization of the magnetoferritin cores [49] failed to unequivocally determine the precise form of the iron oxide present, that is, distinguish between maghemite (γ -Fe₂O₃) and magnetite (Fe₃O₄). Dominic Dickson [51] used Mössbauer spectroscopy, in the absence and presence of an externally applied magnetic field parallel to the γ -ray direction, to characterize HoSFderived magnetoferritin in an attempt to determine the precise nature of the iron oxide phase. The spectra obtained are shown in Fig. 1.21.

Between $H_{app} = 0$ T to 9 T the spectra evolve from a single sextet to two superimposed sextets. With increasing applied field strength the intensity of the second and fifth absorption lines of each subspectrum diminishes to almost zero at the highest applied field of 9 T. The two sextets represent two interpenetrating magnetic sublattices, with their magnetization directions approximately parallel and antiparallel to the applied magnetic field, leading to increasing separation of the outer absorption lines with increasing magnetic field. This behavior is characteristic of antiferromagnetically coupled irons. Furthermore, the fact that the two antiferromagnetic sublattices exhibit unequal absorption intensities indicates a ferrimagnetic material rather than an antiferromagnetic one. The model used in fitting the spectra assumes a system of uniaxial ferrimagnetic small particles, in which the local magnetic moments orient in response to the applied magnetic field to an amount determined by the competing interactions of anisotropy and exchange fields. The fits gave estimates of the exchange field to be 850 T, the ratio of sublattice spins of 0.68 and anisotropy fields of 1.0 T and 2.2 T in the two sublattices. These values are very close to those obtained for maghemite, giving credence to a γ -Fe₂O₃ core for magnetoferritin.



Figure 1.21 Mössbauer spectra of magnetoferritin at T = 4.2 K in various magnetic fields applied parallel to the direction of the γ -ray beam. (Reproduced with permission from D. P. E. Dickson (1999) Nanostructured magnetism in living systems, *J. Magn. Magn. Mater.*, **203**, 46–49 [51]).

1.5.2 Beyond Iron Oxides

In living systems ferritin has evolved to exclusively sequester iron; however, in the laboratory additional synthetic pathways have been identified for the production of various inorganic nanophases within apoferritin, as depicted in Fig. 1.22. For example, Mn^{2+} and Co^{2+} ions undergo oxidation and mineralization, following a path analogous to Fe^{2+} , by forming $Mn(O)OH \rightarrow Mn_3O_4$ and $Co(O)OH \rightarrow Co_3O_4$ phases, respectively, while bubbling of hydrogen sulfide gas into solutions of magnetoferritin results in the production of nonmagnetic iron sulfide [50]. To date many other phases have been synthesized within apoferritin, both magnetic and semiconducting, further supporting the notion that the reactions are not specific to iron and that electrostatic properties of the protein play a significant role in the process of mineralization.



Figure 1.22 Schematic of various synthetic pathways possible for the production of a variety of nanophases within the apoferritin cage. (Reproduced with permission from M. T. Klem, M. Young and T. Douglas, (2005) Biomimetic magnetic nanoparticles, *Mater. Today*, 8, 28–37 [50]).

1.5.3 Metal and Metal Alloy Nanoparticles

In addition to metal oxide and hydroxide phases, metallic nanoparticles of Ni and Co have been produced within horse spleen apoferritin [52], as indicated schematically in Fig. 1.23. Once the Ni²⁺ and Co²⁺ ions have entered the protein cavity, they can react with NaBH₄, which is small enough to pass through the threefold channels and enter the apoferritin interior. Thus, the divalent metal ions, complexed onto the interior wall of the apoferritin cage, undergo reduction to zero-valent, metal nanoparticles. Transmission electron micrographs and energy-dispersive X-ray spectroscopy (EDS) data of the resulting nanoparticles are shown in Fig. 1.24. As seen, metallic nanoparticles of an average diameter of ~3.5 nm, for both Co and Ni, were obtained under the experimental conditions used.



Figure 1.23 Schematic representation of apoferritin encapsulated Ni and Co metal nanoparticles. M^{II} = Ni²⁺ or Co²⁺, M⁰ = Co or Ni. 1) Dialysis and chromatography. 2) Addition of NaBH₄. (Reproduced with permission from N. Gálvez, P. Sánchez, J. M. Domínguez-Vera, A. Sorianno-Portillo, M. Clemente-Léon and E. Coronado, (2006) Apoferritin-encapsulated Ni and Co superparamagnetic nanoparticles, *J. Mater. Chem.*, 16, 2757 [52]).

Metal-alloy magnetic nanoparticles have also been produced within apoferritin. An example is shown in Fig. 1.25, where TEM micrographs of Co:Pt composite nanoparticles formed within apoferritin are shown [53]. The nanoparticles were prepared by using 0.1 M salt solutions of ammonium tetrachloroplatinate, 32 Biogenic and Biomimetic Magnetic Nanoparticles and Their Assemblies



Figure 1.24 TEM images of Co (a) and Ni (b) nanoparticles produced within the ferritin cage. Scale bars 10 nm. Inset (lower): size-distributions and EDS spectra; Cu peaks are due to the microscope grids. Inset (upper) in (b): electron diffraction pattern of the Ni nanoparticles. (Reproduced with permission from N. Gálvez, P. Sánchez, J. M. Domínguez-Vera, A. Sorianno-Portillo, M. Clemente-Léon and E. Coronado, (2006) Apoferritinencapsulated Ni and Co superparamagnetic nanoparticles, J. Mater. Chem., 16, 2757 [52]).

 $(HN_4)_2PtCl_4$, and cobalt acetate tetrahydrate, $(CH_3COO)_2Co\cdot 4H_2O$, as precursors of the metal ions. They were slowly added to the apoferritin solution in 1:1, 2:1, and 3:1 Co:Pt ratios. After allowing time for the metal ions to enter the apoferritin cavity (~30 min) a stoichiometric amount of 0.1 M sodium borohydride was added at pH 8.3 to reduce the metal ions to metal. Nanoparticles containing core sizes corresponding to 1000 atoms were thus prepared. The resulting solutions were freeze-dried to a powder, and TEM pictures were taken before and after annealing the powder at 650°C for 60 minutes under a reducing atmosphere. Spherical morphology is observed with an average particle size of 4.1 nm, which does not increase appreciably upon annealing. At this temperature, the protein shell appears to carbonize, protecting the particles from both sintering, which leads to particle growth, and oxidizing.



Figure 1.25 TEM micrographs of Co:Pt composite nanoparticles before (a) and after (b) annealing for 60 minutes in hydrogen at 650°C. Scale bars are 50 nm, and the average particle diameter from multiple micrographs is 4.1 nm, σ = 2.4 nm. (Reproduced with permission from B. Warne, O. I. Kasyutich, E. L. Mayes, J. A. L. Wiggins and K. K. W. Wong, (2000) Self assembled nanoparticulate Co:Pt for data storage applications, *IEEE Trans. Magn.*, **36**, 3009 [53]).

The composition of the metal-alloy nanoparticles was determined by EDS, as indicated in Table 1.1. With an increasing Co:Pt ratio the particle cobalt content increases, but for the experimental conditions used, the metal stoichiometry of the resulting nanoparticles does not correspond to that of the precursor salts. In addition, it was observed that the as-prepared nanoparticles were superparamagnetic and exhibited no distinct crystallinity. Upon annealing at 650°C in a hydrogen atmosphere the nanoparticles became highly crystalline and exhibited a range of magnetic behavior, as indicated in Table 1.1. These experimental observations can be partially explained by the well-known structural transition of CoPt from a face-centered cubic (fcc) (cubic) to a face-centered tetragonal (fct) (uniaxial) phase upon annealing, with the latter exhibiting high uniaxial magnetic anisotropy of the order of $K \approx 5 \times 10^6$ J/m³.

Co:Pt	Со	Pt	H _c	<i>M</i> _r
addition	(atomic %)	(atomic %)	(0e)	(emu/g)
1:1	27.2	72.8	SP	SP
2:1	30.4	69.6	246	2.3
3:1	37.0	63.1	315	3.2

Table 1.1Metal-alloy CoPt nanostructures synthesized by biomimetic
processes (EDS and magnetization data^a)

^aAfter annealing at 650°C in a hydrogen atmosphere. *Source*: From Ref. [53].

1.6 Nanoparticle Superstructures

Nanoparticle size uniformity is a prerequisite to the formation of ordered, packed arrays, or superlattices. The symmetry of self-assembled arrays of monodispersed nanoparticles can vary depending on the nature of the particles and the media in which they are dispersed. For nanoparticles with a diameter less than 10 nm, van der Waals forces are of the order of thermal energies (kT) such that self-assembly can be driven by intermolecular interactions. For charged or magnetic nanoparticles, electrostatic repulsion and/or magnetostatic interactions can lead to a variety of packing arrangements. When magnetostatic interactions dominate, highly anisotropic, one-dimensional arrays are formed, like the linearchain arrangements or rings seen in Fig. 1.6. As opposed to hard spheres, the packing characteristics of protein-coated inorganic nanoparticles can be considerably more involved because the soft organic coats can overlap [54, 55]. For instance, even though free volume entropy considerations favor fcc packing of neutral hard spheres, ligand-coated, neutral nanocrystals have been often found to form body-centered cubic (bcc) arrays, implying that the ligand packing around each particle pushes the structure to the less dense bcc lattice. Recently, reversible solvent-vapor-mediated fcc \leftrightarrow bcc phase changes in nanocrystal superlattices have been reported [56].

Stable dispersions of nanoparticles can self-assemble into 2D arrays when drop-cast onto wettable surfaces, but long-range order depends critically on the solvent evaporation rate. In addition, "programmed" nanoparticle self-assembly on solid substrates can be mediated by encapsulating surfactants or protein shells endowed with molecular surface recognition properties, thus affording controlled particle organization onto 2D superlattices. Liquid interfaces and air/water interfaces have been proven especially useful in the formation of densely packed, self-assembled films of nanoparticles, which can then be transferred onto solid surfaces [32]. The resulting nanoscale ensembles are of immense interest because they can exhibit unique materials properties as a result of electronic or magnetic coupling between unit particles within the arrays. These collective states can differ from those of either individual nanoparticles or the bulk solid, giving rise to new properties not found in naturally occurring materials. For this reason such nanoparticle assemblies have been coined "metamaterials."

Bioinspired routes to nanoparticle formation can take advantage of the ability to assemble protein cages or bacterial capsids into hierarchically ordered arrays. In principle, this offers the potential to direct the assembly and organization of any material that could be encapsulated inside the cage. We discuss next magnetoferritin arrays in three and two dimensions.

1.6.1 Magnetoferritin Arrays

1.6.1.1 3D arrays

The classical and most direct way to form 3D arrays of ferritin is the process of crystallization. Under supersaturation conditions in the protein solution, the addition of a small amount of $CdSO_4$ as a precipitating agent initiates crystallization and the growth of functional crystals. Over a relatively short time, typically hours or days, large crystals of a few tens to hundreds of micrometers are obtained. Kasyutich et al. [57] produced bioengineered nanocrystals of magnetoferritin through this process. Figure 1.26 gives a schematic of the experimental concept, while Fig. 1.27 shows typical optical and scanning electron microscopy (SEM) images of the crystals obtained. Evidence of internal order is provided by the regular shape and clear facets of these perfect, freestanding octahedral crystals of fcc crystallographic structure, typical of apo- and native ferritin crystals.



Figure 1.26 Scheme of the experimental concept- from nano- to mesoscale: (A) apoferritin templates, (B) filled with functional core and (C) crystallized to produce a highly ordered 3D array. (Reproduced with permission from O. Kasyutich, A. Sarua and W. Schwarzacher, (2008) Bioengineered magnetic crystals, *J. Phys. D: App. Phys.*, 41, 134022 (3pp) [57]).



Figure 1.27 Typical optical (a) and SEM (b) images of magnetoferritin crystals removed from the mother liquor and dried. Each crystal is a fcc array of ~8 nm ferrimagnetic particles. Scale bar = 100 μm. (Reproduced with permission from O. Kasyutich, A. Sarua and W. Schwarzacher, (2008) Bioengineered magnetic crystals, J. Phys. D: App. Phys., 41, 134022 (3pp) [57]).

Formation of 3D arrays by protein crystallization offers advantages over colloidal particle crystallization. The process is

much faster and allows for the formation of much larger arrays; pure protein crystals have been prepared with lengths up to several millimeters [57]. In addition it is possible to control the structure, since apoferritin can crystallize in cubic, tetragonal, and orthorhombic forms, depending on the salt concentration used to induce crystallization.

The magnetic properties of a dilute dispersion of magnetoferritin were compared with those of the magnetoferritin crystals. Figure 1.28 shows hysteresis loops obtained at T = 10 K. Ferritin crystals exhibit substantially lower coercivity and remanence compared to the dilute ferritin solution. These differences must arise from interparticle magnetic interactions within the crystal, where the magnetoferritin molecules are closely packed, resulting in interparticle distances much smaller than those in the dilute dispersion. Given that the magnetic nanoparticles are isolated from each other by the protein coat, these interactions must be purely magnetostatic in origin.



Figure 1.28 Measured hysteresis loop for (a) a dilute dispersion of magnetoferritin and (b) an ordered fcc array of magnetoferritin, both at T = 10 K. (Reproduced with permission from O. Kasyutich, A. Sarua and W. Schwarzacher, (2008) Bioengineered magnetic crystals, *J. Phys. D: App. Phys.*, **41**, 134022 (3pp) [57]. Corrected figure shown in *J. Phys. D: Appl. Phys.*, **43** (2010) 179801).

Interestingly, similar differences in hysteresis loop behavior were observed by Kasyutich et al. [58] for 3 nm magnetoferritin cores forming ordered 3D arrays and corresponding disordered arrays with comparable interparticle distance. These differences were attributed to the effect of nanoparticle ordering and collective behavior within the crystalline magnetic assembly rather than simply to random interparticle magnetic interactions [38].

In another study that clearly exemplifies the power of the biomimetic method, Kostiainen et al. took advantage of the demonstrated differences in magnetic behavior between disordered and ordered arrays of magnetoferritin to produce controlled switching of magnetoferritin nanoparticle magnetism [59]. Magnetoferritin was prepared by encapsulating $Fe_3O_4-\gamma$ - Fe_2O_3 within the ferritin cage of the hyperthermophylic bacterium Pvrococcus furiosus rather than of HoSF. The advantage of using ferritin from hyperthermophylic bacteria is that their ferritin cage is stable at even higher temperatures than that of mammalian ferritin, allowing for a large variety of reactions requiring higher temperatures. Kostiainen et al. [59] subsequently induced directed self-assembly of the recombinant magnetoferritin particles (RMPs) into micrometer-size complexes with an fcc superstructure by using dendritic scaffolds (G1). Furthermore, they functionalized the dendrons with photolabile o-nitrobenzyl linkers, which can be cleaved by short exposure to ultraviolet (UV) light, providing for an optically induced disassembly of the fcc array. Figure 1.29 compares magnetic data collected for (a) disordered RMPs, (b) fccarrayed RMP-G1 complexes, and (c) UV radiation-exposed fcc RMPs destroying the o-nitrobenzyl linkers and thus the superimposed fcc array structure. It is clearly seen that the hysteresis loop of the fcc-ordered RMPs (inner loop with smaller coercivity) reverts to that of the disordered assemblies of magnetoferritin molecules (outer loop with higher coercivity) after exposure to UV radiation. This data provides direct evidence that the magnetic properties of magnetoferritin assemblies are affected directly by the hierarchical organization.

Whether disordered or fcc-arrayed iron oxide magnetoferritin cores interact strongly through dipolar interactions to produce similarly broad ZFC/FC magnetization curves, but detailed analysis indicates differences. It is interesting to contrast the ZFC/FC curves of Fig. 1.29, characteristic of strongly interacting spin-glass-like magnetic nanoparticle ensembles [38], with those obtained for closely packed, disordered assemblies of native ferritin molecules shown in Fig. 1.13, the latter being characteristic of assemblies of isolated, noninteracting magnetic nanoparticles. Furthermore, at T = 10 K the magnetization of the strongly interacting assemblies of Fig. 1.29 saturates above an applied field of 0.5 T, while the magnetization of native HoSF remains unsaturated at T = 5 K up to an applied field of 4 T, as seen in Fig. 1.15.



Figure 1.29 Magnetic properties of disordered and fcc arrayed recombinant magnetoferritin particles (RMP) complexed with dendritic scaffolds (G1). (a) Hysteresis loops at T = 2 K (top) and T =10 K (bottom) for the free RMPs, the RMP-G1 complexes with fcc array configuration, and RMP-G1 complexes disassembled with 60 s of UV irradiation (free RMPs). The inset at the bottom figure shows the full ±1 T loop taken at 10 K for all three systems identifying clear magnetic saturation with fields greater than ± 0.5 T. (b) Temperature dependence of the low field magnetization (M) when the systems were zerofield-cooled an field-cooled from 300 K in a 0.01 T applied field. (Adapted from Kostiainen, M. A., Ceci, P., Fornana, M., Hiekkataipale, P., Kasyutich, O., Nolte, R. J. M., Cornelissen, J. J. L. M., Desautels, R. D., and van Lierop, J. (2011) Hierchecal self-assembly and optical disassembly for controlled switching of magnetoferritin nanoparticle magnetism, ACS Nano, 5(8), 6394-6402 [59]).

1.6.1.2 2D arrays

Yamashita et al. have formed hexagonally close-packed 2D arrays of magnetoferritin molecules by self-assembly at an air/water interface and successfully transferred it onto a Si substrate coated with a hydrophobic layer [33]. Figure 1.30 shows a high-resolution SEM (HRSEM) image of the resulting 2D array. The white dots represent iron oxide cores. The protein shell was subsequently eliminated by one-hour heat treatment at 500°C in a nitrogen atmosphere. The protein coat cannot be imaged by this method, but atomic force microscopy (AFM) in contact mode indicated that the protein shell was indeed eliminated by the heat treatment, leaving a 2D superlattice of the magnetic cores.



Figure 1.30 High resolution scanning electron microscopy image of a magnetoferritin 2D-superlattice formed on a hydrophobic Si substrate. The distance between the cores is about 12 nm. (Reproduced with permission from Yashamita, I. (2001) Fabrication of two-dimensional array of nano-particles using ferritin molecules. *Thin Solid Films*, **393**, 12–18 [33]).

In a similar study a 2D hexagonally close-packed magnetoferritin array was formed directly onto a hydrophilic carbonaceous solid substrate by genetically modifying the outer surface of the protein with binding peptides, endowing the magnetoferritins with specific protein–substrate interactions. Specifically, the Yamashita group used L-type recombinant horse spleen apoferritin, exposing targetspecific affinity peptides on its surface by genetic modification, to form hexagonally close-packed 2D arrays of magnetoferritin [34]. The target surface was a silicon substrate covered with a vacuumdeposited 10 nm thick carbon film. The researchers demonstrated that the interplay between two interactions, (a) the attractive protein–protein interaction that could be adjusted by selecting buffer conditions and (b) the attractive force between ferritin and the substrate via the surface-site-recognition-specific interactions, allowed for protein rearrangement, or directed self-assembly, on the substrate. With proper subsequent heat treatment protein elimination could result in the formation of 2D arrays of the encapsulated inorganic magnetic nanoparticles on a solid substrate. This bioinspired method of nanoparticle array fabrication provides extraordinary control over arraying nanoparticles on a flat surface. It has been coined the "bionano process" and holds promise in future device fabrication for nanoelectronics [61].

1.7 Conclusion

We explored biogenic and biomimetic magnetic nanoparticle formation and self-assembly into superlattices. We demonstrated that biomimetic processes can produce superior nanocrystalline materials and enable directed self-assembly on solid supports. Biological nanotemplates can be used as nanoreactors within which monodispersed magnetic nanocrystals are produced. Utilization of wild-type and recombinant apoferritin cages, combined with genetic engineering of interior and exterior surfaces, offers unprecedented control over directed self-assembly into superlattices. Use of ferritin cages from hyperthermophylic bacteria greatly extends the temperature range of accessible reactions for the production of a variety of magnetic phases within the apoferritin cage. Genetic engineering of the interior surfaces can provide for nucleation and growth of diverse magnetic phases, while the exterior surfaces afford additional degrees of freedom for incorporating molecular recognition properties, leading to directed magnetic nanoparticle arraying. It is expected that the bionano process for the formation of ordered arrays on solid supports, currently in its infancy, will be further pursued and perfected in the near future for applications in nanoelectronics, biosensors, and heterogeneous catalysis.

Acknowledgments

The author thanks the National Science Foundation for support under contract # DMR-0604049.

References

- 1. Lowenstam, H. A. (1981). Science, 211, 1126–1131.
- 2. Mann, S. (1981). Struct. Bonding, 54, 125–174.
- 3. Mann, S. (2001). *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*, Oxford University Press, Oxford.
- 4. Bazylinski, D. A., Frankel, R. B. (2004). Nat. Rev. Microbiol., 2, 217–230.
- 5. Frankel, R. B., Blakemore, R. P., Wolfe, R. S. (1979). Science, 203, 1355.
- 6. Schüler, D. (2004). Arch. Microbiol., 181, 1.
- 7. Chasteen, N. D., Harrison, P. M. (1999). J. Struct. Biol., 126, 182.
- Waldo G. S., Theil, E. C. (1996). Ferritin and iron biomineralization, in *Comprehensive Supramolecular Chemistry* (Suslick, K. S., ed.), Vol., 5, pp. 65–89, Pergamon Press, Oxford, U.K.
- 9. Harrison P. M., Arosio, P. (1996). Biochim. Biophys. Acta, 1275, 161.
- Sohn, B. H., Cohen, R. E., Papaefthymiou, G. C. (1998). J. Magn. Magn. Mater., 182, 216.
- 11. Papaefthymiou, G. C., Ahmed, S. R., Kofinas, P. (2005). *Rev. Adv. Mater. Sci.*, **10**, 306.
- 12. Petit, C. Taleb, A., Pileni, M. P. (1999). J. Phys. Chem. B, 103, 1805–1810.
- Wilcoxon, J. P., Provencio, P. P. (1999). J. Phys. Chem. B, 103(45), 9809– 9812.
- 14. Yi, D. K., Lee, S. S., Papaefthymiou G. C., Ying, J. Y. (2006). *Chem. Mater.*, **18**, 614.
- Yi, D. K., Selvan, S. T., Lee, S. S., Papaefthymiou, G. C., Kundaliya, D., Ying, J. Y. (2005). *J. Am. Chem. Soc.*, **127**, 4990.
- 16. Douglas, T., Young M. (2006). Science, 312(5775), 873-875.
- 17. Bou-Abdallah, F. (Guest ed.) (2010). *Biochim. Biophys. Acta*, **1800**(8), special issue.
- 18. Laufberger V. (1937). Bull. Soc. Chim. Biol., 19, 1575–1582.
- 19. Lowenstam, H. A., Rossma, G. R. (1975), Chem. Geol., 15, 15–51.
- 20. Lowenstam, H. A. (1962). Geol. Soc. Am. Bull., 73, 435-438.
- 21. Kirschvink, J. L., Lowenstam, H. A. (1979). *Earth Planet. Sci. Lett.*, 44, 193–204.

- 22. Lindauer, M., Martin, H. (1972). *Animal Orientation and Navigation* (Galler, S. R., et al., eds.), p. 559, NASA, Washington, DC.
- 23. Blakemore, R. P. (1975). Science, 190, 377-379.
- 24. Tanaka, M., Mazuyama, E., Arakaki, A., Matsunaga, T. (2011). *In Vivo J. Biol. Chem.*, **286**(8), 6386–6392.
- 25. Bazylinski, D. A., Frankel, R. B. (2004). Nat. Rev. Microbiol., 2, 217–230.
- 26. Komeili, A. (2007). Annu. Rev. Biochem., 76, 351-366.
- 27. Lang, C., Schüler, D., Faivre, D. (2007). Macromol. Biosci., 7, 144–151.
- Heywood, B. R., Bazylinski, D. A., Garratt-Reed, A., Mann, S., Frankel, R. B. (1990). *Naturwissenschaften*, **77**(11), 536–538.
- 29. Ofer, S., Nowik, I., Bauminger, E. R., Papaefthymiou, G. C., Frankel, R. B., Blakemore, R. P. (1984). *Biophys. J.*, **46**, 57–64.
- Han, L., Li, S., Yang, Y., Zhao, F., Huang, J., Chang, J. (2007). J. Magn. Magn. Mater., 313, 236.
- 31. Lee, H., Purdon, A. M., Chu, V., Westervelt, R. M. (2004). *Nano Lett.*, **4**(5), 995–998.
- Lawson, D. M., Artymiuk, P. J., Yewdall, S. J., Smith, J. M. A., Livingstone, J. C., Treffry, A., Luzzago, A., Levi, S., Arosio, P., Cesareni, G., Thomas, C. D., Shaw, W. V., Harrison, P. M. (1991). *Nature*, 349, 541–544.
- 33. Yamashita, I. (2001). Thin Solid Films, 393, 12-18.
- 34. Yamashita, I. (2008). J. Mater. Chem., 18, 3813-3820.
- Drits, V. A., Sakharov, B. A. Salyn, A. L., Manceau, A. (1993). *Clay Miner.*, 28, 185.
- Michel, F. M., Hosein, H.-A., Hausner, D. B., Debnath, S., Parise, J. B., Strongin, D. R. (2010). *Biochim. Biophys. Acta*, **1800**(8), 871–885.
- 37. Papaefthymiou, G. C. (2010). Biochim. Biophys. Acta, 1800, 886-897.
- Papaefthymiou, G. C., Devlin, E., Simopoulos, A., Yi, D. K., Riduan, S. N., Lee, S. S., Ying, J. Y. (2009). *Phys. Rev. B*, **80** 024406(1–10) and references therein.
- Néel, L. (1961). *Comptes Rendus Acad. Sci.*, **252**(1961), 4075–4081 (translated in *Selected Works of Louis Néel* (Kurti, N., ed.), pp. 107–110, Gordon and Breach, New York, 1988).
- Néel, L. (1961). Comptes Rendus Acad. Sci., 253, 203–208 (translated in Selected Works of Louis Néel (Kurti, N., ed.), pp. 114–117, Gordon and Breach, New York, 1988).
- Néel, L. (1961). Comptes Rendus Acad. Sci., 253, 1286–1291 (translated in Selected Works of Louis Néel (Kurti, N., ed.), pp. 118–121, Gordon and Breach, New York, 1988).

- 42. Makhlouf, S. A., Parker, F. T., Berkowitz, A. E. (1997). *Phys. Rev. B*, **55**, R14717.
- Kilcoyne, S. H., Cywinski, R. (1995). J. Magn. Magn. Mater., 140–144, 1466–11467.
- 44. Harris, J. G. E., Grimaldi, J. E., Awschalom, D. D., Chiolero A., Loss, D. (1999-I). Spin *Phys. Rev. B*, **60**, 3453–3456.
- 45. Madsen, D. E., Hansen, M. F., Bendix, J., Mørup, S. (2008). *Nanotechnology*, **19**, 315712(1–7).
- 46. Papaefthymiou, G. C., Viescas, A. J., Devlin, E., Simopoulos, A. (2007). Electronic and magnetic characterization of in vivo produced vs. in vitro reconstituted horse spleen ferritin, in *Nanophase and Nanocomposite Materials V (Materials Research Society Symposium Proceedings*) (Komarneni, S., Kaneko, K., Parker, J. C., O'Brien, P., eds.), Volume 1056E, pp. HH03–HH27, Warrendale, PA.
- 47. Mørup, S., Topsøe, H. (1976). Appl. Phys., 11, 63-66.
- 48. Meldrum, F. C., Cölfen, C. (2008). Chem. Rev., 108, 4332-4432.
- 49. Meldrum, F. C., Heywood B. R., Mann S. (1992). Science, 257, 522.
- 50. Klem, M. T., Young, M., Douglas, T. (2005). Mater. Today, 8(9), 28-37.
- 51. Dickson, D. P. E. (1999). J. Magn. Magn. Mater., 203, 46-49.
- 52. Gálvez, N., Sánchez, P., Domínguez-Vera, J. M., Sorianno-Portillo, A., Clemente-Léon, M., Coronado, E. (2006). *J. Mater. Chem.*, **16**, 2757.
- Warne, B., Kasyutich, O. I., Mayes, E. L., Wiggins, J. A. L., Wong, K. K. W. (2000). *IEEE Trans. Magn.*, 36, 3009.
- Li, Y. Lin, S.-T., Godard, W. A., III (2004). J. Am. Chem. Soc., 126, 1872– 1885.
- 55. Mann, S. (2009). Nat. Mater., 8, 781-792.
- 56. Goodfellow, B. W., Korgel, B. A. (2011). ACS Nano, 5(4), 2419–2424.
- Kasyutich, O., Sarua A., Schwarzacher, W. (2008). J. Phys. D: Appl. Phys., 41, 134022 (3pp).
- Kasyutich, O., Tatchev, D., Hoell, A., Ogrin, F., Dewhurst, C., Schwarzacher, W. (2009). *J. Appl. Phys.*, **105**, 07B528.
- Kostiainen, M. A., Ceci, P., Fornana, M., Hiekkataipale, P., Kasyutich, O., Nolte, R. J. M., Cornelissen, J. J. L. M., Desautels, R. D., van Lierop, J. (2011). ACS Nano, 5(8), 6394–6402.
- Matsui, T. Matsukawa, N., Iwahori, Sano, K.-I., Shiba, K., Yamashita, I. (2007). *Langmuir*, 23, 1615–1618.
- 61. Yamazaki, G., Uraoka, Y., Fuyuki, T., Yamashita, I. (2003). J. Polym. Sci. Technol., 16(3), 439-444.

Chapter 2

Controlling the Structure and Properties of Nanostructured Magnetic Materials Produced by Depositing Gas-Phase Nanoparticles

Chris Binns

Department of Physics and Astronomy, University of Leicester, Leicester LE1 7RH, UK cb12@le.ac.uk

2.1 Introduction

Since the 1980s there has been enormous interest in the fundamental properties of gas-phase atomic clusters with diameters in the size range of 1–10 nm due to the novel behavior of these systems arising from quantum size effects and the high proportion of undercoordinated surface atoms. The field developed rapidly following the design of cluster sources able to produce size-selected particles containing a specific number of atoms as this afforded a wonderful opportunity to study how the properties of a material

develop as it is built atom by atom from the monomer. Several reviews of the technology of cluster sources are available [1–4]. The fundamental studies of free nanoparticles revealed a rich variety of novel behavior, including magic numbers based on electronic shells [5] or atomic packing [6], leading to atomic structures not found in the bulk. Several properties that could be useful in practical applications were demonstrated, including enhanced magnetic moments in transition metal nanoparticles [7–9] and the appearance of magnetism in nanoparticles of bulk paramagnetic metals [10].

The electronic, optical, magnetic, and chemical properties of nanoparticles are a sensitive function of their size, and this gradually let to the concept of using the preformed nanoparticles as "building blocks" of new materials. They can be regarded as artificial atoms whose behavior can be adjusted over a wide range by controlling their size or, as shown below, building them out of more than one material. Obviously in a material the strong interactions between the nanoparticles or the matrix in which they are embedded also determines the macroscopic behavior of the material, but using nanoparticles introduces an extra fundamental parameter to be varied, almost as if there were an extra dimension to the periodic table.

Over the last two decades a number of reviews have appeared of nanoparticles deposited onto surfaces to produce nanostructured thin films [3, 11, 12], and the versatility of the materials produced was expanded further by codepositing the nanoparticles with an atomic beam of a different material [11, 12] so that the nanoparticles are embedded in a matrix of choice, as illustrated in Fig. 2.1. This is a powerful method of making granular materials, as there is free choice over the elements in the nanosized grains and the matrix and there is independent control over the grain size and volume fraction (VF). It is even possible to affect some control over the cluster shape by adjusting the impact energy on the surface [13], which will have a significant effect on the magnetic anisotropy. It has also been demonstrated that the choice of matrix material can be used to control the atomic structure of the embedded nanoparticles [14]. The flexibility of control increases further if the clusters are functionalized in the gas phase by making them out of more than one material [15, 16] or as core-shell particles, for example, by controlled oxidation [17]. One can also modify the deposited films by postprocessing, such as heating or oxidation [18]. Recently the codeposition method has been extended to using liquid matrices [19] so that magnetic nanoparticle hydrosols (ferrofluids) can be produced with the full flexibility over the nanoparticle properties available with gas-phase synthesis.

In this chapter the state of the art in using the flexibility of gas-phase synthesis to control the properties of nanostructured films will be reviewed. This control can be exercised by modifying the structure of nanoparticle building blocks, adjusting their size, choosing a matrix, and varying the VF of embedded nanoparticles. This level of control is not available with any other material synthesis method and holds the promise of the production of materials with very high performance in specific applications. This has already been demonstrated by the manufacture of thin nanostructured Fe-Co films whose magnetization exceeds the Slater-Pauling (SP) limit [12] and hydrosols of magnetic nanoparticles that produce more heat per gram than any available ferrofluids [19], to quote a couple of examples. The former material will be valuable in any electric machine, and the latter can be used for magnetic nanoparticle hyperthermia treatment of tumors. Clearly there are many breakthroughs to come, and this chapter presents the toolkit of control methods that can be used to optimize performance for practical applications.

Section 2.2 describes the properties of the simplest possible films produced by depositing just elemental magnetic nanoparticles on surfaces. Even these films display remarkable properties, for example, the absence of magnetic domains [20] and ultrafast magnetic switching [21]. Section 2.3 extends the description to codeposition of nanoparticles and matrix materials (Fig. 2.1), which enables control of the nanoparticle atomic structure [22] and interparticle interactions [23]. The section will include the synthesis of hydrosols from gas-phase nanoparticles by using a liquid matrix [19].

2.2 Pure Magnetic Nanoparticle Films

In this section the magnetic properties of films produced by depositing preformed gas-phase nanoparticles of Fe or Co directly

onto a substrate with no matrix material will be described. It is assumed throughout that the gas-phase clusters are produced and deposited in ultrahigh vacuum (UHV) conditions so that there is no oxide present during synthesis. If it is necessary to remove the film from vacuum, it must be protected by an impervious capping layer prior to exposure to air to maintain the pristine state of the film. As shown below, however, the nonmagnetic capping layer can alter magnetic behavior.



Figure 2.1 Synthesis of a nanostructured material by codepositing preformed gas-phase nanoparticles and an atomic beam from a conventional deposition source onto a common substrate.

2.2.1 Morphology of Pure Deposited Nanoparticle Films

The magnetic properties of pure elemental nanoparticle films are determined to a large extent by the morphology that arises from nanoparticle deposition. Most gas-phase cluster sources condense the nanoparticles in a supersaturated metal vapor, which is typically mixed with a cooled rare gas (He or Ar) at a pressure of a few millibars. The particles are formed into a beam by nozzles and differential pumping and can then be ionized (if they are not already) for a charged particle mass selector before being deposited onto a substrate. Throughout this chapter we will deal entirely with the so-called "soft landing" regime ($\leq 0.1 \text{ eV/atom}$) in which it can be assumed that the nanoparticles are not fragmented or embedded into the substrate, which is the normal situation unless one deliberately accelerates the particles using electric fields. Enhanced energy deposition provides extra flexibility in terms of "flattening" the clusters [13] and also some technological advantages such as very smooth films or the ability to coat high-aspect-ratio holes but is beyond the scope of this chapter.

The typical morphology of a film of soft-landed nanoparticles is shown in Fig. 2.2, which illustrates that the nanoparticles are simply piled on top of each other [24]. Although in certain specific cases, for example, small Sb clusters [25], the deposited nanoparticles can coalesce like liquid drops to form larger particles, this has not been observed for magnetic transition metals. The grain size within the film is thus the same as that of the free gas-phase nanoparticles. It can also be assumed that the anisotropy of each particle is uniaxial, even in the case of elements, like Fe, that have cubic anisotropy in the bulk. Only perfectly formed clusters containing magic numbers of atoms would maintain cubic anisotropy, since, as shown by Xie and Blackman [26], adding a few atoms to a facet is sufficient to induce uniaxial anisotropy. Even in the case of the small proportion of clusters that contain magic numbers, the process of depositing and embedding nanoparticles will induce stresses that lower the symmetry of the anisotropy. The uniaxial anisotropy in deposited clusters was demonstrated by dispersing them in a nonmagnetic Ag matrix using the process shown in Fig. 2.1 and modeling the approach to saturation at low temperatures well below the blocking temperature [23, 27] (see Section 2.3.2).

2.2.2 Magnetic Behavior of Pure Deposited Nanoparticle Films

From the discussion in the previous section, it is clear that within the film of deposited nanoparticles, each one will have a uniaxial anisotropy, and since the gas-phase clusters are rotating about all three axes, the anisotropy axis of each deposited nanoparticle will be randomly oriented. In addition there is usually a coherent anisotropy due to the strain induced in every cluster in the same direction due to the deposition process. Up to now the best description of the

50 Controlling the Structure and Properties of Nanostructured Magnetic Materials

magnetic behavior of films with this type of morphology has been with reference to the random anisotropy (RA) model described by Chudnovsky et al. and Saslow [28–31]. This was originally developed to describe the magnetic properties of amorphous materials in which it is supposed that the randomized atomic structure creates a local magnetic anisotropy, which is randomly oriented with respect to neighboring local anisotropies. It is even better suited to clusterassembled materials in which the local anisotropy changes direction randomly on a well-defined distance scale, that is, the size of an individual deposited nanoparticle.



Figure 2.2 AFM image $(2 \times 2 \mu m)$ of a 375 nm thick film of Co nanoparticles deposited on Si. The measured typical particle size, including tip convolution, is 30–35 nm. Reproduced with permission from Ref. [24]. *Abbreviation*: AFM, atomic force microscopy.

In the RA formalism, the magnetic ground state in a granular film is determined by the relative strength of an RA field

$$H_{\rm r} = \frac{2K_{\rm r}}{M_{\rm s}} \tag{2.1}$$

and an exchange field

$$H_{\rm ex} = \frac{2A}{M_{\rm s}R_{\rm a}^2},\tag{2.2}$$

where K_r is the (randomly oriented) anisotropy of the grains, M_s is their saturation magnetization, A is the exchange constant for the interaction between the grains, and R_a is the nanometer-size region over which the local anisotropy axis is correlated. When applied to a film of deposited nanoparticles, R_a can simply be taken as the characteristic particle size, and it is straightforward to include a size distribution [27]. The relative strength of the RA and exchange fields is given by the dimensionless parameter

$$\lambda_{\rm r} = \frac{H_{\rm r}}{H_{\rm ex}} = \frac{K_{\rm r} R_{\rm a}^2}{A} \,. \tag{2.3}$$

In a bulk material the exchange energy per atom is orders of magnitude larger than the anisotropy energy per atom, but in a pile of deposited nanoparticles the exchange field is given by the exchange interaction between neighboring particles in which only a few atoms participate. Thus exchange in a nanoparticle film acts strongly within each particle to induce internal alignment in what is effectively a "superatom" but has relatively "weak links" between particles. In addition the anisotropy energy per atom of nanoparticles is an order of magnitude greater than in the bulk [23, 27] due to the high proportion of surface atoms, and so the exchange and anisotropy fields in a nanoparticle film are comparable.

The ground-state magnetic configuration in the film depends on the value of λ_r and can be delineated into two regimes. If $\lambda_r >> 1$, anisotropy dominates and the magnetization within each nanoparticle is aligned along the local intraparticle anisotropy axis, so the film forms a simple superspin glass, as illustrated in Fig. 2.3a. The direction of magnetization may be forced slightly away from perfect alignment with the anisotropy axis by the exchange interaction with neighboring particles, but the magnetic correlation length is still the nanoparticle diameter. In the case where $\lambda_r << 1$, the exchange field dominates and the tendency is for the magnetization in all particles to line up irrespective of the direction of the local anisotropy. The anisotropy, however, pulls the local magnetization into a slight random misalignment in going from nanoparticle to nanoparticle so that magnetic correlation is lost after a few particles, as illustrated in Fig. 2.3b. This state has been called a correlated superspin glass (CSSG) [28-31], and the correlation length is given

by
$$\frac{R_{\rm a}}{\lambda_{\rm r}^2}$$



Figure 2.3 (a) Magnetic configuration in a nanoparticle film when anisotropy dominates so that the magnetic correlation length is the diameter of a single nanoparticle. This is a simple superspin glass. (b) Magnetic configuration in a nanoparticle film when exchange dominates, so there is nominal magnetic alignment between particles; however, the local anisotropy produces a small random misalignment, and so alignment is lost after a few particles. This is a CSSG [28–31]. *Abbreviation*: CSSG, correlated superspin glass.

The magnetic correlation length in a film of deposited Co nanoparticles, each with a diameter of \sim 30 nm, has been directly measured by magnetic force microscope (MFM) imaging [24]. Figures 2.4a and 2.4b show, respectively, the topography and phase (magnetic force) images of the Co nanoparticles at low coverage, and it is observed that for isolated nanoparticles the magnetic force contrast coincides with the diameter of the nanoparticles. When the nanoparticles are assembled into a thick film (Fig. 2.4c,d) the individual nanoparticles can still be distinguished in the topography image, but the phase-contrast image shows magnetic domains spread over several particles, though the domain boundaries are localized around nanoparticle edges. Comparing the correlation length in the topography and phase-contrast images enables a direct determination of λ_r , which in this case was found to be $\lambda_r = 0.67$. This value can be entered into the RA model to determine how the magnetization of the film approaches saturation [32], and the results are shown in Fig. 2.4e, indicating agreement between the prediction of the RA model and the measured magnetization. These results come with some provisos, one being that the field from the MFM tip may well perturb the ground-state magnetic pattern. The other is that in this study there was an oxide shell on the Co nanoparticles, so the exchange coupling between particles is more complex than for pure metal nanoparticles, but the origin of the magnetization pattern in a nanoparticle films is clearly illustrated.



Figure 2.4 (a and b) Topography and phase-contrast (magnetic force) images $(1 \times 1 \ \mu m)$ of deposited Co nanoparticles (~30 nm) on Si at low coverage. (c and d) Topography and phase-contrast (magnetic force) images $(1 \times 1 \ \mu m)$ of a continuous film (375 nm thick) of deposited Co nanoparticles on Si. The magnetic correlation is larger than a single nanoparticle. (e) Measured approach to saturation of the magnetization from the thick film (circles) compared to a calculation using the RA model for the value of $\lambda_r = 0.67$ measured from the images. Reproduced with permission from Ref. [32].

Thus in essence, nanoparticle films do not develop domains in the normal sense. In a macroscopic material the domains form to minimize magnetostatic energy in the bulk at the expense of some increase in exchange energy at the domain boundaries. The delicate balance between magnetostatic, exchange, and anisotropy energies determines the domain pattern and the size of the domains, which are typically of micron size. In a nanoparticle film the competition between exchange (interparticle) and local intraparticle anisotropy produces magnetic correlation that varies from the nanoparticle diameter to the ~ 100 nm scale, giving a magnetization pattern

54 Controlling the Structure and Properties of Nanostructured Magnetic Materials

that averages to zero at larger scales, and so the system naturally minimizes its magnetostatic energy from local interactions. This difference between conventional and nanoparticle films is illustrated clearly in Fig. 2.5, which shows X-ray photoemission electron microscope (XPEEM) images of a conventional molecular beam epitaxy (MBE)-grown Fe film and a similar-thickness nanoparticle film. composed of 2 nm diameter nanoparticles deposited on Si and compared side by side [20]. Both films were deposited in situ in UHV conditions. In these measurements, magnetic contrast was obtained by using soft X-rays around the Fe L_3 edge (708 eV) and taking two images with either the photon helicity or magnetization reversed. After subtracting them the spatial distribution of X-ray magnetic circular dichroism (XMCD) of the sample (i.e., its magnetization pattern) is revealed. Generally this method is not able to achieve the spatial resolution of an MFM, but it is much less intrusive. While the normal metal film clearly shows micron-size domains the nanoparticle film shows a smooth image, indicating that the "domains" or magnetic correlations are below the resolution limit (~100 nm). Assuming it is spread over a few nanoparticles, the magnetic correlation length would be ~ 10 nm. Magnetization data from the nanoparticle films in this experiment also showed an approach to saturation that could be predicted using the RA model [20].

Since the source of the anisotropy is generally due to shape and surface effects the magnetic behavior is relatively independent of temperature, and in addition the random orientation of the anisotropy on the nanoscale produces soft magnetic behavior. The weak temperature dependence is demonstrated in Fig. 2.6, which shows the approach to magnetization of films of 2-3 nm diameter Fe and Co clusters at different temperatures, along with the calculated curves using the RA model with the fit parameters specified in the figure [27]. In all cases the λ_r parameter is close to 1, indicating that the ground-state magnetic configuration of the films is close to the crossover region between a simple superspin glass and a CSSG. The inset for each type of sample shows the intraparticle anisotropy, obtained from the fitted value of H_r and Eq. 2.1, and in each case the flat line shows the value of anisotropy measured for isolated nanoparticles of the same size dispersed in a Ag matrix [27] (see Section 2.3.2). For the Fe nanoparticle films the intraparticle anisotropy is similar to that of the isolated nanoparticles, whereas for the Co nanoparticle films the intraparticle anisotropy is significantly less than that of the isolated nanoparticles.



Figure 2.5 XPEEM images of Fe films taken at the Fe L₃ edge and exploiting XMCD to determine the magnetization pattern. (a) A 200 Å thick Fe film deposited by MBE onto Si, exhibiting a domain pattern. (b) A similar-thickness film of 2 nm diameter Fe nanoparticles deposited onto Si. Both films were deposited in situ in UHV. The absence of domains in the nanoparticle film down to the resolution limit of the XPEEM (~100 nm) is evident. Reproduced with permission from Ref. [20]. Abbreviations: XPEEM, X-ray photoemission electron microscope; MBE, molecular beam epitaxy; XMCD, X-ray magnetic circular dichroism.

In this experiment the Fe and Co nanoparticle samples were transferred from the UHV deposition chamber into the magnetometer, while maintaining UHV conditions, so the films were uncapped. A similar study, carried out on Fe nanoparticle films, compared the behavior of films that were capped with Ag and transferred through air and others that were uncapped and transferred in UHV [23]. It was found that the H_r parameter (and thus the intraparticle anisotropy) is significantly higher in the capped films, showing that the capping layer introduces strain, which increases the intraparticle anisotropy and is transmitted through the film.

The mechanism for magnetization reversal of films composed of nanoparticles is different to that of conventional films in which the motion of domain walls plays a significant part. Since nanoparticle films do not form domains in a conventional sense their reversal processes are more complex and not so well understood. It is known, from time-resolved spin-polarized photoemission measurements using synchrotron radiation [21], that the switching dynamics in a film of Fe nanoparticles is significantly faster than a conventional magnetic film.



Figure 2.6 Measured approach to saturation of uncapped 2–3 nm Fe and Co cluster films as a function of temperature (filled circles) compared to the predictions of the RA model (lines) with the fit parameters displayed by each curve. The insets show the intraparticle anisotropy of the Fe or Co nanoparticles (circles) compared to the anisotropy of isolated nanoparticles of the same size dispersed in Ag (lines). Reproduced with permission from Ref. [27].

2.3 Magnetic Nanoparticles in Matrices

Whereas the previous section described the properties of films composed of deposited nanoparticles of a single element, in this section, the properties of nanoparticles codeposited with matrices of other materials will be presented. The process used is as described in Fig. 2.1, and by this method, size-selected magnetic nanoparticles have been deposited with a controlled VF into nonmagnetic [11, 12, 14, 22, 23, 27, 33], ferromagnetic [12, 34], antiferromagnetic [35–38], rare-earth [39], and liquid [19] matrices.

2.3.1 Controlling the Atomic Structure of Nanoparticles in Matrices

It has become clear from a number of studies of cluster-assembled materials produced by codeposition of clusters and a matrix material that the interaction between the clusters and the matrix can modify the atomic structure of the nanoparticles. This not only includes strain but in some cases a transformation of the atomic structure to a new phase. For clusters dispersed at a low VF in a matrix a simple picture emerges that enables the prediction of which structure the nanoparticles will adopt. In the dilute limit the matrix will always adopt the bulk structure, while the high proportion of surface atoms in the nanoparticles will minimize the structural energy for surface atomic arrangements that are epitaxial with the matrix.

For example, there is a close lattice match between the bulk body-centered cubic (bcc) Fe and bulk face-centered cubic (fcc) Ag structures, so it was found that 1.85 nm diameter Fe nanoparticles embedded in Ag matrices [14] maintain the bulk bcc structure. On the other hand Fe nanoparticles in Cu matrices adopt an fcc structure due to the close lattice match between fcc γ -Fe and fccCu [40]. Interestingly, it was demonstrated that Fe nanoparticles embedded in amorphous carbon, in which there is no epitaxy between the cluster surface and the matrix, showed a mixture of bcc and fcc phases [14], implying that this size (1.85 nm or ~120 atoms) is close to the critical value for the transition from the fcc to the bcc phase in the free clusters. On increasing the nanoparticle VF above the nanoparticle dilute limit, as the percolation threshold is reached and most nanoparticles are in contact with neighbors, the energy balance changes and the structure can change. For example, the structure of Fe clusters in Cu changes from fcc to bcc as the VF increases beyond $\sim 25\%$ [40]. As shown in the left portion of Fig. 2.7 the structural transition of Fe clusters in Cu matrices produces a significant change in their magnetic moment.



Figure 2.7 (Left) Measured magnetic moment per atom of Fe nanoparticles (260 atoms) embedded in Cu as a function of VF. EXAFS shows that the low-VF Fe structure is fcc, while at high VF it is bcc. (Right) TB-LMTO calculations of the magnetic moment in fcc Fe clusters surrounded by a thick Cu shell as a function of the Fe lattice constant. The two sizes of Fe core bracket the experimental size distribution. The vertical line shows the fcc lattice constant obtained by EXAFS, revealing that the calculated (low-spin) magnetic moment in the fcc structure at the correct lattice constant agrees with the measured one. Reproduced with permission from Ref. [40]. *Abbreviations*: EXAFS, extended x-ray absorption fine structure; TB-LMTO, tight binding linear muffin-tin orbital.

In the fcc structure, the magnetic moment per atom of the Fe nanoparticles is predicted to undergo a transition from a low-spin to a high-spin state with increasing lattice constant. The right-hand portion of Fig. 2.7 shows the results of the calculated magnetic moment for fcc Fe nanoparticles of two different sizes, each including a thick Cu shell, carried out using the TB-LTMO method. The two sizes were chosen to bracket the experimentally observed size distribution for the data in the left portion. The vertical line in the theory shows the measured lattice constant of 3.58 Å obtained by EXAFS for the fcc Fe clusters at a low VF, and it is evident that the calculated magnetic moment agrees with the experimentally obtained one.
The same method can be used to prepare other nanoparticles in atomic structures different from the bulk material. Co nanoparticles deposited into Fe matrices adopt the Fe bcc structure rather than the bulk Co hexagonal close-packed (hcp) arrangement [34]. Interestingly this is observed across the Co VF range up to 40%, that is, well above the percolation threshold. The EXAFS measurements for the films indicated no significant degree of alloying between the clusters and the matrix. The more open Co structure leads to an increased magnetic moment [12], which is an important factor in producing very-high-magnetization nanostructured films (see Section 2.3.2).

As well as being able to modify the atomic structure of nanoparticles by choosing the right matrix, it is even possible to exercise control over the lattice constant within the modified structure by using alloy matrices, as demonstrated recently by Baker et al. [22] for Fe nanoparticles in CuAu alloy matrices. In general it is found experimentally [41] that the lattice constant of $Cu_{1,y}Au_{y}$ alloys varies linearly with *x*, as predicted by Vegard's rule [42, 43]. It thus provides a host matrix in which the lattice structure stays fcc but the lattice constant can be continuously varied by changing the Au content. It was found that Fe nanoparticles with a diameter of 2 nm embedded in CuAu matrices adopt the fcc (or face-centered tetragonal [fct]—see below) structure throughout the composition range studied [22], and Fig. 2.8 shows the measured magnetic moment as a function of Au content. It is observed that the moment varies from the low-spin fcc value of 1.1 $\mu_{\rm B}$ /atom in the pure Cu matrix (lattice constant = 3.58 Å) to 2.5 $\mu_{\rm B}$ /atom at a Au content of 25% (lattice constant = 3.7 Å), which is significantly higher than the bulk Fe bcc value. The unfilled circles in Fig. 2.8 show the measured Cu lattice constant as a function of Au content.

In pure Cu films the Fe nanoparticles adopt an fcc structure and throughout the composition range never revert to the bulk Fe bcc structure; however, it was found that the change in Fe clusters with increasing Au content was not simply a uniform stretch of the fcc structure but rather a tetragonal distortion in which there is a stretch in one direction and a compression in the orthogonal direction. Despite this, changing the lattice parameter of the matrix does enable the preparation of fct Fe nanoparticles in the high-spin state. Tables 2.1 and 2.2 show a summary of structures of Fe and Co nanoparticles embedded in various matrices.



Figure 2.8 Magnetic moment per atom of Fe nanoparticles embedded in CuAu alloy matrices as a function of Au content (filled circles). The variation in the fcc Cu lattice constant of CuAu films containing Fe nanoparticles as a function of Au content is show by the open circles. The Fe atomic structure is fcc or fct (see text) at all Cu lattice constants.

The discussion in this section has so far been restricted to embedded nanoparticle systems that have sharp interfaces and no detectable intermixing with the matrix material; thus the nanoparticles can be considered as discrete entities with a modified atomic structure. In many embedded nanoparticle systems this is not the case and significant surface alloying takes place at room temperature, as found in, for example, Fe nanoparticles embedded in Dy [45] and Co particles embedded in Mn [46] matrices. These highly inhomogeneous alloys can also display unusual properties, as demonstrated in the case of Co nanoparticles in Mn matrices [46]. The morphology inferred from EXAFS data is illustrated schematically in Fig. 2.9. Each deposited Co nanoparticle becomes a nanoscale region of a $Co_{1-x}Mn_x$ alloy in which x varies continuously from 0 at the middle of the region to 1 where it merges with the Mn matrix. At the radius where *x* crosses 0.3, the alloy switches from ferromagnetic (F) to antiferromagnetic (AF), thus creating an F/AF interface, and the films show a magnetic exchange bias [46].

Matrix material	VF (%)	Nanoparticle atomic structure	Lattice constant (Å)	Ref.	Bulk material structure and lattice constant
Ag	5 40	bcc bcc	2.85 ± 0.01 2.85 ± 0.01	[14]	
Cu	6	γ-fcc	3.57 ± 0.02	[40]	
Amorphous-C	4 40	mixed bcc and fcc	2.56 ± 0.02 2.57 ± 0.01	[14]	
Со	9	bcc	2.84 ± 0.02	[34]	hcc 287Å
Cr	5	bcc	2.85 ± 0.01	[44]	500, 210, 11
CuAu alloy	5	fcc-fct (increasing fct distortion	3.58 - 3.70	[22]	
		with Au content)		[]	

Table 2.1	Atomic structure of Fe nanoparticles with a diameter of 1.85 nm
	embedded in various matrices

Table 2.2Atomic structure of Co nanoparticles with a diameter of1.85 nm embedded in various matrices

					Bulk material
		Nanoparticle			structure
Matrix	VF	atomic	Lattice		and lattice
material	(%)	structure	constant (Å)	Ref.	constant
Ag	5	hcp or fcc	2.49 ± 0.02	[34]	hen 2 E1 Å
Fe	9	bcc	2.86 ± 0.02	[34]	ncp, 2.51 A

Finally in this section, it is worth pointing out that although the discussion about modifying the nanoparticle atomic structure has focused on particles embedded in solid matrices, it may be possible to produce these structural changes within core-shell nanoparticles. Thus, for example, it may be possible to stabilize the high-spin fcc Fe structure in an Fe nanoparticle coated in a CuAu alloy shell, and gas-phase sources have been built that are specialized to produce such core-shell particles [19, 47]. Coupled with the technology to deposit

these into water to form liquid suspensions (see Section 2.3.3), these could make high-performance nanovectors for medical applications such as tumor hyperthermia.



Figure 2.9 Structure inferred for the highly alloyed system of Co nanoparticles embedded in Mn matrices [46].

2.3.2 Controlling the Magnetic Properties of Isolated Nanoparticles in Matrices

In this section we will consider the magnetic behavior of films of isolated nanoparticles embedded in a matrix of a different, nonmagnetic material produced by the cluster deposition method (Fig. 2.1). This enables the preparation of close to "ideal" systems of size-selected noninteracting nanoparticles, whose magnetic properties can be accurately described by well-understood models. Thus a range of important parameters for the isolated buried nanoparticles can be extracted, which aids interpretation of the data from films in which there are significant interactions.

Particles with a diameter of less than \sim 50 nm will be a single magnetic domain. In addition for diameters significantly smaller than the domain wall width, *t*, of the equivalent bulk material, given by

$$t = \pi a \left(\frac{W}{3K}\right)^{\frac{1}{2}}$$
(2.4)

where *a* is the atomic diameter, *W* is the exchange energy/unit volume, and *K* is the anisotropy energy density, one can ignore canting of spins at the particle surface. Typically, $W \approx 10^9$ Jm⁻³ while $K \approx 10^5$ Jm⁻³, so the domain wall thickness is ~25 nm, and since the nanoparticles we are considering here are <10 nm, we can assume that the magnetic moment in each is a single giant moment derived from the individual magnetic moments locked together by exchange. The nanoparticle magnetic moment will have an anisotropy that can be assumed to be uniaxial (see discussion in Section 2.2.1).

At T = 0 K, reversing the direction of the cluster magnetization requires an external field to drive the magnetization vector across the anisotropy boundary *KV* separating different magnetic alignments, where *K* is the anisotropy constant and *V* is the particle volume. At finite temperatures, the external field acts in the presence of thermal fluctuations of the moment. When a saturating field is removed from a particle (or a dilute assembly) at temperature *T*, the magnetization decays with a relaxation time, τ , that can be approximated by the Arrhenius relationship:

$$\tau = \tau_0 \exp\left(\frac{KV}{k_{\rm B}T}\right),\tag{2.5}$$

where τ_0 is the natural lifetime of the particle, that is, the value at the high-temperature limit. This has been measured by muon spin resonance spectroscopy [48] to be 12 ns for 2.85 nm diameter Fe nanoparticles embedded in Ag matrices at a VF of 0.1%. For this order of particle size, observations must be made at cryogenic temperatures (≤ 5 K) for the magnetic relaxation to be slower than typical measurement times for conventional magnetometry.

As the temperature is lowered the thermal energy becomes too small to excite the magnetization vector over the barrier and in zero field the magnetization is static in each nanoparticle and lies along the easy axis in either direction. In this regime it is also possible for the magnetization vector to form a superposition by quantum mechanical tunneling through the anisotropy barrier [49, 50]. This is a fascinating phenomenon but difficult to observe with the size of particles discussed in this chapter and will not be considered further. The temperature at which the magnetic moments become static is known as the blocking temperature, and this depends on the measurement time but not very sensitively. For example, Fe nanoparticles with a diameter of 2 nm have $K = 2 \times 10^5 \text{ Jm}^{-3}$ (see below), and using the measured value of $\tau_0 = 12 \text{ ns}$, the blocking temperature at a measurement time of 1,000 seconds (typical for measuring an M–H loop) is 2.4 K, while if the measurement time is increased to a year the blocking temperature is 1.7 K. Thus this narrow range delineates essentially permanent static moments from fluctuating ones.

The magnetization of an assembly of nanoparticles below their blocking temperature is determined by the competition between the particle moment aligning with the direction of the applied field or the direction of the local anisotropy axis. Considering an individual particle with a uniaxial anisotropy (Fig. 2.10) one can assume that the (uniaxial) anisotropy axis (labeled \hat{e}_i in Fig. 2.10) is randomly aligned and is at an angle θ with respect to the applied field direction (*z* axis). Assuming the magnetization vector (labeled \hat{S}_i in Fig. 2.10) makes an angle ϕ with respect to the *x* axis, the energy above the ground state of the magnetization vector of the particle in zero field is

$$E_{\varphi} = KV \sin^2(\theta - \varphi), \qquad (2.6)$$

and when the field is applied

$$E_{\varphi} = KV \sin^2(\theta - \varphi) - \mu B \cos\varphi. \qquad (2.7)$$

So the particle moment will rotate to minimize E_{φ} , and this will be at some angle between the directions of the field and the anisotropy axis. For small fields and/or large anisotropies the moment will be close to the anisotropy axis, but as the field is increased the magnetic moment will align more closely with it.

To calculate the magnetization of an ensemble in which the particles (i.e., their anisotropy axes) are randomly oriented, for each field and particle orientation θ , the direction (ϕ) of the magnetic moment is determined by minimizing the energy in Eq. 2.7. This determines the measured magnetic moment along the field direction, $\mu_z = \mu \cos \phi$, where μ is the magnitude of the particle magnetic moment. The values of μ_z are then averaged over all possible particle orientations θ to get the magnetization of the ensemble.



Figure 2.10 (a) Dependence of uniaxial anisotropy energy on the magnetization direction in zero field in a nanoparticle whose axis is at an angle to the direction in which the field will be applied. (b) After the field is applied.

Figure 2.11 shows magnetization isotherms obtained at 2 K from low-VF assemblies of Fe and Co nanoparticles with diameters of 3 nm and 2.8 nm, respectively embedded in Ag matrices [27]. In Fig. 2.11a the field is applied in the plane to the assembly of Fe nanoparticles, and the data obtained with the decreasing field has been fitted to the model described above. The only unknown parameter is the particle anisotropy, and this is adjusted to optimize the fit and the obtained value shown in the inset. In Fig. 2.11b the process has been repeated for an out-of-plane applied field and shows a larger value of K for the Fe nanoparticles, indicating an additional in-plane anisotropy term resulting from strain or shape distortion induced by the deposition process. This will be related to the coherent anisotropy discussed in the description of the RA model (Section 2.2.2). Figure 2.11c shows the out-of-plane data and model fit for Co nanoparticles, indicating a much larger value of the anisotropy. The remanence of an assembly of nanoparticles with uniaxial anisotropy should be 50%, and it is noticeable that the remanence in the data is below 50% for both Fe and Co nanoparticles. This is ascribed to the proportion of small particles within the size distribution that are not blocked at 2 K.



Figure 2.11 (a) In-plane magnetization isotherms at 2 K for 0.8% VF 3.0 nm diameter Fe nanoparticles in a Ag matrix compared to the model described in the text. The inset details the fit and shows the value of the anisotropy that optimizes it. (b) As (a) but with the field applied out of plane. (c) As (b) but for 2% VF 2.8 nm diameter Co nanoparticles. Reproduced with permission from Ref. [27].

The magnetization of a dilute nanoparticle assembly well above the blocking temperature can also be calculated precisely. The nanoparticle moment, μ , is quantized into discrete μ_z values (i.e., discrete directions), but the number of allowed states between the ground state, $E = -\mu B$ and the maximum energy $E = +\mu B$ is given by 2J+ 1, where *J* is the angular momentum. Since this is the total angular momentum of the nanoparticle, its value is typically hundreds or thousands and the discrete values form a quasi-continuum. Thus the variation of the energy as a function of the orientation of the moment can be treated classically, as illustrated in Fig. 2.12a.

In an applied field, B, the energy of the moment is

$$E = -\mu B \cos\theta \,, \tag{2.8}$$

which is minimized when the moment and the field are aligned, but perfect alignment at all times is prevented by thermal excitations away from the minimum energy direction. This is a standard problem in classical statistics, which predicts that the probability of the moment pointing along a direction, θ , is proportional to

$$\exp\left(\frac{-E}{kT}\right) = \exp\left(\frac{-\mu B \cos\theta}{kT}\right) = e^{m\cos\theta}, \qquad (2.9)$$

where $m = \mu B/kT$. The angle, θ , can vary between 0 and π for an ensemble of particles, and the average angle made with the field, $\langle \cos \theta \rangle$, is obtained by integrating the factor $\langle \cos \theta \rangle = \cos \theta e^{m\cos \theta} / e^{m\cos \theta}$ over a spherical shell defined by $\theta = 0 - \pi$. A suitable shell element is shown in Fig. 2.12b. The average angle the moment makes with the field is thus

$$(\cos\theta) = \frac{\int_0^{\pi} \cos\theta e^{m\cos\theta} \sin\theta d\theta}{\int_0^{\pi} e^{m\cos\theta} \sin\theta d\theta},$$
(2.10)

and integrating by parts gives

$$(\cos\theta) = \cot hm - \frac{1}{m} = L(m), \qquad (2.11)$$

where L(m) is the Langevin function. Thus at a given temperature and applied field the magnetization of an assembly of *N* nanoparticles in the direction of the applied field is

$$N(\mu) = \mu N(\cos\theta) = \mu N L\left(\frac{\mu B}{kT}\right).$$
(2.12)



Figure 2.12 (a) In a nanoparticle, the magnetic moment is large and the energy states of the different μ_z values (different pointing directions of the moment) form a quasi-continuum, so the moment can be treated as a classical vector. (b) Suitable shell element to integrate over a spherical shell defined by $\theta = 0 - \pi$.

At a given field and temperature the magnetization depends only on μ , which, enhanced moments, etc., depends only on the size of the particle.

Thus the magnetization curves for a dilute monosized nanoparticle assembly well above the blocking temperature can be fitted to a Langevin function and optimized to find the average particle size. With sufficiently good-quality data, it is possible to go further and fit a family of Langevin functions, each representing a different size and where the weighting of each function is a fitting parameter, allowing the size distribution to be determined. This has been done using the dilute Fe nanoparticle sample shown in Fig. 2.11a, and the result is displayed in Fig. 2.13a, which shows isotherms for temperatures in the range 50-300 K. Each of these has been fitted with a set of Langevin functions, and the weight of these as a function of particle size is shown in the inset fitted to a log-normal distribution. The same data is plotted against 1/Tin Fig. 2.13b, demonstrating that the curves all lie on top of each other, as required for a superparamagnetic system. The inset in Fig. 2.13b shows the median particle size for the size distribution obtained from the isotherms at different temperatures and shows a constant value of 3 nm. As a check that the sizes obtained in this wav are reasonable the images obtained by scanning tunneling microscopy (STM) of the Fe nanoparticles deposited in UHV onto Si(111) with the source operating at the same conditions is shown in Fig. 2.13c. The size distribution obtained directly from the images and corrected for tip effects is plotted in Fig. 2.13d (filled circles) and compared to the size distribution obtained from the magnetic data (open circles). There is agreement within the uncertainty of tip correction and source conditions, providing confidence that the size obtained from the magnetic data is accurate.

Figure 2.14a shows isotherms for temperatures in the range 50–300 K for the 2% VF assembly of Co nanoparticles in Ag. Again, each isotherm has been fitted with a set of Langevin functions, and the weight of these as a function of particle size is shown in the inset fitted to a log-normal distribution. Plotting the data against 1/T (Fig. 2.14b) reveals that in the scans of Co nanoparticles the curves only lie on top of each other for temperatures greater than 100 K, demonstrating that the sample can only be considered to be perfectly superparamagnetic above this temperature. This is due to the higher

anisotropy of the Co nanoparticles and may also be due to increased interaction at the higher VF. The inset in Fig. 2.14b, which plots the median size distribution obtained by fitting Langevin functions to the data, only reveals a constant size (2.9 nm) above 100 K.



Figure 2.13 (a) Isotherms from an assembly of a 0.8% VF of Fe nanoparticles in a Ag matrix for temperatures in the range 50–300 K along with fits using a number of Langevin functions representing the size distribution. The inset shows the size distribution obtained (averaged over all temperatures) fitted to a log-normal curve. (b) The same data plotted against 1/Tto demonstrate the curves lie on top of each other, as required for a superparamagnetic system. The inset shows the median size obtained from the fitted distribution, demonstrating the temperature independence. (c) STM image of a deposit of Fe nanoparticles produced under similar source conditions and deposited onto Si(111) [51]. (d) Comparison of the size distribution obtained from the STM images (filled circles) and the magnetic data (open circles). Reproduced with permission from Refs. [27, 51].

In summary, in this section, it has been shown that the size distribution of a dilute assembly of noninteracting nanoparticles in a nonmagnetic matrix can be determined from the magnetization curves at temperatures above 100 K. At low temperature the magnetization yields precise values for the intraparticle anisotropy energy and also the symmetry of the anisotropy, which has been found to be uniaxial in the case of Fe and Co nanoparticles in Ag.



Figure 2.14 (a) Isotherms from an assembly of a 2% VF of Co nanoparticles in a Ag matrix for temperatures in the range 50–300 K along with fits using a number of Langevin functions representing the size distribution. The inset shows the size distribution obtained (averaged over all temperatures) fitted to a lognormal curve. (b) The same data plotted against 1/T to check whether the curves lie on top of each other, as required for a superparamagnetic system. In this case the data at 50 K and 100 K is separate from the rest, indicating that the system does not have ideal superparamagnetic behavior for T < 100K. The inset shows the median size obtained from the fitted distribution and shows temperature independence in the superparagnetic regime. Reproduced with permission from Ref. [27].

2.3.3 Controlling the Magnetic Properties by Nanoparticle Volume Fraction

The previous two sections considered isolated nanoparticles dispersed at low VFs in matrices. Section 2.3.1 described changes in the atomic structure of individual nanoparticles that can be induced by using different matrix materials, and Section 2.3.2 discussed the magnetic properties of isolated nanoparticles in nonmagnetic matrices. In this section the focus will be on changes in the magnetic properties of the film produced by changing the VF of nanoparticles and increasing the importance of interparticle interactions. We

have already considered the two extremes of this variation, that is, pure cluster films (Section 2.2.1) for which VF = 1 and isolated nanoparticles where VF < 0.1 (Sections 2.3.1 and 2.3.2), but here we look at how magnetic behavior varies with intermediate values of VF.

When the interparticle interactions become significant in a system of nanoparticles, it displays a rich variety of magnetic configurations resulting from competing energy terms. The dipolar interaction introduces frustration as it is impossible to produce an optimum alignment for every particle. In addition there is frustration resulting from the competition between the interparticle dipolar and exchange terms and the intraparticle anisotropy energy (magnetocrystalline, shape, magnetoelastic, etc.) that requires the magnetization vector to be aligned along specific axes in each particle. Apart from scientific curiosity it is important to understand the behavior produced by these interactions, since many applications of granular magnetic materials require the VF to be close to or above the percolation threshold in which there are strong interactions.

This is a topic that has been studied for many decades using a variety of measurement techniques, including magnetometry, susceptibility measurements, muon spin resonance, and Mössbauer spectroscopy and samples, including frozen ferrofluids, cosputtered metal/insulator films, annealed melt-spun alloys, and ball-milled alloys [52–67]. In most preparation methods, however, it is difficult to control the size of the embedded magnetic grains independently of the VF. It is only with the advent of preformed nanoparticle deposition that it has been possible to maintain the particle size fixed while varying the VF within the matrix as a single parameter. An extreme example of magnetic changes with the VF was illustrated in Fig. 2.7, where the atomic structure of the nanoparticles changed with the VF, producing a transition from a low-spin to a high-spin state. In this section, however, we will assume that the structure of the constituent nanoparticles does not change with the VF and study the evolution of magnetic properties brought about purely by interactions. A good model system for this is Fe nanoparticles codeposited with a Ag matrix in which, as discussed in the previous section, the Fe nanoparticles maintain the bulk bcc structure throughout the VF range.

72 Controlling the Structure and Properties of Nanostructured Magnetic Materials

Figure 2.15 shows how the room temperature magnetization curves evolve with the VF in the range 0.8%–19% for 3 nm diameter Fe nanoparticle assemblies in Ag matrices and the most apparent change is an increase in the low-field susceptibility with higher packing densities. The basic nanoparticle building blocks in the films are well characterized with the size distribution and intraparticle anisotropy energies known, as discussed in Section 2.3.2.



Figure 2.15 Evolution of the magnetization curves for 3 nm diameter Fe nanoparticles in Ag as the VF is varied in the range 0.8%–19%. The inset shows the measured susceptibility value (open circles) compared to a MC simulation (filled circles/line). Reproduced with permission from Ref. [23]. *Abbreviation*: MC, Monte Carlo.

The set of films can be modeled by MC simulations, and to describe the system realistically, both dipolar and exchange interactions must be included [23]. Note that in the discussion below, "exchange" refers only to the interparticle exchange force, and it is assumed that intraparticle exchange serves only to lock the atomic spins into a single nanoparticle moment. The predicted susceptibility is displayed in the inset (filled circles/line) and qualitatively predicts the experimentally observed trend (open circles). The quantitative disagreement can be ascribed to a difference in the time associated with the experiment and model. In the MC simulation the calculation is extended to 10,000 MC steps, which roughly corresponds to an experimental measurement time of 10^{-4} seconds [68] and compares to time scales of minutes for the measurement. It is interesting to note that both experimental measurements [66] and theoretical modeling [69] predict a decrease in low-field susceptibility in the presence of dipolar interactions alone, emphasizing the importance of exchange forces in determining the macroscopic behavior of the material.

In this relatively low VF range (i.e., below the percolation threshold at VF $\approx 25\%$), one can also gain a qualitative understanding of the behavior of interacting nanoparticle assemblies by applying the Curie-Weiss model, as shown by Allia et al. [66]. As discussed in Section 2.3.2, the very low VF (0.8%) data in Fig. 2.15 displays perfect superparamagnetism and shows a qualitatively good fit to a Langevin function with a particle size of 3 nm (the median diameter in Fig. 2.13a,b). Repeating the fit for magnetization curves from the dilute film at different temperatures shows that the fitted particle size remains constant as a function of the temperature of the curve used, as shown in Fig. 2.13b. Curves at higher VFs also show qualitatively good fits to single Langevin functions using larger particle sizes, but it is erroneous to describe the higher VF films as superparamagnetic with larger particle sizes. When the fit to a higher VF curve is carried out at different temperatures, each temperature requires a different particle size for optimization. In addition the isotherms plotted against 1/T do not lie on top of each other, and both indications show that the system is not superparamagnetic.

In the low VF range (<25%), the system consists of nanoparticle aggregates whose moments are locked together by exchange that interact with other aggregates by dipolar forces. The dipolar interactions can be characterized by a temperature parameter T^* , proportional to the mean dipolar energy between particles and included in the denominator of the Langevin function. Thus for the interacting assembly, Eq. 2.12, which was derived for a superparamagnetic system, is replaced by

$$M = \mu NL \left(\frac{\mu B}{k(T+T^*)} \right), \tag{2.13}$$

where in this case μ is the moment of the nanoparticle aggregates. It is straightforward to show that the average diameter, d, of the nanoparticle aggregates is related to the "apparent" (or wrong) diameter, d_a , obtained if one fits a pure Langevin function to the interacting particle magnetization data through the equation [66]:

$$d_{\rm a} = \left(\frac{1}{1 + \frac{T}{T^*}}\right)^{\frac{1}{3}} d \tag{2.14}$$

Thus if one fits simple Langevin functions to the data over a range of temperatures, the apparent diameter will vary with temperature and the variation can be used to determine the true aggregate diameter and T^* . This procedure is illustrated for two films of 3 nm diameter Fe nanoparticles in Ag with VF = 0.8% and VF = 10% in Fig. 2.16.



Figure 2.16 Median particle diameter *d* obtained by fitting unmodified Langevin functions to the magnetization curves taken at 50–300 K of Fe_{0.8}Ag_{99.2} (open circles) and Fe₁₀Ag₉₀ (filled circles) films. The variation of d_a vs. *T* can be used to obtain the interaction parameter *T*^{*} and the true particle size, *d*, from Eq. 2.14. Reproduced with permission from Ref. [23].

In the noninteracting VF = 0.8% system, *d* remains at the isolated nanoparticle diameter of 3 nm and $T^* = 0$, as required. When the VF is

10% the change of d_a with temperature is apparent and the variation can be modeled by Eq. 2.14 to yield a true aggregate diameter of 5.7 nm with an interaction temperature of 94 K. To check that this number is sensible it is straightforward to make a rough estimate of T^* since the dipolar interaction energy is given by

$$E_{\rm dip} = \frac{\mu_0 \mu^2}{4\pi r^3} \,, \tag{2.15}$$

where μ is the total moment of the nanoparticles or aggregates of nanoparticles and *r* is their separation. Thus we can write

$$T^* = \frac{\mu_0 \mu^2}{4\pi r^3 k} \,. \tag{2.16}$$

Assuming random packing, for the isolated nanoparticles with a diameter of 3 nm (VF = 0.8%), one obtains $\langle r \rangle = 13.6$ nm and $T^* \approx$ 3K, which is undetectable in the fit in Fig. 2.16. On the other hand for a VF of 10% and a mean aggregate diameter of 5.7 nm, one obtains $\langle r \rangle = 11.1$ nm and $T^* \approx 100$ K, which is close to the fitted value in Fig. 2.16. Thus the aggregate diameters and dipolar interaction energies yielded by the scheme outlined above are consistent with each other. An aggregate with a diameter of 5.7 nm consists of around six to seven of the constituent nanoparticles. These are exchange coupled into single supermoments that interact with each other via dipolar forces.

The magnetic isotherms obtained at low temperature (T = 2 K) form the same films as used for Fig. 2.15, are plotted in Fig. 2.17, and reveal the appearance of hysteresis. An important feature of the data is that the remanence remains close to 50% so that assuming the above picture, that is, aggregates coupled together to form supermoments, the anisotropy of the aggregates is uniaxial and the data between saturation and remanence can be fitted using Eq. 2.7 to extract the magnitude, K, of the aggregate anisotropy as a function of VF using the procedure described in Section 2.3.2. The values are indicated on the figure and show a reducing value of K with VF. This is expected due to an averaging of the individual cluster anisotropies to produce a resultant value along the anisotropy axis of the whole aggregate. In addition areal decrease in the intracluster magnetocrystalline anisotropy may be expected as a result of a decreasing orbital moment with increasing nanoparticle density, as shown by previous XMCD measurements of exposed Fe clusters on graphite [70].

Also shown in Fig. 2.17 are the results of an MC model that includes both dipolar and exchange forces, which shows fairly good agreement with the measurements and in particular is able to predict the observed increase in the coercive field with the VF (inset).



Figure 2.17 Magnetic isotherms at T = 2 K of 3 nm diameter Fe nanoparticles embedded in Ag as a function of VF (dots). The values of anisotropy, *K* are obtained by fitting the approach to saturation (thick lines) by the procedure described in the text. MC modeling that includes exchange and dipolar interactions has been used to determine the entire hysteresis loop (thin lines). The inset shows the measured (open circles) and predicted (line) variation in the coercive field with VF. The parameter *b* obtained from the MC model at zero field, Eq. 2.17, indicates the influence of exchange forces and can take values between 1 (no exchange) and 0.5 (exchange dominates). Reproduced with permission from Ref. [12].

The MC model can be used to determine how the influence of exchange varies with VF by evaluating the global parameter

$$b = \frac{1}{N} \sum_{i} \hat{s}_{i} \cdot \hat{e}_{i}$$
, (2.17)

in zero field at T = 0, where S_i and e_i are the unit vectors along the magnetic moment and anisotropy axis of particle *i*. Thus in the absence of exchange interactions and thermal fluctuations, every nanoparticle moment would point along the local anisotropy axis, giving b = 1. In an assembly with a random distribution of anisotropy axes in which exchange is dominant, b = 0.5. At each VF in Fig. 2.17 the value of *b* at H = 0 obtained is indicated by the respective curve and shows a steady reduction from b = 0.89 at a VF of 0.8% (exchange unimportant) to b = 0.54 at a VF of 19% (exchange dominant).

Thus in the VF range up to the percolation threshold a clear picture of the magnetic behavior of embedded \sim 3 nm diameter nanoparticle assemblies emerges. At the limit of low VF, each nanoparticle has a uniaxial anisotropy, with an anisotropy constant in the range $2-3 \times$ 10^{5} Im⁻³ for Fe and around 7–8 × 10^{5} Im⁻³ for Co. At temperatures above 50 K in the case of Fe nanoparticles and above 100 K for Co nanoparticles the system displays ideal superparamagnetism. As the VF is increased to values in the range 10%, the assembly can be considered to be aggregates of a few nanoparticles, where the nanoparticle moments within each aggregate are aligned by exchange and the aggregates have a uniaxial anisotropy. The anisotropy constant is less than the isolated particle value and decreases with the size of the aggregate. The measured remanence of 50% indicates that the anisotropy axes of the aggregates are randomly aligned. The aggregates experience a significant dipolar interaction between them, and the magnetic behavior in this VF range has been labeled "interacting superparamagnetic" [66]. An illustration of the magnetic moments in the isolated particles and in 10% VF assemblies is shown in Fig. 2.18.

With further increases in the VF toward the percolation threshold the assembly gradually evolves into an exchange-coupled network, as indicated by parameter b tending to b = 0.5. Above the percolation threshold, simple intuitive pictures are absent till the formation of a correlated superspin glass (Section 3.2.2), and the properties can only be understood with reference to an accurate MC model. At VFs 78 Controlling the Structure and Properties of Nanostructured Magnetic Materials



Figure 2.18 Schematic of Fe nanoparticle assemblies dispersed in Ag with a uniaxial anisotropy and a random orientation of the anisotropy axes at T = 0 and zero field. (a) 1% VF: the MC model yields b = 0.89, Eq. 2.17, indicating that all the particle moments are oriented close to the local anisotropy axis. (b) 10% VF: Eq. 2.14 indicates that the deposited nanoparticles from aggregates containing on average about 7 particles and the MC model give b = 0.63, indicating that the aggregates are strongly exchange-coupled to form single magnetic entities. The measured remanence of 50% shows that the aggregate moments are randomly oriented. Reproduced with permission from Ref. [12].

above 70% [23], the system forms a correlated superspin glass well described by the RA model (Section 3.2.2) in which the magnetic properties arise from the competition between interparticle exchange and intraparticle anisotropy, with dipolar interactions not playing a significant role. This is in contrast to normal bulk systems where dipolar forces lead to the formation of magnetic domains. The magnetic state of Fe nanoparticles embedded in Ag at room temperature throughout the whole VF range is illustrated in Fig. 2.19, superimposed on a plot of the measured initial susceptibility of the films [72].



Figure 2.19 Initial susceptibility of Fe nanoparticles in Ag vs. VF with an indication of regions of different magnetic behavior.

The discussion has so far focused on magnetic nanoparticles in nonmagnetic matrices; however, as mentioned in Section 2.3.1, a technologically important material is Fe nanoparticles embedded in Co matrices (and vice versa). In the case of magnetic nanoparticles embedded in magnetic matrices in which there is not a significant degree of alloying (as is the case here—see Section 2.3.1), the spaces between the magnetic nanoparticles are packed with a ferromagnetic material and exchange dominates even at low VFs. Thus it has been shown that films of Fe nanoparticles in Co matrices in the Fe VF range 5%–25% are well described by the RA model [71].

The measured saturation magnetization of films of Fe nanoparticles embedded in Co matrices and Co nanoparticles

80 Controlling the Structure and Properties of Nanostructured Magnetic Materials

embedded in Fe matrices is shown in Fig. 2.20 as a function of the Fe VF (either as nanoparticles or as the matrix) [12]. Also plotted is the SP curve, which shows the saturation magnetization of conventional FeCo alloys as a function of the Fe fraction. The alloy with a composition around $Fe_{60}Co_{40}$ shows a peak magnetization of 2.45 µB/atom, and since the 1920s this has been the highest saturation magnetization available with conventional transition metal alloys. The nanostructured film produced by embedding Fe nanoparticles in Co matrices initially shows a higher magnetization than the conventional alloy, but around the percolation threshold, the moment drops to below the SP curve and shows a value close to the weighted average of bulk Fe and Co magnetic moments. This is simply due to phase separation above the percolation threshold. The Fe-rich end can be produced as a nanostructured material by embedding Co nanoparticles in Fe matrices, and this data shows values well above the peak of the SP curve.



Figure 2.20 Saturation magnetization in μ B/atom of Fe nanoparticles embedded in Co matrices (filled circles) and Co nanoparticles embedded in Fe matrices (open circles) as a function of Fe VF. The line is the SP curve showing the magnetization of conventional FeCo alloys. Reproduced with permission from Ref. [12].

2.3.4 Producing Nanoparticle Hydrosols by Deposition of Gas-Phase Particles into Liquid Matrices

The application of nanoparticles in medicine and biology has become an important area in a diverse variety of methods ranging from in vitro biomarkers to complex in vivo theranostic nanovectors that can both detect and treat disease [73–76]. For all such applications nanoparticles need to be dispersed in a liquid matrix, preferably water. Methods have been developed to produce nanoparticles that are monodisperse (or at least have a narrow size distribution) by a large number of techniques, including chemical and biological routes [77–83]. These have the advantage that they can produce large quantities of nanoparticle suspensions relatively cheaply.

In contrast the high-vacuum gas-phase method described in this chapter produces relatively small quantities of nanoparticles in UHV and at first sight does not seem suitable for the synthesis of nanomaterials in medicine. Its overriding strength is the flexibility of nanoparticle manufacture with very tight size control. Not only is there free choice of material in the core nanoparticles, but the method can produce core-shell structures in which there is free choice of core and shell materials and independent control over the core size and shell thickness [19, 84]. It is also straightforward to use alloys in either the core [85] or the shell, and as discussed in Section 2.3.1 it is even possible to modify the internal atomic structure of the nanoparticles [22]. An important feature of a vacuum gas-phase nanoparticle source is that it can operate in UHV conditions so that either the core or the shell can be a reactive material without being converted to oxide. It is thus possible to "design" an ideal nanoparticle by modeling and then manufacturing it using the required materials with a predetermined size and structure. The main technical problem is forming a hydrosol out of the nanoparticles in the beam since the vast majority of liquids have a vapor pressure that is incompatible with UHV operation.

Various methods for depositing gas-phase nanoparticles into liquids have been tested, including the use of very-low-vaporpressure ionic liquids [86, 87]. The most versatile method, developed at the University of Leicester [19, 88], is illustrated in Fig. 2.21. A UHV nanoparticle source (in this case a sputter gas aggregation source) produces preformed nanoparticles that are deposited onto a substrate maintained at 77 K. Simultaneously a molecular beam of water is injected from outside the vacuum and directed onto the same substrate, thus forming an ice layer embedding the nanoparticles. The vapor pressure of ice at 77 K is in the range 10^{-12} – 10^{-14} mbar [89]; thus the film does not contaminate the UHV environment in the rest of the source. When the sample is finished the deposition chamber can be valved off and vented, and the sample is collected by allowing the ice to melt and collecting the water containing nanoparticles. Stable suspensions can be produced by adding a suitable ligand to the collected water [19]. Note the similarity between this method and Fig. 2.1, in which the matrix was a metal. It is essentially the same technique, except the solid matrix in this case is ice at 77 K. In principle the method could work with any liquid as long as it was maintained at a temperature at which its vapor pressure is in the UHV range.



Figure 2.21 Synthesis of a nanoparticle suspension by codepositing preformed gas-phase nanoparticles and a molecular beam of water onto a common substrate maintained at 77 K. The vapor pressure of the ice at 77 K is in the range 10^{-12} – 10^{-14} mbar [89]. Reproduced with permission from Ref. [19].

The ice layer is formed under conditions where it will be amorphous, and Fig. 2.22 shows the results of molecular dynamics modeling of Au nanoparticles impacting an amorphous ice layer. The velocity of the particles produced by a sputter gas aggregation source is not precisely known but has an upper limit of around 400 ms⁻¹ [19]. It is evident that the penetration depth increases with nanoparticle velocity, but even the fastest particles are not fully embedded, indicating that nanoparticle agglomeration is unlikely during the deposition phase. In addition the nanoparticles suffer only minimal distortion upon impact.



Figure 2.22 Molecular dynamics simulations of 5 nm diameter Au nanoparticles incident at the velocities shown, coming to rest on the amorphous ice substrate. Even the fastest particles (which represent the upper limit of possible velocities) show little damage and less than a particle diameter penetration into the substrate. Reproduced with permission from Ref. [19].

The method was used to deposit Fe nanoparticles directly into water without a protective shell, thus allowing the particles to oxidize naturally. Figure 2.23a shows bright-field (BF) transmission electron microscopy (TEM) images of Fe nanoparticles deposited onto carbon in UHV conditions and exposed to air, and in comparison Fig. 2.23c is an image of nanoparticles deposited into water in UHV conditions and extracted and dried. It is clear from the high-resolution images of individual nanoparticles from these samples (Fig. 2.23b and Fig. 2.23d) that in both cases the oxide is restricted to a 2 nm thick shell around the nanoparticles, which have a typical size of 10 nm. These nanoparticles were shown to have an exceptionally high value of the specific absorption rate of an applied ~ 100 kHz alternating current (AC) magnetic field [19], indicating that they would be particularly suited to magnetic nanoparticle hyperthermia treatment of tumors. The high performance is due to the large proportion of pure metallic Fe within each nanoparticle with a magnetic moment per atom much higher than the oxides. It is likely that the Fe oxide shell will render the nanoparticles biocompatible, though so far no toxicity tests have been done with this ferrofluid. It was also shown that suspensions of core-shell nanoparticles could also be produced by the method.



Figure 2.23 (a and b) BF-STEM images of Fe nanoparticles extracted from water with dimercapto-succinic acid and dried on a TEM grid, with each showing a pure Fe core, a thin oxide shell, and a thicker surfactant shell. (c and d) BF-STEM images of Fe nanoparticles deposited in vacuum directly onto TEM grids, allowing higher resolution. The same core-shell Fe@Fe oxide structure is observed, and a lattice spacing corresponding to bulk bcc Fe is visible in the core. *Abbreviation*: STEM, scanning transmission electron microscopy.

References

- 1. De Heer, W. A. (1993). Rev. Mod. Phys., 65(3), 611-676.
- 2. Milani, P., Iannotta, S. (1999). *Cluster Beam Synthesis of Nanostructured Materials*, Springer, Berlin.
- 3. Binns, C. (2001). Surf. Sci. Rep., 44(1-2), 1-49.

- Binns, C. (2008). Cluster/island production, in *Metallic Nanoparticles* (Blackman, J., ed.), Elsevier.
- Knight, W. D., Clemenger, K., de Heer, W. A., Saunders, W. A., Chou, M. Y., Cohen, M. L. (1984). *Phys. Rev. Lett.*, **52**(24), 2141–2143.
- Sakurai, M., Watanabe, K., Sumiyama, K., Suzuki, K. (1999). J. Chem. Phys., 111(1), 235–238.
- Billas, I. M. L., Chtelain, A., de Heer, W. A. (1994). Science, 265, 1682– 1684.
- Billas, I. M. L., deHeer, W. A., Chatelain, A. (1994). J. Non-Cryst. Sol., 179, 316–323.
- Billas, I. M. L., Becker, J. A., Chatelain, A., deHeer, W. A. (1993). *Phys. Rev. Lett.*, **71**(24), 4067–4070.
- Cox, A. J., Louderback, J. G., Apsel, S. E., Bloomfield, L. A. (1994) *Phys. Rev. B*, **49**(17), 12295–12298.
- Perez, A., Melinon, P., Dupuis, V., Jensen, P., Prevel, B., Tuaillon, J., Bardotti, L., Martet, C., Treilleux, M., Broyer, M., Pellarin, M., Vialle, J. L., Palpant, B., Lerme, J. (1997). *J. Phys. D: Appl. Phys.*, **30**(5), 709–721.
- Binns, C., Trohidou, K. N., Bansmann, J., Baker, S. H., Blackman, J. A., Bucher, J.-P., Kechrakos, D., Kleibert, A., Louch, S., Meiwes-Broer, K.-H., Pastor, G. M., Perez, A., Xie, Y. (2005). *J. Phys. D: Appl. Phys.*, 38(22), R357–R379.
- Haberland, H., Insepov, Z., Moseler, M. (1995). *Phys. Rev. B*, **51**(16), 11061–11067.
- Baker, S. H., Roy, M., Gurman, S. J., Louch, S., Bleloch, A., Binns, C. (2004). J. Phys.: Condens. Matter, 16(43), 7813 –7821.
- 15. Getzlaff, M., Kleibert, A., Methling, R. P., Bansmann, J., Meiwes-Broer, K.-H. (2004). *Surf. Sci.*, **566–568**(1), 332–336.
- Dupuis, V., Favre, L., Stanescu, S., Tuaillon-Combes, J., Bernstein, E., Perez, A. (2004). *J. Phys.: Condens. Matter*, **16**(22), S2231–S2240.
- Peng, D. L., Sumiyama, K., Hihara, T., Yamamuro, S., Konno, T. J. (2000). *Phys. Rev. B*, **61**(4), 3103–3109.
- Kholmanov, I. N., Barborini, E., Vinati, S., Piseri, P., Podesta, A., Ducati, C., Lenardi, C., Milani, P. (2003). *Nanotechnology*, 14(14), 1168–1173.
- Binns, C., Prieto, P., Baker, S. H., Howes, P., Dondi, R., Burley, G., Lari, L., Kröger, R., Pratt, A., Aktas, S., Mellon, J. K. (2012). *J. Nanopart. Res.*, 14(9), 1136.
- Binns, C., Howes, P. B., Baker, S. H., Marchetto, H., Potenza, A., Steadman, P., Dhesi, S. S., Roy, M., Everard, M. J., Rushforth, A. (2008). *J. Phys.: Condens. Matter*, **20**(5), 05521.

- Binns, C., Sirotti, F., Gruegel, H., Prieto, P., Baker, S. H., Thornton, S. C. (2003). J. Phys: Condens. Matter, 15(25), 4287–4299.
- 22. Baker, S. H., Roy, M., Thornton, S. C., Binns, C. (2012). J. Phys.: Condens. Matter, 24(17), 176001 (8pp).
- Binns, C., Maher, M. J., Pankhurst, Q. A., Kechrakos, D., Trohidou, K. N. (2002). *Phys. Rev. B*, 66(18), 184413.
- 24. Koch, S. A., teVelde, R. H., Palasantzas, G., De Hosson, J. Th. M. (2004). *Appl. Surf. Sci.*, **226**, 185–190.
- Yoon, B., Akulin, V. M. Cahuzac, Ph., Carlier, F., de Frutos, M., Masson, A., Mory, C., Colliex, C., Bréchignac, C. (1999). *Surf. Sci.*, 443(1–2), 76–88.
- Xie, Y., Blackman, J. (2004). J. Phys.: Condens. Matter, 16(18), 3163– 3172.
- 27. Binns, C., Maher, M. J. (2002). New J. Phys., 4, 85.1-85.15.
- Chudnovsky, E. M., Saslow, W. M., Serota, R. A. (1986). *Phys. Rev. B*, 33(1), 251–261.
- 29. Saslow, W. M. (1987). Phys. Rev. B, 35(7), 3454-3460.
- 30. Chudnovsky, E. M. (1988). J. Appl. Phys., 64(10), 5770-5775.
- 31. Chudnovsky, E. M. (1995). *The Magnetism of Amorphous Metalsand Alloys* (Fernandez-Baca, J. A., Ching, W-Y., eds.) Vol. 80, Springer Series in Solid-State Sciences, World Scientific, Singapore.
- Koch, S. A., Palasantzas, G., Vystavel, T., De Hosson, J. Th. M., Binns, C., Louch, S. (2005). *Phys. Rev. B*, **71**(8), 085410.
- Binns, C., Baker, S. H., Louch, S. (2007). J. Magn. Magn. Mater., 312(2), 379–385.
- Baker, S. H., Roy, M., Louch, S., Binns, C. (2006). *J.Phys: Condens. Matter*, 18(8), 2385–2399.
- Domingo, N., Testa, A. M., Fiorani, D., Binns, C., Baker, S. H., Tejada, J. (2007). *J. Magn. Magn. Mater.*, **316**(2), 155–158.
- Domingo, N., Fiorani, D., Testa, A. M., Binns, C., Baker, S. H., Tejada, J. (2008). *J. Phys. D*, **41**(13), 134009.
- Binns, C., Domingo, N., Testa, A. M., Fiorani, D., Trohidou, K. N., Vasilakaki, M., Blackman, J. A., Asaduzzaman, A. M., Baker, S. H., Roy, M., Peddis, D. (2010). *J. Phys.: Condens. Matter*, **22**(43), 436005.
- Laureti, S., Peddis, D., Del Bianco, L., Testa, A. M., Varvaro, G., Agostinelli,
 E., Binns, C., Baker, S. H., Fiorani, D. (2012). *J. Magn. Magn. Mater.*,
 324(21), 3503–3507.
- Iles, G. N., Binns, C., Baker, S. H., Roy, M. (2010). *J. Magn. Magn. Mater.*, 322(17), 2509–2515.

- 40. Baker, S. H., Asaduzzama, A. M., Roy, M., Gurman, S. J., Binns, C., Blackman, J. A., Xie, Y. (2008). *Phys. Rev. B*, **78**(1), 014422.
- 41. Gradmann, U., Isbert, H. O. (1980). *J. Magn. Magn. Mater.*, **15–18**(2), 1109–1111.
- 42. Vegard, L. (1921). Z. Phys., 5(1), 17-26.
- 43. Denton, A. R., Ashcroft, N. W. (1991). Phys. Rev. A, 43(6), 3161-3164.
- 44. Qureshi, M. T., Baker, S. H., Binns, C., Peddis, D., (2013) J. Magn. Magn. Mater., (unpublished).
- 45. Iles, G. N., Binns, C., Baker, S, H., Roy, M. (2010). *J. Magn. Magn. Mater.*, **322**(17), 2509–2515.
- Binns, C., Domingo, N., Testa, A. M., Fiorani, D., Trohidou, K. N., Vasilakaki, N., Blackman, J. A., Asaduzzaman, A. M., Baker, S. H., Roy, M., Peddis, D. (2010). *J. Phys.: Condens. Matter*, **22**(43), 436005.
- 47. Bai, J., Wang, J.-P. (2005). App. Phys. Lett., 87(15), 152502.
- Jackson, T. J., Binns, C., Forgan, E. M., Morenzoni, E., Niedermayer, Ch., Glückler, H., Hofer, A., Luetkens, H., Prokscha, T., Riseman, T. M., Schatz, A., Birke, M., Litterst, J., Schatz, G., Weber, H. P. (2000). *J. Phys: Cond. Matter*, **12**(7), 1399–1411.
- 49. Chudnovsky, E. M., Tejada, J. (1998). *Macroscopic Quantum Tunneling* of the Magnetic Moment, Cambridge University Press, U.K.
- 50. Chudnovsky, E. M., Friedman, J. R. (2000). *Phys. Rev. Lett.*, **85**(24), 5206.
- 51. Upward, M. D., Cotier B. N., Moriarty, P., Beton, P. H., Baker, S. H., Binns, C., Edmonds, K. W. (2000). *J. Vac. Sci. Technol. B*, **18**(6), 2646–2650.
- Gittelman, J. J., Abelas, B., Bozowski, S. (1974). *Phys. Rev. B*, 9(9), 3891– 3897.
- 53. Fiorani, D., Tholence, J. L., Dormann, J. L. (1981). *Physica B*, **107**(1–3), 643–644.
- Dormann, J. L., Bessais, L., Fiorani, D. (1988). J. Phys. C, 21(10), 2015– 2034.
- 55. Luo, W., Nagel, S. R, Rosenbaum, T. F., Rosensweig, R. E. (1991). *Phys. Rev. Lett.*, **67**(19), 2721–2724.
- Chantrell, R. W., El-Hilo, M., O'Grady, K. (1991). *IEEE Trans. Magn.*, 27(4), 3570–3578.
- El-Hilo, M., O'Grady, K., Chantrell, R. W. (1992). J. Magn. Magn. Mater., 114(3), 295–306.
- Gangopadhyay, S., Hadjipanayis, G. C., Sorensen, C. M., Klabunde, K. J. (1993). *IEEE Trans. Magn.*, **29**(6), 2619–2621.

- O'Grady, K., El-Hilo, M., Chantrell, R. W. (1993). *IEEE Trans. Magn.*, 29(6), 2608–2613.
- 60. Mørup, S., Tronc, E. (1994). Phys. Rev. Lett., 72(20), 3278-3281.
- Mørup, S., Bodker, F., Hendriksen, P. V., Linderoth, S. (1995). *Phys. Rev. B*, **52**(1), 287–294.
- 62. Djurberg, C., Svedlindh, P., Nordblad, P., Hansen, M. F., Bødker, F., Mørup, S. (1997). *Phys. Rev. Lett.*, **79**(25), 5154–5157.
- 63. Jonsson, T., Svedlindh, P., Hansen, M. F. (1998). *Phys. Rev. Lett.*, **81(**18**)**, 3976–3979.
- Dormann, J. L., Fiorani, D., Cherkaoui, R., Tronc, E., Lucari, F., D'Orazio, F., Spinu, L., Nogues, M., Kachkachi, H., Jolivet, J. P. (1999). *J. Magn. Magn. Mater.*, **203**(1–3), 23–27.
- Kleemann, W., Petracic, O., Binek, Ch., Kakazei, G. N, Pogorelov, Yu. G., Sousa, J. B., Cardoso, S., Freitas, P. P. (2001). *Phys. Rev. B*, 63(13), 134423.
- Allia, P., Coisson, M., Tiberto, P., Vinai, F., Knobel, M., Novak, M. A., Nunes, W. C. (2001). *Phys. Rev. B*, 64(14), 144420.
- Ucko, D. H., Pankhurst, Q. A., Barquin, L. F., Fernández, J. R., Cos, S. F. J. (2001). *Phys. Rev. B*, 64(10), 104433.
- 68. Dimitrov, D. A., Wysin, G. M. (1996). Phys. Rev. B, 54(13), 9237-9241.
- 69. Kechrakos, D., Trohidou K. N. (2000). Phys. Rev. B, 62(6), 3941-3951.
- Edmonds, K. W., Binns, C., Baker, S. H., Thornton, S. C., Norris, C.,Goedkoop, J. B., Finazzi, M., Brookes, N. B. (1999). *Phys. Rev. B*, 60(1), 472–476.
- 71. Qureshi, M. (2012). *Nanostructured Magnetic Films Produced by Magnetic Nanoparticles*, PhD thesis, University of Leicester.
- Binns, C., Maher, M. J., Baker, S. H., Louch, S. C., Thornton, S. C., Dhesi, S. S., Brookes, N. B. (2003). *IEE Proc. Sci. Meas. Tech.*, **150**(5), 247–251.
- 73. Rosi, L., Mirkin, C. A. (2005). Chem. Rev., 105(4), 1547-1562.
- Haun, J. B., Yoon, T.-J., Lee, H., Weissleder, R. (2010). Nanomed. Nanobiotech., 2(3), 291–304.
- Solokov, K., Follen, M., Aaron, J., Pavlova, I., Malpica, R., Lotan, R., Richards-Kortum, R. (2003). *Cancer Res.*, 63(9), 1999–2004.
- 76. Binns, C. (2010). Chapter 6, in *Introduction to Nanoscience and Nanotechnology*, Wiley.
- 77. Hyeon, T. (2003). Chem. Commun., 2003(8), 927-934.
- Sun, S., Murray, C, B, Weller, D., Folks, L., Moser, A. (2000). Science, 287(5460), 1989–1992.

- Boatman, E. M., Lisensky, G. C., Nordell, K. J. (2005). J. Chem. Edu., 829(11), 1697–1699.
- Garcia-Martinez, J. C., Scott, R. W. J., Crooks, R. M. (2003). J. Am. Chem. Soc., 125(37), 11190–11191.
- Tsang, E. (2008). Synthesis of clusters and nanoparticles by chemical methods, in *Metallic Nanoparticles (Handbook of Metal Physics)*, (Blackman, J., ed.), Vol. 5, Elsevier.
- Coker, V. S., Telling, N. D., Van Der Laan, G., Pattrick, R. A. D., Pearce, C. I., Arenholz, E., Tuna, F., Winpenny, R. E. P., Lloyd, J. R. (2009). *ACS Nano*, 3(7), 1922–1928.
- Narayanan, K. B., Sakthivel, N. (2010). Adv. Colloid Interface Sci., 156 (1-2), 1-13.
- Baker, S. H., Roy, M., Qureshi, M., Binns, C. (2010). J. Phys: Condens. Matter, 22(38), 385301.
- Bouwen, W.Thoen. P., Vanhoutte, F., Bouckaert, S., Despa, F., Weidele, H., Silverans, R. E., Lievens, P. (2000). *Rev. Sci. Instrum.*, 71(1), 54–58.
- Hamm, S. C., Shankaran, R., Korampally, V., Bok, S., Praharaj, S., Baker,
 G. A., Robertson, J. D., Lee, B. D., Sengupta, S., Gangopadhyay, K.,
 Gangopadhyay, S. (2012). ACS Appl. Mater. Interfaces, 4(1), 178–184.
- Vanecht, E., Binnemans, K., Seo, J.-W., Stappers, L., Fransaer, J. (2011). *Phys. Chem. Chem. Phys.*, **13**(30), 13565–13571.
- Von Haeften, K., Binns, C., Brewer, A., Crisan, O., Howes, P. B., Lowe, M. P., Sibbley-Allen, C., Thornton, S. C. (2009). *Eur. Phys. J. D*, 52(1–3), 11–14.
- 89. Kouchi, A. (1987). Nature, 330, 550-552.

Chapter 3

Time-Dependent Phenomena in Nanoparticle Assemblies

Òscar Iglesias

Departament de Física Fonamental and IN²UB, Universitat de Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain oscar@ffn.ub.es

Magnetic nanoparticle assemblies are difficult systems to model due to the interplay between intrinsic and collective effects. The first ones are associated with the magnetic properties of an individual particle and require considering the atomic spins of the magnetic ions, their mutual exchange interactions, and magnetocrytalline anisotropy. Due to its finite size, an individual particle has magnetic properties different from the bulk counterpart material. Moreover, the high proportion of surface spins with reduced coordination influences the equilibrium magnetic configuration of an individual particle, with spin noncollinearities being a consequence of the distinct surface anisotropy. The collective effects have to do with interactions among the nanoparticles in an ensemble, such as long-range dipole-dipole interactions, and can be tackled more easily by considering each nanoparticle as one effective spin having the magnitude of the total magnization of the particle. Therefore, at this level of description, nanoparticle ensembles can be modeled by a collection of macrospins having their own anisotropy axes and interacting through dipolar interactions, neglecting their internal structure, which in turn is equivalent to assuming that the interactomic exchange coupling is strong enough to keep atomic magnetic ions aligned along the global magnetization direction. Whereas in atomic magnetic materials the exchange interaction usually dominates over dipolar interactions, the opposite happens in many nanoscale particle or clustered magnetic systems, for which interparticle interactions are mainly of dipolar origin. Therefore, one-spin (OSP) models should, in principle, provide a correct description of noninteracting systems and, to a first approximation, be valid also to account for the main features observed in more concentrated samples where interactions cannot be neglected. It has been shown also recently [17, 54] that spin noncollinearities due to surface anisotropy can even be incorporated within the OSP approach if an effective cubic anisotropy term is added to the original uniaxial anisotropy energy. However, incorporation of dipolar interactions along these lines does not seem feasible within the present theoretical frameworks.

While we have a valid theoretical framework to compute equilibrium magnetic properties for noninteracting systems (such as thermal dependence M(T), isothermal field dependence M(H), and low-temperature configurations), analytically or numerically within the scope of OSP models [19] models including dipolar interactions can only compute these quantities using perturbative thermodynamic theory and, even so, anaytical expressions can only be obtained under certain limits and approximations. In contrast, dynamic properties [such as hysteresis loops, field-cooled-zero-field-cooled (FC-ZFC) processes, susceptibility, or magnetic relaxation] are nonequilibrium phenomena for which a unique theoretical framework covering the wide range of time scales involved is not available, even for noninteracting systems. Therefore, most studies on dynamics revert to numerical simulations of ensembles of macrospins [3, 14, 15, 18, 26, 46, 50, 52] based on

Monte Carlo (MC) methods, since simulations based on the Landau– Lifschitz equation cannot access the long time scales involved in these phenomena.

The main difficulty in modeling the long-time dynamics of magnetic nanoparticle ensembles is the calculation of the relaxation rates between metastable states as they depend on the energy barriers that have to be overcome by thermal fluctuations and, consequently, they depend on the orientation of the nanoparticle easy axis with respect to the field axis. At the same time, the presence of interparticle interactions modifies in a complex manner the energy landscape due to the long-range character of the dipolar interactions, and several escape paths out of a metastable minimum may coexist. Therefore, in general, the energy barriers responsible for the thermal relaxation of the nanoparticle ensemble toward equilibrium cannot be computed analytically and numerical simulations have to be used.

While dilute systems are well understood, experimental results for dense systems are still a matter of controversy. Some of their peculiar magnetic properties have been attributed to dipolar interactions, although many of the issues are still controversial. Different experimental results measuring the same physical quantities give contradictory results, and theoretical explanations are many times inconclusive or unclear. In the following section, we briefly outline some of the issues that are still under debate:

 The complexity of dipolar interactions and the frustration provided by the randomness in particle positions and anisotropy axes directions present in highly concentrated ferrofluids seem enough ingredients to create a collective glassy dynamics in these kinds of systems. Experiments probing the relaxation of the thermoremanent magnetization [23, 24, 35] have evidenced magnetic aging. Studies of the dynamic and nonlinear susceptibilities [10, 24, 27] have also found evidence of a critical behavior typical of spin-glass-like freezing. All these studies have attributed this collective spin-glass behavior to dipolar interactions, although surface exchange may also be at the origin of this phenomenon. However, MC simulations of a system of interacting monodomain particles [18] show that, while the dependence of ZFC/FC curves on interaction and cooling rates are reminiscent of a spin-glass transition at $T_{\rm B}$, the relaxational behavior is not in accordance with the picture of cooperative freezing.

- 2. It is still not clear what the dependence of the blocking temperature and remanent magnetization with concentration, ε , in ferrofluids is. While most experiments [6, 7, 11, 13, 16, 18, 32, 42] find an increase of $T_{\rm B}$ and a decrease of $M_{\rm R}$ with ε , others [38, 39] observe the contrary variation in similar systems.
- 3. The dependence of the effective energy barriers with concentration is unclear. While theoretical studies by the group of Dormann [11, 12] and experimental results by Luis [31] on Co clusters predict an increase of the barriers for magnetization reversal, Mørup [39] et al. argue for a reduction of $T_{\rm B}$ with ε .
- 4. Although magnetic hysteresis is usually reported in experimental studies of nanoparticle ensembles for a wide range of sizes and concentrations and varied compositions, a general theoretical framework able to account for the observed phenomenology is still lacking. However, we can say that, in general, for disordered systems, the dipolar interaction diminishes the coercive field and decreases the remanent magnetization [6, 16].

In this contribution, we will review of our works on the time dependence of magnetization in nanoparticle systems, starting from noninteracting systems, presenting a general theoretical framework for the analysis of relaxation curves, which is based on the so-called scaling method. We will detail the basics and explain its range of validity, showing also its application in experimental measurements of magnetic relaxation. We will also discuss how it can be applied to determine the energy barrier distributions responsible for relaxation. Next, we will show how the proposed methodology can be extended to include dipolar interactions between nanoparticles. A thorough introduction of the method will be presented and exemplified for a 1D chain of interacting spins, with emphasis on showing the microscopic origin of the observed macroscopic time dependence of the magnetization. Experimental application examples will be given, showing that the validity of the method is not limited to a 1D case.
3.1 Magnetic Relaxation in Noninteracting Nanoparticle Ensembles

Let us consider a general magnetic system, not necessarily a system of small particles. We will only assume that, whatever is the underlying microscopic model used to describe it, it can be thought in terms of effective energy barriers that separate the metastable states of the appropriate degrees of freedom of the constituents. Therefore, we will be thinking now of a magnetic system as a collection of energy barriers *E* that can be characterized by a certain distribution function f(E), which contains the specific composition of the system. We are interested in the time dependence of the order parameter m(t), which we will call magnetization thinking in applications to small-particle systems. In particular, in single-domain particles and granular materials, the energy barriers due to anisotropy are, in principle, proportional to the volume of the particle or grain. In this case, f(E) reflects the scattering of particle volumes or anisotropy constants. It should be noted that using a distribution of energies or of relaxation times is better and more general than using a distribution of volumes or particle sizes, since in this way no assumption about the relation between these parameters has to be made.

The decay of the magnetization of a distribution of single-domain particles is given by the relaxation law

$$m(t) = \int_0^\infty dE \ f(E) e^{-t/\tau(E)}$$
(3.1)

where f(E) is the distribution function of energy barriers that have to be overcome by thermal fluctuations in order to change the equilibrium magnetization direction of the particles. The exponential factor is the classical Boltzmann probability for a particle to change its equilibrium magnetization value, and $\tau(E)$ is the relaxation time used in Neél's theory [40], given by

$$\tau(E) = \tau_0 e^{E/k_{\rm B}T} \tag{3.2}$$

where $1/\tau_0$ is an attempt frequency of the order $10^8 - 10^{12}$ s⁻¹, k_B the Boltzmann constant, and *T* the temperature.

Let us introduce the function p(t, E) defined by

$$p(t, E) = e^{-(t/\tau_0)\exp(-E/k_B T)}$$
(3.3)

Taking into account that p(t, E), for a given time t, varies abruptly from 0 to 1, as the energy barrier E increases, the usual simplification [51] consists on approximating p(t, E) by a step function whose discontinuity $E_{\rm C}(t)$ moves to higher values of E as time elapses. As a consequence, the integral is cut off at the lower limit by the value of $E_{\rm C}(t)$, which is the only time-dependent parameter, and the expression 3.1 is approximated by [28]

$$m(t) \simeq \int_{E_{\mathbb{C}}(t)}^{\infty} dE f(E) \,. \tag{3.4}$$

 $E_{\rm C}(t)$ corresponds to the energy barrier value for which the function p(t, E) has the inflection point and is given by

$$E_{\rm c} = k_{\rm B} T \ln(t/\tau_0). \tag{3.5}$$

From Eq. 3.4, we conclude that the remanent magnetization M(t) obtained after integration over the energy barriers E is a function of the parameter $E_{\rm C}(t) = k_{\rm B}T \ln(t/\tau_0)$. The existence of this scaling variable implies that measuring the magnetization as a function of temperature at a given time is equivalent to measuring the magnetization as a function of $\ln(t)$ at a fixed temperature. This time-temperature correspondence is characteristic of activated processes governed by the Arrhenius law.

Moreover, in [21] we demostrated that the logarithmic relaxation rate $S(t) = \frac{\partial M(t)}{\partial (\ln(t))}$ (also called magnetic viscosity) is related to the

energy barrier distribution through the expression

$$S(t) = k_{\rm B} T f(\overline{E}_{\rm c}) (1 + S^{(1)} + S^{(2)} + \cdots),$$
(3.6)

where $S^{(n)}$ is proportional to $(k_{\rm B}T/\sigma)^n$, σ being the characteristic width of the energy barrier distribution. Therefore, at low enough temperatures, the corrections introduced by the $S^{(n)}$ terms can be neglected and the magnetic viscosity becomes directly proportional to the distribution of energy barriers.

Magnetic relaxation experiments are limited to a range of at most four decades in time, but during this range of times the magnetization of most physical systems only varies in a small percentage of the initial value, so the range of energy barriers explored during the experiment is limited to a small fraction of the real distribution f(E). This is so because of the spread of the physical properties of the systems and the exponential variation of the relaxation times with the energy. So, it would be interesting to find a method to extend the experimental relaxation curves to much longer times without having to perform impossibly long measurements. This is what the phenomenological $T \ln(t/\tau_0)$ scaling pretends.

The method relies on the fact that under certain conditions there is a natural scaling variable in the relaxation law that relates temporal to temperature scales, thus making it possible to deduce relaxation curves at long times and a given temperature from the knowledge of the short time relaxations at different higher temperatures. The idea ressembles that found in earlier works by Préjean et al. in the context of relaxation in spin glasses at the beginning of the 1980s [44].



Figure 3.1 Illustration of the origin of the $T \ln(t/\tau_0)$ scaling for relaxation curves at different *T*. (a) Relaxations curves at different *T* (the lowest *T* is for the uppermost curve) in a logarithmic time scale, as measured in an experiment. (b) Details of low, medium, and high *T* curves. The dashed lines correspond to logarithmic time dependence; departures from this law are clearly seen at low and high *T*. (c) Diagram showing the fraction of energy barriers that contribute to the relaxation curves in (b).

In order to illustrate its origin, let us start from a real experimental example. Let us consider a set of relaxation curves measured at different temperatures, as the ones displayed in Fig. 3.1a. At first glance, they all seem to follow a logarithmic law. One is even tempted to make linear fits, which probably would be accurate enough, and that is what is usually done in the literature [49]. But let us make a closer inspection of every particular curve. In Fig. 3.1b we have selected low, intermediate, and high temperature curves and plotted them separately. It can be clearly seen that only at intermediate temperatures the curves are straight lines corresponding to a logarithmic law but that, at high and low *T*, they are curved downward and upward, respectively, showing a clear deviation from a logarithmic law.

In order to understand this change of curvature, let us notice that during the time of the experiment only a small fraction of all the energy barriers of the system is sampled. Moreover, this fraction is not the same at different temperatures. The typical energy barriers explored during the measuring time of the experiment, $t_{\rm m}$, are of the order of $E_m = T \ln(t_m/\tau_0)$ and therefore, proportional to the temperature. So that relaxation curves at different temperatures are not directly comparable, because they collect results from different portions of the energy barrier distribution of the system. As Fig. 3.1c illustrates, the low-temperature curve samples the low-energy part of the energy barrier distribution f(E), at intermediate temperatures the mean energy barriers are explored, and at high temperatures the high-energy part of f(E) is sampled. Moreover, this explains why only relaxations at intermediate temperatures are logarithmic, since, in this range, the fraction of barriers explored are near the maximum of the distribution where f(E) is almost flat. The curvature of the relaxation curves is, therefore, directly related to the curvature of the energy distribution. This clearly indicates that, even though all the measurements have been performed during the same time window, the energy barriers responsible for the relaxation are not the same at every temperature.

To verify the validity of the $T \ln(t/\tau_0)$ scaling law in real smallparticle systems, a sample was cooled from above the blocking to the measurement temperature under a magnetic field, the magnetic relaxation was measured after switching off the field and subsequently analyzed within the scope of the scaling hypothesis [28]. According to the scaling hypothesis discussed previously, all the different curves corresponding to different temperatures should scale onto one single master curve when plotted as a function of the scaling variable $T\ln(t/\tau_0)$. In order to verify the validity of this model, we tried to scale the relaxation data of the referred samples. The procedure used for this purpose consists of plotting the relaxation curves in an *M* vs $\ln(t)$ plot and trying to connect each of them continuously with the adjoining curves corresponding to the nearest measured temperatures. To do that, we shifted the experimental curves in the *T* $\ln(t)$ axis by an amount equal to $T \ln(\tau_0)$, where τ_0 is a characteristic time that governs the relaxation processes on an atomic scale. τ_0 is the same for all the measured temperatures, and it was chosen to be the best in bringing all the curves into one.



Figure 3.2 (Left) Master curve obtained by $T \ln(t/\tau_0)$ scaling of the relaxation curves for a ferrofluid composed of FeC particles [28]. The figure shows reduced magnetization as a function of the scaling variable. The corresponding temperatures are indicated above the corresponding interval. The solid line is the theoretical curve calculated by using Eq. 3.1. (Right) Numerical derivative of the master curve with respect to the scaling variable (open circles) and the energy distribution functions as obtained by fitting the master relaxation curve to the expression (3.1), assuming a single logarithmic-normal distributions. The differential of the thermoremanence relative to the saturation magnetization versus the temperature is also shown in full circles for comparison.

In Fig. 3.2 the results of this scaling are shown. One of the most interesting aspects of these results is that, in fact, measuring the relaxation at a given temperature is completely equivalent to measuring it at a different temperature but shifting the observation

time window according to the law $T \ln(t/\tau_0)$. In this sense, the method enables us to obtain the relaxation curve at a certain temperature. in a time range that is not experimentally accessible, by simply rescaling the $T \ln(t/\tau_0)$ axis by this temperature. In this particular example, we can obtain the relaxation curve at the lowest measured temperature of 1.8 K at a time as large as 10^{119} s, which is obviously inaccessible experimentally. For sample 1, where the highest temperature that we have measured was 37 K, we are observing the relaxation curve corresponding to 2 K at a time as large as 10^{173} s. According to the expression 3.6, viscosity is a function of the scaling variable $T \ln(t/\tau_0)$ and it is proportional to T. So, if we plot *S*/*T* as a function of $T \ln(t/\tau_0)$ at low enough temperatures, the resulting curve will be the energy distribution function of the sample. As it has already been mentioned, it is not possible to obtain an experimental relaxation curve covering enough time decades to map the whole energy barrier distribution at any temperature. However, the master curve can be used to obtain the relaxation curve at the lowest-measured temperature extrapolated to experimentally inaccessible times. We have obtained S by making the numerical derivative of the master curve. The results are shown in Fig. 3.2, where we also show the derivative of the thermoremanence relative to the saturation magnetization versus the temperature (dM_r/dT) [29], which is known to be proportional to the distribution function of blocking temperatures [7] and consequently to the distribution function of energy barriers. The results obtained by the two methods are in very good agreement.

One way to check the self-consistency of the method is to compare f(E) as obtained from the viscosity with the one obtained by fitting the master relaxation curve to Eq. 3.1, assuming only a logarithmic-linear distribution of energy barriers. The resulting distribution function is shown in Fig. 3.2 in dashed lines.

3.2 Models of Interacting 1D Chains of Nanoparticles

To study the effect of long-range interactions on the dynamics of spin systems, we will start with the simplest model capturing the essential physics of the problem. Let us consider a linear chain of *N*

Heisenberg spins S_i (i = 1, ..., N), each one representing a monodomain particle with magnetic moment $\mu_i = \mu S_i$. As indicated in Fig. 3.3, each spin has uniaxial anisotropy pointing along the direction \hat{n}_i , which may be the same for all and is oriented at random, and anisotropy constants, K_i , distributed according to a distribution function f(K). An external magnetic field **H** may act on all the spins with the same value and point along the direction perpendicular to the chain. For simplicity, we will consider that particles have no internal structure, so the only interaction taken into account will be the dipolar longrange interaction. The corresponding Hamiltonian is therefore

$$\mathcal{H} = -\sum_{i=1}^{N} \left\{ K_i (\mathbf{S}_i \cdot \hat{n})^2 + \mathbf{S}_i \cdot \mathbf{H} \right\} + g \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left\{ \frac{\mathbf{S}_i \cdot \mathbf{S}_j}{\mathbf{r}_{ij}^3} - 3 \frac{(\mathbf{S}_i \cdot \mathbf{r}_{ij})(\mathbf{S}_j \cdot \mathbf{r}_{ji})}{\mathbf{r}_{ij}^5} \right\}, \quad (3.7)$$

where $g = \mu_0^2/4\pi a^3$ characterizes the strength of the dipolar energy, r_{ij} is the distance separating spins *i* and *j*, *a* is the lattice spacing, here chosen as 1.



Figure 3.3 1D chain of spins S_i with random anisotropy directions n_i .

We will consider systems with either uniform anisotropy $K_i = K_0$ = 1 or with a log-normal distribution of anisotropies, f(K), of width σ and centered at $K_0 = 1$. We will also study the effect of the random orientation of the anisotropy axis \mathbf{n}_i and compare this case with the case of aligned particles. Moreover, two different spin models will be considered:

- a. **Model I** Spins in the same (x z) plane with $\varphi_i = 0$ characterized only by the angle θ_i (see Fig. 3.4a).
- b. **Model II** Spins with 3 dimensional orientations characterized by the spherical angles θ_i , φ_i (see Fig. 3.4b).

Besides the dimensionality of the spin vector, the difference between the two models lies in the fact that for Model I it is possible to write down an algorithm to find the exact values of the minima of the energy function and the energy barriers, whereas for Model II this becomes extremely difficult since a new degree of freedom comes into play.



Figure 3.4 The two 1D models considered. (a) Model I: 1D chain of planar spins. (b) Model II: 1D chain of 3D spins.

We will consider periodic boundary conditions along the chain, so the restriction

$$\mathbf{S}_1 = \mathbf{S}_N \tag{3.8}$$

will be imposed in the simulations. In this way, we get rid of the possibility of spin reversal at the boundaries of the system because of the reduced coordination there. For this kind of boundary condition, the evaluation of dipolar fields for two dimensional or three dimensional spins would require replicating the system with several identical copies to minimize the rounding-off errors caused by the finite size of the system, but for our 1D model this will not be necessary.

The effect of dipolar interaction can be more easily understood if we define the dipolar fields acting on each spin *i* (see Fig. 3.5)

$$\mathbf{H}_{i}^{dip} = -\sum_{j \neq i}^{N} \left\{ \frac{\mathbf{S}_{j}}{\mathbf{r}_{ij}^{3}} - 3 \frac{(\mathbf{S}_{j} \cdot \mathbf{r}_{ji})\mathbf{r}_{ij}}{\mathbf{r}_{ij}^{5}} \right\}$$
(3.9)

and so, by rewriting the dipolar energy as

$$\mathcal{H}_{\rm dip} = -g \sum_{i=1}^{\rm N} \mathbf{S}_i \cdot \mathbf{H}_i^{\rm dip}, \qquad (3.10)$$

the total energy of the system can be expressed in the simpler form

$$\mathcal{H} = -\sum_{i=1}^{N} \left\{ K_i (\mathbf{S}_i \cdot \hat{n}_i)^2 - (\mathbf{S}_i \cdot \mathbf{H}_i^{\text{eff}}) \right\}.$$
(3.11)



Figure 3.5 Definition of the dipolar field H_{ij}^{dip} generated by the spin S_j on the spin S_i .

Now, the system can be thought as an ensemble of noninteracting spins feeling an effective field which is the sum of an external and a locally changing dipolar field $H_i^{\text{eff}} = H + H_i^{\text{dip}}$. Note now that the first term in (3.9) is a demagnetizing term since it is minimized when the spins are antiparallel, while the second one tends to align the spins parallel and along the direction of the chain. For systems of aligned Ising spins only the first term is nonzero and, consequently, the dipolar field tends to induce antiferromagnetic (AF) order along the direction of the chain (for this case). However, for Heisenberg or planar spins, the competition between the two terms give rise to frustrating interactions, which can induce other equilibrium configuration, depending on the interplay between anisotropy and dipolar energies.

3.3 Computational Details

3.3.1 Calculation of Dipolar Energies

The long-range character of dipolar interactions, due to the double sum over N in (3.9), makes the energy computation in the standard MC algorithm extremely costly in central processing unit (CPU) time in comparison with other local energy terms. So one is forced to find some way to reduce the time spent in the calculation of dipolar energy. The first thing one can think of is to cut off the interaction range to a sufficiently large (but still small, let us say 10) number of neighbors, with the hope that the contribution of the

furthest spins will be negligible. But it turns out that, even in 1D,

sums of the kind $\sum_{n=1}^{\infty} 1/n^{\alpha}$ are very poorly convergent so that truncation may result in considerable rounding-off errors and also to the formation of artificial surface charges or magnetic poles at the truncation distance, which lead to nonphysical solutions.

Another strategy is to keep the exact calculation but to find an algorithm that avoids, in some way, the longest part of the calculation, that is, the evaluation of the double sum in (3.2) at every MC trial jump. Our algorithmic implementation for the calculation of dipolar energies is based on the following considerations:

1. Let us first note that it is not necessary to recalculate the dipolar energy each time a spin flip attempt is tried during the MC procedure. By rewriting the dipolar energy as

$$\mathcal{H}^{\rm dip} = g \sum_{i,j=1}^{N} S_i^{\alpha} W_{ij}^{\alpha\beta} S_j^{\beta}, \qquad (3.12)$$

where *W* is the dipolar interaction matrix

$$W_{ij}^{\alpha\beta} = \frac{\delta_{\alpha\beta}}{r_{ij}^3} - 3 \frac{\delta_{\alpha\gamma} \delta_{\beta\eta} r_{ij}^{\gamma} r_{ij}^{\eta}}{r_{ij}^5}, \qquad (3.13)$$

that represents the dipolar interaction between spins *i* and *j*, these quantities can be calculated before starting the MC part of the program and stored in an array for later use, as they only depend on the position of the spins along the chain and not on the particular spin value.

2. With these quantities at hand, it is more convenient to work with the dipolar fields as they are can be simply written as

$$H_{\mathrm{dip}_{i}}^{\alpha} = \sum_{j=1}^{N} W_{ij}^{\alpha\beta} S_{j}^{\beta}.$$
(3.14)

The dipolar fields may be calculated once for the initial spin configuration before entering the MC part of the simulation and stored in an array.

3. Therefore, in the MC algorithm, the dipolar energy of a spin can be calculated simply by multiplying the stored dipolar field by the value of the spin as

$$\mathcal{H}_{dip_i} = -\mathbf{S}_i \cdot \mathbf{H}_{dip_i}.$$
 (3.15)

4. Finally, let us note that, only if the trial jump is accepted, the dipolar fields have to be updated by a specific subroutine as

$$\mathbf{H}_{dip_{i}}^{new} = \mathbf{H}_{dip_{i}}^{old} - W_{ij}(\mathbf{S}_{j}^{old} - \mathbf{S}_{j}^{new})(i = 1, ..., N)$$
(3.16)

where S_j is the spin that has been changed. This requires only N evaluations instead of the double N sum involved in the calculation of the dipolar energy. This strategy is particularly efficient at low temperatures, when the acceptance rate can be very low.

Note that this implementation of the calculation of dipolar energies is not limited to 1D systems. It can be applied to spin systems in two or three dimensions and independently of their spatial arrangement in the nodes of a regular lattice or in random positions in space as long as they remain fixed in space.

3.3.2 The Monte Carlo Algorithm

In MC simulations of continuous spins, special care has to be taken in the way the attempt jumps are done and in the way the energy difference ΔE appearing in the Boltzmann probability is calculated. There are mainly two choices for the dynamics of the MC procedure, independent of the way the attempt jumps are done: (a) Either ΔE is directly calculated as the energy difference between the old S^{old} and the attempted S^{new} values of the spin, or (b) ΔE is chosen as the energy barrier that separates S^{old} and S^{new} (see Fig. 3.6). Note that the second choice gives ΔE 's that are higher than in the first if there is an energy maximum separating the two states.

Each of the two models previously considered is suited to probe these two different choices:

1. In Model I, the energy minima and the barriers separating them can be explicitly calculated since, in this case, there is only one degree of freedom for each spin and its energy can be written as in the Stoner–Wohlfarth particle model

$$E_{i} = -K_{i} \cos^{2}(\theta_{i} - \psi_{i}) - H_{i}^{\text{eff}} \cos(\theta_{i}^{h} - \theta_{i}), \qquad (3.17)$$

with an effective field which is the sum of the external and dipolar fields. Although the energy barriers cannot be analytically calculated for all the values of ψ_i and θ_i^h , it is not

difficult to build up an algorithm that finds the minima and maxima of the energy function (3.3.2) and their respective energies. Thus, we can build an MC algorithm that considers trial jumps only between orientations corresponding to energy minima randomly chosen with equal probabilities. In this case, the ΔE in the transition probability are always to one of the actual energy barriers of the system.

2. In Model II, the 3D character of the spins and the dipolar field makes it difficult to devise an efficient algorithm to find the energy minima. Then, the trial jump must be done in this case to a random orientation inside a cone of aperture $\delta\theta$ around the current spin direction.



Figure 3.6 Different choices of ΔE for the transition probability.

Of course, when the MC simulation is used to simulate the evolution in time, the link between the computer artificial MC step and real time will depend on how the ΔE is computed, but it is well known that in either case, only in some specific situations [37, 41], this correspondence can be established.

3.3.3 Dipolar Fields in 1D

• In a 1D chain of Ising spins with directions perpendicular to the line joining the spins, the ground state is AF, giving an

energy $E_{din}^{AF} = -g/a^3$ for n.n spins. For spins pointing along the chain direction, the ground state is ferromagnetic (FM), giving now an energy $E_{dip}^{FM} = -2g/a^3$ for n.n. spins. • The local field felt by spins in a FM chain is

$$H_{\rm dip}^{\rm FM} = -2g\zeta(3) = -2.4041g \tag{3.18}$$

where $\zeta(s)$ is Riemann's zeta function [1]. While if the spins are AF ordered the dipolar fields are

$$H_{\rm dip}^{\rm AF} = \pm 2g \sum_{n=1}^{\infty} \frac{-1^n}{n^3} = \mp \frac{3}{2} \zeta(3) = \mp 1.8031g.$$
(3.19)

If the spins point along the chain, these values are doubled.

Effective Energy Barrier Distributions 3.4

Before starting to simulate the time dependence of magnetization, we will study first the influence of dipolar interactions on the energy distribution. With this purpose, in this section we will compute the distribution of energy barriers of interacting systems with distributed properties in a way similar to what we did when the effect of an homogeneous external magnetic field was considered [22]. As in that case, we can expect that the dipolar fields acting on each particle will modify the energy barrier distribution in the absence of interactions. But now, since the local dipolar fields may vary depending on the spin configuration, the effective distributions will be different from those for a homogeneous magnetic field. We will concentrate on Model I, since in this case the energy barriers can be computed exactly and can be compared to those extracted from relaxation curves. Moreover, we will consider a system with a log-normal distribution ($\sigma = 0.5$) of anisotropies f(K) and random anisotropy axes.

• Let us first consider the case of a FM chain of spins pointing along the positive y axis ($\theta_i = 0$). In Fig. 3.7 (left panel), we present the calculated energy barrier distributions for several values of the dipolar interaction g and compare them with that for the noninteracting case g = 0. The distributions have been obtained from histograms for a system with 40,000 particles and normalized to the total area of the distribution.



Figure 3.7 Energy barrier distributions $f(E_b)$ for a system with log-normal distribution of anisotropy constants ($\sigma = 0.5$) and random anisotropy axes directions. (Left) spins pointing toward the positive *y* direction. (Right) Spin configuration achieved after an equilibration at T = 0 in which spins have been replaced iteratively toward the nearest energy minimum direction starting from an initial FM configuration.

In this case, the local dipolar fields on all the spins are exactly the same since periodic boundaries are assumed at the ends of the 1D chain. The dipolar field is given in this case by $H_{\text{dip}_i}^{\text{FM}} = -2g\zeta(3)\hat{y}$. The existence of one or two energy minima and the height of the energy barriers is ruled by the ratio of the dipolar to anisotropy energies, since the reduced field reads now

$$h_{\rm dip_i}^{\rm FM} = \zeta(3) \frac{g}{K_i}.$$
 (3.20)

Therefore, particles with $h_{dip_i} < h_{ci}(\varphi_i)$ have two energy minima, while the rest will have only one.

For small g (= 0.1) there are slight changes on the $f(E_b)$ with respect to the noninteracting case. As it was the case for an external homogeneous field, the dipolar fields shift the peak of the distribution, while its shape is undisturbed. However, when increasing g, the smallest energy barriers of particles having the smallest K start to disappear. This leads to the appearance of a peak at zero energy, an increase in the number of low energy barriers due to the reduction by the field, and to the appearance of a longer tail at high energies. As the dipolar interaction is increased further (g = 0.3, 0.4) the original peak around $E_b \simeq 1$ is progressively suppressed as more barriers are destroyed, and a secondary distribution peaked at high energies appears due to the existence of barriers against rotations out of the field direction.

• The previously analyzed configuration is highly metastable even at T = 0 since, in general, the spin orientations are not along the energy minima. If a strong external field was applied to align the particles, they would instantaneously reorientate their magnetizations so that they lie along the nearest minimum. This accommodation process occurs in a time scale of the order of τ_0 , much shorter than the thermal overbarrier relaxation times τ . Therefore, in real experiments probing magnetization at time scales of the order of 1-10 seconds (i.e., SOUID magnetometry), this will not be observed. In order to get rid of this ultrafast relaxation during the first instants of the simulations, we submit the system to a previous equilibration process at T = 0, during which the spins are consecutively placed in the nearest energy minima. Since the dipolar field after each of this movement changes on all the spins, the energy minima positions change continuously, but after a certain number of MC simulations, the total magnetization changes become negligible and the system reaches a final equilibrated state. The effective energy barrier distributions after equilibration are displayed in the right panel of Fig. 3.7. As we see, the high energy peaks observed in the FM configuration disappear almost completely after this process, indicating that they were due to the "misplacement" of the spins away from the local nearest minima.

3.5 Relaxation Curves: $T \ln(t/\tau_0)$ Scaling with Interactions

Here we would like to answer the following questions. How is the relaxation rate affected by dipolar interactions between the particles? And is $T \ln(t/\tau_0)$ scaling still accomplished, even though the energy barrier landscape changes as time elapses in this case? If so, what is the meaning of the effective energy barrier distribution derived from the scaled relaxation curves?

3.5.1 Simulations of the Time Dependence of Magnetization

Let us start with the simple case of a system with an anisotropy distribution f(K) and anisotropy axes distributed at random. As already mentioned in the previous section, if the system is initially prepared with all spins aligned in the field direction, the spins relax to the nearest minimum within a time of the order of τ_0 that is not usually accessible in most relaxation experiments. Therefore, the simulated relaxation will not be exactly as in typical experiments measuring the variation of the magnetization after saturation in a strong magnetic field.

We will run the simulations starting from the equilibrated states achieved by the previously described procedure. At nonzero *T*, thermal fluctuations will drive the system toward the equilibrium state, which for aligned particles would be AF. For a disordered system, however, the equilibrium state will have zero net magnetization. The final expected configuration will have neighboring particles with almost parallel easy axes in the *y* direction with antiparallel spins and neighboring particles with almost parallel easy axes in the *x* direction with parallel spins.

The relaxation curves at different temperatures and values of the interaction g are shown in Fig. 3.8. Temperature is measured in reduced units $(k_{\rm B}T/K_0)$, the chosen values of the interaction parameter range from the weak (g = 0.1) to the strong (g = 0.5) interaction regime. We observe that the stronger the interaction, the smaller the magnetization of the initial configuration due to increasing strength of the local dipolar fields that tend to depart the equilibrium directions from the direction of the anisotropy axis. Thus, we point out that, if one is to compare relaxation curves for different g at the same T, they have to be properly normalized by the corresponding m(0) value. As it is evidenced by the logarithmic time scale used in the figure, the relaxation is slowed down by the intrinsic frustration of the interaction and the randomness of the particle orientations.

More remarkable is the fact that the magnetization decay is faster the stronger the interaction is, which agrees well with the experimental results of Refs. [4, 9, 39] and also with other simulation works that model dipolar interactions by a mean field



Figure 3.8 Upper panels: Relaxation curves for several temperatures ranging from T = 0.02 (uppermost curves) to T = 0.2 (lowermost curves) in 0.02 steps for a system of interacting particles with distribution of anisotropies f(K) and random orientations. g is the dipolar interaction strength. The initial state for all of them is the one achieved after the equilibration process described in the text. Lower panels: Master relaxation curves corresponding to the relaxations shown above obtained by the multiplicative scaling factor T.

[8, 30, 33, 36]. However, at difference with these works, the quasilogarithmic relaxation regime is only found in our simulations in the strong interaction regime, for short times, and within a narrow time window that depends on *T*. This can be understood because of the short duration of the relaxations in other works compared to ours, which were extended up to 10,000 MC simulations, thus confirming the limitation of the logarithmic approximation to narrow time windows.

3.5.2 $T \ln(t/\tau_0)$ Scaling in the Presence of Interactions

Following the ideas exposed in Section 3.1, we will try to analyze the relaxation curves at different temperatures according to the phenomenological approach of $T \ln(t/\tau_0)$ scaling. The underlying hypothesis of the method was that the dynamics of the system can be described in terms of thermal activation of the Arrhenius type over the effective local energy barriers induced by the interaction. Although one could think that this assumption is only valid in noninteracting particle systems, we would like to stress that the T $\ln(t/\tau_0)$ scaling approach was first successfully introduced in studies of spin glasses [5, 43, 44]. Although it is true that dipolar interaction, being long ranged, changes the energy barrier landscape in a dynamic way during the relaxation, this does not imply that the low T relaxations will not scale. In fact, if this scaling is accomplished, it will give us information on the energy barriers that are effectively probed during the relaxation process, even if they keep on changing during the process.

The results of the master curves obtained from Fig. 3.8 (upper panels) by scaling the curves along the horizontal axis by multiplicative factors T are presented in Fig. 3.8 (lower panels) for a range of temperatures covering one order of magnitude. First, we observe that, in all cases, there is a wide range of times for which overlapping is observed. Below the inflection point of the master curve, the overlap is better for low T curves, whereas high T curves overlap only at long times above the inflection point, as it was also in the noninteracting case. Moreover, it seems that scaling is accomplished over a wider range of T, the stronger the interaction is, whereas in the weak interaction regime, scaling is fulfilled over a narrower range of times and T. As we will explain later, this fact

is due to the different variation of the effective energy barriers, contributing to the relaxation in the two regimes.

In order to see the influence of *g* on the relaxation laws, in Fig. 3.9, we have plotted together the master relaxation curves for different values of the interaction parameter *g* after smoothing and filtering of the curves in Fig. 3.8. We can clearly see the qualitative change in the relaxation law with increasing *g*. In the weak interaction regime (g = 0.1, 0.2), the magnetization decays slowly to the equilibrium with an inflection point around which the decay law is quasi-logarithmic. In the strong interaction regime, however, the relaxation curves have always downward curvature with no inflection point. When plotted in a $\ln(M)$ vs $\ln t/\tau_0$ scale they are linear (see inset of Fig. 3.9), indicating a power-law decay of the magnetization with time, since the energy scale can be converted to time through the $T \ln(t/\tau_0)$ variable.



Figure 3.9 Master relaxation curves for different values of the dipolar interaction strength *g*. (Inset) The same curves in a log-log plot in order to make evident the power-law behavior of the relaxation at high values of *g*.

This power-law behavior has also been found by Ribas et al. [46] in a 1D model of Ising spins and by Sampaio et al. [47, 48] in an MC simulation of the time dependence of the magnetic relaxation of a 2D

array of Ising spins under a reversed magnetic field. It has also been observed experimentally in arrays of micromagnetic dots tracked by focused ion beam irradiation on a Co layer with perpendicular anisotropy [2, 20].

3.6 Evolution of $f_{eff}(E_b)$ and of Dipolar Fields

To gain some insight into what microscopic mechanisms rule the relaxation processes in weak and strong interaction regimes, we will examine how the distribution of energy barriers and the dipolar fields change during the relaxation process. The initial distributions of energy barriers have already been shown in Fig. 3.7, but since the starting configurations are not uniform, it is not easy to infer their microscopic origin. Let us notice that the distribution of dipolar fields does not depend on the anisotropy or easy-axis directions of the particles, so it is only sensitive to the spin orientations and their positions in the lattice. For this purpose, it turns useful to perform histograms of the strength of the dipolar fields felt by all the spins at different values of g. We show the results in Fig. 3.10, where the dipolar fields having a component in the negative y direction have been given a negative sign. This means that the local field is pointing in the opposite direction with respect to the original spin orientation, which was along the positive y axis. Therefore, the existence of negative dipolar fields indicates a higher probability for the spin to jump toward the equilibrium state.

For weak interaction (g = 0.1), the initial $f(H_{dip})$ are strongly peaked at a value that is very close to the dipolar field for a FM configuration $H_{dip}^{FM} = -2.0411381632g$, and there are very few negative dipolar fields. This indicates that the equilibrated configuration is not far from the initial FM one. In this case, since the dipolar fields are weak, the spins will point near the anisotropy axis direction since the energy minima and the energy barriers between them do not depart very too from the noninteracting case. This is also corroborated by the shape of $f(E_b)$, which resembles that for g = 0.

However, in the strong interaction regime, the local fields start to destroy the energy barriers of the particles with lower *K*, and so negative dipolar fields originated by the particles that have rotated into the field direction are numerous. There are still positive fields, but now the peak due to collinear spins blurs out with increasing g at the same time that a second peak, centered at higher field values, starts to appear and finally swallows the first (see the case g = 0.5). This last peak tends to a value equal to $H_{dip}^{AF} = \mp 4.808 g$, that would correspond to FM alignment along the chain.

All these features are also supported by the distributions of dipolar field angles (right panel in Fig. 3.10). Now we can understand how the initial stages of the relaxation proceed. To gain a deeper insight into the microscopic evolution of the system during relaxation, histograms of energy barriers of intermediate configurations have been recorded at different MC steps. In Fig. 3.11, the time evolution of the energy barriers separating the occupied state of each spin from the other allowed state is shown for a relaxation at an intermediate temperature T = 0.1. In Fig. 3.11, we have also kept track of the time dependence of the dipolar field histograms $f(H_{dip})$.



Figure 3.10 (Left) Initial distribution of dipolar fields for a system of particles equilibrated at T = 0 for different values of the interaction parameter *g*. All the magnetic moments are pointing along the local energy minima. (Right) Initial distribution of dipolar field angles for the same system.

These evolutions are markedly different in the two interaction regimes. In the weak interaction regime, the relaxation is dominated by anisotropy barriers, so the distributions are similar to the noninteracting case. As time elapses, particles with the lowest energy barriers relax toward a state with higher energy barriers. However, although during the relaxation process the energy barriers change locally, this change is compensated by the average over the anisotropy distribution and random orientations of the easy axes. Thus, the global $f(E_b)$ does not change significantly as the system relaxes, although the final configuration is much more disordered than the initial one. In spite of this, the distribution of dipolar fields, which is more sensitive to the local changes in spin configuration, presents evident changes with time. As relaxation proceeds, the high peak of positive H_{dip} progressively flattens, since it corresponds to particles whose magnetization is not pointing along the equilibrium direction. Particles that have already relaxed create dipolar fields in the negative direction, which give rise to a subdistribution of negative H_{dip} of increasing importance as time evolves. Near the equilibrium state of zero magnetization, the relative contributions of positive and negative fields tend to be equal, since, on average, there are equal number of "up" and "down" pointing spins.



Figure 3.11 Left columns: Evolution with time of the energy barrier histograms during the relaxation process at T = 0.1. The initial distribution is shown in dashed lines. Right columns: Time dependence of the distribution of dipolar fields during the relaxation process.

In the strong interaction regime, dipolar fields are stronger than anisotropy fields for the majority of the particles, even at the earlier stages of the relaxation process. As time elapses, the number of small energy barriers, corresponding to the particles with smaller anisotropies, continuously diminishes as they are overcame by thermal activation. When relaxing to their equilibrium state, now closer to the dipolar field direction, the particles with initially a small E_b give rise to higher energy barriers and also higher dipolar fields on their neighbors. This is reflected in the increasingly higher peak in the $f(E_b)$ that practically does not relax as time elapses, causing the final distribution to be completely different from the initial one. What is more, as more particles relax, more particles feel an $H_{dip}>H_{anis}$ and, therefore, higher E_b for reversal against the local field. This leads to faster changes in the dipolar field distribution and also is at the origin of the power-law character of the relaxations. Equilibrium is reached when $f(H_{dip})$ presents equal sharp-peaked contributions from negative and positive fields, since in this case there will be an equal number of particles with magnetizations with positive and negative components along the *y* axis.

3.7 Effective Energy Barrier Distributions from $T \ln(t/\tau_0)$ Scaling

In Section 3.1, we described a method to obtain an effective distribution of energy barriers from the master curves, showing that they can be obtained by performing the logarithmc time derivative of the master curves. The resulting effective energy barrier distributions obtained from the master curves in Fig. 3.9 are given in Fig. 3.12. It is worth remembering that these are not the real-time evolving energy barrier distributions. Instead, they represent time-independent distributions giving rise to the same relaxation curves obtained in the scaling regime. At a difference with the noninteracting cases analyzed in previous sections, these curves do not match the energy barrier distribution. The microscopic information given by them will be clarified in what follows.

For weak interaction (g = 0.1), the effective distribution of energy barriers has essentially the same shape as for the noninteracting case. However, the distribution narrows as g increases up to a value where almost zero barriers start to appear, and the mean effective barrier is shifted toward lower values of the scaling variable. In some sense, this resembles the situation for the noninteracting system in an external magnetic field, in which this shift was associated with the decrease of the energy barriers for rotation toward the field direction.



Figure 3.12 Derivatives of the master relaxation curves of Fig. 3.9 for different dipolar interaction strengths *g*.

When entering the strong interacting regime, an increasing number of low energy barriers appear that finally change the shape of the effective distribution into a quasi-exponential dependence. This change in the effective distribution is of course due to the power-law behavior of the relaxation law in the strong *g* regime and, therefore, a genuine effect of the dipolar interaction. This striking behavior has important consequences on the experimental interpretation of relaxation curves. As we already mentioned in Section 3.1, if magnetic relaxation is analyzed in terms of viscosity (i.e., the slope of the logarithmic time dependence), it turns out that, since $S \sim Tf[T \ln(t/\tau_0)]$, an energy distribution diverging as $f(E) \sim 1/E$ would give a constant viscosity at low *T* that could be erroneously interpreted as an indication of quantum *T*-independent relaxation phenomenon.

Both the change of behavior in the effective energy barrier distributions and the evidence of $T \ln(t/\tau_0)$ scaling of the relaxation have been observed experimentally in ensembles of Ba ferrite fine particles [4]. The relevance of demagnetizing interactions in this sample was established by means of Henkel plots at different *T*. The relaxation curves of the thermoremanent magnetization for

temperatures between 9 K and 230 K can be scaled when plotted against the $T \ln(t/\tau_0)$ variable with $\tau_0=10^{-12}$ seconds (see Fig. 3.13, left panel). From the derivative of the master relaxation curve the distribution of effective energy barriers (see Fig. 3.13, right panel) was obtained and fitted a sum of two log-normal distributions. The additional low energy barrier contribution to the energy barrier distribution can be associated with the demagnetizing interactions. since the other contribution centered at higher energies can be ascribed to the volume and anisotropy distributions. Moreover, when cooling the sample in different external magnetic fields before the relaxation process was recorded (see Fig. 3.14), the authors found that, when increasing the cooling field, the effective distributions changed from a function with a maximum that extends to high energies to a narrower distribution with a peak at much lower-energy scales for high-cooling fields. The effective distribution at high $H_{\rm FC}$, which was there argued to be given by the intrinsic anisotropy barriers of the particles, appears shifted toward lower-energy values with respect to the anisotropy distribution, as derived from transmission electron microscopy (TEM) due to the demagnetizing dipolar fields generated by the almost aligned spin configuration induced by the $H_{\rm FC}$.



Figure 3.13 (Left) panel M/M0 vs $T \ln(t/\tau_0)$ scaling with $\tau_0=10^{-12}$ s for 27 temperatures within 9 K and 230 K. The solid line represents the best fit of data to Eq. 3.1, considering two log-normal distributions of energy barriers. (Right) Energy barrier distributions obtained from the derivative of the experimental master curve with respect to the scaling variable (filled circles). The solid line indicates the fitted distributions.



Figure 3.14 Effective energy barrier distributions obtained from relaxation measurements in a Ba ferrite fine-particle system after field cooling. The sample at 200 Oe (a), 500 Oe (b), 10 kOe (c), and 50 kOe (d). *M*120 is an arbitrary normalization factor.

As we have established that the effective energy barrier distributions derived from the master relaxation curves do not coincide with the real energy barrier distributions, now we will try to further clarify their meaning. To this end, we have computed the cumulative histograms of energy barriers that have been really jumped during the relaxation processes. The corresponding results are presented in Fig. 3.15 for systems in the weak and strong interaction regimes and T = 0.1, 0.2. As it is clear by comparison of the curves in this figure with those of Fig. 3.12, although one could think that the derivative of the master curves collects jumped energy barriers of the order of $T \ln(t/\tau_0)$ as time elapses, the cumulative histograms overcount the number of small energy barriers at all the studied *T* and *g*. This small energy barriers that are not seen by the relaxation correspond to the those jumped by the superparamagnetic (SP) particles.

In fact, when the cumulative histograms are computed by counting only the E_b jumped by particles that have not jumped up to a given time *t*, the contribution of SP particles that have already relaxed to the equilibrium state is no longer taken into account. The histograms computed in this way are presented in Fig. 3.16. There, we see that when only the energy barriers jumped by the blocked particles are taken into account, the resulting histograms at advanced stages of the relaxation process tend to the effective

energy barriers derived from the master relaxation curves (dashed lines in the figure). The difference between both quantities at high energy values is due to the existence of very high energy barriers, which can only be surmounted at temperatures higher than the one considered here.



Figure 3.15 Cumulative histograms of the jumped energy barriers during the relaxation process. All the jumped energy barriers are taken into account. The temperature is T = 0.1. The value of the interaction parameter is g = 0.1 on left panels and g = 0.4 on right panels.



Figure 3.16 Cumulative histograms of the jumped energy barriers during the relaxation process. Only the E_b jumped by particles that have not jumped up to time *t* are taken into account. Symbols correspond to T = 0.1. The dashed lines stand for the derivatives of the master relaxation curves shown in Fig. 3.16. The value of the interaction parameter is g = 0.1 on left panels and g = 0.3 on right panels.

3.8 Hysteresis Loops

Besides the time dependence of magnetization, it is also interesting to study the effects of dipolar interactions on hysteresis loops, since they give information about the reversal processes of the magnetization and are usual measurements in real samples. Since in this case we are not interested in how the system evolves with time but in finding the value of thermodynamic average of M at a given H, we will implement the MC dynamics by choosing Model II previously introduced in Section 3.3. In this way, the phase space is sampled more efficiently, minimizing computation and improving the quality of thermal averages. The studied system consists again of an ensemble of 10,000 randomly oriented particles with log-normal distribution of anisotropy constants with $\sigma = 0.5$. We start the loop at high enough fields with a FM configuration and subsequently decrease the field in constant steps $\delta H = 0.05$. At every field value, thermodynamic averages of the magnetization along the field direction are measured during a large but fixed number of MC steps.

In Fig. 3.17, we present simulated hysteresis loops at different temperatures for values of g ranging from 0.1 to 0.4. As it is apparent from the figures, the area of the hysteresis loops decreases with increasing temperature, as expected. The loops become more elongated with increasing interactions, resembling the ones for a system with frustrated interactions. The closure field becomes higher, and the system becomes harder as it is more difficult to reach saturation.

The thermal dependence of the coercive field H_c shown in Fig. 3.18 (upper panels) for different values of the interaction parameter *g* shows that, at low *T*, H_c decreases linearly with increasing *T* and also with increasing interactions. This observation is in agreement with experiments in interacting systems and simulations [25, 53]. However, at higher *T* (see the *T* = 0.1, 0.14 curves in the right panel of Fig. 3.18), $H_c(g)$ seems to have a maximum value at an intermediate *g* value before starting to decrease for higher values of *g*. Further evidence of the influence of the frustration induced by dipolar interaction is given by thermal dependence of the remanent magnetization M_R . As shown in Fig. 3.18 (lower panels), remanence values decrease with increasing interactions at all the considered *T*. Moreover, the thermal dependence of M_R displays an inflection point at intermediate *T* values, decaying smoothly toward zero for higher

T and similarly to experimental results for the thermoremanent magnetization of FeN ferrofluids of different concentrations [34].



Figure 3.17 Hysteresis loops for different values of dipolar coupling: g = 0.1 (black), g = 0.2 (red), g = 0.3 (blue), and g = 0.4 (orange, discontinuous line).



Figure 3.18 (Left) Temperature dependence of the coercive field and remanent magnetization for g = 0.1, 0.2, 0.3, and 0.4 (from the uppermost curve). (Right) Dependence of the coercive field and remanent magnetization on the interaction parameter g from temperatures T = 0.01, 0.05, 0.1, and 0.14 (starting from the uppermost curve).

3.9 Conclusions

We have presented a review of a description of the long-time relaxation of the magnetization of nanoparticle ensembles on the basis of a phenomenological approach to their dynamics that focuses on effective energy barriers. The approach is based on a scaling property of the relaxation curves at different temperatures that profits from the natural link between temperature and energy barriers through the Arrhenius law. We have also presented a way to obtain microcopy energy barrier distributions from the master relaxation curves obtained frmo the $T \ln(t/\tau_0)$ scaling. A proposal of extension of this methodology to interacting systems has been presented in detail, as applied to a 1D chain of spins, which has been shown to be valid in spite of the fact that energy barriers keep on changing through the relaxation process.

We have shown that dipolar interaction induces a faster relaxation of the magnetization, changing the time dependence of the magnetic relaxation from quasi-logarithmic to a power law as *g* increases, due to the intrinsic disorder of the system and the frustration induced by dipolar interactions. $T \ln(t/\tau_0)$ scaling of the relaxation curves at different T is accomplished even in the presence of interactions. From the obtained master curves, effective energy barrier distributions can be obtained, giving valuable information about the microscopic energy barriers and the change induced on them by the dipolar interaction, which cannot be directly obtained experimentally. As the strength of the dipolar interaction g increases, the effective energy barrier distribution shifts toward lower $E_{\rm b}$ values and becomes wider, in qualitative agreement with experimental results. In spite of the dynamic change of the dipolar fields, the energy barrier distribution does not change appreciably during the relaxation due to the disorder induced by randomness of interaction. Moreover, the results of simulations of the hysteresis loops display a decrease of the coercive field and remanence with increasing interaction in agreement with most of the experimental findings. The hysteresis loops of this system resemble those of frustrated systems, with elongated shapes and high closure fields. A reduction in the coercive field and the remanent magnetization with increasing interaction is in agreement with experimental findings.

Acknowledgments

The authors acknowledge funding of the Spanish MICINN and MINECO through Grant projects MAT2009-08667 and MAT2012-33037, European, Union FEDER funds ("Una manera de hacer Europa"), Generalitat de Catalunya through Project 2009SGR876, and CESCA and CEPBA under coordination of C4 for supercomputer facilities.

References

- 1. Abramowitz, M., Stegun, I. (1972). *Handbook of Mathematical Functions*, Dover Publications, New York.
- Aign, T., Meyer, P., Lemerle, S., Jamet, J., Ferré, J., Mathet, V., Chappert, C., Gierak, J., Vieu, C., Rousseaux, F., Launois, H., Bernas, H. (1998). *Phys. Rev. Lett.*, 81, 5656.
- 3. Alonso, J. J., Fernández, J. F. (2010). *Phys. Rev. B*, **81**, 064408.
- 4. Batlle, X., García del Muro, M., Labarta, A. (1997). Phys. Rev. B, 55, 6440.
- 5. Castaign, B., Souletie, J. (1991). J. Phys. (France) I, 1, 403.
- 6. Chantrell, R. W. (1997). *Magnetic Hysteresis in Novel Magnetic Materials Science and Technology of Nanostructured Magnetic Materials, NATO ASI Series E* (Hadjipanajys, G. C., ed.), Vol., 338, p. 21, Kluwer Academic, Dordrecht, the Netherlands.
- 7. Chantrell, R. W., El-Hilo, M., O'Grady, K. (1991). *IEEE Trans. Magn.*, **27**, 3570.
- Dahlberg, E. D., Lottis, D. K., White, R. M., Matson, M., Engle, E. (1994). J. Appl. Phys., 76, 6396.
- 9. del Muro, M. G., Batlle, X., Labarta, A. (1999). Phys. Rev. B, 59, 13584.
- Djurberg, C., Svedlindh, P., P.Nordblad, Hansen, M. F., Bödker, F., Mørup, S. (1997). *Phys. Rev. Lett.*, **79**, 5154.
- 11. Dormann, J. L., Bessais, L., Fiorani, D. (1988). J. Phys. C, 21, 2015.
- 12. Dormann, J. L., Fiorani, D., Tronc, E. (1997). Adv. Chem. Phys., 98, 283.
- 13. El-Hilo, M., O'Grady, K., Chantrell, R. W. (1992). *J. Magn. Magn. Mater.*, **117**, 21.
- 14. Fernández, J., Alonso, J. J. (2000). Phys. Rev. Lett., 63, 53.
- 15. Fernández, J. F., Alonso, J. J. (2009). Phys. Rev. B, 79, 214424.
- Gangopadhyay, S., Hadjipanajys, G. C., Sorensen, C. M., Klabunde, K. J. (1993). *IEEE Trans. Magn.*, 29, 2619.

- 17. Garanin, D. A., Kachkachi, H. (2003). Phys. Rev. Lett., 90, 065504.
- García-Otero, J., Porto, M., Rivas, J., Bunde, A. (2000). *Phys. Rev. Lett.*, 84, 167.
- 19. García-Palacios, J. L. (2000). Adv. Chem. Phys., 112, 1.
- Hyndman, R., Mougin, A., Sampaio, L. C., Ferré, J., Jamet, J. P., Meyer, P., Mathet, V., Chappert, C., Mailly, D., Gierak, J. (2002). *J. Magn. Magn. Mater.*, 240, 34.
- 21. Iglesias, O., Badia, F., Labarta, A., Balcells, L. (1996). Z. Phys. B, 100, 173.
- 22. Iglesias, O., Labarta, A. (2002). J. Appl. Phys., 91, 4409-4418.
- Jonsson, T., Mattsson, J., Djurberg, C., Khan, F., Nordblad, P., Svedlindh, P. (1995). *Phys. Rev. Lett.*, **75**, 4138.
- 24. Jonsson, T., Svedlindh, P., Hansen, M. F. (1998). *Phys. Rev. Lett.*, **81**, 3976.
- Kechrakos, D., Trohidou, K. N. (1998a). J. Magn. Magn. Mater., 177– 181, 943.
- 26. Kechrakos, D., Trohidou, K. N. (1998b). Phys. Rev. B, 58, 12169-12177.
- 27. Kleemann, W., Petracic, O., Binek, C., Kakazei, G. N., Pogorelov, Y. G., Sousa, J. B., Cardoso, S., Freitas, P. P. (2001). *Phys. Rev. B*, **63**, 134423.
- 28. Labarta, A., Iglesias, O., Balcells, L., Badia, F. (1993). *Phys. Rev. B*, **48**, 10240.
- Linderoth, S., Balcells, L., Labarta, A., Tejada, J., Hendriksen, P. V., Sethi, S. A. (1993). *J. Magn. Magn. Mater.*, **124**, 269.
- 30. Lottis, D. K., White, R. M., Dahlberg, E. D. (1991). *Phys. Rev. Lett.*, **67**, 362.
- Luis, F., Torres, J. M., García, L. M., Bartolome, J., Stankiewicz, J., Petroff, F., Fettar, F., Maurice, J., Vaurés, A. (2002). *Phys. Rev. B*, 65, 094409.
- Luo, W., Nagel, S. R., Rosenbaum, T. F., Rosensweig, R. E. (1991). *Phys. Rev. Lett.*, 67, 2721.
- 33. Lyberatos, A. (2000). J. Phys. D: Appl. Phys., 33, R117.
- 34. Mamiya, H., Nakatani, I. (1997). J. Appl. Phys., 81, 4733.
- Mamiya, H., Nakatani, I., Furubayashi, T. (1998). Phys. Rev. Lett., 80, 177.
- Matson, M. E., Lottis, D. K., Dahlberg, E. D. (1994). J. Appl. Phys., 75, 5475.
- Miltényi, P., Gierlings, M., Keller, J., Beschoten, B., Guntherodt, G., Nowak, U., Usadel, K. D. (2000). *Phys. Rev. Lett.*, 84, 4224.

- Mørup, S., Bødker, F., Hendriksen, P. V., Linderoth, S. (1995). *Phys. Rev. B*, 52, 287.
- 39. Mørup, S., Tronc, E. (1994). Phys. Rev. Lett., 72, 3278.
- 40. Néel, L. (1949). C. R. Acad. Sci. Paris, 228, 664.
- 41. Nowak, U. (2001). Ann. Rev. Comp. Phys., 9, 105.
- 42. O'Grady, K., El-Hilo, M., Chantrell, R. W. (1993). *IEEE Trans. Magn.*, **29**, 2608.
- 43. Omari, R., Préjean, J. J., Souletie, J. (1984). J. Phys. (France), 45, 11809.
- 44. Préjean, J. J., Souletie, J. (1980). J. Phys. (France), 41, 1335.
- 45. Ribas, R., Labarta, A. (1996). J. Appl. Phys., 80, 5192.
- 46. Russ, S., Bunde, A. (2006). Phys. Rev. B, 74, 064426.
- 47. Sampaio, L. C., de Albuquerque, M. P., de Menezes, F. S. (1996). *Phys. Rev. B*, **54**, 6465.
- Sampaio, L. C., Hyndman, R., de Menezes, F. S., Jamet, J. P., Meyer, P., Gierak, J., Chappert, C., Mathet, V., Ferré, J. (2001). *Phys. Rev. B*, 64, 184440.
- Sappey, R., Vincent, E., Ocio, M., Hammann, J. (1998). J. Magn. Magn. Mater., 221, 87.
- Serantes, D., Baldomir, D., Pereiro, M., Hernando, B., Prida, V. M., Sánchez Llamazares, J. L., Zhukov, A., Ilyn, M., González, J. (2009). *Phys. Rev. B*, 80, 134421.
- 51. Street, R., Wooley, J. C. (1949). Phys. Soc. A, 62, 562.
- 52. Ulrich, M., García-Otero, J., Rivas, J., Bunde, A. (2003). *Phys. Rev. B*, **67**, 024416.
- 53. Xu, C., Li, Z. Y., Hui, P. M. (2001). J. Appl. Phys., 89, 3403.
- 54. Yanes, R., Chubykalo-Fesenko, O., Kachkachi, H., Garanin, D. A., Evans, R., Chantrell, R. W. (2007). *Phys. Rev. B*, **76**, 064416.

Chapter 4

Elementary Excitations in Magnetic Nanoparticles Probed with ⁵⁷Fe Nuclear Magnetic Resonance and Mössbauer Spectroscopy

Michael Fardis,^a Alexios P. Douvalis,^b George Diamantopoulos,^a Ioannis Rabias,^a Thomas Bakas,^b Hae Jin Kim,^c and

Georgios Papavassiliou^a

^aInstitute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, Department of Materials Science, National Centre for Scientific Research "Demokritos," 153 10 Aghia Paraskevi, Attiki, Greece ^bDepartment of Physics, University of Ioannina, 451 10 Ioannina, Greece ^cKorea Basic Science Institute, 350-333 Daejeon, Republic of Korea mfardis@ims.demokritos.gr

4.1 Introduction

The concept of elementary excitations is at the heart of condensed matter physics since it is related to such important issues as the many-body effects and the idea of broken symmetry [1]. As Anderson points out [2], historically the idea of elementary excitations has grown rather gradually, but the names of Debye (Debye phonon

130 Elementary Excitations in Magnetic Nanoparticles

theory) and Landau (he introduced the term) are intimately related with the generalization of the approach. Central to the concept of elementary excitations is the idea that the very important physical quantity is not the ground state of a system but rather the behavior of the lower excited states relative to the ground state [2]. These states are weakly excited energy levels in the sense that they are situated not too high above the ground state, for example, excited at relatively low temperatures or by weak external fields. The elementary excitations may be regarded to behave as "quasi-particles," moving in the volume occupied by the body and having definite energies and momenta [3]. For example, in a solid at nonzero temperature, the longitudinal and transverse phonons are the elementary excitations corresponding to the lattice vibrations of the crystals and when regarded as "quasi-particles" they are propagated through the lattice with definite energies and directions of motion. In a ferromagnet, the ordered state at T = 0 is disturbed at nonzero temperatures by spin waves quantized as magnons quasi-particles.

Actually, in magnetic ordered systems, there are two kinds of magnetic excitations, the collective spin excitations (spin waves) and spin-flip particle-hole excitations (Stoner excitations). Spin waves have collective character, can be described using the Heisenberg model, and form a branch in k- ω space, which is gapless if the system is isotropic. The Stoner excitation is spin-dependent single-particle excitation and is described within a simple electronic band structure appropriate for itinerant-electron ferromagnets.

Elementary excitations from the ground state may be described by a harmonic Hamiltonian. In Heisenberg ferromagnets these excitations are wavelike propagating modes, and a spin wave state of wave vector **k** may be constructed. Figure 4.1 shows schematic representations of spin wave modes with different **k** values and directions. The $k \neq 0$ traveling waves (Fig. 4.1b,c) correspond to spin waves propagating parallel and perpendicular to an effective field direction. The direction of the phase variation of the precessing spins corresponds to the direction of travel. The uniform mode (Fig. 4.1a) may be considered of a spin wave of infinite wavelength (k = 0) and corresponds to the in-phase precession of all the spins throughout the sample. Such a precession is called the uniform or Kittel mode. We will now show how long-wavelength (uniform-mode), lowfrequency excitations are associated with conservation laws and
broken symmetry. In the absence of an external magnetic field, in a Heisenberg ferromagnet, the energy of the system cannot depend on the orientation of the spin with respect to an arbitrary axis fixed in space. Excitation of a spin wave of zero wave vector corresponds to such rotation and therefore cannot change the energy of the system. This result is also a consequence of the Golstone theorem, which states that there must be a zero frequency–zero wave number mode in systems with a continuous broken symmetry [5]. In the present case, the Hamiltonian is invariant under rotations about any axis; however, the ferromagnetic ground state assumes a definite value for S_{z_2} and it is thus not invariant. Consequently states of zero excitation energy must exist; in our case, there are spin waves of k = 0 [6].



Figure 4.1 Schematic representation of (a) the uniform mode and spin waves propagating (b) parallel and (c) perpendicular to the effective static magnetic field direction (adapted from Ref. [4]).

It has been suggested that the uniform mode is the primary mode of elementary excitations in ferromagnetic or ferrimagnetic nanoparticles [7–9]. Generally, for spin waves with finite k values to propagate in nanoparticles, quite low wavelengths (high frequencies)

are required, as the wavelength λ is given by $\lambda = 2L/n$, where L is the dimension of the particle in the direction of propagation and *n* is an integer. The spin wave with the largest finite wavelength (first excited spin wave level for n = 1) has a λ value of 2L, and since L for nanoparticles is quite reduced relative to the bulk particles, spin waves with quite short wavelengths (high frequencies) are required relative to the available long wavelengths (low frequencies) for bulk particles. This demands consequently a relatively larger amount of energy, $E_n = \hbar \omega_n k_n^2 \approx D k_n^2$, where D is a constant of the order of a few hundreds of meVÅ² [10], to be offered to the spin system of the nanoparticle just to excite it to the first (n = 1) spin wave $k \neq 0$ level, which is usually not available from thermal energy sources at low temperatures. Thus the spin system prefers to diverge from the uniform mode in the form of uniform-mode excitations induced by thermal energy [9]. In this work we will focus on nuclear magnetic resonance (NMR) and Mössbauer experiments on maghemite $(\gamma - Fe_2O_3)$ nanoparticles and discuss the implications of the uniformmode excitations induced by thermal energy on the experimental results.

4.2 Magnetization Dynamics in Magnetic Nanoparticles

4.2.1 Superparamagnetic and Blocking States

It is well known that below a certain critical size, magnetic particles exhibit a single-domain structure with uniform magnetization *M*. In the absence of an applied field the magnetization is along some easy direction of magnetization. Néel [11] first pointed out that in these subdomain particles, even in the absence of an external magnetic field, the magnetization can be reversed by thermal fluctuations over the energy barrier *KV* (where *K* is the magnetic anisotropy constant and *V* the volume of the particle) between different directions of easy magnetization. In these single-domain particles the internal magnetization depends only on the orientation of the magnetic moment with respect to certain axes. The efficiency of the disorientation action of the fluctuations depends on the ratio σ = *KV*/*k*_B*T* of the magnetic anisotropy energy to the thermal energy (where *k*_B is Boltzmann's constant and *T* the temperature).

For an ensemble of such particles having a statistical distribution of magnetization orientations, thermal equilibrium is attained within a characteristic relaxation time τ . When τ is smaller than the experimental measuring time, the particles are called "superparamagnetic" with respect to that experiment. The calculation of the relaxation time τ was first considered by Néel [11] and later by Brown [12, 13]. They both assumed a ferromagnetic particle with uniaxial anisotropy where the internal magnetization energy is given by $E = KV \sin^2 \theta$, where θ is the angle between magnetization and the easy axis. Néel considered magnetostriction and demagnetization fluctuations induced by vibrations. Brown considered a random walk scheme for the magnetization direction and solved the Fokker-Plank equation. Brown, assuming uniform rotation of the magnetization, obtained for the asymptotic behavior of $1/\tau$ for a large σ in the case of uniaxial anisotropy (see, e.g., [14])

$$\frac{1}{\tau} = \frac{2K\gamma}{\sqrt{\pi}M_{\rm s}} \left(\frac{KV_{\rm M}}{k_{\rm B}T}\right)^{1/2} \exp\left(-\frac{KV_{\rm M}}{k_{\rm B}T}\right),\tag{4.1}$$

where γ is the gyromagnetic ratio (*e/mc*), *K* is the magnetic anisotropy constant, $V_{\rm M}$ is the volume of the magnetic core of the particle, and $M_{\rm s}$ is the saturation magnetization. For a comparison and a re-examination of the Néel–Brown model see Jones and Srivastava [15]. An experimental evidence of the Néel–Brown model of magnetization reversal on individual ferromagnetic cobalt nanoparticles has been recently reported [16]. A review on the magnetic relaxation in nanoparticles is given by Dormann et al. [17].

For bulk ferromagnets at room temperature the ratio σ is of the order 10^{20} . This means that the probability of the magnetic moment to overcome the barrier due to thermal fluctuations is extremely small, and the system is observed always in the "magnetic" state. For subdomain particles, the ratio σ at room temperature is not large and the probability of rotation of the magnetic moment due to thermal fluctuations becomes substantial. The relaxation time τ is thus quite shorter relative to the bulk case, and the system is in the superparamagnetic state. The transition between the magnetic and the superparamagnetic state is very well demonstrated experimentally with the use of ⁵⁷Fe Mössbauer spectroscopy in maghemite (γ -Fe₂O₃) single-domain nanoparticles. In the case of ⁵⁷Fe Mössbauer (and NMR) spectroscopy, the characteristic experimental

measurement time, $t \approx 10^{-8}$ seconds, is determined by the period of the Larmor precession of the spin of the ⁵⁷Fe nuclei, under the influence of the hyperfine magnetic field $H_{\rm hfr}$. At low temperatures, magnetically split sextets appear in the ⁵⁷Fe Mössbauer spectra for this type of single-domain nanoparticles, meaning that $\tau >> t$ and σ >> 1. With increasing temperature, the frequency of the hyperfine fluctuations increases, and when $\tau \approx t$, collapsing of the sextets occurs, which becomes complete (the $H_{\rm hf}$ vanishes) when $\tau << t$.

In the low-temperature magnetic state, the intrinsic motion of the magnetic moments originate from the regular precession of the magnetic moment around the easy direction of the magnetization (i.e., around an effective field H_a due to anisotropy) at an energy minimum and chaotic reorientations of the moment under the action of small thermal fluctuations. These motions have been termed by Mørup as collective magnetic excitations (Fig. 4.2) and correspond to the uniform-mode excitations referred to in the "Introduction" section [7, 8, 18].



Figure 4.2 Schematic representation of magnetic fluctuations in magnetic nanoparticles (adapted from Ref. [18]).

The regular motion of magnetization relative to the effective field may be described using the phenomenological Landau–Lifshitz equation [19]

$$\frac{dM}{dt} = \gamma \left(M \times H_{\text{eff}} \right) - \alpha \frac{\gamma}{M} \left[M \times (M \times H_{\text{eff}}) \right], \qquad (4.2)$$

where α is the dimensionless damping constant, γ is the gyromagnetic ratio, and the magnetic field H_{eff} consists of applied fields and the anisotropy field H_{a} . The first term in Eq. 4.2 describes the free precession of the magnetic moment around the effective field H_{eff} with the Larmor frequency $\omega_{\text{L}} = \gamma H_{\text{eff}}$ while the second term represents the decay of this precession with a characteristic relaxation time $\tau_0 = (\alpha \omega_{\text{L}})^{-1}$. This time is then given by $\tau_0 = (\alpha \gamma H_{\text{eff}})^{-1}$, and if the effective field is composed only from the anisotropy field $H_a = 2K/M_s$, then τ_0 is given by $\tau_0 = M_s/2\alpha\gamma K$.

In Chapter 4 we will discuss the connection of this relaxation time τ_0 with the characteristic time τ_c in the NMR T_2 spin–spin relaxation rate given in the motional narrowing regime by $1/T_2 = \langle \Delta \omega^2 \rangle \tau_c$, where $\langle \Delta \omega^2 \rangle$ is the mean-square fluctuation of the NMR line.

4.2.2 Uniform Mode in Mössbauer and Nuclear Magnetic Resonance Spectroscopies

4.2.2.1 Hyperfine magnetic field in Mössbauer spectroscopy

⁵⁷Fe Mössbauer spectroscopy has been an excellent tool for the magnetic characterization of both bulk and nanoparticle systems containing a Mössbauer isotope, like ⁵⁷Fe. The hyperfine structure in ⁵⁷Fe Mössbauer spectroscopy results from the interactions of the nuclear electric monopole (Coulombic), magnetic dipole, and electric quadrupole moments with the electronic charge density, the magnetic field (H_{hf}) , and the electric field gradient (EFG) at the nucleus, respectively. The first term (E_0) shifts the nuclear ground and excited states' energy levels according to the number and properties of electrons surrounding the nucleus and gives rise to the hyperfine parameter called isomer shift (IS), while the magnetic dipole (M_1) and the electric quadrupole (E_2) interactions both unfold the degeneracy of the nuclear energy levels and generate multipleline spectra, uncovering important information on the properties of the material in study. A comprehensive review of Mössbauer spectroscopy in nanoparticle systems has been given by Dormann et al. [17].

Mørup et al. have extensively applied the concept of uniform-mode excitations in ferromagnetic, ferrimagnetic, and antiferromagnetic nanoparticles and explained their Mössbauer and inelastic neutronscattering experiments according to this model (for a recent review see [18]).

We will give a brief description of this initial simple approach. A particle with uniaxial magnetic anisotropy is assumed, and if θ is the angle between the magnetization of the particle and the easy axis of the magnetization, then the anisotropy energy may be written in the form $E(\vartheta) = -KV \cos^2 \vartheta$. Then in Mørup's model [7], the essential idea is that at low temperatures below the blocking temperature ($k_BT << KV$) there is a finite probability that the magnetization makes an angle between θ and $\theta + d\theta$ with the easy direction and thus the average magnetization may be given as $M(T) = M_0 \langle \cos \vartheta \rangle_T$, where M_0 is the saturation magnetization and $\langle \cos \vartheta \rangle_T$ is the thermal average of $\cos \theta$, which can be evaluated using Boltzmann statistics.

The prime result of this classical approach is that for ferromagnetic and ferrimagnetic nanoparticles, the *z* component of the magnetization in the limit of low temperatures is given by

$$\langle M \rangle \cong M_0 \left[1 - \frac{k_{\rm B}T}{2KV} \right],$$
 (4.3)

contrary to the $T^{3/2}$ dependence of the Bloch law in bulk ferromagnets. Assuming that these fluctuations are of much higher frequency than the Larmor precession frequency of the ⁵⁷Fe Mössbauer nucleus, the magnetic hyperfine field is expected to be proportional to the magnetization. Thus, at low temperatures the observed hyperfine field in ⁵⁷Fe Mössbauer spectroscopy is consequently given by

$$\langle H_{\rm hf} \rangle \cong H_0 \left[1 - \frac{k_{\rm B}T}{2KV} \right]$$
 (4.4)

A high field approximation of the Langevin function produces also the same result [38]. Later on, Mørup and Hansen [9] used the spin wave model for nanoparticles and showed that to a first approximation, the results are similar to the classical model described above.

4.2.2.2 Nuclear relaxation in nuclear magnetic resonance spectroscopy

NMR in magnetic materials elucidates the static and hyperfine coupling in the ordered system at a local level, through the timeaverage field produced by electron spin and orbital currents at the site of the nuclei [20, 21]. Examples of the static magnetic information mainly obtained from the NMR spectrum include the magnitude and direction of the hyperfine field (H_{hf}), its temperature and pressure dependence, etc. The dynamics of the magnetic system can be observed through dynamic interactions of the nuclear spins by the characteristic relaxation times for spin–spin (T_2) and spin–lattice (T_1) coupling. Spin diffusion and spin wave processes may also be observed [20].

The first observation of NMR in magnetically ordered material has been reported by Gossard and Portis in 1959 [22], namely, the observation of ⁵⁹Co from face-centered cubic (fcc) metallic cobalt powder in a zero external magnetic field. The very first ⁵⁹Co resonance traced at room temperature appeared to be much more intense than expected, due to the strong domain wall enhancement factor. Following this, very quickly the ⁵⁷Fe NMR in metallic iron [23, 24] and ⁶¹Ni in metallic nickel [25] has been reported.

Although the first NMR experiments on single-domain particles were reported as early as 1965, by Gossard et al. [26] on cobalt particles in the range of 10 nm, relatively few NMR studies on magnetic nanoparticles and nanowires have appeared in the literature compared to the numerous NMR studies on bulk magnets ([27] and references therein). As mentioned above, the NMR signal in ferromagnets is strongly enhanced and therefore easily observable because the nuclear resonance excitation is produced indirectly by the sample magnetization rather by the radio-frequency (rf) field. In multidomain particles the principal magnetization process in the rf range is the displacement of domain walls and is usually controlled by the magnetic anisotropy and wall-pinning effects. On the other hand, for particles too small to form walls, the principal magnetization process is the rotation of the magnetization, which is controlled by the magnetic anisotropy field. Despite the domain rotation enhancement factor, in his early study Gossard found that the only way to produce a detectable ⁵⁹Co NMR signal in single-domain fcc cobalt particles was the cooling of the particles at liquid nitrogen temperatures because of the very short T_2 transverse relaxation time [26]. Gossard attributed this reduction of the T_2 relaxation time to the rapid thermal fluctuations of the longitudinal magnetization of the nanoparticles.

Gossard was able to show that the T_2 spin–spin relaxation time of a single-domain particle depends on the square of the volume of the particle and on the inverse square of the temperature. He assumed that single-domain particles obey the Langevin equation, and he considered the thermal average of the square of the fluctuation of the longitudinal magnetization $\langle \Delta M_z^2 \rangle_{\text{thermal}}$.

According to Kambe and Usui [28] this can be written as

$$\left\langle \Delta M_{\rm z}^2 \right\rangle_{\rm thermal} = \left\langle M_{\rm z}^2 \right\rangle_{\rm thermal} - \left\langle M_{\rm z} \right\rangle_{\rm thermal}^2$$
,

an expression that has been frequently employed in the calculation of the second-order moment in the investigations of the line shape of paramagnetic resonance lines at arbitrary temperatures.

Assuming an ideal superparamagnetic assembly of singledomain particles with particle volume *V* and magnetic anisotropy field H_a , the magnetization M_z is proportional to the Langevin function, and it can be proved that the mean-square fluctuation of the magnetization is given by the derivative of the Langevin function $\langle \Delta M_z^2 \rangle_{\text{thermal}} = d(L(x))/dx$, which after some algebra gives

$$\left\langle \Delta M_{z}^{2} \right\rangle_{\text{thermal}} = M^{2} \left[1 - 2L(x) / x - L^{2}(x) \right],$$

where $x = MVH_a/k_BT$ and L(x) is the Langevin function of the variable x.

In a very-small-thermal-fluctuation regime, $x = MVH_a/k_BT>>1$, the mean-square fluctuation of the magnetization becomes

$$\left\langle \Delta M_{\rm z}^2 \right\rangle_{\rm thermal} = M^2 \left[\frac{k_{\rm B}T}{MVH_{\rm a}} \right]^2.$$
 (4.5)

Equation (4.5) shows that the small thermal fluctuations of the magnetic moment around the easy direction of the magnetization in the low-temperature regime result in a finite second moment of the fluctuations of the longitudinal magnetization, which is proportional to $[k_{\rm B}T/MVH_{\rm a}]^2$.

These fluctuations are the collective magnetic excitations discussed by Mørup, and we have seen that within the classical model both the average magnetization and the mean-square fluctuation of the magnetization can be derived by the high field approximation of the Langevin function.

At this point it should be also mentioned that neutron-scattering experiments of the spin precession of ferrimagnetic (maghemite) nanoparticles [29] were also analyzed in terms of Boltzmann statistics. Namely, the intensity of the inelastic peaks in terms of the total magnetic intensity was given by $\langle \sin^2 \vartheta \rangle_{\rm T}$.

Returning now to the calculation of the nuclear T_2 relaxation time, according to Eq. 4.5, the mean-square fluctuation in the nuclear resonance in the limit of very small thermal fluctuations is then given by

$$\left\langle \Delta \omega^2 \right\rangle_{\text{thermal}} = \omega^2 \left[\frac{k_{\text{B}}T}{MVH_{\text{a}}} \right]^2,$$
 (4.6)

where ω is the NMR Larmor frequency.

In the motional narrowing regime $\langle \Delta \omega^2 \rangle^{1/2} \tau_c \ll 1$, the nuclear relaxation rate is given by the motional averaging expression

$$1/T_2 = \left\langle \Delta \omega^2 \right\rangle \tau_c \,, \tag{4.7}$$

where τ_c is an electronic relaxation time. Finally combining Eqs. 4.6 and 4.7 one obtains for the $1/T_2$ spin–spin nuclear relaxation rate

$$\frac{1}{T_2} = \omega^2 \left[\frac{k_{\rm B} T}{M V H_{\rm a}} \right]^2 \tau_{\rm c} \,. \tag{4.8}$$

Finally, assuming uniaxial anisotropy for the particles, the anisotropy field may be given by $H_a = 2K/M$; therefore Eq. 4.8 becomes

$$\frac{1}{T_2} = \omega^2 \left[\frac{k_{\rm B} T}{2KV} \right]^2 \tau_{\rm c} \,. \tag{4.9}$$

This is the result of Gossard, which shows that for small nanoparticles at room temperature the NMR signal is undetectable due to the very short T_2 relaxation time. Indeed for τ_c of the order of 10^{-9} seconds and for a cobalt particle of 9 nm, Eq. 4.8 gives T_2 at liquid nitrogen temperatures of the order of 1 µs. One has to cool at liquid helium temperatures in order to observe the NMR signal, because

the relaxation time increases with cooling. However, later, Yasoka and Lewis [30] managed to measure the temperature dependence of single-domain cobalt particles with sizes between 12 nm and 22 nm. They reported that the ⁵⁹Co nuclear resonance frequency followed the $T^{3/2}$ Bloch law up to temperatures as high as 450 K.

4.3 ⁵⁷Fe Mössbauer Spectroscopy Experiments

We have applied ⁵⁷Fe Mössbauer spectroscopy on 3 nm dextrancoated γ -Fe₂O₃ nanoparticles to elucidate the dynamic magnetic properties of the system through the uniform-mode excitation model and to estimate the value of the magnetic anisotropy constant *K*.

Selected Mössbauer spectra of the 3 nm maghemite nanoparticles are shown in Figs. 4.3 and 4.4 for high and low temperatures representing the superparamagnetic and the blocked regime, respectively.



Figure 4.3 $^{57}\mbox{Fe}$ Mössbauer spectra of the 3 nm dextran-coated $\gamma\mbox{-Fe}_2O_3$ nanoparticles at the high-temperature superparamagnetic regime.



Figure 4.4 5^{7} Fe Mössbauer spectra of the 3 nm dextran-coated γ -Fe₂O₃ nanoparticles at the low-temperature blocked regime.

The temperature dependence of the average hyperfine field, $\langle H_{\rm hf}(T) \rangle / \langle H_{\rm hf}(0) \rangle$ (scaled to the extrapolated value at T = 0), for the 3 nm nanoparticles is shown in Fig. 4.5, alongside with previous Mössbauer studies on Fe₃O₄ magnetite nanoparticles [7]. The linear relation of $H_{\rm hf}$ with temperature according to Eq. 4.4 is thus easily verified.

Assuming uniaxial anisotropy for the maghemite nanoparticles, the calculation of an effective magnetic anisotropy constant using Eq. 4.4 gives $K_{\text{eff}} = 6.1 \times 10^5 \text{ erg/cm}^3$ for the 3 nm maghemite nanoparticles. A similar Mössbauer study for 10 nm maghemite

nanoparticles gave $K_{\rm eff} = 1.4 \times 10^5 \, {\rm erg/cm^3}$, in good agreement with the one obtained from magnetization measurements [27]. Finally, a reduced plot of Eq. 4.4, that is, $<H_{\rm hf}(T)>/<H_{\rm hf}(0)>$ as a function of the dimensionless parameter $k_{\rm B}T/2K_{\rm eff}V$, for all the data is shown in Fig. 4.6.



Figure 4.5 Temperature dependence of the reduced average hyperfine field $\langle H_{hf} \rangle / \langle H_0 \rangle$ as obtained from Mössbauer measurements for 3 nm dextran-coated γ -Fe₂O₃ nanoparticles (filled inverted triangles, this work) as well as for Fe₃O₄ magnetite nanoparticles (circles, inverted triangles [7]). The lines are linear fits to the data according to Eq. 4.4.



Figure 4.6 Reduced plot of the average scaled hyperfine field $\langle H_{hf}(T) \rangle / \langle H_{hf}(0) \rangle$ as a function of the dimensionless parameter $k_{\rm B}T/2K_{\rm eff}V$, as obtained from Mössbauer measurements for 3 nm dextran-coated γ -Fe₂O₃ nanoparticles (filled inverted triangles, this work) as well as for Fe₃O₄ magnetite nanoparticles (circles, inverted triangles, [7]). The line is given according to Eq. 4.4.

4.4 ⁵⁷Fe Nuclear Magnetic Resonance Spectroscopy Experiments

4.4.1 Nuclear Magnetic Resonance Line Shapes

The NMR technique has been frequently employed for the study of bulk magnetic materials, and as an example of 57 Fe NMR on iron oxides, we show in Fig. 4.7 representative spectra (obtained by the spin-echo point-to-point method) of powder magnetite (Fe₃O₄).

It is well known that magnetite in the cubic phase above 118 K is an inverse spinel with all tetrahedral sites occupied by Fe^{3+} ions and with Fe^{2+} and Fe^{3+} ions in octahedral sites. The two resonances observed in Fig. 4.7 could be readily attributed to these crystallographic sites. Since the resonance frequencies are expected to be proportional to the sublattice magnetizations, the temperature dependence of the NMR frequencies could be directly compared with the predictions of spin wave theory ($T^{3/2}$ Bloch's law). Boyd [31] has indeed shown that the resonance frequency from tetrahedral sites and the distribution of resonance frequencies from octahedral sites follow the $T^{3/2}$ law, as shown in Fig. 4.8.



Figure 4.7 Zero external field ⁵⁷Fe NMR spectra of bulk Fe₃O₄ powder at selected temperatures. The lines are fits to the data using a superposition of two Gaussian functions.

NMR has thus been frequently used for the comparison of experiments with the predictions of spin wave theory for the temperature dependence of the magnetization in magnetically ordered systems. The first experimental test of spin wave theory for ferromagnets using NMR was performed by Gossard et al. with $CrBr_3$, the first insulating ferromagnet [32]. Other examples include EuS—another model system for Heisenberg ferromagnets [33], ferrimagnetic $MnFe_2O_4$ [34], antiferromagnetic MnF_2 [35], etc. It is important to note that in ferrites of garnet-type structure, the NMR method follows separately the temperature dependence of



the sublattice magnetizations and not the total magnetization as in conventional magnetic measurements (see, e.g., [36, 37]).

Figure 4.8 Magnetic moment, ⁵⁷Fe NMR resonance frequency from tetrahedral sites, and distribution of resonance frequencies from octahedral sites vs. $T^{3/2}$ for bulk powder Fe₃O₄ (adapted from [31]).

Despite the fact that many iron oxides have been extensively studied by ⁵⁷Fe NMR as early as 1962, a few studies have been reported for maghemite (γ -Fe₂O₃), either for bulk or for nanoparticles ([27] and references therein). Examples of zero external magnetic field ⁵⁷Fe NMR spectra of bulk maghemite are shown in Fig. 4.9.

The maghemite NMR spectra could be readily resolved into two hyperfine field components as in magnetite. According to Lee [39] the lower-resonance-frequency component can be attributed to nuclei from the A-site (tetrahedral) and the higher-frequency one to nuclei from the B-site (octahedral) due to the stronger covalent bonding of an Fe ion in a tetrahedral site than in an octahedral one. As expected, there is good agreement of the hyperfine field values for the two sites as obtained from NMR and Mössbauer measurements.

Figure 4.10 shows ⁵⁷Fe zero field NMR spectra of a series of maghemite nanoparticles of various sizes compared to the bulk one.



Figure 4.9 Zero external field 57 Fe NMR spectra of bulk γ -Fe₂O₃ at selected temperatures. The lines are fits to the data using a superposition of two Gaussian functions.

It is shown in Fig. 4.10 that the basic features of the nuclear resonance of ⁵⁷Fe in maghemite nanoparticles are essentially the same as that of bulk maghemite. Nevertheless, there is a gradual decrease of the hyperfine field values with decreasing particle size, particularly for tetrahedral sites.

This is shown in Fig. 4.11 where the NMR frequencies of the nuclei in tetrahedral and octahedral sites are plotted as a function of particle diameter for maghemite nanoparticles of various sizes at T = 5 K. These observations are in accord with Mössbauer experiments in 3–10 nm γ -Fe₂O₃/PVA particles where the average hyperfine field $\langle H_{hf} \rangle$ value extrapolated to zero temperatures slightly decreases with decreasing particle size, a behavior observed in other relative studies [17].



Figure 4.10 Zero external field ⁵⁷Fe NMR spectra of dextran-coated (3 nm and 10 nm), uncoated (16 nm), and bulk γ -Fe₂O₃ at *T* = 5 K. The solid lines are fits to the data using a superposition of two Gaussian functions. The dashed lines in the spectra correspond to hyperfine fields of 52 T and 53.4 T.

Finally, a crystallographically based analysis [40], as well as the vacancy ordering [41, 42] in bulk and nanosized maghemite, as observed in ⁵⁷Fe NMR spectra, have been recently appeared.

4.4.2 Nuclear T₂ Transverse Relaxation

Insights into the dynamics of magnetically ordered systems can be gained from the measurements of the T_2 transverse spin-spin relaxation times. The ⁵⁷Fe nuclei with nuclear spin I = 1/2 have pure dipole magnetic moments; hence the relaxation mechanism is solely attributed to the fluctuations of local magnetic fields. As we shall see in the following, magnetic nanoparticles exhibit considerably different spin dynamics of the nuclear spins when compared to their bulk counterparts. Figure 4.12 shows ⁵⁷Fe NMR spectra and spin-spin relaxation decays (obtained by the spin-echo method) of 10 nm dextran-coated and uncoated as well as bulk maghemite, obtained in a zero external magnetic field at 5 K.



Figure 4.11 ⁵⁷Fe NMR frequencies corresponding to nuclei from tetrahedral and octahedral sites as a function of diameter for maghemite nanoparticles of various sizes at T = 5 K. Data points: circles this work; inverted triangles, [39].

Despite the similarity of the observed hyperfine fields, there is a clear distinction of the nuclear T_2 spin–spin relaxation time between the magnetic nanoparticles and the bulk material, as clearly demonstrated in the right column of Fig. 4.12.

It is observed that the spin-echo relaxation decays are increasingly longer as one proceeds from the coated to the uncoated and the bulk samples. The T_2 value of the coated nanoparticles $(T_2^{\text{coated}} = 0.09 \text{ ms})$ is three times shorter than that of the uncoated one $(T_2^{\text{uncoated}} = 0.3 \text{ ms})$, and both are two orders of magnitude shorter than the corresponding T_2 for the bulk maghemite $(T_2^{\text{bulk}} = 10 \text{ ms})$.

Actually, due to the short T_2 relaxation time, the NMR signal in the 10 nm dextran-coated maghemite nanoparticles could only be detected up to temperatures of 15 K, whereas that of the uncoated sample was found up to about 50 K, and that of the bulk maghemite powder was already observable at room temperature. These values correspond to the time where the NMR decay signal has dropped to the 1/e of its initial value, since the spin-echo relaxation decays are not exponential functions.



Figure 4.12 Zero magnetic field ⁵⁷Fe NMR spectra (left column) and T_2 relaxation decays (right column) of 10 nm coated (a, b), 10 nm uncoated (c, d) maghemite nanoparticles and bulk maghemite (e, f), respectively. The dashed lines in the NMR spectra correspond to hyperfine fields of 52 T and 53.4 T. In the T_2 decays, note the difference in scale for the bulk material. The time scale of the spin-echo decay for the bulk material is two orders of magnitudes longer than that of the maghemite nanoparticles. The measuring temperature is 5 K.

T = 5 K

A similar reduction of the T_2 relaxation time is observed when the particle diameter decreases. Figure 4.13 shows the measured 1/ T_2 relaxation rates for the 3 nm coated and 10 nm, 16 nm, 26 nm, and 37 nm uncoated maghemite nanoparticles and bulk maghemite (3 μ) as a function of inverse diameter 1/*D*.



Figure 4.13 Nuclear $1/T_2$ relaxation rates as a function of inverse diameter 1/D for γ -Fe₂O₃ at 71 MHz (tetrahedral sites) and T = 5 K. In the inset the $1/T_2$ rates are plotted as a function of the fraction of the atoms residing at the particle surface. The lines serve as guides to the eye.

The significant increase of the $1/T_2$ relaxation rate with particle diameter is obvious. In the inset of Fig. 4.13 the $1/T_2$ relaxation rates are plotted as a function of the fraction c of the atoms residing at the particle surface. This fraction c was estimated according to $c \sim 6a_0/(D - 6a_0)$, where α_0 is the interatomic distance (about 0.2 nm) [43]. Due to this considerable reduction of T_2 with increasing temperature and decreasing particle size, experimental verification of deviations of the spin wave $T^{3/2}$ Bloch law in maghemite nanoparticles using the ⁵⁷Fe NMR is not possible for single-domain particles with a mean size less than 10–20 nm. For digression of the thermal dependence

of magnetization from the $T^{3/2}$ law in nanostructured ferromagnets see, for example, Della Torre et al. [44] and Zhang et al. [45].

As mentioned above, the spin-echo relaxation decays for maghemite nanoparticles were found to be nonexponentials as also observed in bulk ferromagnets. It is possible to analyze these decays using a double exponential function yielding a short T_2^{short} and a long T_2^{long} relaxation time. These relaxation times as a function of temperature for the 10 nm dextran-coated maghemite nanoparticles and for the bulk maghemite are shown in Fig. 4.14.



Figure 4.14 Nuclear spin-spin relaxation times T_2 as a function of temperature T for 10 nm dextran-coated nanoparticles (circles and inverted triangles) and bulk γ -Fe₂O₃ (squares and triangles), measured at the tetrahedral sites. The straight lines for bulk γ -Fe₂O₃ are linear fits to the data. The curves for the coated nanoparticles correspond to fits described in the text (adapted from [27]).

The transverse relaxation rates $1/T_2^{\text{short}}$ and $1/T_2^{\text{long}}$ measured at the tetrahedral sites (at NMR frequency of 71 MHz) as a function

of temperature for the 10 nm dextran-coated γ -Fe₂O₃ nanoparticles are shown in Fig. 4.15.



Figure 4.15 Temperature dependence of the nuclear spin–spin relaxation rates $1/T_2$ for 10 nm dextran-coated nanoparticles γ -Fe₂O₃, measured at the tetrahedral sites. The straight lines are linear fits to the data, as described in the text (adapted from [27]).

It is observed that the relaxation rate of the short component, $1/T_2^{\text{short}}$, scales linearly with temperature (Fig. 4.15b), whereas the rate of the long component, $1/T_2^{\text{long}}$, scales linearly with the square of the temperature (Fig. 4.15a). From the analysis of the double exponential fits of the relaxation decays for the 10 nm nanoparticles, it is observed that the weight of the short component (corresponding to T_2^{short}) is on average (for the different temperatures concerned) 70%–80% of the total NMR magnetization and that of the long component (corresponding to T_2^{long}) is 20%–30%. The analysis of

the 16 nm uncoated maghemite nanoparticles gave equal weights of the short and long T_2 components and that of the 26 nm nanoparticles gave 20% and 80% for the short and long components, respectively. A single T_2 relaxation time was observed in the 37 nm nanoparticle assembly. These findings clearly indicate that the weight of the short component of T_2 could be tentatively associated with the number of Fe³⁺ ions in the surface of the nanoparticles, since, as also mentioned earlier, this number increases as the particle diameter decreases. Therefore it could be argued that the T_2^{short} component is influenced by the surface spins of the nanoparticles, and the T_2^{short} relaxation mechanism is modulated by electronic fluctuations of the surface spins generally regarded as noncollinear or disordered. The linear temperature dependence of T_2^{short} is also reminiscent of the linear dependence of the domain wall relaxation in bulk ferromagnets. Indeed it can be assumed that even in a single-domain particle, a transition region may exist between the well-ordered core spins and the disordered surface spins in analogy to a domain wall in bulk multidomain materials. This transition region will respond to the exciting rf field and give linear temperature dependence similar to that of bulk maghemite.

The $1/T_2^{\text{long}}$ relaxation rate scales with the square of temperature and thus follows the temperature dependence of the small thermal fluctuations in the collective magnetic excitations described by Eq. 4.9. Also the model explains the disappearance of the NMR signal of the larger-diameter particles at higher temperatures than the smaller-diameter ones. It is also possible to carry out a numerical estimation of the T_2^{long} value using the parameters in Eq. 4.9 estimated from other experiments. Indeed the effective anisotropy constant can be evaluated both from magnetization and Mössbauer experiments, Eq. 4.4. For the 10 nm coated maghemite nanoparticles the anisotropy constant is $K_{\rm eff} = 1.6 \times 10^5 \, \rm erg/cm^3$ [27]. The other parameters are all known: the bulk saturation magnetization M = 400 emu/cm³, the particle volume $V = 5.2 \times 10^{-19}$ cm³, and the nuclear frequency $\omega/2\pi = 71$ MHz. The only adjustable parameter is the electronic relaxation time τ_c . Using the above parameters, the best fit of the analysis using Eq. 4.3 (shown as solid line in Fig. 4.15b) yields a value for the relaxation time $\tau_c = 2 \times 10^{-10}$ seconds. This value is within the range of theoretical predictions of the gyromagnetic precession time τ_0 (between 10^{-9} s and 10^{-11} s) [17], which is the dominant microscopic relaxation time in the low-temperature region of spin fluctuations.

Thus it has been shown that thermal fluctuations in the longitudinal magnetization of nanoparticles in the low-temperature limit may account for the shortening and temperature dependence of the long component of the T_2 relaxation time. As we have shown it can be asserted that this NMR relaxation mechanism originates from the concept of collective magnetic excitations due to the precession of the magnetization around an energy minimum.

4.5 Concluding Remarks

The concept of elementary excitations in magnetic nanoparticles is examined in this work using atomic-level probing techniques such as ⁵⁷Fe NMR and Mössbauer spectroscopies. It is well known that ⁵⁷Fe Mössbauer spectroscopy is an ideal technique to elucidate the magnetic behaviour of single-domain ferrimagnetic oxide nanoparticles. In particular, the low-temperature ⁵⁷Fe Mössbauer spectra of this system exhibit a six-line magnetically split hyperfine structure, typical of an ordered ferromagnetic system, whereas by increasing temperature the sextet collapses into a doublet resembling a paramagnetic state, far below the ferromagnetic ordering temperature of the material. It is the increasing thermal fluctuations of the orientation of the nanoparticles' magnetic moments that cause the early collapse of the magnetic hyperfine splitting in these materials—the well-known phenomenon of superparamagnetism.

Fluctuations of the orientation of the magnetization still exist in the low-temperature region. These collective magnetic excitations originate from the regular precession of the magnetic moment around the easy direction of the magnetization at an energy minimum and chaotic reorientations of the moment under the action of small thermal fluctuations. As we have shown, Mössbauer spectroscopy probes these collective excitations by the temperature dependence of the average magnetic hyperfine field obtained from the static Mössbauer spectra recorded at different temperatures. Examples were provided for γ -Fe₂O₃ maghemite nanoparticles. The same procedure can be applied in NMR experiments; however, the T_2 nuclear transverse relaxation time is the limiting factor that determines the temperature range where NMR spectra could be obtained. Nevertheless, this relaxation mechanism is an additional time domain relaxation probe for the study of the dynamic magnetic behavior of nanoparticles. It has been shown that the temperature dependence of T_2 originates from the mean-square fluctuations of the collective magnetic excitations present in nanoparticles at the lowtemperature regime and the NMR experimental data nicely combines with the Mössbauer ones. The combined NMR and Mössbauer experiments are thus suitable and complementary probes for the microscopic investigation of the electronic fluctuations of iron oxide magnetic nanoparticles. Under this aspect, future research could involve the investigation of core-shell structures and in particular the iron-iron oxide case, the vacancy order or disorder of the octahedral sites in maghemite, T_1 spin-lattice NMR relaxation, and enhancement of the NMR signal in tetrahedral and octahedral sites, in relation to the corresponding Mössbauer spectral line shape, as well as the influence of interparticle dipolar magnetic interactions on uniform-mode excitations in the case of ferromagnetic, ferrimagnetic or antiferromagnetic iron oxide nanoparticles.

Acknowledgments

This research was supported by a Marie Curie International Research Staff Exchange Scheme Fellowship within the 7th European Community Framework Programme.

References

- 1. Anderson, P. W. (1984). *Basic Notions of Condensed Matter Physics*, Benjamin-Cummings, London.
- 2. Anderson, P. W. (1997). Concepts in Solids, World Scientific, Singapore.
- 3. Landau, L. D., Lifshitz, E. M. (1958). *Statistical Physics, Course of Theoretical Physics*, Vol., 5, Pergamon, London.
- 4. Patton, C. E. (1975). *Microwave Resonance and Relaxation* (Craik, D. J., ed.), John Wiley, London.
- 5. Chaikin, P. M., Lubensky, T. C. (1995). *Principles of Condensed Matter Physics*, Cambridge University Press, U.K.

- 6. Callaway, J. (1974). *Quantum Theory of the Solid State, Part A*, Academic Press, New York and London.
- 7. Mørup, S., Topsøe, H. (1976). Appl. Phys., 11, 63-66.
- 8. Mørup, S., Topsøe, H., Lipka, J. (1976). J. Phys. Colloq., 37(C6), 287-290.
- 9. Mørup, S., Hansen, B. R. (2005). Phys. Rev. B, 72, 0244181-0244186.
- 10. Kittel, C. (2005). *Introduction to Solid State Physics*, John Wiley & Sons, New York.
- 11. Néel, L. (1955). Adv. Phys., 4, 191–243 and references therein.
- 12. Brown, W. F. (1959). J. Appl. Phys., 30S, 130–132.
- 13. Brown, W. F. (1963). Phys. Rev., 130, 1677-1686.
- 14. Aharoni, A., Eisenstein, I. (1975). Phys. Rev. B, 11, 514-519.
- Jones, D. H., Srivastava, K. K. P. (1989). J. Magn. Magn. Mater., 78, 320– 328.
- Wernsdorfer, W., Orozco, E. B., Hasselbach, K., Benoit, A., Barbara, B., Demoncy, N., Loiseau, A., Pascard, H., Mailly, D. (1997). *Phys. Rev. Lett.*, 78(9), 1791–1794.
- 17. Dormann, J. L., Fiorani, D., Tronc, E. (1997). *Adv. Chem. Phys.*, **98**, 283–494.
- Mørup, S., Frandsen, C., Hansen, M. (2010). *Beilstein J. Nanotechnol.*, 1, 48–54.
- 19. Morrish, A. H. (1965). *The Physical Properties of Magnetism*, John Wiley & Sons, New York.
- Portis, A. M., Lindquist, R. H. (1965). Nuclear resonance in ferromagnetic materials, in *Magnetism: A Treatise on Modern Theory and Materials* (Rado, G. T., Suhl, H., ed.), Vol. IIA, pp. 357–383, Academic Press, New York and London.
- 21. Turov, E. A., Petrov, M. P. (1972). *Nuclear Magnetic Resonance in Ferroand Antiferromagnets*, Halsted, New York.
- 22. Gossard, A. C., Portis, A. M. (1959). Phys. Rev. Lett., 3(4), 164-166.
- 23. Robert, C., Winter, J. M. (1960). Compt. Rend., 250, 3831.
- Budnick, J. I., Bruner, L. J., Blume, R. J., Boyd, E. L. (1961). J. Appl. Phys., 32(3), S120–S121.
- 25. Bruner, L. J., Budnick, J. I., Blume, R. J. (1961). Phys. Rev., 121, 83-83.
- Gossard, A. C., Portis, A. M., Rubinstein, M., Lindquist, G. H. (1965). *Phys. Rev.*, **138**(5), A1415–A1421.
- 27. Fardis, M., Douvalis, A. P., Tsitrouli, D., Rabias, I., Stamopoulos, D., Kehagias, Th., Karakosta, E., Diamantopoulos, G., Bakas, T.,

Papavassiliou, G. (2012). J. Phys.: Condens. Matter, **24**(15), 156001(1–16).

- 28. Kambe, K., Usui, T. (1952). Prog. Theor. Phys., 8(3), 302-316.
- 29. Lefmann, K., Bødker, F., Klausen, S. N., Hansen, M. F., Clausen, K. N., Lindgård, P.-A., Mørup, S. (2001). *Europhys. Lett.*, **54**(4), 526–532.
- 30. Yasuoka, H., Lewis, R. T. (1969). Phys. Rev., 183(2), 559-562.
- 31. Boyd, E. L. (1963). Phys. Rev., 129(5), 1961-1964.
- 32. Gossard, A. C., Jaccarino, V., Remeika, I. P. (1961). *Phys. Rev. Lett.*, 7, 122–124.
- 33. Charap, S. H., Boyd, E. L. (1964). Phys. Rev., 133(3), A811-A818.
- 34. Heeger, A. J., Houston, T. (1964). J. Appl. Phys., 35(3) (Part 2), 836–837.
- Jaccarino, V. (1965). Nuclear Resonance in Antiferromagnets, in Magnetism: A Treatise on Modern Theory and Materials (Rado, G. T., Suhl, H., ed.), Vol. IIA, pp. 307–355, Academic Press, New York and London.
- 36. Gonano, R., Hunt, E., Meyer, H. (1967). Phys. Rev., 156(2), 521-533.
- 37. Petrov, M. P., Turov, E. A. (1972). Appl. Spectrosc. Rev., 5(1), 265–330.
- Mørup, S., Christensen, P. H., Clausen, B. S. (1987). J. Magn. Magn. Mater., 68, 160–170.
- 39. Lee, S.-J., Lee, S. (2009). New J. Phys., 8, 98(1-7).
- Spiers, K. M., Cashion, J. D. (2012). J. Magn. Magn. Mater., 324(5), 862– 868.
- 41. Bastow, T. J., Trinchi, A. (2009). Solid State Nucl. Magn., Reson., 35, 25– 31.
- Bastow, T. J., Trinchi, A., Hill, M. R., Harris, R., Muster, T. H. (2009). J. Magn. Magn. Mater., 321, 2677–2681.
- Perzynski, R., Raikher, Y. L. (2005). Effect of surface anisotropy on the magnetic resonance properties of nanosize ferroparticles, in *Surface Effects in Magnetic Nanoparticles* (Fiorani, D., ed.), pp. 141–187, Springer, New York.
- 44. Della Torre, E, Bennett, L. H., Watson, R. E. (2005). *Phys. Rev. Lett.*, **94**, 147210(1–3).
- 45. Zhang, D., Klabunde, K. J., Sorensen, C. M., Hadjipanayis, G. C. (1998). *Phys. Rev. B*, **58**, 14167–14170.

Chapter 5

Magnetic Properties of Spinel Ferrite Nanoparticles: Influence of the Magnetic Structure

Davide Peddis

ISM-CNR, Area della Ricerca Roma1, Via Salaria km 29.300, C.P. 10, 00016 Monterotondo, Scalo (RM), Italy david.peddis@ism.cnr.it

5.1 Introduction

On entering the nanometer-scale regime the magnetic properties of condensed matter show substantial differences with respect to the bulk state, leading to new physics [1, 2] and applications [3]. Among nanostructured magnetic materials, nanoparticles are unique complex physical objects. In fact, at the nanoscale, a multidomain organization is energetically unfavorable and singlemagnetic-domain particles are formed, each one with a large magnetic moment named *supermoment*. The behavior of a random assembly of nanoparticles depends on the type and strength of interparticle interactions, evolving from ferromagnetic (FM)-like to paramagnetic-like, including a spin-glass-like behavior. Due to the enhanced time and magnetization scale with respect to atomic systems, the magnetism of nanoparticle assembly has been often called *supermagnetism* [4].

Beyond magnetic interparticle interactions, the physics of nanoparticle assemblies is influenced by finite-size effects on the properties of the particle's core and by the modification of structural and electronic properties at the particle surface [5, 6]. The breaking of lattice symmetry and broken bonds at the surface gives rise to sitespecific surface anisotropy, weakened exchange coupling, magnetic frustration, and a noncollinear spin structure (i.e., spin canting) [7, 8]. The presence of spin canting deserves special attention, as it determines strong modifications in the magnetic properties. In fact, it may propagate from the surface to the particle core, so the picture of the particle as a perfectly ordered magnetic single domain, whose spins rotate in a synchronous way as a large single spin, is no longer valid [8–11].

Among nanoscaled magnetic materials, nanoparticles of iron oxide with a spinel structure (MeFe₂O₄, Me = Fe²⁺, Co²⁺, Ni²⁺, Mg²⁺, Mn²⁺, Zn²⁺, etc.) have generated great interest. Spinel ferrite nanoparticles are important in ferrofluid technology, catalysts, color imaging [12], and biomedicine [13] (magnetically guided drug delivery and hyperthermic treatments) [3, 14-16]. Furthermore, iron oxide nanoparticles (Fe₃O₄, γ -Fe₂O₃) play an important role in nature; indeed, they are commonly found in soils and rocks and are also important in several ways for the functioning of living organisms [17]. These systems are interesting also from a fundamental point of view because they are good model systems for studies on the relationship between magnetic behavior and magnetic structure at the atomic level [18]. In addition, the structural properties and the rich crystal chemistry of spinels offer excellent opportunities for understanding and fine-tuning the magnetic properties [19, 20]. The spinel ferrite structure is based on a closed-packed oxygen lattice, in which tetrahedral (T_d) and octahedral (O_h) interstices are occupied by cations.

Thus, the magnetic properties of ferrite nanoparticles with a spinel structure are due to a complex interplay of several effects, where cationic distribution and spin canting are fundamental factors [11, 21].

Among spinel ferrites $CoFe_2O_4$ is especially interesting because of its mechanical hardness, remarkable chemical stability, and high anisotropy ($K_a = 3 \times 10^5$ J/m³) [22] due to a strong cubic anisotropy of magnetocrystalline origin, mainly attributed to Co^{2+} ions, which have nonzero orbital momentum [23]. At the nanoscale, the coexistence of cubic and uniaxial anisotropy is observed, with a pure uniaxial anisotropy for small particles [24, 25]. In the last years, $CoFe_2O_4$ has been considered very attractive in the biomedical field for its high magnetic anisotropy and saturation magnetization, which give rise to a suitable magnetic behavior at room temperature, despite the presence of cobalt making it potentially toxic. In any case, great advances in surface modification both for protection and for functionalization needs, open an interesting perspective for this material in the biomedical field [26–28].

The aim of this chapter is to gain a better insight into the effect of the complex interplay between cationic distribution and spin canting on magnetic properties in spinel ferrite nanoparticles using $CoFe_2O_4$ as a model system. The presented data results from wide research on magnetic properties of CoFe₂O₄ nanoparticles, unsupported or embedded in a silica matrix, prepared by a sol-gel autocombustion method [11, 20, 21, 29-34]. After a short overview on nanoparticle magnetism (Section 5.1), in Section 5.2 new experimental results elucidating the effects of cationic distribution and spin canting on magnetic properties are discussed. In this section the potentiality of neutron powder diffraction (NPD) and Mössbauer spectroscopy under an intense magnetic field (MSiF) in the study of the magnetic structure of spinels is discussed. Section 5.3 is devoted to the influence of the nanoparticle magnetic structure on magnetic properties, focusing on magnetic anisotropy and saturation magnetization. All the results on CoFe₂O₄ nanoparticles will be discussed in the general framework of spinel ferrites.

5.2 Magnetism in Nanoparticles: An Introduction

5.2.1 Magnetism in Condensed Matter

In condensed matter, atomic magnetic moments can mutually act together (*cooperative magnetism*), leading to a different behavior

from what would be observed if all magnetic moments were reciprocally isolated (*noncooperative magnetism*). This, coupled together with different types of magnetic interactions that can be found, leads to a rich variety of magnetic properties in real systems [3, 35–37].

The two basic types of noncooperative magnetism are paramagnetism and diamagnetism. Paramagnetism arises from identical, uncoupled atomic moments located in an isotropic environment. Hence, in a paramagnetic material, there is no longrange order and the magnetic moments tend to align under an external magnetic field. Diamagnetism, instead, is just due to the effect of an external magnetic field on the motion of the atomic inner electrons [37, 38]. It is manifested by repulsion by a magnetic field, which is observable when paramagnetism is not present.

In a cooperative magnetic system, the interactions between adjacent magnetic moments determines magnetic order in the material. Two classes of interactions can be distinguished, direct and indirect exchange interaction. *Direct exchange* occurs between moments that are close enough to have a significant overlap of their wave functions, whereas *indirect exchange* arises when the atomic magnetic moments are coupled over relatively large distances. It can be mediated also by a nonmagnetic ion that is placed in between the magnetic ions (e.g., oxygen atoms in oxides), and in this case it is called *superexchange* [35]. Generally speaking, exchange interactions between magnetic centers in a three-dimensional solid can be quantitatively described by the Heisenberg spin Hamiltonian [35]:

$$H_{\text{exch}} = -2\sum_{i\langle j} J_{ij} S_i \cdot S_j , \qquad (5.1)$$

where J_{ij} is the exchange integral describing the magnitude of coupling between the spins S_i and S_j . If the exchange integral has a positive value, below a critical temperature T_C (*Curie temperature*), the magnetic moments align parallel to each other and the substance is said to be *ferromagnetic* (FM). Above the T_C , the material is no longer FM but reverts to paramagnetic because the thermal energy becomes higher than the exchange energy, destroying the magnetic order. On the contrary, if J_{ij} is negative, the spins are aligned antiparallel to each other, and below a critical temperature called *Néel*

temperature (T_N) the material is said to be *antiferromagnetic* (AFM, if the total magnetic moments is zero and the moments are perfectly compensated) or *ferrimagnetic* (FiM, if there is no compensation due to some difference between the individual moments). Then, in principle, magnetic properties in condensed matter can be explained by different kinds of magnetic coupling that are closely related to the chemical composition and crystalline structure of the material [39, 40].

Minimization of energy provides a basis for predicting the direction of events in the universe. This is why a bulk cooperative magnetic system, to minimize its energy, will organize in a certain number of small regions, with different sizes and shapes, called domains, that is, uniformly magnetized regions having atomic magnetic moments oriented in the same direction [34]. Two adjacent domains are separated by transition regions, called *domain walls*, in which the spins gradually rotate (coherently or incoherently^a) from one domain to the other. In an unmagnetized FM or FiM material, magnetic domains have random directions so that the sum of the overall domain moments is essentially zero [35].

5.2.2 Magnetic Single-Domain Particles

Generally speaking, a physical property depends on the size of an object whenever its size is comparable to a dimension relevant to that property. In magnetism, typical sizes are, for example, the length of exchange-coupling interactions or the dimension of magnetic domains, the latter being typically in the range of 10–1000 nm for a spherical sample of FM materials [4]. This is why nanoscaled magnetic particles are so unique and why their physical properties differ so much from those shown by their parent massive materials. Indeed, by reducing the particle size below a critical value, a magnetic single-domain organization is energetically more favorable with respect to the multidomain one. The critical radius (r_c), below which the formation of single domains is observed, depends on the physical properties of the material [41 4, 17]. Typical values for r_c are about 10 nm for Fe, 30 nm for γ -Fe₂O₃, 60 nm for Fe₃O₄, and 750 nm for SmCo₅ [4, 17].

^aIn the coherent rotation mode all the spins remain parallel to each other, while in the incoherent reversal mode a nonuniform magnetization process occurs.

A magnetic single-domain particle (i.e., *particle that is in a state of uniform magnetization at any field* [42]) can be considered as a large magnetic unit (namely, a *superspin*) with a magnetic moment (μ_p), expected in the range of 10^3 – 10^5 Bohr magneton (μ_B), proportional to the particle volume, V_P ($\mu_p = M_s \times V_p$, where M_s is the saturation magnetization of the material) [4].

The magnetic behavior of an assembly of superspins is strongly affected by interparticle interactions that can be dipole-dipole or exchange coupling, involving surface atoms. The strength of such interactions plays a fundamental role in the physics of these systems that might show collective behavior. Generally speaking, strong interparticle interactions can lead to some kind of FM state. FM-like correlations can indeed arise among the supermoments of nanoparticles, in addition to those among the atomic moments within the particles; this FM-like state has been called superferromagnetism (SFM) [43]. The intermediate strength of interparticle interactions, frustration, and random distribution of particle moments correlated on the long range lead to magnetic properties similar to those of atomic spin-glass systems in bulk [4, 44, 45]. For this reason such behavior was called superspin glass (SSG). Finally, in a system consisting of noninteracting singledomain particles, the magnetic supermoment associated at each particle acts independently. Such a state is characterized by the instability of magnetization due to thermal agitation that, for isolated spherical particles, results in the flip of magnetization between its antiparallel easy directions, separated by an energy barrier (ΔE_a) . Then, on a certain time scale, above a certain temperature (blocking temperature, $T_{\rm B}$), the particle moment can undergo a thermally activated transition. The superparamagnetic relaxation of an assembly of noninteracting nanoparticles can be described according to the Néel-Brown model [30, 46] by the equation

$$\tau = \tau_0 \exp\left(\frac{\Delta E_a}{k_{\rm B}T}\right),\tag{5.2}$$

where τ is the superparamagnetic relaxation time (i.e., the average time between the reorientation of the magnetization direction), τ_0 is the characteristic relaxation time, *T* is the absolute temperature, and $k_{\rm B}$ is the Boltzmann constant. This phenomenon is analogous

to paramagnetism, but involving superspins, it is characterized by different time and magnetization scales, and for this reason it is called superparamagnetism (SPM). The ensemble of SFM, SSG, and SPM magnetic regimes has been called *supermagnetism* [4].

Stoner and Wohlfarth [47] gave a complete treatment of the magnetization reversal process of single-domain isolated particles: the energy of the particle is generally dependent on the magnetization direction, and for uniaxial anisotropy and easy axis aligned along the direction of the external field (*H*) it can be written as

$$E = K_{\rm a} V_{\rm p} \sin^2 \theta - M_{\rm s} V_{\rm p} H \cos \theta, \qquad (5.3)$$

where K_a is the anisotropy constant and θ is the angle between the magnetization vector and the field direction. Below T_B the particle's moment is blocked and unable to rotate over the barrier in the typical time of a measurement. From Eq. 5.3 the height of the energy barrier can be derived [47, 48]:

$$\Delta E_{\rm a} = K_{\rm a} V \left(1 \pm \frac{H}{H_{\rm K}} \right)^2, \tag{5.4}$$
where $H_{\rm K} = \frac{2K_{\rm a}}{M}$.

 M_s Equations (5.3) and (5.4) show that the energy barrier (ΔE_a) is the key parameter to understand and to tune magnetic properties (e.g., T_B , magnetic anisotropy) of nanoparticle-based magnetic materials. For an isolated particle, ΔE_a can be generally considered proportional to V_p and K_a , which are two strongly intercorrelated parameters.

5.2.3 Magnetic Anisotropy

Generally speaking, the term "magnetic anisotropy" describes the dependence of internal energy on the magnetization's direction, leading to the formation of *easy* (minimum of energy) and *hard* (maximum of energy) anisotropy axes. For bulk materials the magnetic anisotropy energy depends mainly on structure and chemical composition (i.e., magnetocrystalline anisotropy); for nanoparticles other factors, such as particle shape (i.e., shape anisotropy) and surface–volume ratio (i.e., surface anisotropy) have

to be taken into consideration as well. A short qualitative discussion of some contributions will be given here, with particular attention to the most important anisotropies in a nanoparticle system. A more complete description of magnetic anisotropy energy can be found in Refs. [39, 49, 50].

5.2.3.1 Magnetocrystalline anisotropy

The exchange interaction among spins described by Eq. 5.1 is purely isotropic (i.e., there is no built-in preferred direction). However, within a crystal not all directions are equivalent due to reduced crystal lattice symmetry. Then spin orientation is found to follow some preferred crystallographic axes because spin–orbit coupling ties the electron spin to the orbital electronic static associated with the crystal structure. Such so-called *magnetocrystalline anisotropies* can be described by an additional anisotropic term to the Hamiltonian:

$$H_{\text{exch}} = -2\sum_{i \langle j} J_{ij} S_i \cdot S_j - K_{\text{mc}} \sum_i (SZ_i)^2$$
(5.5)

Here, the second term does not correspond to any particular crystal symmetry, since we have taken into account a simple uniaxial anisotropy. Magnetocrystalline anisotropy can show various symmetries, but uniaxial and cubic symmetries cover the majority of cases.

5.2.3.2 Magnetostatic anisotropy (shape anisotropy)

This contribution is due to the presence of free magnetic poles on the surface of a magnetized body. The poles create a magnetic field inside the system, called *demagnetizing field*, which is responsible for the magnetostatic energy. Thus, the shape determines the magnitude of magnetostatic energy, and this kind of anisotropy is often called *shape anisotropy* [38].

5.2.3.3 Surface anisotropy

Surface atoms have lower symmetry compared to atoms within the bulk. This leads to a break of symmetry and a reduction of nearest-neighbor coordination at the surface, giving rise to an additional term to the anisotropy, called *surface anisotropy*. It increases with
an increase of the surface–volume ratio (i.e., a decrease of particle size), and it may be predominant for a particle diameter below ~ 10 nm [17, 51–53]. In fact, the effective magnetic anisotropy can be expressed as [4, 51]

$$< K_{\rm eff} > = K_{\rm V} + \frac{S}{V} K_{\rm S}, \tag{5.6}$$

where $\langle K_{\text{eff}} \rangle$ represents the mean value of the effective anisotropy constant and $\langle K_v \rangle$ and $\langle K_s \rangle$ represent the mean volume and surface components of magnetic anisotropy, respectively. The diameter dependence of the surface–volume ratio for spherical particles (Fig. 5.1) shows a sudden increase below 10 nm, leading to the prevalence of surface anisotropy. For example $\langle K_{\text{eff}} \rangle$ increases by more than one order of magnitude for CoFe_2O_4 nanoparticles with a diameter of ~ 3 nm, measured by transmission electron microscopy (TEM), achieving 1.7×10^6 J/m³ to be compared with the bulk value of 3.0×10^5 J/m³ [11]. Surface anisotropy is also strictly related to the chemical and/or physical interactions between surface atoms and others chemical species [54, 55].



Figure 5.1 Calculated surface-volume ratio for spherical particles with mean diameters (*<D>*) in the range of 1–20 nm.

5.3 Magnetic Structure of Nanoparticles

5.3.1 Spin Canting

As already discussed in the previous paragraphs, magnetic properties are particularly sensitive to the particle size, being determined by finite-size effects and surface effects [2]. Magnetic atoms at the surface experience a breaking of symmetry, originating from broken exchange bonds. This induces changes in exchange integrals, related to variation of superexchange angles and/or distances among moments, giving rise to topological magnetic frustration. Consequently a noncollinear spin structure (spin canting) at the particle surface occurs. In the seventies J. M. D. Coey wrote that "ultrafine particles may be visualized as having a core with the normal spin arrangement, and a surface layer in which the spin of the ions are not oriented at random, but are inclined at some angle to their normal direction" [8]. In this paper ⁵⁷Fe Mössbauer spectroscopy under an intense magnetic field was used to investigate the magnetic structure of maghemite (γ -Fe₂O₃) nanoparticles.

In a Mössbauer experiment the resonant absorption of γ -rays, emitted from a radioactive nucleus, by nuclei identical to those of the ground state of the emitting nuclei, is measured. Then, Mössbauer spectroscopy detects transition within nuclear rather than electronic energy states. Although there are around 100 nuclear transitions that can be used, the majority of Mössbauer studies are carried out using the 14.4 keV transition of ⁵⁷Fe.

Mössbauer spectroscopy is very powerful tool in the study of magnetic dynamics (due to the very-short-time experimental window, 5×10^{-9} s) and magnetic structures of iron-based nanoparticles. The ⁵⁷Fe nucleus in a magnetically ordered material will be exposed to a magnetic hyperfine field ($B_{\rm hyp}$), usually antiparallel to the magnetic moment (Fig. 5.2), which gives rise to a Zeeman splitting of the nuclear states, resulting in a Mössbauer spectrum with six lines. This splitting is proportional to the magnetic structure. In addition, the interactions between the nuclear charge and the electronic charge result in a shift of all the transition energies. This shift, called *isomer shift* (δ) and measured in *mm/s*, is proportional to the density of the s-electron at the nucleus. The isomer shift is used to measure

the difference in the s-electron density (ED) at the nucleus between different environmental states of the same kind of atoms. Finally, the electrostatic interaction between the electric quadrupole moment of a nonspherical nucleus and the electric field gradient due to the surrounding charges can result in shifts of the six lines of spectra of magnetic materials, the so-called *quadrupole shift* (ε). ε is used in many Mössbauer spectroscopy studies for helping to solve the structure, ligand position, and even behavior of unbound electron pairs.



Figure 5.2 Schematic representation of the vector diagram of the hyperfine fields B_{hyp} of ${}^{57}\text{Fe}^{3+}$ ions located in T_d (O_h) interstitial sites under an applied magnetic field (B_{app}) parallel to the γ -ray direction.

When Mössbauer spectra of ferrites are collected under an intense magnetic field (B_{app}), magnetic splitting of the T_d site Fe³⁺ ions increases and the O_h site splitting decreases, allowing us to distinguish iron ions located in tetrahedral and octahedral interstitial sites. Figure 5.3 shows Mössbauer spectra of maghemite nanoparticles recorded at 5 K without (Fig. 5.3a) and under (Fig. 5.3b) an intense magnetic field (5 T) [8]. A spectrum recorded in a zero field shows a sextet with a slight asymmetry of the peaks due to small difference of the hyperfine field of the ions in the two sites. Under an intense magnetic field (b) the spectrum is clearly resolved into two components. At low temperatures the recoilless fractions

for iron ions in the $T_{\rm d}$ and $O_{\rm h}$ sites are essentially equal [56], and therefore the area of the different components can give information about the cationic distribution. Furthermore, such spectra can also give information about the degree of alignment of magnetization with the applied field. In particular, a direct estimation of the angle defined by the direction of the effective magnetic field ($B_{\rm efc}$) at the nucleus and the γ -beam direction for both tetrahedral and octahedral components can be obtained. The effective hyperfine field at the nucleus is given by the vector sum of $B_{\rm app}$ and $B_{\rm hyp}$:

$$B_{\rm hyp} = B_{\rm efc}^2 + B_{\rm app}^2 - 2B_{\rm efc}B_{\rm app}\cos\theta$$
(5.7)

where θ is the angle between the effective magnetic field at the nucleus and the γ -ray direction (Fig. 5.2).

For a thin absorber, the relative area of the six lines is given by 3:p:1:1:p:3, where

$$p = \frac{4\sin^2\theta}{1+\cos^2\theta} \,. \tag{5.8}$$

From Eq. 5.8 it is evident that, if B_{efc} is perfectly aligned along the γ -ray direction, the intensity of lines 2 and 5 vanishes. The nonzero intensity of lines 2 and 5 in the spectrum (Fig. 5.3b) indicates the presence of a noncollinear magnetic structure, with some spins that are not aligned parallel or antiparallel to the external magnetic field. Using Eq. 5.5 it is possible to calculate the average value of the canting angles. This spin canting was attributed by Coey to surface ions for which the reduced number of magnetic neighbor ions results in magnetic frustration, which leads to a noncollinear spin structure [8]. Later, spin canting has been also observed in many studies in several nanostructured FiM systems, and generally speaking, it was attributed to competing interactions between sublattices, yielding magnetic disorder at the particle surface [2, 9, 57]. This hypothesis has also been confirmed by polarized neutron scattering [58] and further Mössbauer experiments [59] in cobalt and nickel ferrite, respectively.

At the end of his pioneering work, Coey claimed that "however some canting in the interior [of the particles] cannot be excluded." This insight was confirmed by subsequent following studies, taking advantage of the selective sensitivity of Mössbauer spectroscopy only to ⁵⁷Fe that has a natural abundance of about 2% [17, 60].

Indeed, by coating the surface of nanoparticles with 57 Fe-enriched iron, Parker et al. showed that the canting can be a finite-size effect, which also occurs in the interior of the particles [61] and this was ascribed to the sublattice anisotropy [62]. Later, Morales et al. investigated maghemite nanoparticles, showing that internal spin canting can arise from structural disorder as well [10, 63]. More recently internal spin canting has been observed also in CoFe₂O₄ nanoparticles, showing the influence of the synthesis procedure on producing a noncollinear spin structure [20].



Figure 5.3 Mössbauer spectra recorded at 5 K on γ -Fe₂O₃ nanoparticles without (a) and under (b) an applied field of 5 T. Reproduced with permission from Coey, J. M. D. (1971). Non-collinear spin arrangement in ultrafine ferrimagnetic crystallites, *Phys. Rev. Lett.*, **27**, 17.

5.3.1.1 Temperature dependence of spin canting

The temperature evolution of Mössbauer spectra under an intense magnetic field indicates that mean canting angles decrease with increasing temperatures and spin canting apparently disappears above a certain temperature. This effect has been observed in several nanoparticles (γ -Fe₂O₃[61, 64], tin-doped γ -Fe₂O₃, Mn_{0.25}Zn_{0.75}Fe₂O₄, Li_{1.125}Ti_{1.25}Fe_{0.625}O₄, iron oxide substituted with diamagnetic ions [65]) and, more recently, in CoFe₂O₄ nanoparticles dispersed in silica matrix [20]. Generally speaking, this trend can be explained by rapid fluctuations of the spin components that are perpendicular

to the applied field (transverse relaxation) such that the average canting angle is zero. Theoretical studies [17, 66] indicated that, due to symmetry, a canted state with canting angle θ_c is commonly accompanied by another canted state with canting angle $-\theta_c$ [66]. At finite temperature, the thermal energy may be sufficient to overcome the energy barrier separating these two canted states, and the ions may then perform transverse relaxation in a certain time (τ_t) between the two states [67]. If τ_t is much higher than the experimental time window of Mössbauer spectroscopy, only the spin components that are perpendicular to the applied field will be sensed, and an apparent collinear structure is observed. Then, a decrease of lines 2 and 5 is observed with an increase in temperature, because the nucleus only experiences an average field parallel to the applied field. In fact, under these conditions, the effective magnetic field at the nucleus will be given by

$$B_{\rm eff} \approx B_{\rm hf}^0 \left< \cos \theta_{\rm c} \right>, \tag{5.9}$$

where B_{hf}^0 is the hyperfine field if the canting is static. An evidence of fast spin fluctuations at high temperature was also given by FM resonance and inelastic neutron-scattering studies [68] on γ -Fe₂O₃.

5.3.2 Iron Oxides with a Spinel Structure

Among magnetic iron oxides compounds with a spinel structure $(Me^{II}Fe^{III}{}_{2}O_{4}; MeII = Fe^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+})$ represent probably the most important class, because the rich crystal chemistry of spinels offers excellent opportunities for fine-tuning of the magnetic properties. Spinels have a face-centered cubic structure in which oxygen atoms are cubic close packed. The structure contains two interstitial sites, occupied by metal cations, with tetrahedral, (T_d) site, and octahedral, $[O_h]$ site, oxygen coordination resulting in different local symmetry. When (T_d) sites are occupied by Me^{II} cations, the structure is called *normal spinel*, (Me^{II}) [Fe^{III}]. If the (T_d) sites are completely occupied by Fe^{III} and $[O_h]$ sites are randomly occupied by Me^{II} and Me^{III} the structure is referred to as *inverse spinel*, (Fe^{III}) [Fe^{III} Me^{II}]. In general cationic distribution in octahedral and tetrahedral sites is quantified by the inversion degree (γ) , which is defined as the

fraction of divalent ions in octahedral sites [36, 69, 70]. A schematic representation of a normal spinel structure is reported in Fig. 5.4a.

The magnetic properties of oxides with a spinel structure can be understood by studying the magnetic coupling among atoms. In fact, exchange interactions between atomic magnetic moments in T_d (J_{TT}) and O_h (J_{00}) interstices give rise to two magnetic sublattices, with FM ordering between the ions located in each site, respectively. On the other hand, interactions between magnetic ions in T_d and O_h sites (J_{TO}) induce AFM order, and they are 10 times higher than J_{TT} and J_{00} interactions. Then the dominant intralattice J_{TO} interaction induces a noncompensated AFM order (ferrimagnetism) between T_d and O_h sublattices. Therefore the net magnetization can be considered proportional to the difference between T_d and O_h sublattice magnetization [67, 69]. Also magnetic anisotropy is related to the cationic distribution because single-ion anisotropy in divalent ions depends on interstitial sites. A schematic representation of a normal spine structure is reported in Fig. 5.4b.



Figure 5.4 (a) Schematic representation of the crystalline normal spinel structure highlighting the two interstitial sites with octahedral (gray) and tetrahedral (blue) oxygen coordination. Blue and red spheres represent Fe³⁺ and divalent cations (Fe²⁺, Co²⁺, Ni²⁺, etc.), respectively. (b) Schematic representation of the magnetic structure in a normal spinel: the dominant intralattice J_{TdTd} interactions induce a noncompensated AFM order between T_d and O_h sublattices (ferrimagnetism). Black arrows represent magnetic moments, with modules proportional to the length, associated with magnetic cations.

From this picture, it is clear that magnetic properties of spinel oxides can be explained by magnetic coupling. This coupling is closely

related to the chemical composition and crystalline structure of the materials. In fact, J_{TT} , J_{00} , and J_{TO} depend on the chemical identity of Me^{II} and on its host interstitial site. As an example, Sawatzky et al., in a systematic study on spinel ferrites [56, 71], showed that in CoFe₂O₄ superexchange interactions [Fe³⁺]–O^{2–}–(Co²⁺) are weaker than [Fe³⁺]–O^{2–}–(Fe³⁺) and in MnFe₂O₄ [Mn²⁺]–O^{2–}–[Mn²⁺] are negligible with respect to (Mn²⁺)–O^{2–}–(Mn²⁺). Then, adjusting the chemical identity of Me^{II} and tuning the cationic distribution the magnetic configuration of Me^{II}Fe^{III}₂O₄ can be chemically engineered to provide a wide range of magnetic behaviors [18, 70]. It should be remarked that the inversion degree depends on the thermal history of the materials [72], and it can also depend on particle size [20], although this dependence is still debated in the literature [11, 20, 73].

5.3.3 Spin Canting and Cationic Distribution: Magnetic Structure of Spinel Ferrite Nanoparticles

Starting from this framework, the magnetic structure of nanostructured spinel ferrite systems is due to the complex interplay between cationic distribution and spin canting. Understanding the intercorrelation between these two elements represents the key point for governing the magnetic structure, and then the magnetic properties, of these systems. In the following section the magnetic structure of $CoFe_2O_4$ nananoparticles (CoFeO) prepared by a thermal decomposition method [29, 74] will be described.

The crystalline and magnetic structures of a sample were investigated by NPD. Neutron powder diffraction is one of the most powerful tools for studying the magnetic and crystalline structure of materials. Indeed, neutrons may interact with both the nucleus and the nuclear magnetic moment in the lattice, giving both the crystal structure and the magnetic order of materials. In addition, the great variation of the neutron-scattering length allows us to distinguish certain adjacent elements on the periodic table and to determine the lattice site composition with high precision. This is very useful in ferrites, Me^{II}Fe₂O₄, that can be chemically engineered using divalent cations with similar ED. As an example, due to the small difference in ED, X-ray diffraction (XRD) cannot distinguish Co²⁺ from Fe³⁺. On the other hand, the neutron-scattering length is very different (Fe 1.10 $\times\,10^{-12}$ cm, Co $0.253\,\times\,10^{-12}$ cm), allowing us to easily determine the cationic distribution.

NPD experiment on a CoFeO sample was carried out at 300 K (Fig. 5.5a). Rietveld refinement indicates only the presence of the $CoFe_2O_4$ phase crystallized in the FdN3m space group with a mean particle size around 6 nm. The obtained cationic distribution was $(Fe_{0.73}Co_{0.27})[Fe_{0.63}Co_{0.37}]_2O_4$, corresponding to an inversion degree of γ_{NPD} = 0.74 (Table 5.1). Structural values obtained by Rietveld refinement are in very good agreement with the expected values for nanostructured CoFe₂O₄ (Table 5.1) [18, 19]. Nanoparticles display the typical FiM structure of the inverse ferrite, with the magnetization of the $O_{\rm h}$ sublattice in the opposite direction with respect to that of the T_d sublattice (Fig. 5.5b). The refined magnetic moments at the T_d and O_h sublattices are lower with respect to the values reported in the literature for CoFe₂O₄ nanoparticles with similar particle size and cationic distribution [18], suggesting that some noncollinear spin components coexist with the ordered spins [75]. To get a complete view of the magnetic structure, a Mössbauer spectrum was recorded at 10 K under a magnetic field of 8 T applied parallel to the γ -beam direction. The spectrum is consistent with an FiM structure without any superparamagnetic relaxation (Fig. 5.6a). The refinement of the in-field spectrum allows us to attribute clearly the two magnetic components to the Fe³⁺ in tetrahedral and octahedral sites, according to the values of the isomer shift (Table 5.1) [20], with a cationic distribution ($Fe_{0.76}Co_{0.24}$) $[Fe_{0.62}Co_{0.38}]_2O_4$ and γ_{MSiF} 0.76. It should be emphasized that the inversion degree obtained by in-field Mössbauer investigation is in good agreement with that estimated from NPD analysis, within the experimental error of the two techniques (Table 5.1). However, MSiF allows us to better describe the magnetic structure of the particle, taking into account the magnetic disorder. In fact, lines 2 and 5 have nonzero intensity and this reveals the presence of a noncollinear spin structure. The modeling of the in-field Mossbauer spectrum allows us to determine both the magnetic effective field and the canting angle of the iron atoms located in T_{d} and O_{h} interstitial sites (Fig. 5.6b). Due to the strong asymmetrical broadening of the lines the chosen fitting-model-involved B_{efc} distribution that has been correlated to the canting angle distribution, showing as the spin canting, is extended over iron atoms in both interstitial sites, as already observed in several ferrites [2, 76, 77].



Figure 5.5 (a) Neutron diffraction pattern (symbols) and Rietveld refinement (line). Reproduced with permission from Ref. [21]. (b) Schematic representation of the crystalline and magnetic structures obtained by NPD. Nanoparticles display the typical FiM structure of inverse ferrites, with magnetization of the O_h sublattice oppositely directed that of the T_d sublattice. Blue and red spheres represent Fe³⁺ and Co²⁺, respectively, and the cationic distribution, (Fe_{0.73}Co_{0.27})[Fe_{0.63}Co_{0.37}]₂O₄, is schematically represented as relative chromatic percentage in each site.



Figure 5.6 (a) 57 Fe Mössbauer spectrum obtained at 10 K in an 8 T magnetic field applied parallel to the γ -beam. Reproduced with permission from Ref. [21]. (b) Schematic representation of the crystalline and magnetic structures obtained by Mössbauer spectroscopy under an intense magnetic field. MSiF confirms the cationic distribution obtained by NPD, allowing us to better describe the magnetic structure, taking into account the canting of the spins.

In FiM structures the spin canting can be explained in terms of the Yafet–Kittel triangular arrangement due to the magnetic frustration resulting from the competition between J_{OT} and J_{TT} exchange interactions. In general, the main features of the spin structure may be understood on the basis of the expression for the magnetic energy of an ion located, for example, in O_h sites [66, 67]:

$$E_{\rm B} = E_{\rm a} + (g\mu_{\rm B}S_{\rm O_{\rm h}} \cdot B_{\rm app}) - S_{\rm O_{\rm h}} \cdot (\sum_{\rm i} J_{\rm T_{\rm d}} \cdot S_{\rm T_{\rm d}} + \sum_{\rm j} J_{\rm O_{\rm h}} \cdot S_{\rm O_{\rm h}} + \cdots), \quad (5.10)$$

where E_a represents the magnetic anisotropy energy and the second term is the interaction of the spin S_{Oh} under an applied field. In the first approximation, it is reasonable to consider only the next neighboring magnetic ions: in the third term J_{Td1} and J_{Oh1} represent the exchange-coupling constants of spin S_{Oh} , with the spins located in the next neighboring T_d and O_h sites, respectively [71]. For the Fe³⁺ ions the contribution of the anisotropy energy to the magnetic energy is expected to be small as compared to the exchange energy [78], and the spin structure can be considered related mainly to the exchange-coupling energy. On the other hand, the high single-ion anisotropy of Co²⁺²⁰ suggests that the canting involves mainly Fe³⁺ ions, as already observed in molecular compounds [32, 79].

Table 5.1 Structural data and cationic distribution obtained from Rietveld refinement of NPD data at 300 K; fitting parameters of in-field Mössbauer spectra (T = 10 K, $H_{appl} = 6$ T) of CoFeO: isomer shift (δ), quadruple shift (2ε), mean canting angle ($<\theta_c >$), and relative fraction of the Fe³⁺ located in T_d and O_h sites. Reproduced with permission from Ref. [21]

Neutron powder diffraction						
Cell size (Å)	O coordinate (x)	<d> (nm)</d>	R-Bragg (%)	R-factor (%)		
8.3777(4)	0.2564(1)	6.0	3.46	1.65		
γ0:74		C.D.: (Fe _{0.73} Co _{0.27}) [Fe _{0.63} Co _{0.37}] ₂ O ₄				
Mössbauer spectroscopy under an intense field						
	<δ> (mm.s ⁻¹) ± 0.01	<2ɛ> (mm.s ⁻¹) ± 0.01	<θ _c > (°) ± 10	$\mathrm{Fe}_{T\mathrm{d},O\mathrm{h}}^{3\mathrm{+}}/\mathrm{Fe}_{\mathrm{total}}^{3\mathrm{+}} \pm 0.01$		
Fe _A ³⁺	0.36	-0.04	41	0.38		
Fe _B ³⁺	0.47	-0.03	36	0.62		
γ0:76		C.D.: (Fe _{0.76} Co _{0.24}) [Fe _{0.62} Co _{0.38}]				

In the spinel ferrite structure each tetrahedral Fe^{3+} ion is surrounded by 12 octahedral ions, while an octahedral Fe^{3+} ion has only 6 tetrahedral nearest neighbours [56]. Starting from the cati-

onic distribution obtained by MSiF and NPD investigation, it can be reasonably assumed that in our nanoparticles each $O_{\rm h}$ -Fe³⁺ has in average two T_d -Co²⁺ and four T_d -Fe³⁺ (Fig. 5.7a) neighbors. On the one hand a T_{d} -Fe³⁺ atom is surrounded in average by seven $O_{\rm h}$ -Fe³⁺ and five $O_{\rm h}$ -Co²⁺ atoms (Fig. 5.7b). Then, Fe atoms located in the octahedral site are surrounded by $\sim 67\%$ iron atoms in the tetrahedral site, while iron atoms on T_d sites have as next neighbors ~59% iron atoms in O_h sites. Calculations based on molecular field theory indicate that the superexchange interactions $[Fe^{3+}]-O^{2-}-(Co^{2+})$, $J_1 = 13.7$ K, are weaker than [Fe³⁺]- O^{2-} -(Fe³⁺), $J_2 = 20.1$ K [56]. Then, Fe3+ ions with octahedral and tetrahedral symmetry feel a similar total superexchange strength. Keeping in mind that *J*_{ObTd} interactions are predominant with respect J_{TdTd} and J_{ObOb} [67], these arguments qualitatively explain why the canting in this sample extends to both $T_{\rm d}$ and $O_{\rm h}$ sites. However, neutron diffraction and Mössbauer studies have provided evidence that spin canting can be also restricted to a single magnetic sublattice [29, 59, 80] and no clear physical explanation has been suggested.

To clarify this point it is useful to discuss the magnetic structure of CoFe₂O₄ nanoparticles dispersed in a silica matrix with a particle size between ~3 nm and ~30 nm and prepared by a similar synthesis procedure [81], showing spin canting mainly restricted to an O_h magnetic sublattice [11, 20]. In particular, two nanocomposites with 10% and 5% of the magnetic phase (CoFeO_{N10} and CoFeO_{N5}, respectively) appear ideal to elucidate this issue. Indeed, TEM and high-resolution transmission electron microscopy (HRTEM) analyses on both samples showed crystalline nanoparticles homogeneously dispersed in a silica matrix with an equal mean particle size ($<D_{\text{TEM}} > \approx 3$ nm) within the experimental error. Despite the same particle size, Mössbauer spectra recorded at low temperature (6 K) under an intense magnetic field (6 T) indicate that the cationic distribution, fraction of canted spins, and mean canting angle are different in the two samples (Table 5.2).

The best fitting was obtained assuming for some of the iron atoms in T_d and O_h sites a perfect FiM local environment. To represent ions with canted spins a third sextet was introduced, showing a value of isomer shift typical for octahedrally coordinated Fe³⁺ in spinels. This indicates that the canted spins are mainly located in the O_h sites [11, 20].



Figure 5.7 Schematic representation of the magnetic environment of iron atoms located in O_h (a, c, e) and T_d (b, d, f) sites for CoFeO, CoFeO_{N10}, and CoFeO_{N5} samples.

Starting from the cationic distribution obtained by MSiF spectra, it is possible to define the chemical surrounding in CoFeO_{N10} and CoFeO_{N5}, as sketched in Figs. 5.7b,c and 5.7d,e, respectively. In CoFeO_{N10} Fe³⁺ ions located in the O_h site are surrounded by ~50% iron atoms in the tetrahedral site, while iron atoms in T_d sites have as near neighbors ~75% of iron atoms in O_h sites. Thus, iron atoms located in the interstitial site with a tetrahedral symmetry feel a total superexchange strength, which is definitely higher than that felt by the iron atoms located in the octahedral site. This explains the reason why this sample shows canting extended only to $O_{\rm h}$ sites. Going to CoFeO_{N5} a further decrease of (Fe³⁺) in the chemical surrounding of [Fe³⁺] is observed, leading to a further decrease of the total superexchange interactions felt by octahedral iron. This is reflected in an increase of the fraction of canted spins and of the mean canting angle.

This experimental framework shows that spin canting, probably localized at the particle surface, in $CoFe_2O_4$ depends on cationic distribution. The physical origin of this dependence has been found in the different strength of superexchange interactions between $[Fe^{3+}]-O^{2-}-(Co^{2+})$ and $[Fe^{3+}]-O^{2-}-(Fe^{3+})$. This model can be extended to other spinel ferrites because important differences in superexchange interactions are found in several divalent cations. As an example, molecular field theory indicates the ratio J_1/J_2 equal to 0.68 and 0.66 for $CoFe_2O_4$ and $MnFe_2O_4$, respectively [56].

5.4 Magnetic Properties of Spinel Ferrite Nanoparticles: Influence of the Magnetic Structure

The first step to understand the influence of magnetic structure on the magnetic properties in spinel ferrites is to discuss the magnetic behavior of canted spins and, more generally, the so-called surface effect in nanoparticles. Then, attention will be focused on the correlation between the magnetic structure and the magnetic properties of $CoFe_2O_4$ nanoparticle assemblies, with particular attention to magnetic anisotropy and saturation magnetization. To exclude the influence of interparticle interactions, the discussion will be focused on nanoparticles dispersed in a silica matrix with low percentage of the magnetic phase (i.e., noninteracting system).

5.4.1 Surface Magnetism

The $CoFeO_{N5}$ sample appears to be an ideal system to discuss the influence of surface magnetism on magnetic properties of a material.

Low-field (5 mT), zero-field-cooling (ZFC), and field-cooling (FC)^b magnetization curves (Fig. 5.8a) exhibit a blocking process typical of an assembly of very weakly interacting single-domain magnetic particles. The temperature corresponding to the maximum in the ZFC curve (T_{max}) is proportional to the mean blocking temperature, with the proportionality constant depending on the type of $T_{\rm b}$ distribution. The temperature below which the ZFC and FC curves show an irreversible behaviour (T_{irr}) is associated with the blocking of the biggest particles [82], and above this temperature a fully superparamagnetic regime is entered into [2, 32]. The continuous increase of $M_{\rm FC}$ with decreasing temperature indicates that interparticle interactions, if present, are negligible. This is confirmed by alternating current (AC) magnetic susceptibility measurements, showing that the Néel-Brown model for superparamagnetic relaxation (Eq. 5.2) well describes the variation of blocking temperature with frequency [11].

The magnetic structure of nanoparticles has been carefully described in Section 5.3.,2 and a summary of the MSiF results is reported in Table 5.2. In particular, the relative area of lines 2 and 5 indicates that 32% of the spins are canted with respect to the direction of the external magnetic field, with a mean canting angle of 42°. Assuming that all canted spins are located at the particles' surface, a core-shell model (ferrimagnetically ordered core and randomly canted magnetic shell) can be considered (Fig. 5.9). Then, it is possible to give an estimation of the thickness of the canted layers (t) using the formula [83]

$$t = \frac{\langle D_{\text{TEM}} \rangle}{4} \sin^2 \theta_{\text{c}} \,. \tag{5.11}$$

A canted layer thickness of 0.3(1) nm and consequently a ferrimagnetically ordered core of 2.3(1) is obtained. To gain a better understanding of the influence of surface spins on the magnetic behavior of nanoparticles a deep magnetic investigation has been carried out below $T_{\rm max}$. At first, nonequilibrium dynamics were investigated by means of ZFC magnetic memory effect measurements.

^bZFC and FC measurements were carried out as follows: The sample was first cooled down from 325 K to 5 K in a zero magnetic field, then a static magnetic field was applied, and $M_{\rm ZFC}$ was measured during warming up from 5 K to 325 K; finally the sample was cooled down to 5 K under the same magnetic field, and $M_{\rm FC}$ was measured during the cooling.



with permission from Ref. [32]. (c) Numerical results of a ZFC reference curve (full circles) and a ZFC memory curve empty circles). (Inset) Percentage of the relative difference ΔM between memory and reference curves as a function of temperature for random shell anisotropy. Reproduced with permission from Trohidou et al. (2012). Memory effects in (a) Zero-field-cooled (empty circles) and field-cooled (full circles) magnetizations (H = 5 mT) of a CoFeO_{N5} sample. Inset) Percentage relative difference $(\Delta M = (M_{ref} - M_{mem})/M_{ref})$ between memory and reference curves. Reproduced Reproduced with permission from Ref. [32]. (b) Reference ZFC (full circles) and memory ZFC (empty circles) magnetization. ultra-small CoFe O nanoparticles, IEEE Trans. Magn., 48, 4. Figure 5.8



- **Figure 5.9** (a) Two-dimensional sketch of a spherical FiM nanoparticle with a ferrimagnetically ordered core and a spin-glass-like surface.
- **Table 5.2**Mean particle size by TEM ($<D_{\text{TEM}}>$), inversion degree (γ),
cationic distribution, relative areas of lines 2 and 5 (A2,5)^a,
mean canting angle ($<\theta_c>$), and effective anisotropy constant
determined by AC measurements

Samples	<d<sub>TEM> nm</d<sub>	γ	Cation distribution	A _{2,5} (%)	<0c>(°)	<i>K</i> a (J/m ³)
CoFeO _{N5}	2.8(3)	0.20	(Co _{0.80} Fe _{0.20}) [Co _{0.20} Fe _{1.80}]O ₄	32(1)	42(1)	1.7×10^{6}
CoFeO _{N10}	2.9(3)	0.44	(Co _{0.56} Fe _{0.44}) [Co _{0.44} Fe _{1.56}]O ₄	17(1)	37(1)	1.6×10^{6}
CoFeO _{N15}	6.7(4)	0.52	(Co _{0.48} Fe _{0.52}) [Co _{0.52} Fe _{1.48}]O ₄	15(1)	38(1)	1.9×10 ⁵

Uncertainties in the last digit are given in parentheses.

^aThe area of lines 2 and 5 is normalized by the total area of the spectrum.

Figure 5.8b shows two ZFC magnetization curves measured with an external magnetic field of 10 mT in the temperature range of 5-60 K. The reference curve (full circles) was recorded with the normal ZFC procedure from 150 K. The memory curve (empty circles) was measured in the same way but after keeping the sample at a constant temperature (5 K) in the zero field for three hours. In the ZFC memory curve, a decrease of magnetization is observed in the range of 5–30 K. In the inset of Fig. 5.8b the thermal dependence of the relative percentage decrease of the memory curve with respect to the reference curve, $M = (M_{ref} - M_{mem})/M_{ref}$ is reported. The aging effect is typical in spin glasses and assembly of interacting magnetic nanoparticles (SSG), and it is due to the relaxation during the waiting time for a more stable spin configuration, as explained by both the hierarchical energy and the droplets model [84-86]. We clearly showed that in our system interparticle interactions are negligible; then, the observed behavior can be ascribed to the anisotropic freezing of surface spins with spin-glass-like features. These results were confirmed by Monte Carlo simulation [33] (Fig. 5.8c). indicating that a random surface anisotropy 20 times bigger than the core can be accounted for the observed aging effect. This frame was completed by a careful study of time dependence of magnetization (i.e., relaxation measurements) that confirms a progressive random spin-glass-like freezing of the surface spin below 30 K [32].

An investigation of magnetization reversal has been performed by relaxation measurements at low temperature (5 K). In particular, the sample was brought to a negative saturation field (-5 T); then a reverse field was applied, and the time dependence of magnetization was measured. As expected for a log-normal distribution of anisotropy energy barriers and particle size [11], a logarithmic decay of the magnetization was observed [87]:

$$M(t) = M_0 S \ln(t), (5.12)$$

where *S* is the magnetic viscosity. By fitting the data to a logarithmic decay (Eq. 5.12), the magnetic viscosity was estimated at different values of the reversing field. By combining S_{max} , obtained for a reverse field of ~1.5 T, with the irreversible susceptibility (χ_{irr}), it is possible to estimate the activation volume by the equation [32, 88, 89]

$$V_{\rm act} = \frac{k_{\rm B}T}{M_{\rm s}H_{\rm f}},\tag{5.13}$$

where all the parameters are as previously defined. The activation volume represents *the smallest volume of material that reverses coherently in an event* [90].

Considering spherical particles, as showed by TEM and HRTEM characterization, the $V_{\rm act}$ value corresponds to a mean *magnetic diameter* of 2.3(1) nm, in agreement with the diameter of a ferrimagnetically ordered core obtained by MSiF. These results indicate that at 5 K a coherent reversal process in the particles involves only a 2.3 nm core ferrimagnetically ordered. Canted spins are frozen in a spin-glass-like state with such high anisotropy (Monte Carlo simulation indicates 20 times bigger that the core) that they don't take part in the reversal process. A substantially similar magnetic behavior has been observed in a CoFeO_{N10} sample [33].

5.4.2 Magnetic Anisotropy

The presence of a shell of canted spins that undergoes a progressive spin-glass-like freezing below 30 K, influences the magnetic anisotropy of the whole system. Virgin magnetization recorded at different temperatures in the range 5-40 K (Fig. 5.10a) shows a nonsaturating character increasingly pronounced with decreasing temperature, as shown by the increase of the magnetization slope at 5 T, $(dM/dH)_{5 T}$, below 30 K (Fig. 5.10b) and more pronounced below 15 K. This trend indicates a strong increase in anisotropy that can be directly correlated with the magnetically disordered surface spins undergoing a freezing process with moments in random directions [91-94]. The formation of an anisotropic frozen disordered shell below 30 K is supported by the observation of interface exchange coupling (IEC) between the FiM core and a more anisotropic phase formed below this temperature. The observed exchange bias (EB) originates from the pinning action exerted by the anisotropic disordered frozen spins on the adjacent ferrimagnetically ordered core spins [7, 95]. Thermal dependence of the EB field ($\mu_0 H_e$), coercive field post-ZFC ($\mu_0 H_c _{ZFC}$), and post-FC ($\mu_0 H_c _{FC}$) is shown in Fig. 5.10c. The appearance of EB is accompanied by a more rapid increase of $\mu_0 H_c$, confirming that an extra source of anisotropy due to the freezing of surface spins appears below 30 K. As clearly shown in Fig. 5.10c, there are no differences between $H_{c_{zFC}}$ and $H_{c_{rFC}}$. This indicates that, as shown by V_{act} measurements, there are no canted spins of the surface layer rotating with the FiM core spins. Surface spins are highly anisotropic below 30 K, and through exchange coupling they exert a torque on the FiM core spins in the FC direction, tending to hinder their reversal when the field is reversed. It is interesting to observe that the effective anisotropy constant measure by AC susceptibility experiment ($K_a = 1.7 \times 10^6 \text{ J/m}^3$) confirms this interpretation, showing a value much larger with respect to the bulk ($K_{a_{a}bulk} = 3.0 \times 10^5 \text{ J/m}^3$).



Figure 5.10 (a) Virgin curves at different temperatures in the range of 5–40 K; (b) thermal dependence of $(dM/dH)_{5 \text{ T}}$; thermal dependence of the EB field (H_{eb}) and coercive field measured post-ZFC $(H_{C_{2}\text{FC}})$ and post-FC $(H_{C_{e}\text{FC}})$. All the figures are reproduced with permission from Ref. [32].

5.4.2.1 Influence of the cationic distribution

As we discussed in Section 5.3.2, independently of the surface effect, cationic distribution can strongly influence the magnetic anisotropy

of iron oxide with a spinel structure. Indeed, single-ion anisotropy, especially of divalent ions, strongly depends on the symmetry of the interstitial site. To take into account this effect it is interesting to discuss the magnetic properties and magnetic structure of CoFe₂O₄@ SiO_2 nanocomposites with 15% of a magnetic phase (CoFeO_{N15}). The XRD pattern clearly shows the presence of a single spinel cubic phase corresponding to CoFe₂O₄ (pdf card 22.1085) [20]. TEM and HRTEM investigations show almost spherical particles, well dispersed in a silica host matrix. The particle size distributions are fitted with log-normal functions, and the mean particle size is 6.7 nm. MSiF investigation shows a magnetic structure that can be discussed in the framework defined in Section 5.3.2 (Table 5.2). In fact, $CoFeO_N$ samples show canting localized in O_h sites, going from CoFeO_{N5} to CoFeO_{N15}, an increase of cobalt corresponding to a decrease of canting. Figure 5.1 clearly shows that the surfacevolume ratio considerable decreases, going from 3 nm to 7 nm, leading to a predominant role of magnetocrystalline anisotropy in the nanocomposite with a 15% magnetic phase. In fact, the effective anisotropy constant determined for CoFeO_{N15} by AC susceptibility is much smaller than that of CoFeO_{N5} and slightly higher with respect to the bulk value. Especially this last result is surprising, because the effective magnetic anisotropy is usually larger in nanoscale particles [20, 51, 67]. The value of the effective anisotropy constant in a $CoFeO_{N15}$ sample can be explained by the cationic distribution. Indeed, Co^{2+} ions located in tetrahedral sites (${}^{4}A_{2}$ crystal field ground energy term) show smaller single-ion anisotropy $(-79 \times 10^{-24} \text{ J/ion})$ with respect to Co^{2+} ions in octahedral sites (+850 × 10⁻²⁴ J/ion), showing larger magnetocrystalline anisotropy due to the orbital contribution in the ${}^{4}T_{1}$ ground energy term [96, 97]. On the contrary, $< K_{eff} >$ is found to increase with decreasing Co occupation of the O_{h} sites (i.e., moving from the CoFeO_{N15} to the CoFeO_{N5} sample). This indicates that other contributions are more important in determining the effective anisotropy of particles, presumably mainly the surface contribution, since $\langle K_{eff} \rangle$ increases with decreasing particle size.

5.4.3 Saturation Magnetization

Saturation magnetization is one of the most important magnetic features for application of nanoparticles in biomedicine and catalysis [3, 98]. In addition, the observed variation of M_s with respect to bulk materials is one of the most controversial issues in the fundamental research on the magnetic behavior of nanoparticles [99]. In many studies on maghemite $(\gamma - Fe_2O_3)$ and magnetite (Fe_3O_4) nanoparticles, a reduction has been observed and attributed to spin canting, due to competing interactions between sublattices that yield magnetic disorder at the particle surface [8, 76, 99]. On the other hand, a steep rise in saturation magnetization at low temperature has been reported for FiM nanoparticles [80, 100]. This phenomenon has been generally explained by the freezing of surface canted spins, and some investigations into the dependence on particle size have been carried out [80, 100]. A clear view of this complex matter is related to a full understanding of the nanoparticles' magnetic structure. Following the drawn line, we will start to discuss magnetic properties of a CoFeO_{N5} sample. In fact, CoFe₂O₄ nanoparticles in this system show at 5 K a saturation magnetization value ($M_{s 5 K}$ = 109 A·m²·kg⁻¹) higher than the bulk system ($M_{\rm s \ bulk \ 5 \ K}$ = 86–93 A·m²·kg⁻¹). The temperature dependence of $M_{\rm s}$ in the range of 5–300 K reveals the appearance of an extra contribution to M_s below 50 K. Using a phenomenological approach [59] the onset temperature (T_{onset}) at which the extra contribution to saturation magnetization appears was determined. By considering the temperature range of 150–300 K, a value of M_s was extrapolated for T = 0 K $M_s(0) = 89$ A·m²·kg⁻¹ (dashed line in figure X11a), and to quantify the increase in M_{s} , the term $M_{s}(T) = M_{s}(T) - M_{s}(0)$ was defined. The thermal dependence of M_s (inset of Fig. 5.11b) is well described by the relation

$$\Delta M \propto 1 - \frac{T}{T_{\text{onset}}} , \qquad (5.14)$$

where $T_{\text{onset}} = 30 \pm 2$ K is obtained.

Thus, an increase of M_s can be correlated with the spin-glass-like surface freezing. Starting from the picture drawn by MSiF and by magnetic measurements, the magnetic structure of nanoparticles is schematically represented (Fig. 5.11b).

Magnetization measurements indicate that at T > 30 K the canted spins can freely fluctuate, giving negligible contribution to M_s [80 100]. Progressive freezing in a disordered structure with high anisotropy is observed with decreasing temperature. At 0 K, 32% of the iron spins will be frozen with a mean angle of 42° with respect to

the external field, and each canted spin will give a mean contribution to saturation:



 $\mu_{\rm eff} = \mu_{\rm atomic} \times \cos 42^{\circ} \tag{5.15}$

Figure 5.11 (a) Thermal dependence of saturation magnetization. (Inset) Dependence of ΔM_s on temperature, where $\Delta M_s(T) = M_s(T) - M_s(0)$. (b) Schematic representation of the magnetic structure in nanoparticles on a CoFeO_{N5} sample. Reproduced with permission from Ref. [32].

Starting from this picture, M_s extrapolated at 0 K, considering the range of 300–50 K (Fig. 5.11a), is due only to the FM core (M_s core). On the other hand, the magnetization extrapolated at 0 K, considering the range 50–5 K, is due to the contribution of both frozen canted spins and magnetically ordered core (M_s) . Some calculations were performed to verify this model quantitatively (Table 5.3). Assuming that Fe^{3+} and Co^{2+} have a moment of 5 μ_B and 3 μ_B , respectively [9,101], and considering that at high temperature the canted spins do not give contribution to magnetization, the theoretical magnetic moment × chemical formula ($\mu_{C,E}$) equal to 3.3 μ_B is obtained. This value is comparable with the value obtained from the M_s core $(3.6 \mu_{\rm B})$. Using Eq. 5.15 to calculate the mean contribution to the saturation magnetization of each canted iron atom, a theoretical μ_{CF} of 5.45 μ_B is obtained at 0 K. A substantial agreement is obtained with the experimental results (5.56 $\mu_{\rm B}$). It is worth nothing that the temperature dependence of M_s in both samples (Fig. 5.12A) has the same trend, although a more rapid increase is observed in the $CoFeO_{N5}$ sample, consistent with the high degree of canting in the most diluted nanocomposites. To validate these results, this model was applied also to the CoFeO_{N10} sample, which shows a similar particle size but a different magnetic structure. Calculations performed on the $CoFeO_{N10}$ sample at low temperature show a good agreement, within experimental error, with experimental data also for this sample (Table 5.3).

Table 5.3	Calculated (th) and experimental (exp) magnetic moment × formula unit ($\mu_{C,F}$) and percentage difference between the two quantities for the sample CoFe, CoFe _{N10} , and CoFe _{N5}
	1

Sample	$\mu_{\text{C.F.}}$ Th (μ_{B})	$\mu_{\text{C.F.}} \exp(\mu_{\text{B}})$	∆µ _{C.F} (%)
CoFeO	4.6	4.2	8.5
$CoFeO_{N10}$	5.0	4.7	6
CoFeO _{N5}	5.4	5.6	3.5

Although a different fitting model was used, the same approach works in explaining the saturation magnetization values of a CoFe sample. In this case the spin canting, extended to both interstitial sites, has been described using a distribution of the canting angle. Then using Eq. 5.15 and the distribution of canting angles it is possible





to obtain the distribution of effective iron magnetic moments for each sublattice (Fig. 5.12b), giving an indication of the influence of spin canting on magnetic moment. The obtained magnetic structure allows us to estimate the values of 2.32 μ_B and 3.44 μ_B for T_d and O_h sublattice mean magnetic moments. They correspond to $\mu_{C.F.}$: 4.56 μ_B , slightly higher (8.5%) than the value obtained by magnetization measurements (4.17 μ_B).

Acknowledgments

This chapter partially reviews studies performed for the last 10 years among several research institutions: Chemistry Department of Cagliari University; Institute of Structure of the Matter (ISM), Italian National Research Council (CNR); Physics Department of the Danish Technical University (DTU), Institute des Molécules et Matériaux du Mans (IMMM), UMRCNRS 6283. It is a sincere pleasure to thank Prof. G. Piccaluga, Prof. A. Musinu, Prof. C. Cannas (University of Cagliari), Dr. D. Fiorani, Dr. E. Agostinelli, Dr. G. Varvaro, Dr. S. Laureti, Dr. A. M. Testa (ISM-CNR), Dr. J. M. Greneche, Dr. N. Yaacoub (IMMM), and Prof. S. Mørup (DTU-Denmark) for their respective contributions in specific publications. Special thanks are due to Prof. G. Piccaluga, Dr. E. Agostinelli, Dr. G. Varvaro, and Dr. S. Laureti for useful discussions during the preparation of this chapter.

References

- 1. Dormann, J. L., Fiorani, D. (1991). Magnetic properties of fine particles, in *Proceedings of Workshop on Studies of Magnetic Properties of Fine Particles and Their Relevance to Materials Science*, North Holland.
- 2. Dormann, J. L., Fiorani, D., Tronc, E. (1997). Magnetic relaxation in fine particle systems, in *Adances in Chemical Physics*, Vol. XCVIII, New York.
- 3. Suber, L., and Peddis, D. (2010). Approaches to synthesis and characterization of spherical and anisometric metal oxide magnetic nanomaterials, in *Magnetic Nanomaterials*, Vol., 4, Wiley, Weinheim.
- 4. Bedanta, S., and Kleeman, W. (2009). J. Phys. D: Appl. Phys., 42, 013001.
- 5. Papaefthymiou, G. C. (2009). Nano Today, 4, 438-447.
- 6. Fiorani, D. (ed.) (2005). *Surface Effects in Magnetic Nanoparticles,* Wiley, New York.
- 7. Kodama, R. H., Berkowitz, A. E. (1999). Phys. Rev. B, 59, 6321.

194 Magnetic Properties of Spinel Ferrite Nanoparticles

- 8. Coey, J. M. D. (1971). Phys. Rev. Lett., 27, 1140.
- 9. Haneda, K., Morrish, A. H. (1988). J. Appl. Phys., 63, 4258-4260.
- Morales, M. P., Serna, C. J., Bodker, F., Mørup, S. (1997). J. Phys.: Condens. Matter, 9, 5461.
- Peddis, D., Mansilla, M. V., Mørup, S., Cannas, C., Musinu, A., Piccaluga, G., Orazio, F., Lucari, F., Fiorani, D. (2008). *J. Phys. Chem. B*, **112**, 8507– 8513.
- 12. Edelstein, A. S., Cammarata, R. C. (1996). *Nanomaterials: Synthesis, Properties and Applications*, I. P. Publishing, Bristol.
- 13. Tartaj P, Del Puerto Morales, M., Veintemillas-Verdaguer, S., Gonzales Carreno, T., Serna, C. J. (2003). *J. Phys. D: Appl. Phys.*, **36**, R182–R197.
- 14. Mathew, D. S., Juang, R. S. (2007). Chem. Eng. J., 129, 51-65.
- 15. Kodama, R. H. (1999). J. Magn. Magn. Mater., 200, 359-372.
- 16. Machala, L., Zboril, R., Gedanken, A. (2007). J. Phys. Chem. B, **111**, 4003-4018.
- 17. Mørup, S., Hansen, M. F., Frandsen, C. (2011). *Magnetic Nanoparticle*, Elsevier.
- Liu, C., Zou, B., Rondinone, A. J., Zhang, Z. J. (2000). J. Am. Chem. Soc., 122, 6263–6267.
- 19. Chao Liu, A. J. R., John Zhang, Z. (2000). Pure Appl. Chem., 72, 37–45.
- Cannas, C., Musinu, A., Piccaluga, G., Fiorani, D., Peddis, D., Rasmussen, H. K., Mørup, S. (2006). *J. Chem. Phys.*, **125**, 164714.
- Peddis, D., Yaacoub, N., Ferretti, M., Martinelli, A., Piccaluga, G., Musinu, A., Cannas, C., Navarra, G., Greneche, J. M., Fiorani, D. (2011). *J. Phys.: Condens. Matter*, 23, 426004.
- Blaskov, V., Petkov, V., Rusanov, V., Mikhov, M., Martinez, L. M., Muñoz, J. S., Martinez, B. (1996). *J. Magn. Magn. Mater.*, **162**, 331–337.
- 23. Slonczewski, J. C. (1961). J. Appl. Phys., 32, S253-S263.
- 24. Peddis, D., Orrù, F., Ardu, A., Cannas, C., Musinu, A., Piccaluga, G. (2012). *Chem. Mater.*, **24**, 1062–1071.
- 25. Moumen, N., Bonville, P., Pileni, M. P. (1996). J. Phys. Chem., 100, 14410-14416.
- 26. Cannas, C., Musinu, A., Ardu, A., Orrù, F., Peddis, D., Casu, M., Sanna, R., Angius, F., Diaz, G., Piccaluga, G. (2010). *Chem. Mater.*, **22**, 3353–3361.
- Baldi, G., Bonacchi, D., Innocenti, C., Lorenzi, G., Sangregorio, C. (2007). *J. Magn. Magn. Mater.*, **311**, 10–16.

- Kukelhaus, S., Reis, S. C., Carneiro, M. F., Tedesco, A. C., Oliveira, D. M., Lima, E. C. D., Morais, P. C., Azevedo, R. B., Lacava, Z. G. M. (2004). *J. Magn. Magn. Mater.*, 272–276, 2402–2403.
- 29. Cannas, C., Falqui, A., Musinu, A., Peddis, D., Piccaluga, G. (2006). J. Nanopart. Res., 8, 255–267.
- Peddis, D., Cannas, C., Musinu, A., Piccaluga, G. (2008). J. Phys. Chem. C, 112, 5141–5147.
- Peddis, D., Cannas, C., Musinu, A., Piccaluga, G. (2009). *Chem.-Eur. J.*, 15, 7822-7829.
- Peddis, D., Cannas, C., Piccaluga, G., Agostinelli, E., Fiorani, D. (2010). Nanotechnology, 21, 125705.
- Trohidou, K. N., Vasilakaki, M., Peddis, D., Fiorani, D. (2012). *IEEE Trans. Magn.*, 48, 1305–1308.
- 34. Cannas, C., Peddis, D. (2012). La Chim. Ind., 4, 109-117.
- 35. Blundell, S. (2003). *Magnetism in Condesed Matter*, Oxford University Press, New York.
- 36. West, A. R. (1984). *Solid State Chemistry and Its Applications*, John Wiley & Sons.
- Morrish, A. H. (1965). *The Physical Principles of Magnetism*, Wiley, New York.
- 38. Crangle, J. (1991). Solid State Magnetism, G. B. Edward Arnold, London.
- 39. Leslie, D. L., Pelecky, R. D. R. (1996). Chem. Mater., 8, 1770-1783.
- Rondinone, A. J., Zhang, Z. J. (2000). Magnetic characterization, in Handbook Nanophase and Nanostructured Materials (Wang, Z. L., Liu, Y., Zhang, Z., eds.), Vol. II, Kluwer Academic, New York.
- 41. Kittel, C. (1946). Phys. Rev., 70, 965–971.
- 42. Bean, C. P., Livingston, J. D. (1959). J. Appl. Phys., 30, S120–S129.
- 43. Rancourt, D. G., Daniels, J. M. (1984). Phys. Rev. B, 29, 2410.
- Dormann, J. L., Cherkaoui, R., Spinu, L., Noguès, M., Lucari, F., D'Orazio, F., Fiorani, D., Garcia, A., Tronc, E., Jolivet, J. P. (1998). *J. Magn. Magn. Mater.*, 187, L139–L144.
- 45. Hansen, M. F., Mørup, S. (1998). J. Magn. Magn. Mater., 184, 262-274.
- 46. Néel, L. (1949). Ann. Gèophys., 5, 99-136.
- 47. Stoner, E. C., Wohlfarth, E. P. (1991). IEEE Trans. Magn., 27, 3475–3518.
- El-Hilo, M., O'Grady, K., Chantrell, R. W. (1992). J. Magn. Magn. Mater., 114, 307–313.

- 49. Solzi, M. (1993). Magnetic anisotropy in nanostructured materials, in *Proceedings of Foundamental Properties of Nanostructured Materials* (Fiorani, G. S. D., ed.).
- 50. Dormann, J. L., Fiorani, D., Tronc, E. (1997). *Advanced in Chemical Physics*, Vol. XCVIII, John Wiley & Sons, New York.
- 51. Bødker, F., Mørup, S., Linderoth, S. (1994). Phys. Rev. Lett., 72, 282–285.
- 52. Néel, L. (1954). J. Phys. Radium, 15, 225-239.
- 53. Berger, L., Labaye, Y., Tamine, M., Coey, J. M. D. (2008). *Phys. Rev. B*, **77**, 104431.
- 54. Eugenii Katz, I. W. (2004). Angew. Chem., Int. Ed., 43, 6042-6108.
- Guardia, P., Batlle-Brugal, B., Roca, A. G., Iglesias, O., Morales, M. P., Serna, C. J., Labarta, A., Batlle, X. (2007). *J. Magn. Magn. Mater.*, **316**, e756–e759.
- Sawatzky, G. A., Van Der Woude, F., Morrish, A. H. (1969). *Phys. Rev.*, 187, 747–757.
- 57. Morrish, A. H., Haneda, K. (1983). J. Magn. Magn. Mater., 35, 105–113.
- Lin, D., Nunes, A. C., Majkrzak, C. F., Berkowitz, A. E. (1995). J. Magn. Magn. Mater., 145, 343–348.
- Alves, C. R., Aquino, R., Depeyrot, J., Cotta, T. A. P., Sousa, M. H., Tourinho, F. A., Rechenberg, H. R., Goya, G. F. (2006). *J. Appl. Phys.*, **99**, 08M905-3.
- Shinjo, T., Kiyama, M., Sugita, N., Watanabe, K., Takada, T. (1983). J. Magn. Magn. Mater., 35, 133–135.
- Parker, F. T., Foster, M. W., Margulies, D. T., Berkowitz, A. E. (1993). *Phys. Rev. B*, 47, 7885–7891.
- 62. Pankhurst, Q. A., Pollard, R. J. (1991). Phys. Rev. Lett., 67, 248-250.
- Morales, M. P., Veintemillas-Verdaguer, S., Montero, M. I., Serna, C. J., Roig, A., Casas, L., Martinez, B., Sandiumenge, F. (1999). *Chem. Mater.*, 11, 3058–3064.
- Tronc, E., Fiorani, D., Noguès M, Testa, A. M., Lucari, F., D'Orazio, F., Grenèche, J. M., Wernsdorfer, W., Galvez, N., Chanéac, C., Mailly, D., Jolivet, J. P. (2003). *J. Magn. Magn. Mater.*, 262, 6–14.
- 65. Dormann, J. L., Nogues, M. (1990). J. Phys.: Condens. Matter, 2, 1223.
- 66. Mørup, S. (2003). J. Magn. Magn. Mater., 266, 110-118.
- Anhøj, T. A., Bilenberg, B., Thomsen, B., Damsgaard, C. D., Rasmussen, H. K., Jacobsen, C. S., Mygind, J., Mørup, S. (2003). *J. Magn. Magn. Mater.*, 260, 115–130.
- Gazeau, F., Bacri, J. C., Gendron, F., Perzynski, R., Raikher, Y. L., Stepanov, V. I., Dubois, E. (1998). *J. Magn. Magn. Mater.*, **186**, 175–187.

- 69. Mathew, D. S., Juang, R.-S. (2007). Chem. Eng. J., 129, 51-65.
- Sun, S., Zeng, H., Robinson, D. B., Raoux, S., Rice, P. M., Wang, S. X., Li, G. (2004). J. Am. Chem. Soc., 126, 273–279.
- Sawatzky, G. A., Van Der Woude, F., Morrish, A. H. (1968). *J. Appl. Phys.*, 39, 1204–1205.
- Chen, J. P., Sorensen, C. M., Klabunde, K. J., Hadjipanayis, G. C., Devlin, E., Kostikas, A. (1996). *Phys. Rev. B*, **54**, 9288–9293.
- 73. Carta, D., Casula, M. F., Falqui, A., Loche, D., Mountjoy, G., Sangregorio, C., Corrias, A. (2009). *J. Phys. Chem. C*, **113**, 8606–8615.
- Cannas, C., Musinu, A., Peddis, D., Piccaluga, G. (2004). J. Nanopart. Res., 6, 223–232.
- 75. Yunus, S. M., Yamauchi, H., Zakaria, A. K. M., Igawa, N., Hoshikawa, A., Ishii, Y. (2007). *J. Magn. Magn. Mater.*, **310**, 2722–2724.
- Lima, J. E., Brandl, A. L., Arelaro, A. D., Goya, G. F. (2006). *J. Appl. Phys.*, 99, 083908–083910.
- Darbandi, M., Stromberg, F., Landers, J., Reckers, N., Sanyal, B., Keune, W., Wende, H. (2012). *J. Phys. D: Appl. Phys.*, 45, 195001.
- Kachkachi, H., Ezzir, A., Nogués, M., Tronc, E. (2000). *Eur. Phys. J. B*, 14, 681–689.
- 79. Bellitto, C., Bauer, E. M., Righini, G. (2008). *Inorg. Chim. Acta*, **361**, 3785–3799.
- Aquino, R., Depeyrot, J., Sousa, M. H., Tourinho, F. A., Dubois, E., Perzynski, R. (2005). *Phys. Rev. B*, **72**, 184435–184446.
- Cannas, C., Musinu, A., Peddis, D., Piccaluga, G. (2006). *Chem. Mater.*, 18, 3835–3842.
- Gittleman, J. I., Abeles, B., Bozowski, S. (1974). *Phys. Rev. B*, 9, 3891– 3897.
- Tronc, E., Prenè, P., Jolivet, J. P., Dormann, J. L., Grenèche, J. M. (1998). *Hyperfine Interact.*, **112**, 97–100.
- Jonsson, T., Mattsson, J., Djurberg, C., Khan, F. A., Nordblad, P., Svedlindh, P. (1995). *Phys. Rev. Lett.*, **75**, 4138–4141.
- Jonason, K., Vincent, E., Hammann, J., Bouchaud, J. P., Nordblad, P. (1998). *Phys. Rev. Lett.*, 81, 3243.
- Mathieu, R., Jönsson, P., Nam, D. N. H., Nordblad, P. (2001). *Phys. Rev. B*, 63, 092401.
- Humfeld, K. D., Giri, A. K., Majestich, A. S., Venturini, E. L. (2001). *IEEE Trans. Magn.*, **37**, 2194–2196.

- 88. Karanasos, V., Panagiotopoulos, I., Niarchos, D., Okumura, H., Hadjipanayis, G. C. (2000). *J. Appl. Phys.*, **88**, 2740–2744.
- 89. Street, R., Brown, S. D. (1994). J. Appl. Phys., 76, 6386-6390.
- 90. O'Grady, K., Laidler, H. (1999). J. Magn. Magn. Mater., 200, 616-633.
- Del Bianco, L., Fiorani, D., Testa, A. M., Bonetti, E., Savini, L., Signoretti, S. (2002). *Phys. Rev. B*, 66, 174418–174429.
- Chen, J. P., Sorensen, C. M., Klabunde, K. J., Hadjipanayis, G. C. (1995). *Phys. Rev. B*, **51**, 11527–11532.
- Tronc, E., Ezzir, A., Cherkaoui, R., Chanéac, C., Noguès, M., Kachkachi, H., Fiorani, D., Testa, A. M., Grenèche, J. M., Jolivet, J. P. (2000). *J. Magn. Magn. Mater.*, **221**, 63–79.
- Kodama, R. H., Berkowitz, A. E., McNiff, J. E. J., Foner, S. (1996). *Phys. Rev. Lett.*, **77**, 394–397.
- Del Bianco, L., Hernando, A., Multigner, M., Prados, C., Sanchez-Lopez, J. C., Fernandez, A., Conde, C. F., Conde, A. (1998). *J. Appl. Phys.*, **84**, 2189– 2192.
- 96 Zhang, H. Y., Gu, B. X., Zhai, H. R., Lu, M., Miao, Y. Z., Zhang, S. Y., Huang, H. B. (1994). *J. Appl. Phys.*, **75**, 7099–7101.
- Sturge, M. D., Gyorgy, E. M., LeCraw, R. C., Remeika, J. P. (1969). *Phys. Rev.*, 180, 413.
- Pankhurst, Q. A., Connelly, J., Jones, S. K., Dobsonb, J. (2003). J. Phys. D: Appl. Phys., 36, R167–R181.
- Martínez, B., Obradors, X., Balcells, L., Rouanet, A., Monty, C. (1998). *Phys. Rev. Lett.*, **80**, 181–184.
- 100. De Biasi, E., Zysler, R. D., Ramos, C. A., Romero, H. (2002). *Phys. B: Condens. Matter*, **320**, 203–205.
- 101. Ngo, A. T., Bonville, P., Pileni, M. P. (2001). J. Appl. Phys., 89, 3370-3376.

Chapter 6

FePt Films with Graded Anisotropy for Magnetic Recording

Th. Speliotis and D. Niarchos

Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, Department of Materials Science, National Centre for Scientific Research "Demokritos," 153 10 Aghia Paraskevi, Attiki, Greece tspeliotis@ims.demokritos.gr, speliotis@outlook.com

6.1 Short History of Magnetic Recording

Magnetic recording was invented over a century ago by Valdemar Poulsen [1]. Although magnetic recording had been invented in 1898, it was not until the late 1920s that the technology was successfully marketed to the public [2]. The recording medium of that era was magnetic tapes for archive files or recording sound, but the major disadvantage was the fast random access capability. The access time was longer than other methods of recording available that period, such as punch cards. In 1956 IBM invented the first hard disk drive (HDD) named RAMAC (the random access memory accounting system) to overcome the random access problem in stored material [3]. RAMAC had a capacity of 5 MB, and after that started the golden age of exponential growth in performance and utilization. The areal density (AD) increased to the order of 10^8 times in a period of 50 years. Nowadays HDDs offer an AD of 600 gigabits per square inch (Gb/in²). Besides Moore's law from the semiconductor industry, which is the most frequently cited metric for information technology advance, magnetic recording has exhibited equally impressive advances in storage (AD) and cost reduction. In both fields, adherence to geometrical scaling is a guiding principle in this advance (Fig. 6.1).



Figure 6.1 AD progress in IBM hard disks. Courtesy of Grochowski, E., Halem, R. D. (2003). *IBM Syst. J.*, **42**, 338.

In the 1970s and 1980s, AD underwent an annual compound growth at a rate of ~30%. It should be noted that the significant improvement came in 1991, with the introduction of thin-film media as well as the magnetoresistive head. This accelerated AD growth from 30% to 60% per annum. Magnetic recording with an AD up to 10 Gbit/in² was demonstrated in 1997.

In data storage devices there has to be a medium for storing information. In magnetic recording the medium is tape or disk and satisfies two basic principles. The first is magnetized grains with north and south poles out of which the magnetic stray field stems and can be sensed by a conventional magnetic field sensor. The second prerequisite is the ability to change the polarity of magnetic grains by applying an external magnetic field, which is usually produced using an electromagnet.

In longitudinal recording technology were needed many grains to store a bit, which are isolated with zigzag transition. The polarities of small multigrain magnets are parallel to the surface of the hard disk. When two identical poles are next to each other a strong magnetic field emerges from the medium, but no field will emerge when opposed poles are next to each other. Therefore when a giant magnetoresistance (GMR) magnetic field sensor flies over the pole-pole transitions a voltage pulse is produced and synchronized with a clock pulse. When during a clock pulse the GMR sensor produces a voltage peak, it is represented by 1, and the opposite case, for example, the absence of voltage, is represented by 0. The volume V of grains typically decreases with an increase of AD. To compensate for a decrease in *V*, higher–magnetocrystallineanisotropy (K_{u}) materials are needed to maintain sufficient stability [4]. However, at the superparamagnetic limit [5], scaling of the grain size necessary to maintain a sufficient signal-to-noise ratio (SNR) can no longer be compensated by increasing $K_{\mu\nu}$ due to the limited write fields achievable with today's write heads. The predicted superparamagnetic limit for conventional longitudinal recording is an AD of 150 Gbit/in² [6].

6.2 Perpendicular Recording Media for 1 Tb/in² and beyond

In perpendicular recording, which is used nowadays for recording information in HDDs, magnetization stands out of plane. In this case the origin of the stray magnetic field is the center of bit cells rather than transitions.

In the mid-1970s, perpendicular magnetic recording technology was proposed as a way to overcome the problem of demagnetized fields from recording transitions [3]. In a ferromagnetic or ferrimagnetic system there exists a demagnetizing field with a direction opposed to that of magnetization. The demagnetized field is $H_d = -N \times \mathbf{M}$, where *N* is the demagnetizing tensor and **M** is the magnetization vector. *N* depends on the shape and direction relative to the magnetic field of the magnet. In longitudinal recording as the linear density increases, the distance between the magnetic charges decreases. When the distance between the charges decreases an increased demagnetized field in the opposite magnetization direction is expected, at higher linear densities (Fig. 6.2). In 1975 Iwasaki and Takemura experimentally observed that magnetic vortices will be produced in longitudinal media because of a stronger demagnetizing field when thicker films are used [8]. This circular magnetization would not be able to produce high output voltages at higher densities.



Figure 6.2 Illustration of magnetic charges and associated demagnetizing fields for longitudinal and perpendicular recording: (a) thin film, (b) low density, and (c) high density. The arrows indicate the direction of the demagnetizing field. Block arrows are used to show the higher strength of the demagnetizing field [7].

After his first publication in 1975, Professor Iwasaki et al. from Tohoku University came up with many other inventions from 1975 to 1980 [9–11]. These inventions were critical for the future of perpendicular recording technology and were also the foundation for some of the current developments. Media based on CoCr alloys with a perpendicular anisotropy, double-layered perpendicular recording media with a CoCr recording layer and NiFe as a soft underlayer (SUL), and the design of several types of heads for perpendicular recording were developed. Iwasaki and Nakamura developed a perpendicular recording medium based on CoCr and
demonstrated that 30 kbits/in² could be achieved with a 1000 nm thick recording layer. This linear density was significantly larger than that supported by longitudinal recording then [12].

The technology of perpendicular magnetic recording developed further from the 1970s until today and was integrated into HDDs in 2005. Perpendicular recording technology has been the dominant technology since 2008. The materials used for perpendicular recording are based on Co alloys. Iwasaki proposes CoCr alloy thin films for the first medium and a NiFe film for the magnetic SUL [13]. Since that time modifications of CoCr. such as CoCrPt. CoCrTa. and CoCrNb, have been used as recording materials. CoCrPt oxide-based media have a composite of Pt 10-20 at%, Cr 5-20 at%, and Co 60-80 at%. The oxide material will be part of the composite target in the form of SiO_2 , Ta_2O_5 , or TiO_2 . When such a composite target is sputtered the thin film consists of small-area grains without oxygen, where Co and Pt materials dominate, and grain boundaries, which have excessive oxygen and maybe small nonmagnetic parts of Co or Pt. The nonmagnetic grain boundaries isolate the magnetic grains from each other and help to reduce the transition noise. Figure 6.3 is a transmission electron microscopy (TEM) image of such a media type, which shows grains and grain boundaries.



Figure 6.3 TEM planar view of a typical CoCrPt:SiO₂ perpendicular recording medium. *Source*: Ref. [7].

At the end of the 1970s Iwasaki discovered that a perpendicular recording medium with an SUL requires a lower head field and produces a high read-back voltage, comparable with a single-layer medium. Figure 6.4 shows various functional layers such as the SUL, the intermediate decoupling layer, and the recording layer.



Figure 6.4 Schematic drawing of different functional layers of a perpendicular recording medium. Courtesy of Khizroev, S., Litvinov, D. (2004). *Perpendicular Magnetic Recording*, p. 18, Kluwer Academic Publishers.

6.3 High K_u Materials

One of the prerequisites of ultrahigh recording densities is high thermal stability. A recording layer also must have high anisotropy and small grain sizes. All ferromagnetic materials are characterized by a critical grain size where thermal fluctuations are dominant at room temperature. To reduce grain size, materials with high magnetocrystalline anisotropy (K_u) have attracted interest.

There are several magnetic material systems for perpendicular magnetic recording, such as $L1_0$ FePt, FePd, CoPt, and MnAl, all of which have high magnetic anisotropy. The origin of high magnetocrystalline anisotropy arises from the crystal symmetry breakdown during transformation from a cubic structure to a tetragonal one. This class of materials requires processing at high temperatures to induce ordering and then to achieve high anisotropy.

Another class of materials is based on rare-earth (RE) intermetallic compounds such as $Nd_2Fe_{14}B$ and $SmCo_5$. This class has been studied systematically for permanent magnet applications and also exhibits very high anisotropy. Here the origin of the high magnetocrystalline anisotropy is the asymmetry of their complex crystal structures. The disadvantages, however, for these materials is the difficulty to process by sputtering and the low corrosion resistance due to their RE content.

Co/X multilayers with X = Pt or Pd are another promising class of materials with superlattices fabricated under different experimental conditions, showing very high values in perpendicular magnetic anisotropy due to interfacial anisotropy in the multilayer structure. Representative high- K_u materials are summarized in Table 6.1; the K_u of FePt almost reaches the value of 10^8 erg cm^{-3} , which is close to that of SmCo₅ and 20 times higher than that of pure Co. Also the high K_u of FePt offers thermally stable grains with diameters down to 2.8 nm as compared to the thermally stable grains of 10 nm diameter of Co. See also Fig. 6.5.



Figure 6.5 Schematic structures and cross-sectional microstructures of three types of perpendicular media. Courtesy of Ref. [14].

native media alloys
alter
potential
ties of
c propei
magneti
rinsic
Int
Table 6.1

		Ku	Ms	H _K			٨		
Alloy system	Material	$10^{7} (erg/cm^{3})$	(emu/cm ³)	(k0e)	$T_{c}(\mathbf{K})$	$\delta_w({A})$	(erg/cm ³)	$D_{\rm c}$ (µm)	$D_{\rm P}$ (nm)
	CoCrPt	0.2	298	13.7	I	222	5.7	.89	10.4
Co alloys	Co	0.45	1400	6.4	1404	148	8.5	.06	8.0
	Co3Pt	2.0	1100	36	I	70	18	.21	4.8
	FePd	1.8	1100	33	760	75	17	.20	5.0
$L1_0$	FePt	6.6-10	1140	116	750	39	32	.34	3.3-2.8
phases	CoPt	4.9	800	123	840	45	28	.61	3.6
	MnAl	1.7	560	69	650	77	16	.71	5.1
	$Nd_2Fe_{14}B$	4.6	1270	73	585	46	27	.23	3.7
RE-TM	SmCo ₅	11 - 12	910	240-400	1000	22-30	42-57	.7196	2.7-2.2
Source: Courtesy of I	Ref. 4.								
Anisotropy field: H	$K = 2K_{\rm u}/M_{\rm s};$	Domain wall width	1: $\delta_{\rm w} = \pi (A/K_{\rm u})$) ^{1/2} ; Domai	n wall en	ergy: $\gamma_{\rm w}$;	$ = 4(A \cdot K_{\rm u})^{1/2}; $ Sin	ngle-particle	domain size:
$D_{\rm c} = 1.4 \gamma_{\rm w}/M_{\rm s}^{2}; {\rm Exct}$	ange coupling	constant: $A = 10^{-6} e$	rg/cm; Minimal	stable grain	size: $D_{\rm p} = ($	$(60 k_{\rm B}T/K_{\rm u})$	$^{1/3}$ ($\tau = 10 \text{ yr}$).		

6.4 Fabrication Methods

Physical vapor deposition is a method for depositing magnetic thin films. The process of deposition of thin films underlies the production of a range of technological products. The deposition technology is a mix of applied science and art, with physics at its heart. Here conventional and typical deposition techniques such as sputtering and thermal evaporation are described in brief.

6.4.1 Sputtering

Sputtering is a versatile and one of the most commonly and widely used techniques for preparing thin films. Its popularity arises from the simplicity of the physical process involved, flexibility for alteration, and customization. It is widely used for magnetic-thinfilm research and in the recording industry. High-melting-point materials like ceramics and refractory metals, which are hard to deposit by evaporation techniques, are easily deposited using sputtering.

Sputtering techniques range from a simple direct current (dc) glow-discharge sputtering, which is limited to the sputtering of conductive targets, to radio-frequency (rf) sputtering, where any kind of target regardless of its conductivity can be sputtered, to the more sophisticated ion beam sputtering (IBS), in which very controlled deposition of material is possible [15].

The nature of the process of sputtering makes available ions that can be utilized for tailoring the chemistry of the structure of the film. Sputtering is carried out in an inert gas atmosphere like Ar, Kr, or Xe, since there is no chemical reaction between the sputtering gas and the target. The sputtering gas pressure is a few milli-Torrs and is ionized by a strong electric field, creating plasma above the target. When a small amount of reactive gas such as oxygen or nitrogen is mixed with the sputtering gas and introduced into the sputtering target during deposition, compound films of oxide or nitride can be prepared. This process is called reactive sputtering. When a composite target is used or codeposition from multiple targets is used, alloy films can be prepared. Sputtering is the preferred method for periodic artificial structures called multilayers comprising alternative layers of two different materials, which anticipate their manufacture for magnetic recording technology, etc.

6.4.2 Thermal Evaporation

The vacuum thermal evaporation deposition technique consists of heating until evaporation of the material to be deposited. Usually low pressures are used, about 10^{-6} Torr or 10^{-5} Torr, to avoid a reaction between the vapor and the atmosphere. The three most important parameters for this method are the pressure, expressed as a mean free path (MFP) which is of the same order as the vacuum chamber dimensions, so these particles travel in straight lines from the evaporation source toward the substrate; the partial pressure of reactive gasses in inert working gases; and the film vapor arrival to the reactive gas impingement rate ratio.

Molecular beam epitaxy (MBE) can be considered to be a refined form and the most reliable deposition process of vacuum evaporation and was first developed by Cho and Arthur [16] for the controlled growth of III–V semiconductor epitaxial layers. It works in an ultrahigh vacuum (UHV) atmosphere, for example, 10^{-7} – 10^{-9} Pa. The primary advantage of MBE is the capability for controlled growth of heterostructures with layer thicknesses down to a single molecular monolayer (ML) and monitoring by reflection high-energy electron diffraction (RHEED) oscillation. This has led to exciting new physics and devices based on reduced dimensionality structures.

6.4.3 Thin-Film Growth

Physical vapor deposition is a method for growing a film or a stack of films on a substrate in high vacuum. When sputtered atoms impinge on the substrate surface, the atoms start to adsorb into the surface; these atoms are referred as ad-atoms. Interaction between the ad-atoms and the atoms of the surface takes place during the deposition of atoms (Fig. 6.6). This interaction depends on the adatoms, used substrates, and substrate temperature. It is responsible for nucleation and the subsequent growth of thin layers on the substrate. In general, depending on the growth parameters, one can distinguish between three different growth modes (Fig. 6.7):

1. Layer, or Franck-van der Merwe, growth mode: A new layer starts to grow only after the preceding one is finished (Fig. 6.7a).

- 2. Island, or Vollmer–Weber, growth mode: The deposited atoms cannot diffuse past the island boundaries. Already after a light coverage multiple MLs can be formed as high islands (Fig. 6.7b).
- 3. Layer plus island, or Stranski–Krastanov, growth mode: This type is a combination of the layer and island growth modes (Fig. 6.7c).



Figure 6.6 Behavior of ad-atoms in the surface deposition process.



Figure 6.7 Growth modes for layer development by sputtering.

6.5 Technologies for Future Recording Media

Ultrahigh densities, in the Tbit/in² regime and beyond, require us to shrink the media's grain diameters and decrease the thickness of the media, as well as the physical dimensions of the read/write heads. However, under a critical grain volume the thermal fluctuations

decrease the signal sensed by the drive's read/write head. If the signal reduction is great enough, thermal fluctuations can easily flip the direction of magnetization in each bit, causing permanent loss of information. This phenomenon is called the superparamagnetic limit.

The superparamagnetic limit intrudes an SNR, thermal stability effects, and writability trade-off, which limit the ability to continue using the current magnetic materials to higher storage densities with acceptable performance.

Today, as the conventional magnetic recording technology is finally facing its fundamental limit due to thermal instabilities in the longitudinal magnetic media, the strong interest for perpendicular recording is increasing.

To overcome the superparamagnetic limit several novel architectures that include bit-patterned media recording (BPMR) [17], heat-assisted magnetic recording (HAMR) [18], and two-dimensional magnetic recording (TDMR) [19–21] have been proposed as potential approaches for ultrahigh densities toward 10 Tbits/in².

In BPMR bits are stored in single-domain, ordered magnetic islands to maintain thermal stability for very small grain sizes. HAMR uses laser heating to decrease the coercivity of a bit, while maintaining ambient temperatures and therefore higher coercivities at adjacent bits. TDMR records a channel bit in very few magnetic grains and relies on two-dimensional signal processing. It can still use conventional Voronoi-type granular media to store data.

Among the large variety of materials for perpendicular recording are, for example, $L1_0$, CoPt, FePt, Co/Pd artificial structures, and SmCo₅. It is well known that ordered FePt with an $L1_0$ crystal structure (face-centered tetragonal [fct] phase) has high magnetocrystalline anisotropy energy, for example, 7×10^7 erg/cm³, for FePt in bulk form [22], strong corrosion resistance, and unique thermal stability for grain diameters less than 3 nm. Therefore, an ordered FePt thin film is expected to be one of the candidates for thermally stable media in future ultrahigh-density magnetic recording media.

Ordered FePt thin films with perpendicular magnetic anisotropy were so far prepared by MBE [23] or conventional sputtering [24] with an epitaxial technique using a single-crystal magnesium oxide (MgO) substrate.

6.6 FePt Graded Media for Perpendicular Magnetic Recording

Our approach is:

- growth of FePt single layers, 10 nm thick, on MgO(200) substrates;
- growth of semicore-shell structures, like L1₀/A1 FePt;
- growth of hard/graded FePt structures on MgO substrates; and
- transfer of this work, on MgO substrates, to amorphous (glass), industrial substrates.

6.7 Fundamental Properties of L1₀ FePt

6.7.1 Optimization of FePt Single Layers on MgO

The key parameter that is essential for the remarkable properties of FePt is its chemically ordered $L1_0$ phase with equiatomic composition in the thermal equilibrium phase diagram, as shown in the phase diagram of FePt (Fig. 6.8) [25].



Figure 6.8 Phase diagram of FePt.

Even if the ordering temperature of the $L1_0$ FePt bulk phase is 1300°C, with annealing times in days [26], the FePt films fabricated by the sputtering method with a substrate temperature at room temperature usually are in a disordered face-centered cubic (fcc) structure. For the transformation from fcc to $L1_0$ postannealing or in situ during deposition, annealing is needed, with temperature depending on the kind of substrate and the lattice misfit between the substrate and the $L1_0$ FePt film. In the case of a MgO substrate the temperature is around to 500°C. The crystal structure of the $L1_0$ phase is fct, consisting of alternating atomic layers of Fe and Pt along the *c* axis.

The epitaxial growth and microstructure of an FePt alloy (CuAu (I) type) films, on MgO substrates, with the *c* axis normal to the film plane was investigated with depositions in UHV sputtering at different substrate temperatures. The morphology of the FePt films at different growth temperatures clearly depends on the temperature. Figure 6.9 shows X-ray diffraction (XRD) patterns of FePt films deposited at various substrate temperatures (T_s), (001) superlattice diffractions observed at around 24°C in all cases. No peaks from the other planes suggest a strong (001) texture. Figure 6.10 shows perpendicular magnetization curves of films deposited on MgO(200) substrates at different temperatures. The coercivity of the films drastically increased with increasing T_s from 300°C to 650°C.



Figure 6.9 XRD patterns of FePt films fabricated on MgO substrates.



Figure 6.10 Perpendicular magnetization curves of FePt films fabricated on MgO substrates.

Figure 6.11 shows cross-sectional images of FePt thin films deposited at 500°C and 200°C. The FePt layer deposited at 500°C is grown forming islands whose diameter is in tens of nanometers, whereas the one grown at 200°C is a continuous film. Due to the lattice mismatch between the MgO(100) and FePt films, periodic edge dislocations are found at the interface. Phase analysis results on both specimens are performed using HRTEM images and FFT patterns in Fig. 6.11c-g compared to the selective diffraction images (not shown). In the specimen grown at 500°C, the A1 phase was not detected at least as a form of an island or coarsened grain. In both specimens, the FePt (001) lattice planes of the films are parallel to the MgO(001) plane of the substrate regardless of the FePt phases. The results are that when FePt films are deposited on a MgO(001) substrate, the FePt films tend to grow epitaxially. If sufficient mobility is ensured for the Fe and Pt atoms, that is, by high temperature, they are aligned to develop an $L1_0$ -ordered phase. In this case the mismatch-induced stress applied on the film makes one part of the film separate from other parts; therefore isolated islands are built [27]. On the contrary, if the mobility of the atoms is not enough, for example, owing to low temperature, the atoms under strong stress but small mobility become a film in the disordered phase [28].



Figure 6.11 HRTEM images on FePt films grown (a) at 500°C and (b) 200°C. The FFT images of the marked boxes are listed on (c-g). The arrows and descriptions on the FFT images stand for orientational directions of the given materials. *Abbreviations*: HRTEM, high-resolution transmission electron microscopy; FFT, fast Fourier transform.

6.7.2 L1₀ FePt on Amorphous Substrates

6.7.2.1 Texture control and seed layer

To obtain FePt with the (001) texture, either a substrate or a suitable underlayer that has a similar atomic configuration to that of the FePt(001) plane and a small lattice misfit is required. Substrates such as MgO(001), SrTiO3(100), Cr(200), and Ag(200) are normally used to induce the FePt(001) texture. The corresponding epitaxial relationship is FePt(001)<001>||MgO(100)<001> for MgO, with lattice misfit 9.07%, and FePt(001)<001>||Cr(100)<110> for Cr, with lattice misfit 5.8%. Development of the Cr(200) texture is a key to obtaining FePt(001)-textured films. An intermediate layer of MgO to prevent Cr diffusion on FePt is required.

In Figs. 6.12–6.15 fully ordered XRD [θ –2 θ] patterns of Cr(200) _{30 nm}/MgO(100)_{2 nm}/FePt(100)_{10 nm}, hysteresis loops of Cr(200)/MgO(100)/FePt(100), and cross-sectional TEM and HRTEM images of glass/Cr(200)/MgO(100)/FePt(100) are presented.



Figure 6.12 XRD scan of Cr(200)/MgO(100)/FePt(100).



Figure 6.13 In-plane and out-of-plane hysteresis loops of Cr(200)/ MgO(100)/FePt(100).



Figure 6.14 Cross-sectional TEM of glass/Cr(200)/MgO(100)/FePt(100).



Figure 6.15 Cross-sectional HRTEM FePt(100).

of glass/Cr(200)/MgO(100)/

We report a systematic study of the epitaxial growth of FePt(001) on textured MgO(200)/Cr(200) with the relationship FePt(001)< 100 > ||MgO(001) < 100 > ||Cr(200) < 110 >through optimization of the deposition temperature and a layer thickness of Cr and MgO underlayers. For FePt we varied the deposition temperature and the argon sputtering pressure.

6.7.3 L1₀ FePt Based Exchange-Spring Phenomenon

The exchange-spring phenomenon, nominated for the ability of a soft magnet to rotate reversibly about its interface with a hard magnet, has the potential for increasing a material's magnetic energy product. This approach proposed since the beginning of the 1990s is based on a nanocomposite material with a hard and a soft phase, mutually dispersed and exchange coupled [29]. Exchange-spring media (ESM) for magnetic recording use the exchange coupling between different magnetic phases at the nanoscale climax. The exchange interactions between a magnetically hard phase and a magnetically soft phase cause novel magnetic properties that can be optimized by changing the intrinsic properties of the different phases [30]. In domain-wallassisted magnetic recording the soft magnetic phase helps nucleate a reversed domain, the exchange interactions help propagate the reversed domain, and the hard magnetic phase provides high thermal stability [31]. Exchange-coupled composite (ECC) media, which are composed of magnetically isolated nanodots, each consisting of a hard magnetic layer and a soft magnetic layer, are coupled by exchange interaction through their common interface. The focus of this chapter is on ECC media. As the hard magnetic phase of ECC media L1₀ FePt nanodots are chosen and as the soft magnetic phase A1 FePt.

6.7.4 Production of Prototype L1₀/A1 FePt Nanostructures

To produce prototype composite $L1_0$ FePt nanostructures with perpendicular magnetization and to realize exchange coupling, two different methods have been used and optimized. We selected as the hard phase the $L1_0$ FePt phase deposited at 700°C, limiting the thickness to only 3.2 nm, to obtain isolated grains by sputtering on a single-crystal MgO substrate. This produces island-like nanoparticles with an average lateral size of 10-15 nm due to surface tension according to the proposed Volmer–Weber growth mode. These types of nanoparticles are covered at room temperature with single layers of soft A1 FePt (fcc) with a thickness in the range of 3.2-50 nm.

Two series of $L1_0$ FePt layers were prepared by first depositing FePt on MgO(001) substrates heated to 500°C (series I) and 700°C (series II). The nominal thickness of the $L1_0$ layer, d_{L1} , was kept to 3.2 nm in all samples to obtain isolated grains [32]. The A1 FePt layers were deposited, after cooling to room temperature, with nominal thicknesses d_{A1} of 3.2 nm, 6.4 nm, 9.6 nm, 20 nm, and 50 nm (Figs. 6.16 and 6.17).



Figure 6.16 Cross-sectional TEM images of the interface in the case of 3.2 nm $L1_0$ FePt/3.2 nm A1 FePt (a) and 3.2 nm $L1_0$ FePt/9.6 nm A1 FePt (b).

6.7.4.1 L1₀/A1 FePt semicore–shell nanocomposites

Structural and magnetic properties of $(L1_0/A1 \text{ FePt})$ exchangecoupled nanocomposites are studied. Semispherical "dome like" nanocomposites with L1₀ FePt isolated nanoparticles and A1 FePt (fcc) cap layers were obtained by depositing A1 FePt on type L1₀ FePt nanoparticles to understand the influence of the soft magnetic layer thickness on the magnetic properties of the system. Epitaxial growth is confirmed by XRD and TEM, while coercivity decreases dramatically for the $L1_0/A1$ FePt system when the thickness of the A1–FePt cap layers is increased. This result can be used to realize ultrahigh magnetic recording media with tunable coercivity, suitable for conventional write heads [33].



Figure 6.17 Coercive and nucleation fields as a function of A1 layer thickness for $L1_0$ in 700°C deposition.

6.7.5 Hard/Graded FePt Granular Layers

Besides the exchange-spring phenomenon, a new approach proposed for reducing the writing field, while retaining high thermal stability, was graded ESM, with thin films grown in a temperature gradient [34–36]—a new class of nanocomposite material for ultrahigh-density recording media. Graded ESM with spatially varying anisotropy $K_u(z)$ offer improved characteristics in comparison to homogeneous, constant-*K* hard/soft bilayer media (Fig. 6.18). There are several examples of graded ESM, depending on the tetragonal phase of FePt as the hard magnetic layer, with the soft layer composed of the cubic phase (A1) of FePt [37–41].



Figure 6.18 (a) The phase-graded media model for linear phase transformations with a 15 nm thick graded layer. (b) Phase profile comparison between linearly, logistically graded media and the bilayer. The bilayer consists of only hard and soft layers [42].

This new technique is based on irreversible growth of (2 + 1)-dimensional magnetic thin films under the influence of a perpendicular temperature gradient. Until now gradients have been studied extensively in diffusion processes, thermal conductivity, and heat conduction problems.

6.7.5.1 Growth of L1₀ FePt/graded FePt nanocomposites prepared using UHV sputtering on MgO(002) substrates

Varying the deposition temperature affects the $L1_0$ -A1 transformation, thus changing the $L1_0$ order parameter and the anisotropy $K_u(z)$. FePt can be grown with (001) orientation, that is, with the *c* axis, the easy anisotropy axis, of the tetragonal phase perpendicular to the film plane. At first a single-phase $L1_0$ FePt layer with a high coercive field, H_c , perpendicular to the film-plane magnetic anisotropy, was deposited on a MgO substrate at 500°C. The next step was the growth of the graded $L1_0$ to the A1 FePt layer on top of the magnetically hard $L1_0$ FePt layer (Figs. 6.19–6.22), [43].



Figure 6.19 XRD patterns of $L1_0$ /graded FePt films fabricated on MgO substrates.



Figure 6.20 Perpendicular magnetization curves of $L1_0$ /graded FePt films fabricated on MgO substrates.



Figure 6.21 Cross-sectional image of hard (10 nm)/graded (10 nm) FePt nanocomposite.



Figure 6.22 Variation of the coercive field, H_c , of hard (10 nm)/graded $(t_x \text{ nm})$ FePt nanocomposite with the thickness of the graded layer, t_x .

Epilogue

- Perpendicular magnetic recording based on FePt nanostructured films is a key technology nowadays and could be support areal densities of 1 Tb/in² and beyond.
- We have described some fundamental properties of $L1_0$ FePt thin films. The ordering degree depends on deposition temperature, stoichiometry, texture control and microstructure with columnar grains.

- For 1 Tb/in² technologies further improvement of the microstructure, reduction of L1₀ FePt grain size, and grain size distribution are required.
- Nanostructured $L1_0$ -FePt/Fe exchange coupled composite media or $L1_0$ FePt graded media, with perpendicular magnetization, where each nanograin consists of a hard magnetic $L1_0$ -FePt part and a soft magnetic part (Fe or FePt A1), can be considered to be very easy for realizing ultrahigh recording densities of at least 1 Tbit/in². The hard magnetic part (storage layer) provides uniaxial anisotropy, out of plane magnetization and long-term thermal stability of the stored information.
- The soft magnetic part or nucleation layer allows systematic tailoring of the coercivity with the thickness of the soft magnetic layer, and therefore enables writeability of the recording medium by conventional writing heads.

References

- 1. Jorgensen, F. (1999). J. Magn. Magn. Mater., 193, 1.
- 2. Clark, M. H. (1999). J. Magn. Magn. Mater., 193, 8.
- 3. Iwasaki, S. (2003). IEEE Trans. Magn., 39(4), 1868.
- Weller, D., Moser, A., Folks, L., Best, M. E., Wen Lee, Toney, M. F., Schwickert, M., Thiele, J. U., Doerner, M. F. (2000). *IEEE Trans. Magn.*, 36, 10.
- Litvinov, D., Kryder, M. H., Khizroev, S. (2002). J. Magn. Magn. Mater., 241, 453.
- 6. Bertram, N. H., Williams, M. (1999). IEEE Trans. Magn., 36, 4.
- 7. Piramanayagam, S. N. (2007). J. Appl. Phys., 102, 011301.
- 8. Iwasaki, S., Takemura, K. (1975). *IEEE Trans. Magn.*, **11**, 1173.
- 9. Iwasaki, S., Nakamura, Y. (1978). IEEE Trans. Magn., 14, 436.
- 10. Iwasaki, S., Nakamura, Y., Ouchi, K. (1979). *IEEE Trans. Magn.*, **15**, 1456.
- 11. Iwasaki, S. (1984). IEEE Trans. Magn., 20, 657.
- 12. Judy, J. H. (2004). J. Magn. Magn. Mater., 287, 16.
- 13. Iwasaki, S., Nakamura, Y., Ouchi, K. (1979). *IEEE Trans. Magn.*, MAG-61, 1456.

- Laughlin, D. E., Kumar, S., Peng, Y., Roy, A. G. (2005). *IEEE Trans. Magn.*, 41, 719.
- 15. Ohring, M. (1992). The Materials Science of Thin Films, Academic Press.
- 16. Cho A. Y., Arthur, J. R. (1975). *Progress in Solid State Chemistry* (Somorjai, G., McCaldin, J., eds.), Pergamon, New York.
- 17. Terris, B. D., Thomson, T. (2005). J. Phys. D: Appl. Phys., 38, R199.
- Rottmayer, R. E., Batra, S., Buechel, D., Challener, W. A., Hohlfeld, J., Kubota, Y., Li, L., Lu, B., Mihalcea, C., Mountfield, K., Pelhos, K., Peng, C., Rausch, T., Seigler, M. A., Weller, D., Yang, X. (2006). *IEEE Trans. Magn.*, 42, 2417.
- Wood, R., Williams, M., Kavcic, A., Miles, J. (2009). *IEEE Trans. Magn.*, 45, 917.
- Chan, K. S., Miles, J. J., Hwang, E., VijayaKumar, B. V. K., Zhu, J. G., Lin, W. C., Negi, R. (2009). *IEEE Trans. Magn.*, 45(10), 3837–3843.
- Chan, K. S., Radhakrishnan, R., Eason, K., Elidrissi, M. R., Miles, J. J., Vasic, B., Krishnan, A. R. (2010). *IEEE Trans. Magn.*, 46(3), 804–811.
- 22. Ivanov, O. A., Solina, L. V., Demshina, V. A., Magat, M. (1973). *Fiz. Metal. Metalloved.*, **35**, 92.
- Farrow, R. F. C., Weller, D., Marks, R. F., Toney, M. F., Hom, S., Harp, G. R., Cebollada, A. (1996). *Appl. Phys. Lett.*, 69, 1166.
- 24. Watanabe, M., Homma, M. (1996). Jpn. J. Appl. Phys., 35, L1264.
- 25. Okamoto, H. (2000). *Phase Diagram of Binary Alloys*, p. 371, ASM International, Cleveland, USA.
- Warren, B. E. (1990). X-Ray Diffraction, p. 210, Dover Publications, New York.
- Ristau, R. A., Barmak, K., Lewis, L. H., Coffey, K. R., Howard, J. K. (1999). J. Appl. Phys., 86, 4527–4533.
- Hsiao, S. N., Yuan, F. T., Chang, H. W., Huang, H. W., Chen, S. K., Lee, H. Y. (2009). Appl. Phys. Lett., 94, 232505.
- 29. Kneller, E. F., Hawing, R. (1991). IEEE Trans. Magn., 27, 3588.
- 30. Schrefl, T., Fidler, J. (1999). J. Magn. Magn. Mater., 138, 15.
- 31. Dobin, A. Y., Richter, H. J. (2006). Appl. Phys. Lett., 89, 062512.
- Ma, B., Wang, H., Zhao, H. B., Sun, C. J., Acharya, R., Wang, J. P. (2010). *IEEE Trans. Magn.*, 46(6), 2345.
- Giannopoulos, G., Speliotis, Th., Li, W. F., Hadjipanayis, G., Niarchos, D. (2013). J. Magn. Magn. Mater., 325, 75–81.
- 34. Suess, D. (2006). Appl. Phys. Lett., 89, 113105.

- 35. Goncharov, A., Schrefl, T., Hrkac, G., Dean, J., Bance, S., Suess, D., Ertl, O., Dorfbauer, F., Fidler, J. (2007). *Appl. Phys. Lett.*, **91**, 222502.
- Skomski, R., George, T. A., Sellmyer, D. J. (2008). J. Appl. Phys., 103, 07F531.
- 37. Hu, J. F., Chen, J. S., Ding, Y. F., Lim, B. C., Lwin, P. W., Liu, B. (2008). *IEEE Trans. Magn.*, **44**, 3547.
- 38. Zhou, T. J., Lim, B. C., Liu, B. (2009). Appl. Phys. Lett., 94, 152505.
- Takahashi, Y. K., Hono, K., Okamoto, S., Kitakami, O. (2006). J. Appl. Phys., 100, 074305.
- 40. George, T. A., Yu, Y., Yue, L., Skomski, R., Sellmyer, D. J. (2010). *IEEE Trans. Magn.*, **46**, 2435.
- 41. Shima, T., Takanashi, K., Takahashi, Y. K., Hono, K. (2002). *Appl. Phys. Lett.*, **81**, 1050.
- 42. Lee, J., Alexandrakis, V., Fuger, M., Dymerska, B., Suess, D., Niarchos, D., Fidler, J. (2011). *Appl. Phys. Lett.*, **98**, 222501.
- 43. Alexandrakis, V., Speliotis, T., Manios, E., Niarchos, D., Fidler, J., Lee, J., Varvaro, G. (2011). *J. Appl. Phys.*, **109**(7), 07B729-07B729-3.

Chapter 7

Fabrication of Patterned Nanoparticle Assemblies via Lithography

Gang Chen

National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Yutian Rd. 500, Shanghai 200083, China gchen@mail.sitp.ac.cn

7.1 Introduction

The size and composition of nanoparticles (NPs) allow tailoring of their electronic [1], optical [2, 3], or magnetic [4–6] properties arising from their finite size and high surface-area-to-volume ratio. Therefore NPs have attracted a lot of interest owing to their potential in diverse fields ranging, for example, from biomedical [7, 8], plasmonic [9], and photonic [10, 11] applications to nanoelectromagnetic devices [12].

Data storage devices [13–19], spin transport devices [20], labon-a-chip concepts [21–23], medical drug delivery [24–26], and magnetic resonance imaging (MRI) [27, 28] are among the most promising applications for magnetic NPs. Single-ferromagnetic-NP-based magnetic media are promoted as a candidate to replace

228 Fabrication of Patterned Nanoparticle Assemblies via Lithography

conventional storage media due to their small dimensions and singledomain magnetism. Meanwhile, due to their low toxicity, magnetic NPs have exhibited great suitability in biomedical applications, such as DNA incubation, molecular detection, cell separation, etc. Toward these aims, significant progress has been made in the synthesis of magnetic NPs with well-defined compositions, shapes, structures, and sizes [29, 30]. Nevertheless, one major challenge remains, namely, to produce assemblies of magnetic NPs with well-controlled positioning, geometry, and organization. Proper techniques have to be developed to achieve separate identification and addressability for magnetic NP singles or blocks that will enable a much more comprehensive study on the shape and size dependence of their magnetic properties as well as the magnetic interaction between magnetic NPs at a desired interparticle distance and organization. Moreover, from an applications point of view, the continuous miniaturization of magnetic NP-based structures on surfaces has advantages in the development of magnetic devices with higher storage densities and faster speeds and the fabrication of new types of magnetoelectronic devices [31, 32].

The accurate positioning of a few, or even single, NPs (not only limited to magnetic NPs) at well-defined sites of a patterned template is thus a precondition for further advances in both basic research and potential application. Throughout the last decade a wide range of positioning methods has been investigated [33-36] involving, for example, magnetic or electrostatic forces [37], sedimentation [38], layer-by-layer growth [39], lithography [40, 41], and selective wetting [42]. Although these early attempts were successful to some extent, the preparation of large-area ordered assemblies of single NPs with low defect density and a size down to or less than 20 nm still presents problems. Other methods taking advantage of selective adhesive host-guest interactions have been also reported [43-45], but they cannot be regarded as generally applicable solutions since they are only effective for a specific type of NPs and substrate materials. The real breakthrough occurs only after the introduction of various lithography-based micro- and nanofabrication techniques, by which scientists started to organize NPs into ordered structures at the nanometer scale. Since then, the number of methodologies and approaches followed has been continuously increasing. To date, many challenges have been overcome, including accurately placing a few or even a single NP on the desired region of a given surface via lithography techniques. Thus this chapter is presented as a comprehensive and detailed description of the methodologies employed for assembling NPs into ordered nanostructures. And the recent progress in the characterization of the magnetic information of single magnetic NPs has also been introduced in the last section of the chapter.

7.2 Fabrication Techniques

In general, two main strategies have been developed to utilize the lithography technique to obtain patterned NP assemblies. One is to achieve the organization of magnetic NP blocks in a desired pattern via the direct patterning technique, such as microcontact printing (μ CP) [46. 47], and scanning probe-based lithographies (SPLs) [48–51]. The other successful strategy is to organize a magnetic NP block or single NP onto patterned templates via mechanisms of capillary forces [52–58], convective flow [56, 59–61], and mechanic polishing [12, 62], which is prepared by standard lithographic techniques, for example, optical lithography, electron beam lithography.

7.2.1 Direct Patterning Assembly

Direct patterning assembly techniques, especially SPLs, were usually dedicated to medical and biological research, which is aiming at the functional and structural study of biomolecular interactions and the fabrication of nanobiosensors and biocompatible materials. A variety of SPLs have been developed to locate nanoscale biomolecules and colloidal NPs. Among them, dip-pen nanolithography (DPN) [50, 63], is the most successful one. The main strategy is to use the tip of an atomic force microscope (AFM) cantilever as a "pen," which is coated with a chemical compound or mixture acting as an "ink" and put in contact with a substrate, the "paper." Thus the mechanism of the DPN technique is the diffusion of the molecular ink from a nanoscale tip to a surface through a water meniscus. In the last decade, DPN has emerged as a particularly attractive tool since it allows the direct transfer of biomolecules onto surfaces with a high registration and

resolution, while preserving their biological activity. Bellido et al. recently reported control of the number of ferritin protein NPs by adjusting the protein concentration used to coat the AFM tip and the dimensions of the dot-like features fabricated by DPN. The schematic illusion is shown in Fig. 7.1 [50].



Figure 7.1 (a) Schematic illustration of ferritin patterning onto the surface of a TEM grid. (b) TEM images of a ferritin nanoarray $(20 \times 20 \ \mu\text{m}, 150 \ \text{nm}$ diameter dots) generated by direct-write DPN on a TEM grid. Scale bars: 2 mm, 500 nm, and 100 nm for the different magnifications. Reproduced with permission from Ref. [50]. *Abbreviation*: TEM, transmission electron microscope.

Meanwhile Chai et al. reported a unique approach, termed "scanning probe block copolymer lithography (SPBCL)," that enables one to control individual NP growth and position in situ by using DPN to pattern tiny volumes of metal ions associated with block copolymers in a massively parallel manner over large areas. Reduction of the metal ions via plasma results in the high-yield formation of single-crystal NPs per block copolymer feature. They also demonstrated that pattern dimensions and metal ion concentration dictate the size of each NP, whose diameter can be controlled with remarkable precision down to 4.8 ± 0.2 nm [63]. The schematic of the technique has been shown in Fig. 7.2a,b. The high quality of the assembly has been proved via AFM, scanning electron microscope (SEM), and TEM images in Fig. 7.2c–f.

7.2.2 Fabrication of NP Assemblies on Patterned Templates

Although SPL techniques are quite successful to prepare highly ordered NP arrays, as shown in the last section, involving the scan probe techniques leads to low efficiency and high cost. Thus further efforts have been dedicated to an alternative approach, that is, fabrication of NP assemblies on patterned templates, which is developed aiming at wafer-scale mass production of NP assemblies with high accuracy.

The patterned templates are solid surfaces with appropriate relief structures, which could trap the segregated NPs into desired assemblies via dewetting or mechanical polishing. The geometric properties of patterning are used to confine the numbers, sizes, and shapes of the NP assemblies. This facile method is ideal for reproducibly fabricating large-scale device arrays with high throughput and low cost. This approach integrates the merits of bottom-up solution-processed nanostructures with top-down lithographically prepared devices. Thus it has the potential to be scaled up to wafer size for a large number of functional nanoelectronics, nanospintronics, and nanophotonics applications.

One of the pioneering works on this method was published by Gleiche et al. in 2000, in which nanoscopic channel lattices with controlled anisotropic wetting were proposed for the first time [52]. Nevertheless the capability and feasibility of this approach were fully



Figure 7.2 Tip-based synthesis of single Au NPs. (A) Structure and molecular weight of the PEO-b-P2VP used in this study. (B) The block copolymer phase separated in aqueous solution to form P2VP cores (blue) surrounded by PEO coronas (red). When HAuCl4 is added to the solution, the protonated P2VP cores become associated with AuCl₄ ions. The hybrid ink is dip-coated onto an AFM tip and patterned on a Si substrate. The Au precursor within the block copolymer micelles is then reduced, and the polymer removed, with plasma treatment. (C) AFM topographical image of a square dot array of PEOb-P2VP/AuCl4 ink on a Si/SiO_x surface patterned by DPN. (D) Height profile of one line of PEO-b-P2VP/AuCl4 dots, demonstrating uniformity of feature size. (E) SEM image of sub-10 nm Au NPs produced by plasma treatment. (Inset) Fourier transform of the SEM image. (F) High-resolution TEM image showing crystalline Au NPs with a diameter of 8 nm. The measured interplanar spacing of the crystal is 0.24 nm. (Inset) Typical electron diffraction pattern of the synthesized Au (111) NPs. Reproduced with permission from Ref. [63]. Copyright 2010, National Academy of Sciences of the United States of America.

exhibited by Yin et al. [53]. Figure 7.3 shows SEM images of typical examples of polygonal aggregates that were formed by templating polystyrene (PS) beads against 2D arrays of cylindrical holes [53]. The structures were fabricated by near-field optic lithography. Although the sizes of the patterned structures and PS beads are still in the microscopic range, the ordering and controllability in the spatial organization and orientation for the PS beads are very impressive, as shown in Fig. 7.4.



Figure 7.3 SEM images of some typical examples of polygonal aggregates that were formed by templating PS beads against 2D arrays of cylindrical holes. The photoresist pattern was still on the substrate. Panels (A–D) correspond to the beads with diameters ranging from 1 μm to 0.9 μm, 0.8 μm, and 0.7 μm. Reproduced with permission from Ref. [53]. Copyright 2001, American Chemical Society.

The mechanism of this method was clarified by Cui et al. in their later work [54]. The interfacial capillary force present during the dewetting/evaporation of an NP suspension forms the basis of the assembly mechanism. Moreover their results demonstrate macromolecule-size particles down to the sub-50 nm diameter range. And complex nanostructures such as nanotetrapods can also be effectively organized by the capillary interaction [54].



Figure 7.4 SEM images of 2D arrays of colloidal aggregates that were assembled under the confinement of templates other than cylindrical holes. Reproduced with permission from Ref. [53]. Copyright 2001, American Chemical Society.

Figure 7.5 is the scheme of the capillary force–induced assembly. Flat substrates are patterned with hole and trench templates using electron beam lithography and subsequently inserted vertically into a solution containing nanostructures (Fig. 7.5 inset).



Figure 7.5 Schematic illustrating the capillary force (F_c) assembly mechanism at the vapor–suspension–substrate three-phase contact line. (Inset) Movement of the three-phase contact line is driven by evaporation in in-house vacuum or by heating of the solution to ~60°C. Reproduced with permission from Ref. [54]. Copyright 2004, American Chemical Society.

Evaporation of the solvent leads to the three-phase contact line moving slowly across the substrate. When the solution film thickness on the substrate is less than the height of the nanostructure, the solution–vapor interface deforms and the resulting capillary force slides the nanostructure toward the thicker part of the solution and pushes the particle toward the substrate. The net result is that particles are selectively forced into the lithographically defined features as the evaporation zone passes over them, but no particles are deposited on the surrounding areas. The contact angle is a critical parameter to getting good assembly of sub–50 nm diameter particles because it determines the direction of the capillary force and thus the strength of parallel and perpendicular components. Figure 7.6 shows SEM images of Au NP assemblies in different geometric configurations with diameters of 8 nm and 2 nm [54].

Further progress was made by Malaquin et al. [58]. In their work, another mechanism, that is, the convective flow of NPs, induced by the evaporation of the solvent at the three-phase contact line of a solution, was revealed to be the key force to create sparse arrays and complex 3D structures on patterned hydrophilic substrates, just like what capillary force performs on patterned hydrophobic substrates, as shown in Fig. 7.7.



Figure 7.6 (A–C) SEM images of 8 nm diameter Au NPs in trenches and holes. The substrates are SiO_x . The depth of the trenches is ~10 nm. (D and E) SEM images of 2 nm diameter Au NPs in trenches and holes. The substrates are polymer resist. The depth of the templates is ~60 nm. The solution interface-moving direction in all images is from bottom to top in all cases. Scale bars: (A) 1 µm, inset 50 nm, (B and C) 30 nm, (D) 2 µm, (E and F) 200 nm, (E) inset 50 nm, (F) inset 1 µm. Reproduced with permission from Ref. [54]. Copyright 2004, American Chemical Society.

In both methods, the hydrodynamic drag exerted on the particles in the suspension plays a key role in the assembly process. They also demonstrate for that the temperature, the NPs' flow velocity, the substrate velocity, wetting properties, and the pattern geometry are also important parameters to influence assembly efficiency.



Figure 7.7 Various assembly mechanisms based on particle confinement at the contact line of a droplet can be distinguished depending on the wetting properties and topographical patterning of the substrate. Convective assembly is obtained on wetting substrates for contact angle values below 20°. The assembly mechanism is driven by the convective flow of the solvent, induced by evaporation at the contact line of the droplet. Reproduced with permission from Ref. [58]. Copyright 2007, American Chemical Society.

A recent improvement on the capillary force technique is the introduction of fixed glass slides above the suspension droplet, as reported by Fan et al. [64], as well as by Kuemin et al. [65], which further increases efficiency of the capillary assembly, as shown in Fig. 7.8. The substrate speed, temperature, and droplet–substrate contact angle are controlled to optimize the clustering process.

By this method, they assembled plasmonic NPs into desired nanostructures on patterned elastomeric substrates and measured the optical properties of three cluster types: Fano-resonant

238 Fabrication of Patterned Nanoparticle Assemblies via Lithography

heptamers, linear chains, and rings of NPs. And the authors believe the success of this method paves the way for new classes of plasmonic nanocircuits (as shown in Fig. 7.9). It should also be noted that the elastomeric templates used in this work were patterned by a molding process, which follows a similar strategy as the nanoimprinting technique, as shown in Fig. 7.10. This method makes patterning transfer onto elastomeric substrates much more convenient.



Figure 7.8 Schematic of an improved capillary assembly. NPs are packed into patterned template voids by sandwiching a water droplet with particles between the substrate and a glass slide and then moving the droplet meniscus across the substrate. During this process, particles are pushed into the voids via capillary forces (inset). Reproduced with permission from Ref. [64]. Copyright 2012, American Chemical Society.


Figure 7.9 Images and spectra of linear chains of NPs. The chains are assembled by using substrate voids with different aspect ratios. As the number of particles in the chain increases, the electric dipole resonance peak experiences a red shift due to enhanced capacitive coupling between the NPs in the cluster and to retardation effects. The theoretical spectra of these NPs chains show the same red-shifting behavior. Reproduced with permission from Ref. [64]. Copyright 2012, American Chemical Society.

Recently this method has been accepted by many other groups [66]. Meanwhile Holzner et al. reported a novel method to prepare patterned templates via the thermal scanning lithography technique, as shown in Fig. 7.11 [67]. In the first step, a PPA polymer film is patterned by a scanning tip with an accurately controlled temperature. After capillary assembly, the polymer film is then

thermally decomposed and the assembled nanorods transferred onto the target substrate, preserving both position and orientation [67].



Figure 7.10 Schematic of template patterning with a molding process. Reproduced with permission from Ref. [64]. Copyright 2012, American Chemical Society.



Figure 7.11 Schematics of thermal scanning lithography. Reproduced with permission from Ref. [67]. Copyright 2011, American Chemical Society.

Besides the above capillary force assembly method, recently electrophoretic effects have been proposed for NP assembly by Siavoshi et al. [68], which provide an alternative single-particle resolution for a simple, fast, and reproducible directed assembly technique. In their work, NPs are size-selectively assembled into prefabricated via arrays using a sequential template-directed electrophoretic assembly method. Polystyrene latex (PSL) NPs with diameters ranging from 200 nm to 50 nm are selectively assembled into vias comparable to the NP diameter. The schematic of the method has been shown in Fig. 7.12.



Figure 7.12 (a) SEM micrograph shows a patterned substrate with assembled 200 nm particles. (b) Schematic diagram of the electrophoretic assembly setup being removed from the particle suspension. (c) Schematic diagram of the cross section of the patterned template, showing various forces acting on the assembled NP during the insertion and removal of the template into the NP suspension. Reproduced with permission from Ref. [68]. Copyright 2011, American Chemical Society.

All the above methods are suspension-based "wet" approaches, in which the hydrodynamic drag, that is, the capillary force and convective flow induced during evaporation of the suspension, exerted on particles in the suspension plays a key role in the assembly process. Thus the quality of structures prepared by using these methods inevitably depends upon flow speed, contact angle, temperature, density, etc.

On the contrary, Chen et al. reported a straightforward "dry" approach [62] for large-scale nanofabrication with high accuracy, following the same strategy as the well-established Damascene process in integrated circuit manufacturing [69]. In the latter, metal interconnects are produced by depositing a thin Cu film on prepatterned Si wafers, and constriction of the Cu film to connecting

242 Fabrication of Patterned Nanoparticle Assemblies via Lithography

lines is achieved via chemical-mechanical back polishing. In Chen et al.'s work [62], the basic idea of this technique is utilized for controlled positioning of NPs by means of deposition on a prepatterned template and subsequent NP removal by polishing, which is practically independent of temperature and suspension conditions. Mechanical polishing generally refers to the use of clothcovered plates and suitable polishing abrasives. Thus the van der Waals force exerted on the NPs is the main mechanism behind the processing method. Moreover the absence of suspensions or any other solvent during the final processing step is an advantage with respect to environment-friendly production.

To demonstrate the feasibility and potential of this technique, assemblies of ordered NPs with a size down to 18 nm were prepared. Si (001) wafers were chosen as substrates. Patterning was achieved by two methods, either electron beam lithography or direct structuring via a charged-particle nanopatterning technique [70]. A schematic illustration of the process can be seen in Fig. 7.13. After natural drying/evaporation of the dispersant, the NPs are closely packed on the whole surface of the template, as indicated in Fig. 7.13B. The corresponding SEM image is shown in Fig. 7.14A. After the mechanical polishing process, the NPs are either swept into the pits or wiped off the surface of the wafers, trapped in the polishing cloth, as shown in Fig. 7.14b. This mechanism also works for a much larger area, for example, 10×10 mm, as shown in Fig. 7.14c, in which the pit diameter has been reduced to 110 nm. Again the flat part is free of NPs, and the pits have been filled with a few NPs. as indicated by the inset.

With decreasing diameter and depth of the pits the number of NPs per pit decreases and more regular arrangements of the NPs are obtained, as indicated in Fig. 7.15. In Fig. 7.15c, single occupation of the pit with a diameter of 25 nm has been achieved. These results show the main challenge of the patterned assembly of NPs has been well addressed and solved.

As introduced in the beginning of the chapter, one of the main motivations for patterned magnetic NP assembly is its potential applications in data storage devices [8, 13–19], in which case the readout of the magnetization of the magnetic NP blocks and singles becomes the basic function of the devices. Thus Chen et al.'s work also demonstrates this capability with magnetic force microscopy



Figure 7.13 Schematic illustration of the whole Damascene process. (A) A solution with NPs is adsorbed onto the patterned template; (B) after drying, layers of closely packed NPs partially cover the surface of the patterned template; (C) the sample with NPs is polished against a cloth-covered plate; and (D) finally, a regular assembly of NPs on the patterned template is achieved. Reproduced with permission from Ref. [62].



Figure 7.14 SEM images for a specimen with a 250 nm pit diameter coated with FeO/CoFe₂O₄.NPs of ~18 nm size before (a) and after (b) mechanical polishing. (c) Large-area SEM image (10×10 mm) of a sample with a 110 nm pit diameter, showing that the NPs have been removed from the flat surface of the sample and the pits have been filled with NPs. Reproduced with permission from Ref. [62].



Figure 7.15 (a-c) SEM images showing the evolution of the number of NCs in a single pit when the pit diameter is reduced from 90 nm to 25 nm. (d) When the diameter of the pit is smaller than the diameter of the FeO/CoFe₂O₄ NPs, no NPs remain at the surface after polishing (except for one that is located at a pattern defect). (e and f) Control of the NC arrangement by using square-shaped pits. Reproduced with permission from Ref. [62]. *Abbreviation*: NC, nanocrystal.

(MFM). The external magnetic field was applied perpendicular to the substrate surface. Figures 7.16a and 7.16b show SEM and AFM images, respectively, of a sample with a pit size of 200 nm, filled with ferrimagnetic Fe₃O₄ NPs. And Figs. 7.16c and 7.16d are the respective MFM images obtained with the external magnetic field exerted and removed. The results clearly demonstrate that the ferrimagnetic moment of Fe₃O₄ NPs can be well detected by MFM.

Furthermore, pit arrays with single-NP occupation were also investigated. SEM and MFM images for an area with nine pits, five of which are occupied by a single NP, while four are left empty, have been recorded and shown in Fig. 7.16e,f. The MFM image in Fig. 7.16f, taken again with an external applied field, clearly exhibits magnetic contrast for each occupied pit and no signal from the empty pits; thus, single Fe₃O₄ NPs can be detected by MFM. The resolution of the MFM images, characterized by the full width at half maximum of the peak in the line profile of the MFM image in Fig. 7.16g, arising from a single NP, is around 80 nm. Therefore the resolution of MFM would allow reduction of the pitch of the structure to 100 nm, enabling us to read data from a storage device with a density of more than 60 Gbit/in². As a final result the authors also demonstrated that their technique for NP positioning works not only for single pits but also for more complex groove structures. For example, the letters "J K U" are written by FeO/CoFe₂O₄ core/shell NPs, making use of this kind of Damascene process (Fig. 7.16h,i).

7.3 Summary and Perspective

In this chapter, we present a detailed description of the lithographybased NP assembly approaches developed over the last decades. For this, two main strategies have been considered, (1) direct patterning assembly and (2) assembly with patterned templates. The first one is developed on the basis of the scanning probe lithography technique, which has achieved very high accuracy. Nevertheless, it is expensive and lacks efficiency. Thus mostly it is used for biomedical applications. On the contrary, the second strategy was aiming at mass production with high throughput and low cost since the very beginning. This approach could be further divided into "wet" and "dry" methods. The mechanism behind the "wet" one is to fabricate the NP assembly



Figure 7.16 (a) SEM and (b) AFM images of a set of nine pits filled with Fe_3O_4 NPs 50 nm in diameter. (c) MFM images measured under an external out-of-plane magnetic field. The tip is magnetized in the same orientation, and the cantilever lift height is 25 nm. (d) MFM image measured in a zero external field, while the tip is magnetized in opposite orientation as the NPs and the cantilever lift height is 25 nm. (e) SEM and (f) MFM images for a set of pits occupied by single Fe_3O4 NPs. The MFM image was obtained under an external magnetic field. (g) Profile extracted from the MFM image in (f). (h) SEM and (i) MFM for a set of grooves patterned into characters of "J K U" and filled by $FeO/CoFe_2O_4$ NCs with a 18 nm diameter under an external magnetic field. [62].

by exerting hydrodynamic drags, that is. capillary force or convective flow, on NPs in the suspension. The quality of structures prepared by using these methods inevitably depends upon flow speed, contact angle, temperature, density, etc. On the other hand, the "dry" one is to use the van der Waals force to drive the NPs into the patterned pits and grooves. Thus the operation conditions are even simplified. Both "wet" and "dry" approaches are quite successful indeed. And patterned single-NP arrays have also been obtained in the past couple of years. Taking advantage of the progress in patterned assembly, the readout function from assembled magnetic NP blocks and singles via MFM has also been achieved. Thus more extensive application of these methods in nanomagnetism research is well expected, for example, the interaction amongst NPs can be studied, either by adjusting the number of NPs per pit and their geometrical arrangement or by adjusting the period in arrays with single-NP occupation. With further improvement of stability, reproducibility, and controllability, the potential for wafer-scale mass production could also be realized.

References

- Burda, C., Chen, X., Narayanan, R., El-Sayed, M. A. (2005). *Chem. Rev.*, 105(4), 1025–1102.
- 2. Alivisatos, A. P. (1996). Science, 271, 933-937.
- Murray, C. B., Kagan, C. R., Bawendi, M. G. (2000). *Annu. Rev. Mater. Sci.*, 30, 545–610.
- 4. Sun, S., Murray, C. B. (1999). J. Appl. Phys., 85, 4325-4330.
- Hyeon, T., Chung Y., Park, J., Lee, S. S., Kim, Y.-W., Park B. H. (2002). J. Phys. Chem. B, 106, 6831–6833.
- 6. Hyeon, T. (2003). Chem. Commun., 8, 927-934.
- 7. Alivisatos, A. P. (2004). Nat. Biotechnol., 22, 47.
- Seo, W. S., Lee, J. H., Sun, X., Suzuki, Y., Mann, D., Liu, Z., Terashima, M. P., Yang, C., McConnell, M. V., Nishimura, D. G., Dai, H. (2006). *Nat. Mater.*, 5, 971.
- 9. Wei, Q. H., Su, K. H., Durant, S., Zhang, X. (2004). Nano Lett., 4, 1067.
- 10. Lopez, C. (2003). Adv. Mater., 15, 1679.
- 11. Vlasov, Y. A., Bo, X. Z., Sturm, J. C., Norris, D. J. (2001). Nature, 414, 289.

- Yarema, M., Pichler, S., Kriegner, D., Stangl, J., Yarema, O., Kirchschlager, R., Tollabimazraehno, S., Humer, M., Haringer, D., Kohl, M., Chen, G., Heiss, W. (2012). ACS Nano, 6(5), 4113–4121.
- 13. Hayashi, T., Hirono, S., Tomita, M., Umemura, S. (1996). *Nature*, **381**, 772.
- 14. Speliotis, D. E. (1999). J. Magn. Magn. Mater., 193, 29-35.
- Sun, S., Murray, C. B., Weller, D., Folks, and L., Moser, A. (2000). *Science*, 287, 1989–1992.
- 16. Ross, C. A. (2001). Annu. Rev. Mater. Res., 31, 203-235.
- 17. Sun, S., Murray, C. B., Weller, D., Folks, L., Moser, A. (2000). *Science*, **287**, 1989.
- 18. Reiss, G., Huetten, A. (2005). Nat. Mater., 4, 725.
- 19. Sun, S. H. (2006). Adv. Mater., 18(4), 393.
- 20. Chappert, C., Fert, A., Van Dau, F. N. (2007). Nat. Mater., 6, 813-823.
- 21. Craighead, H. (2006). Nature, 442, 387.
- 22. Dekker, C. (2007). Nat. Nanotechnol., 2, 209.
- 23. Lee, H., Yoon, T. J., Weissleder, R. (2009). *Angew. Chem., Int. Ed.*, **48**, 5657.
- 24. Gupta, P. K., Hung, C. T., Lam, F. C., Perrier, D. G. (1988). *Int. J. Pharm.*, **43**, 167–177.
- 25. Torchilin, V. P. (2000). Eur. J. Pharm. Sci., 11, S81-S91.
- Song, H. T., Choi, J. S., Huh, Y. M., Kim, S., Jun, Y. W., Suh, J. S., Cheon, J. (2005). J. Am. Chem. Soc., 127, 9992–9993.
- 27. Bonnemain, B. (1998). J. Drug Target, 6, 167-174.
- Tromsdorf, U. I., Bigall, N. C., Kaul, M. G., Bruns, O. T., Nikolic, M. S., Mollwitz, B., Sperling, R. A., Reimer, R., Hohenberg, H., Parak, W. J., Förster, S., Beisiegel, U., Adam, G., Weller, H. (2007). *Nano Lett.*, 7, 2422–2427.
- Tan, R. P., Carrey, J., Desvaux, C., Grisolia, J., Renaud, P., Chaudret, B., Respaud, M. (2007). *Phys. Rev. Lett.*, **99**, 176805.
- Hofmann, C., Rusakova, I., Ould-Ely, T., Prieto-Centurion, D., Hartman, K. B., Kelly, A. T., Luettge, A., Whitmire, K. H. (2008). *Adv. Funct. Mater.*, 18, 1661.
- 31. Cowburn, R. P., Welland, M. E. (2000). Science, 287, 1466–1468.
- Zeng, H., Black, C. T., Sandstrom, R. L., Rice, P. M., Murray, C. B., Sun, S. (2006). *Phys. Rev. B*, **73**, 020402.
- 33. Xia, Y., Gates, B., Yin, Y., Lu, Y. (2000). Adv. Mater., 12, 693.

- Norris, D. J., Arlinghaus, E. G., Meng, L., Heiny, R., Scriven, L. E. (2004). *Adv. Mater.*, 16, 1393.
- 35. Roldughin, V. I. (2004). Russ. Chem. Rev., 73, 115.
- 36. Dziomkina, N. V., Vancso, G. J. (2005). Soft Matter, 1, 265.
- 37. Bailey, R. C., Stevenson, K. J., Hupp, J. T. (2000). Adv. Mater., 12, 1930.
- 38. van Blaaderen, A., Ruel, R., Wiltzius, P. (1997). Nature, 385, 321.
- 39. Velikov, K. P., Christova, C. G. (2000). Science, 296, 106.
- 40. Xia, D., Brueck, S. R. J. (2004). Nano Lett., 4, 1295.
- 41. Xia, D., Biswas, A., Li, D., Brueck, S. R. J. (2004). Adv. Mater., 16, 1427.
- 42. Suh, K. Y., Khademhosseini, A., Eng, G., Langer, R. (2004). *Langmuir*, **20**, 6080.
- Mahalingam, V., Onclin, S., Peter, M., Ravoo, B. J., Huskens, J., Reinhoudt, D. N. (2004). *Langmuir*, 20, 11756.
- Ling, X., Zhu, X., Zhang, J., Zhu, T., Liu, M., L. Tong, and Z. F. Liu (2005). *J. Phys. Chem. B*, **109**, 2657.
- 45. Ruan, W. D., Wang, C. X., Wang, N. J., Lu, Z. C., Zhou, T. L., Zhao, B., Lombardi, J. R. (2008). *Langmuir*, **24**, 8417.
- Palacin, S., Hidber, P. C., Bourgoin, J. P., Miramond, C., Fermon, C., Whitesides, G. M. (1996). *Chem. Mater.*, 8, 1316–1325.
- 47. An, L., Li, W., Nie, Y., Xie, B., Li, Z., Zhang, J., Yang, B., J. (2005). *Colloid Interface Sci.*, **288**, 503–507.
- 48. Liu, X., Fu, L., Hong, S., Dravid, V. P., Mirkin, C. A. (2002). *Adv. Mater.*, **14**, 231–234.
- 49. Wang, Y., Wei, W., Maspoch, D., Wu, J., Dravid, V. P., Mirkin, C. A. (2008). *Nano Lett.*, **8**, 3761–3765.
- 50. Bellido, E., de Miguel, R., Ruiz-Molina, D., Lostao, A., Maspoch, D. (2010). *Adv. Mater.*, **22**, 352–355.
- Martínez, R. V., Martínez, J., Chiesa, M., Garcia, R., Coronado, E., Pinilla-Cienfuegos, E., Tatay, S. (2010). *Adv. Mater.*, 22, 588–591.
- 52. Gleiche, M., Chi, L. F., Fuchs, H. (2000). Nature, 403, 173.
- 53. Yin, Y. D., Lu, Y., Xia, B. (2001). J. Am. Chem. Soc., 123, 8718.
- 54. Cui, Y., Bjoerk, M. T., Liddle, A., Soennichsen, C., Boussert, B., Alivisatos, A. P. (2004). *Nano Lett.*, **4**, 1093.
- 55. Hoogenboom, J. P., Retif, C., de Bres, E., van de Boer, M., Van Langen-Suurling, A. K., Romijn, J., van Blaaderen, A. (2004). *Nano Lett.*, **4**, 205.
- Juillerat, F., Solak, H. H., Bowen, P., Hofmann, H. (2005). *Nanotechnology*, 16, 1311.

- Cheng, J. Y., Zhang, F., Chuang, V. P., Mayes, A. M., Ross, C. A. (2006). Nano Lett., 6, 2099.
- 58. Malaquin, L., Kraus, T., Schmid, H., Delamarche, E., Wolf, H. (2007). *Langmuir*, **23**, 11513.
- 59. Denkov, N. D., Velev, O. D., Kralchevsky, P. A., Ivanov, I. B., Yoshimura, H., Nagayama, K (1992). *Langmuir*, **8**, 3183.
- Denkov, N. D., Velev, O. D., Kralchevsky, P. A., Ivanov, I. B., Yoshimura, H., Nagayama, K. (1993). *Nature*, **361**, 26.
- 61. Prevo, B. G., Hwang, Y., Velev, O. D. (2005). Chem. Mater., 17, 3642.
- Chen, G., Bodnarchuk, M. I., Kovalenko, M. V., Springholz, G., Heiss, W., Jantsch, W., Platzgummer, E., Loeschner, H., Schotter, J. (2010). *Adv. Mater.*, 22, 1364–1368.
- Chai, J. N., Huo, F. W., Zheng, Z. J., Giamb, L. R., Shim, W. Y., Mirkin, C. A. (2010). PNAS, 107(47), 20202–20206.
- 64. Fan, J. A., Bao, K., Sun, L., Bao J., Manoharan, V. N., Nordlander, P., Capasso, F. (2012). *Nano Lett.*, **12**, 5318–5324.
- 65. Kuemin, C., Stutz, R., Spencer, N. D., Wolf, H. (2011). *Langmuir*, **27**, 6305–6310.
- He, Q., Severac, F., Hajjoul, H., Viero, Y., Bancaud, A. (2011). *Langmuir*, 27, 6598–6605.
- Holzner, F., Kuemin, C., Paul, P., Hedrick, J. L., Wolf, H., Spencer, N. D., Duerig, U., Knoll, A. W. (2011). *Nano Lett.*, **11**, 3957–3962.
- Siavoshi, S., Yilmaz, C., Somu, S., Musacchio, T., Upponi, J. R., Torchilin, V. P., Busnaina, A. (2011). *Langmuir*, 27, 7301–7306.
- 69. Cui, Z. (2008). *Nanofabrication: Principles, Capabilities and Limits*, p. 229, Springer, New York.
- Platzgummer, E., Loeschner, H. (2009). J. Vac. Sci. Techno. B, 27(6), 2707–2710.

Chapter 8

Magnetic Behavior of Composite Nanoparticle Assemblies

Marianna Vasilakaki, George Margaris, and Kalliopi N. Trohidou

Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, Department of Materials Science, National Centre for Scientific Research "Demokritos," 153 10 Aghia Paraskevi, Attiki, Greece trohidou@ims.demokritos.gr

8.1 Introduction

Magnetic nanoparticles with diameters in the range of a few nanometers are today at the cutting edge of modern technology and innovation due to their use in numerous applications ranging from engineering (magnetic recording media or magnetic seals [1], magnetic refrigerants [2], magnetic random access memory devices, or spin logic devices [3, 4]) to biomedical applications (magnetic resonance imaging, drug delivery, or hyperthermia [5]).

Their magnetic properties that differ from those of bulk materials and make them attractive for technological applications stem from the fact that they consist of a single magnetic domain. This singledomain structure is the outcome of the high energy cost for the formation of a domain wall in their volume, and it occurs as long as their size is smaller than the exchange correlation length. In the single-domain regime, the magnetization process of a nanoparticle is realized by the coherent rotation of the magnetic moment instead of domain wall motion. The magnetization coherent rotation model was introduced and studied theoretically by Stoner and Wohlfarth [6] and provides an indispensable tool for interpretation of lowtemperature hysteresis measurements in dilute samples. At finite temperature, reversal of magnetization is achieved by thermal activation over the single-particle anisotropy barrier that leads to temperature and time dependence of the magnetization. This effect was first analyzed by Néel [7], who expressed the relaxation time for reversal by means of the Arrhenius–Néel law $\tau = f_0 \exp(-\Delta E/$ $k_{\rm B}T$), where ΔE is the anisotropy energy barrier and $f_0 \approx 10^9 \text{ s}^{-1}$ is the attempt frequency. Bean and Livingston [8] assumed further that the criterion for thermal stability of a magnetic nanoparticle against thermal fluctuations is the value of the ratio of the relaxation time to the measuring time (t_m) , which is characteristic of the experimental probe used (Mössbauer, etc). Thermal stability is lost when $\tau = t_m$, which for most experimental probes corresponds to $\tau \approx 100$ seconds and, consequently, to a characteristic temperature $T_{\rm B} \approx 25 (\Delta E/k_{\rm B})$ called blocking temperature. For temperatures $T > T_{\rm B}$, the ensemble of single-domain particles behaves as a gas of paramagnetic molecules with a giant magnetic moment ($m \approx 10^3 \mu_{\rm B}$) and the corresponding equilibrium state is known as superparamagnetism [9]. The conceptual framework composed by the models of Stoner-Wohlfarth and Néel has been an invaluable theoretical tool for the interpretation and prediction of the temporal and thermal evolution of the magnetic properties of isolated nanoparticles or dilute assemblies in association with energy barriers and particle size distribution [10, 11]. Also the model consists of a valid starting point for further multiple modifications to describe more complex phenomena [12-16].

Nowadays, the technological demand for retaining the magnetic behavior of very small particles (a few nanometers) stable at room temperature, namely, an increase in their blocking temperature by overcoming the "superparamagnetic limit" [17], has led to the research of bimagnetic core/shell nanoparticles, whose core and shell consist of a soft and a hard magnetic phase of a ferromagnetic (FM), ferrimagnetic (FiM), antiferromagnetic (AFM), or even spinglass-like structure [18, 19]. The synergetic combination of the properties of these two constituents and their interaction [18, 20] can further improve and tune single-phase properties. There are already promising results that show enhancement of the coercive field, enhanced blocking temperatures, [21], increased energy products, [22] superior microwave absorption [23], or optimized hyperthermia [24]. In addition, recent advances in synthesis of these particles, which allow an unprecedented control of the structural parameters (e.g., size, shape, and composition), give further the possibility to fine-tune the new overcoming functionalities of these two phase systems [25–27].

The origin of the enhanced properties of bimagnetic nanoparticles is considered to be the interface exchange interaction between the two different magnetic phases that gives the so-called exchange bias effect. This effect consists of one of the most fascinating and complex phenomena in nanostructured materials—not only nanoparticles, that include the well-known hysteresis loop shift (H_{ex}) and an increased coercive field (H_c) defined as half the loop width, when the two different materials are in contact and field-cooled (FC) in a static magnetic field (H_{cool}) from a temperature lying between their high and low critical temperatures.

More than 50 years have passed since Meiklejohn and Bean [28] discovered the exchange bias mechanism in Co/CoO nanoparticles, and they have interpreted it as an extra kind of unidirectional anisotropy induced by exchange coupling at the interface between the soft and the hard phase. During these years extensive studies were conducted on this effect of several systems, mainly on layered systems [29, 30]. Various models have been developed to explain exchange anisotropy here, but still there is no definitive theory to account for the observed effects—something that is attributed to the diversity of the studied magnetic nanostructured materials [31]. In the approach introduced by Malozemoff [32] the exchange bias effect does not appear in the perfect FM/AFM interface of a spin valve due to a lack of interface roughness. According to other models exchange anisotropy is attributed to additional mechanisms such as uncompensated spins at the interface of the antiferromagnet [33] or to the motion of magnetic domains that are created in a diluted

256 Magnetic Behavior of Composite Nanoparticle Assemblies

antiferromagnet [34]. Though these models and theories were suited for an explanation of the shifted hysteresis loops in layered systems, the same physical arguments were expected to hold for nanoparticles. Indeed, the fact that the spins of the AFM shell that are coupled to the spins of the FM core are not equally distributed on the FM/AFM interface of the nanoparticle has as a result led to the creation of an imperfect interface, even in the absence of additional roughness [32] or lattice vacancies [34]. Also it has been found [35] that the AFM shell itself induces exchange anisotropy along the interface, which is in turn responsible for the fact that smaller nanoparticles have higher coercive fields than bigger ones at low temperatures. In addition, the vertical shift of hysteresis loops usually observed in FM/AFM core/shell nanoparticles has been attributed to uncompensated spins of the AFM shell [36, 37]. So the explanation of the exchange bias effect in the case of core/ shell nanoparticles bears similarities to the layered systems but still is a different complex matter due to the intrinsic inhomogeneity in main particles' parameters caused by finite-size and surface effects.

Magnetic nanoparticles are commonly formed in assemblies, with either random or ordered structure. In the first group belong systems such as ferrofluids and granular solids (discontinuous metal insulator multilayers, cosputtered metal insulator films, cluster-assembled films) [38, 39], while in the second group belong patterned media (or magnetic dots) [40] and self-assembled arrays [41]. In the assemblies of magnetic nanoparticles the crucial role of interparticle interactions in determining their response to an externally applied field as well as the temperature dependence of magnetic properties has been recognized long ago [42]. In fact, various experiments have demonstrated that the presence of magnetostatic interactions leads to a reduction of remanence at low temperature, an increase of the blocking temperature, an increase of the barrier distribution width, deviations of the zero-field-cooled (ZFC) magnetization curves from Curie behavior, difference between in-plane and out-of-plane remanence, and an increase of the blocking temperature with frequency of the applied field.

Experiments have revealed the importance of magnetostatic interparticle interactions and have brought about very early the necessity of a theoretical study of the magnetic properties of interacting magnetic nanoparticle assemblies. The first attempt to include interaction effects on the height of the energy barrier was made by Shtrikmann and Wohlfarth [43] using a mean statistical interaction field. For weak interparticle interactions, this formalism leads to the Vogel-Fulcher law for relaxation of the magnetic moment. Its more general approach was developed by Dormann [42], where dipolar interactions result in an increase of the height of the energy barrier and a consequent increase in the magnetic relaxation time, while another analytical model [44] predicts the opposite trend. Moreover, the interacting superparamagnetic model [45-47] was proposed to describe the effect of interactions on the magnetization value by adding a phenomenological temperature to the real one, or a modified random anisotropy model has been introduced [48, 49] to describe field dependence of the blocking temperature. Bertram and Bhatia [50] have used a spatial-mean interaction field to show that dipolar effects cause an increase of the remanent magnetization, which can reach the saturation value, while Stamps and Camley [51] have shown that the interplay of dipolar interaction and perpendicular anisotropy induces a reorientation transition below a critical temperature.

Moreover, Monte Carlo (MC) simulations of random assemblies of uniform nanoparticles have demonstrated the important role of dipolar interactions in their magnetic behavior. As far as the hysteresis behavior is concerned, there are results that show contradictory behaviors of the coercive field as a function of dipolar coupling strength. Russier [52] found that H_c decreases with an increase in dipolar strength independently of the array topology (square or hexagonal) despite the fact that the ground-state configuration is determined by the array topology. On the other hand Figueiredo and Schwarzacher [53] found that for a triangular lattice H_c exhibits a slight minimum for a small value of the dipolar strength and then increases, while other results indicate a nonmonotonic behavior [54–56]. As far as the blocking temperature is concerned, MC results show that for all nanoparticle concentrations the blocking temperature increases linearly with both the nanoparticle size [57] and the ratio of dipolar to mean uniaxial anisotropy energy contributions [53]. Higher-order (quadrupolar) magnetostatic interactions were shown to act in synergy with dipolar interactions, stabilizing the long-range order of the ground state in a nanoparticle array [58]. In the case of ordered arrays, MC simulations show that the blocking temperature is increased and scales with the inverse cube of the nanoparticle distance, and it remains almost unchanged with film thickness above one monolayer [59]. In addition the presence of an incomplete second layer with hexagonal structure does not destroy the long-range FM ordering of the ground state [59], while even slight structural disorder within the array destroys that ordering [60].

While magnetostatic interactions between particles are always present and due to their long-range character they can only be neglected in very dilute samples, exchange interactions between particles appear only when there is a physical contact between them, due to the overlap of the wave functions of the surface atoms. The short-range direct exchange interactions are expected to play an important role in samples with a concentration close to and above the percolation threshold. Indeed, as the concentration of the nanoparticles increases interparticle interactions appear and modify the height and distribution of the energy barriers arising from the anisotropy contributions of each nanoparticle. The reversal of one particle moment may change all energy barriers within the assembly, so individual energy barriers can no longer be considered but only the total energy of the assembly through an energy landscape with a complex hierarchy of local minima similar to that of spin glasses. Actually in a dense ensemble of single-domain nanoparticles interparticle interactions can dominate over singleparticle blocking and may lead to collective behavior [9].

When long-range dipolar and short-range direct exchange interactions coexist, MC simulations show that interactions among uniform nanoparticles suppress coercivity, while they have opposite effects on the remanence of the sample [61]. The crossover from dipolar-coupled to exchange-coupled behavior occurs when the two types of interactions have comparable strengths. The blocking temperature is always enhanced due to interactions, except for the case that particles coalesce and the sample is above the percolation threshold. Nevertheless, an open question remains as to whether blocking of the individual magnetic moments or collective freezing due to interparticle interactions is the appropriate description of low-temperature magnetic behavior [62]. To this end a series of experiments and theoretical works have attempted to reveal similarities in the dynamical properties of fine-particle assemblies and canonical spin glasses [42, 44].

Lately exploitation of the exchange bias effect in assemblies of core/shell nanoparticles has attracted a lot of interest. Despite the research effort focused on the microscopic mechanism of this effect in individual nanoparticles, much less attention has been paid so far to the modification of the magnetic hysteresis behavior due to interparticle interactions arising in assemblies. In this direction, Co nanoparticles embedded in a Mn matrix [63] were shown to freeze below a temperature, owing to the competition between the exchange anisotropy at the core-shell interface and the interparticle dipolar interactions, and an increase in the exchange field was reported. Similarly, increase of the exchange bias field due to magnetostatic interparticle coupling was found in stripes of Co/CoO nanoparticles [64] and interdot magnetostatic interactions were shown to produce asymmetric anomalies in the magnetization reversal mechanism of Co/CoO dot arrays [65]. Also Margaris et al. [66] have shown that in 2D random assemblies of FM/AFM nanoparticles the exchange interpaticle interactions play a major role, causing an increase in H_c and H_{ex} with the concentration of the nanoparticles. Modification of the coercive and exchange bias fields in assembled nanoparticles with core-shell morphology as a result of the competition between exchange anisotropy and interparticle interactions consists of a challenging issue. We believe that a basic understanding of the magnetic properties of bimagnetic nanoparticles in ordered and disordered structurally assemblies is currently highly demanded.

In what follows we review our MC simulation technique and the standard Metropolis algorithm. We then describe the model we use to simulate the magnetic behavior of single FM/AFM nanoparticles in an atomic-scale approach and that of assembled nanoparticles in ordered and random structures in a mesoscopic-scale approach. We discuss our MC simulation results for atomic-scale modeling on spherical composite nanoparticles, which consist of a spherical FM core surrounded by an AFM shell, and give the most important characteristics of their magnetic behavior. The magnetization dependence on external parameters (temperature, applied field) and the intrinsic particle properties (size, size of shell and core, size of interface exchange interaction) will be discussed. Finite-size effects and the role of the interface are studied. In this way we can put our discussion for the case of FM core/AFM shell nanoparticle assemblies into a context. The effect of exchange interface coupling

on the macroscopic magnetic behavior of these nanoparticle assemblies and its interplay with interparticle interactions will be analyzed. Characteristics of the hysteresis loop and temperaturedependent magnetization (FC, ZFC) are studied. Results will be shown for granular assemblies and ordered arrays of bimagnetic FM/AFM nanoparticles. A discussion on potential applications and a comparison with experimental findings will be given in all cases.

8.2 The Model and Simulation Method

The MC simulation technique with the implementation of the Metropolis algorithm [67–69] has been proved to be a very powerful tool for the systematic study of the magnetic behavior of nanoparticles and nanoparticle assemblies. It offers the possibility for atomic-scale treatment of nanoparticles in order to study details of their microstructure and the ability of the implementation of finite temperature.

The MC simulation technique is a standard method to study models of equilibrium or nonequilibrium thermodynamic systems with many degrees of freedom by stochastic computer simulation. The starting point of the simulation is the appropriate choice of a model Hamiltonian and then the use of random numbers to simulate statistical fluctuations in order to generate the correct thermodynamical probability distribution according to a canonical ensemble [70]. In this way one may obtain microscopic information about complex systems that cannot be studied analytically or that might not be accessible in a real system. Contrary to Landau–Lifshitz or Langevin equations, the MC scheme provides a straightforward implementation of temperature.

To simulate magnetic nanoparticles and nanoparticle assemblies and to derive thermodynamic averages, the elementary physical quantity that we use is the spin. In the case of single nanoparticles we consider a classical spin at each atomic site and we simulate using the MC technique the stochastic movement of the system in the phase space. In the case of assemblies of nanoparticles, we consider one or more effective spins for each nanoparticle, depending on its morphology to represent its magnetic state.

The MC simulation consists of many elementary steps. In every elementary step a spin \hat{S}_{idd} is randomly chosen from a system of N spins and an attempted new orientation \hat{S}_{inew} of the spin is generated with a small random deviation δs . Then the energy difference ΔE between the attempted and the present orientation is calculated. In the Metropolis MC algorithm, if $\Delta E \le 0$ the new orientation is accepted. If $\Delta E > 0$ the attempted new orientation is accepted, provided that a random number *u*, generated uniformly in the interval (0,1), is less than the probability $\exp(-\Delta E/k_{\rm B}T)$, otherwise the system remains in its present state [68]. A complete MC step per spin (MCSS) consists of N elementary steps so that in any MCSS on average every spin is considered once. With this algorithm, states are generated with a certain probability (importance sampling), and rejecting the first MCSS that corresponds to the thermalization process, the desired average of a variable, namely, the sum of the products of each value times the corresponded probability, simply becomes the arithmetic average over the entire sample of states that is kept.

One common problem that appears during the MC simulation is that if we draw the attempted direction of every spin independently of the previous one, the system will always be superparamagnetic and no hysteresis will result, since it will be possible to explore the whole phase space independently of the temperature and due to the large fluctuations in every MCSS it will escape very quickly from any metastable state responsible for hysteresis. By fixing to a certain limit the deviation δs , it is possible to modify the range of acceptance and model the real system more accurately [68, 71, 72] than choosing \hat{S}_{inew} completely randomly and independently from \hat{S}_{iold} . The MC acceptance rate can be set to some desired value (40%-60%) (setting effectively the rate of motion in phase space. The use of such a kind of local dynamics permits to detect confinement in metastable states responsible for hysteresis and to achieve true relaxation at different temperatures. Therefore we choose to perform the Metropolis MC simulation in such a way that it samples the phase space "locally" with an accepted ratio of 50%, and we do it for all the examined temperatures; otherwise the direct comparison between obtained hysteresis loops for different temperatures would not be possible.

To avoid trapping of the system at local minima, we start the numerical procedure from an unmagnetized sample at a high temperature above the critical temperature of the sample and we reduce the temperature gradually at a constant rate. At high temperatures we use more MC steps than at lower temperatures in order to let the system relax, surpassing probable metastable states. Special care has been taken of the time and ensemble averaging of the magnetization of the system by properly choosing the number of MC steps and a rather big number of different samples, namely, independent random number sequences corresponding to different realizations of thermal fluctuations.

8.2.1 Simulations of the Magnetic Behavior of Noninteracting Core/Shell Nanoparticles in the Atomic Scale

We consider spherical nanoparticles that consist of an assembly of *N* classical spins placed on the sites of a 3D simple cubic (sc) lattice within a radius of *R* lattice spacings of the central site consisting of a FM core and an AFM shell surrounding the core (Fig. 8.1). The interface between the core and the shell is defined by the spins in the outer layer of the core being one-lattice-spacing thick and the surrounding AFM layer of one-lattice-spacing thickness, too. The surface of the particle is defined again by the spins in the outer layer of the particle-spacing thickness. The classical spins in the particles interact with nearest-neighbor Heisenberg exchange interaction, and at each crystal site they experience a uniaxial anisotropy. We take into account explicitly the exchange interaction between the spins in the core, at the interface, in the shell, and at the surface [36, 73, 74]. In the presence of an external magnetic field, the total energy of the system is

$$E = -J_{FM} \sum_{(i,j\in FM)} \mathbf{S}_{i} \cdot \mathbf{S}_{j} - \sum_{i\in FM} K_{iFM} (\mathbf{S}_{i} \cdot \hat{e}_{i})^{2} - J_{AFM} \sum_{(i,j\in AFM)} \mathbf{S}_{i} \cdot \mathbf{S}_{j}$$
$$- \sum_{i\in AFM} K_{iAFM} (\mathbf{S}_{i} \cdot \hat{e}_{i})^{2} - J_{IF} \sum_{(i\in FM, j\in AFM)} \mathbf{S}_{i} \cdot \mathbf{S}_{j} - \mathbf{H} \cdot \sum_{i} \mathbf{S}_{i}$$
(8.1)

Here **S**_i is the atomic spin at site *i* and \hat{e}_i is the unit vector in the direction of the easy axis at site *i*. The angular brackets in the

sums denote a summation over the nearest neighbors only. The first term gives the exchange interaction between the spins in the FM core with the exchange-coupling constant $J_{\rm FM}$ to be taken equal to 1. The second term gives the anisotropy energy of the FM core. For nanoparticles, there is some evidence that the easy axis is along one of the crystallographic directions, even though in cubic bulk materials the easy axis is not uniaxial but along the three cubic axes [75]. The core and interface anisotropies are therefore considered uniaxial along the z axis with the anisotropy coupling constant K_c . If site *i* lies in the outer layer of the FM core $K_{iFM} = K_{iF} = 0.5$, and $K_{iFM} =$ $K_{\rm C}$ = 0.05 elsewhere. The third term gives the exchange interaction in the AFM shell (the exchange-coupling constant J_{AFM}), and the fourth term gives the anisotropy energy of the AFM shell. Many studies have shown that, due to the reduced symmetry of the surface, the surface crystal anisotropy is stronger than the bulk [76, 77]. So if i lies in the outer layer of the AFM shell then $K_{iAFM} = K_s = 1$ and $K_{iAFM} = K_{SH} = 0.5$ inside the shell. We take the anisotropy uniaxial along the z axis in the shell and random at the surface of the nanoparticles [78]. The fifth term gives the exchange interaction at the interface between the core and the shell (the exchange-coupling constant J_{IF}), and the last term is the energy in the presence of an external magnetic field. We set $J_{AFM} = -J_{FM}/2$, because the Néel temperature of the AFM oxide is lower than the Curie temperature of the corresponding ferromagnet. The interface exchange-coupling constant $J_{\rm IF}$ is equal to $J_{\rm AFM}$ in size, in agreement with theoretical studies in layered systems [34, 79, 80], and the interaction is considered FM.

To obtain the coercive and exchange bias fields we calculate the complete hysteresis loop. FC procedure is performed initially: we start at temperature T = 2.5, which is between the Curie temperature $T_{\rm C}$ of the FM core and the critical temperature of the AFM shell (for the sc lattice, $T_{\rm C} = 2.9$ and $T_{\rm N} = 1.5$ [81]); consequently we cool the nanoparticle at a constant rate in the presence of a magnetic field $H_{\rm cool} = 0.7$ along the *z* axis. Once the desired temperature is reached, we slowly vary a magnetic field starting from a maximum value along the +*z* direction, reducing it in very small constant steps. At each field step, several MCSSs are executed after thermalization, and then the magnetization is calculated, the field is changing again, and so on. The resulting hysteresis loops have horizontal asymmetry.

The value of the loop shift along the field axis is expressed by the exchange bias field $H_{\text{ex}} = -(H_{\text{right}} + H_{\text{left}})/2$, and the coercive field is defined as $H_{\text{c}} = (H_{\text{right}} - H_{\text{left}})/2$, H_{right} and H_{left} being the points where the loop intersects the field axis. Magnetization is normalized to the magnetization at saturation (M_{s}).



Figure 8.1 Transition from the atomic-scale model of a FM/AFM nanoparticle (left) where the spins of the core, interface, shell, and surface layers are explicitly included to the mesoscopic model (right), where each nanoparticle layer corresponds to one or two macrospins, to describe adequately the core/shell morphology of the nanoparticles in the assembly.

In the presented simulations 18×10^3 MCSSs up to 4×10^4 MCSSs, depending on the system size, were found to be sufficient to produce results as compared to results for a number of MCSSs an order of magnitude higher. For each temperature, the amount of change in the direction of a selected spin is chosen such that on average one half of the selected moves are successful. Results have been checked by calculating the magnetization and coercivity for different sequences of random numbers (10–40 runs). The statistical error found was very small even at high temperatures. Including the corresponding error bars in our figures would not affect the information obtained from them, so they are omitted. In our results, the temperature *T* is measured in dimensionless units of $J_{\rm FM}/k_{\rm B}$, the magnetic field *H* in units of $J_{\rm FM}/g\mu_{\rm B}$, and the anisotropy-coupling constants in units of $J_{\rm FM}$.

8.2.2 Simulations of the Magnetic Behavior of Interacting Core/Shell Nanoparticles in the Mesoscopic Scale

In the atomic-scale MC modeling, a nanoparticle is described by assigning a classical unit spin vector on each site of a 3D lattice that has been cut out to the shape of the nanoparticle [82, 83]. Thus, if assemblies of nanoparticles are simulated the number of spins becomes so large that it quickly turns computationally impossible to treat, impeding the study of large volume fractions in nanoparticle assemblies. To circumvent this problem and to include also timeconsuming interparticle interactions usually arrays of uniform nanoparticles are studied by assigning a macrospin and an anisotropy energy term to each nanoparticle, neglecting the surface effects [84]. This representation is adequate in the case of assemblies of singledomain FM particles where exchange interactions dominate over the anisotropy and all spins are almost collinear. Indeed, a vast majority of numerical investigations have been carried out on assemblies of uniform nanoparticles, including interparticle interactions [85, 86] that have been shown to play a key role in the magnetic properties [87-89] and that are, in fact, essential for applications such as magnetic cellular automata [90].

Nevertheless, taking into account that large technological interest focuses on applications that involve bimagnetic core/shell nanoparticles (e.g., magnetic recording or permanent magnets) in large numbers, there is an increasing need now to simulate arrays of core/shell nanoparticles, including also their internal characteristics (interface, surface), because they are expected to play an important role in the total magnetic behavior of the ensemble. As it becomes clear the above numerical approach of a macrospin for each nanoparticle of the assembly is no longer valid in the case of complex nanoparticle morphologies. Here we present our mesoscopic method based on an MC approach to easily simulate large ensembles of bimagnetic core/shell nanoparticles by reducing the number of spins to be simulated to the minimum necessary to satisfactorily represent their magnetic structure and introducing adequate exchange parameters between them (Fig. 8.1).

In what follows we present two different models for spatial arrangements of the core/shell particle assemblies: 3D or 2D

randomly placed magnetic nanoparticle assemblies and quasi-2Dordered arrays of magnetic nanoparticles. In the first model, spherical FM/AFM particles are located randomly with occupation probability p inside a box or square of edge length L. To avoid the overlap problem, the space inside the box is discretized by a hexagonal lattice or a tetragonal lattice with a lattice constant equal to the particle diameter. This geometrical model describes the morphology of films formed by codeposition of preformed particles with nonmagnetic atoms [91]. In the second model, the particles form a 2D hexagonal lattice in the xy plane with a lattice constant d. This model describes adequately the morphology of self-assembled ordered arrays of magnetic nanoparticles [92, 93]. The particle assembly is assumed monodisperse in accordance with experimental evidence that both films grown by cluster beam [91] or by self-assembly on surfaces [92, 93] are characterized by extremely low size dispersion.

We go beyond the classical model of coherent rotation of a particle's magnetization of Stoner-Wohlfarth [6] in which each nanoparticle is described by a classical spin vector (S_i) . Our mesoscopic model contains of a set of two, three, or six classical spin vectors for each nanoparticle in the assembly, depending on the exact morphology of the particle and the magnetic character (FM, AFM) of the constituents. The values of the different parameters in the simulation are set on the basis of their bulk values, if they exist, and their modifications are established considering the nanoparticles' morphology (e.g., reduced symmetry and reduced size) using a mean field approach. Some parameters that do not exist in the literature have been introduced in a phenomenological way and are also based on experimental evidence. The total energy of the system is defined as the sum of the energy contributions of the N nanoparticles in the assembly with a total diameter *d* in lattice spacings. The energy contribution of the *n*th nanoparticle of the assembly is given by the general equation

$$E_{n} = -\sum_{\langle i,j \rangle} J_{ij}(\mathbf{S}_{i} \cdot \mathbf{S}_{j}) - \sum_{i} K_{i}(\mathbf{S}_{i} \cdot \hat{e}_{i})^{2} - H \sum_{i} (\mathbf{S}_{i} \cdot \hat{H})$$
$$-g \sum_{k,k \neq n} \left(\left(\sum_{i} \mathbf{S}_{i} \right) D_{nk} \left(\sum_{j} \mathbf{S}_{jk} \right) \right) - J_{out} \sum_{\langle i,ik \rangle} (\mathbf{S}_{i} \cdot \mathbf{S}_{ik})$$
(8.2)

where \mathbf{S}_{i} is the *i* mesoscopic classical spin vector inside the *n*th particle and \hat{e}_{i} is its anisotropy easy-axis direction. Each particle

is described by a number of spins S_i . This number depends on the characteristics of the nanoparticles in the system. The first three energy terms correspond to the intraparticle interactions of the spins inside the nanoparticle, namely, the nearest-neighbor Heisenberg exchange interaction, the anisotropy energy, and the Zeeman energy of the spins describing one nanoparticle. The fourth term corresponds to the dipolar interactions among the *n*th and the rest nanoparticles (k) of the assembly where D_{nk} is the dipolar interaction tensor. The last term corresponds to the short-range exchange interactions that decay within a few lattice constants of the parent magnetic material; therefore, it is restricted in our model to the particles in contact (nearest neighbors of the *k*th particle) to the *n*th particle. Consequently this does not occur in the model that describes ordered arrays, where the particles are not in contact [59]. The energy parameters entering Eq. 8.2 are the intraparticle exchange energy J_{ii} , the anisotropy energy K_{i} , the external field *H*, the dipolar energy strength $g = m^2/d^3$, where $m = M_s V$ is the particle's magnetic moment, the exchange interparticle energy I_{out} between spins of nanoparticles in contact, and the temperature T. These parameters are normalized by the core anisotropy parameter (K_c) , so they are dimensionless. When the interface is considered, the FM core and the FM/AFM interface have uniaxial anisotropy and the AFM shell has random anisotropy much higher than the core anisotropy. Otherwise each nanoparticle is assigned a uniaxial easy axis common for all spins in the particle pointing in a random direction.

To deal with the long-range character of dipolar interactions the Ewald summation technique is implemented [94]. Satisfactory convergence with the Ewald technique is obtained using repetitions of the central MC cell along each of the three Cartesian axes [55]. In the model of randomly placed interacting nanoparticles periodic boundaries in all directions are assumed, while in the second model mixed periodic boundaries (*xy* plane) and open boundaries (*z* axis) are considered. The dipolar interactions were treated without truncation using the Ewald summation method [95]. The spin configuration is obtained by a Metropolis MC algorithm [67]. At a given temperature and applied field, the system is allowed to relax toward equilibrium for the first 10^3 MCSSs and thermal averages are calculated over the subsequent 10^4 steps. The results are averaged over 10–30 samples with different realizations of the easy-axes distribution and in the case of random assemblies with different spatial configurations for nanoparticles.

The ZFC/FC magnetization curves are obtained by the following steps: a) Initially we start with the sample at a very high temperature (above its critical temperature), and we gradually reduce the temperature up to a very low value (close to 0) to obtain its ground state; b) at this very low temperature we apply a magnetic field, and we start raising the temperature up to the maximum value that we had started; in this way we obtain the ZFC curve; c) finally, in the presence of a magnetic field we reduce the temperature gradually down to the minimum value, and in this way we obtain the FC magnetization curve.

The hysteresis loop and ZFC/FC magnetization curves are repeated for a large number of different random numbers in order to produce uncorrelated data and thus independent configurations to perform an ensemble average. There are studies [96] that saw the importance of the constant step rate of the magnetic field in the case of the calculation of hysteresis loops and the importance of temperature in the calculation of ZFC/FC magnetization curves.

8.3 Magnetic Behavior of Noninteracting Core/ Shell Nanoparticles: Study of Intraparticle Characteristics

We first investigate the exchange bias mechanism in single spherical FM core/AFM shell nanoparticles and the influence of the interface structure, the shell thickness, and the exchange interface coupling strength on their magnetic behavior [35, 73].

We consider a single FM/AFM nanoparticle with a shell thickness equal to four lattice spacings. Assuming that the exchange interaction along the interface is FM, the bond energy for the spins across the FM/AFM interface is minimum when they are aligned as parallel and maximum when aligned as antiparallel. The opposite would happen in the case of an AFM interaction along the interface. During the field-cooling procedure the spins are aligned in such a way that the energy of the system is minimum. Along these lines, for

a FM interface interaction the parallel spin alignment is favorable. This alignment together with the strong interface anisotropy makes it hard for the spins to turn when the field goes from *H* to -H, and this results in a high coercive field. When the spins align along the negative direction, by changing the field again from -H to *H* they need less energy to turn. Developing this picture we will call up-bonds the pairs of spins along the FM/AFM interface that are parallel and down-bonds the antiparallel ones. So according to our calculations, a nanoparticle with a radius R = 10.0 has up bonds = 360 and down bonds = 318, and a nanoparticle with a radius R = 11.0has up bonds = 606 and down bonds = 288. We can see that though these two particles are very close in size they have very different numbers of up and down bonds. The same holds for nanoparticles with sizes 17.0 (up bonds = 1590, down bonds = 1584) and 19.0(up bonds = 2502, down bonds = 1752) and 12.0 (up bonds = 552, down bonds = 630) and 12.35 (up bonds = 840, down bonds = 486) where the difference is more pronounced. In Fig. 8.2 we show our results for the exchange bias field and the coercive field as a function of temperature for these pairs of particles with radii of 10.0 and 11.0 (circles), 12.0 and 12.35 (squares), and 17.0 and 19.0 (triangles). If we compare each pair of particles of similar size, the ones with a bigger proportion of up bonds have higher coercive fields. The difference is more pronounced in the pair of particles with sizes 12.0 and 12.35. They have the biggest difference in the proportion of up bonds. As the temperature increases the thermal fluctuations cancel the interface effects. Moreover, if we compare the pair of particles, the size dependence of the coercive field as a function of temperature has no difference in behavior from the one observed previously [35]. The smaller particles have a higher coercive field at low temperatures than the bigger ones, and this behavior is reversed at higher temperatures. In the exchange bias field curves, however, we observe that the size dependence on the number of bonds and not so much on the actual size of the particle plays an important role in the temperature dependence of the exchange bias field. When the difference of the up and down bonds is big, such as R = 11.0, 12.35, and 19.0, the particle magnetization turns easily by going from the -H to the H field. H_{ex} is stronger, and it follows the temperature dependence of H_c, while in the case of small up or down bonds, the difference in the behavior of the two branches of the hysteresis loop is similar. This results in a reduced H_{ex} with strong temperature dependence.



Figure 8.2 Coercive field (H_c) and exchange bias field (H_{ex}) versus temperature for three sets of particles with similar sizes but very different proportions of up and down bonds at the interface. R = 10 (closed circles) and R = 11.0 (open circles), R = 12.0 (closed squares) and R = 12.35 (open squares), and R = 17.0 (closed triangles) and R = 19.0 (open triangles).

The temperature dependence of the exchange field is in good agreement with the experimental findings of Ref. [97].

So, our simulations show that it is the number of uncompensated bonds, namely, the difference between FM and AFM bonds, along the interface that plays the key role in the appearance of $H_{\rm ex}$ and not the number of uncompensated spins.

To study the effect of the shell thickness on the exchange bias field we have considered a particle with a core thickness of seven lattice spacings, and we start to add AFM layers. In Fig. 8.3 we have plotted the exchange bias field as a function of the shell thickness at a low temperature $T = 0.05 J_{FM}/k_B$. We observe that this field is approximately constant after the second layer. This result is agreement with the experimental findings of Ref. [98], where they observe very fast stabilization of H_{ex} with the oxygen dose in Co/CoO nanoparticles.

However, in Ref. [73] we found that with an increase of the temperature to $T = 1.0 J_{FM}/k_B$, more AFM layers need to increase and stabilize the exchange bias field, because the thermal fluctuations at the interface make necessary a thicker shell to stabilize the interface contribution. Also in Fig. 8.4 we observe that after a certain number

of AFM layers, roughly when the shell size becomes initially equal and then further increases, the exchange bias field is decreasing because of the enhancement of the AFM contribution that masks the interface role.



Figure 8.3 Exchange bias field as a function of shell thickness, starting from a particle with a ferromagnetic radii $R_{\text{FM}} = 7.0$ at T = 0.05 $J_{\text{FM}}/k_{\text{B}}$. The solid line is a guide to the eye.



Figure 8.4 Coercive field (left) and exchange bias field (right) versus temperatures for a particle with radius R = 11.0 with (a) $J_{IF} = J_{FM}/2$ and $J_{AFM} = -J_{FM}/2$ (squares), (b) $J_{IF} = J_{FM}$ and $J_{AFM} = -J_{FM}/2$ (circles), and (c) $J_{IF} = J_{FM}$ and $J_{AFM} = -J_{FM}$ (triangles).

Finally, we examine the effect of the strength of the interface exchange-coupling and the AFM exchange-coupling constant, keeping the shell thickness of four lattice spacings and the other parameters as they were previously. We first increase the interfacecoupling constant J_{IF} , taking it now as equal to J_{FM} . The results for the temperature dependence of the coercive and the exchange bias fields for a particle with radius R = 11.0 are shown in Fig. 8.4 (circles). In the same figure the results for $J_{IF} = J_{FM}/2$ (squares) are shown for comparison. From this figure we can see that an increase in the strength of the interface exchange coupling results in a reduction of the coercive field at low temperatures and an enhancement of the exchange bias field. This is due to the fact that the stronger interface exchange coupling results in faster reversal of the ferromagnetically aligned spins with the AFM shell. At temperatures higher than T_N the behavior is similar to that of $J_{IF} = J_{FM}/2$, because at these temperatures the shell becomes paramagnetic and does not influence the FM core.

Keeping the interface exchange-coupling constant enhanced as previously and increasing also the exchange-coupling constant for the AFM shell, we take $J_{AFM} = -J_{FM}$, and we calculate the exchange bias and the coercive fields for R = 11.0 as functions of temperature. In this case the T_N and T_C are identical. Results are also shown in Fig. 8.4 (triangles). The increase in the AFM exchange-coupling constant strength results in a reduction of coercivity. The exchange bias field is increased and also persists at high temperatures, as expected, because now T_N is higher than it was in the previous cases. We note here that we have changed the kind of surface anisotropy from random to radial [99, 100] in our simulations to see its influence, but it has a minor effect on our results. This is expected because, as we showed above in composite nanoparticles, the major contribution to the exchange bias effects comes from the interface and the first shell layer.

So in this section, the physics emerging from structural characteristics of the interface, the shell thickness, and the exchange interface interaction of single core/shell nanoparticles were discussed. Our simulations showed that the number of uncompensated bonds and their exchange-coupling strength defines the exchange bias field value and the coercivity. Increasing the exchange-coupling constant of the AFM shell and/or at the FM/AFM interface leads to a reduction of H_c and an increase and thermal stability of H_{ex} . The exchange bias field disappears at temperatures above the Néel temperature of the AFM in agreement with experimental results [101]. Moreover, the AFM shell thickness is a factor of stabilization of the exchange bias effect as long as its

size is more than two lattice spacings and less than twice the core radius. So controlling the shell thickness of these nanoparticles can stabilize the exchange bias field successfully.

8.4 Magnetic Behavior of Interacting Core/Shell Nanoparticles: Interparticle Interactions Effects

8.4.1 Random Assemblies

We start our study of magnetic nanoparticle assemblies by examining the effect of the interplay between single-particle characteristics and interparticle interactions on the magnetic behavior of an assembly of nanoparticles with a FM core/AFM shell morphology [102] that are randomly distributed in a lattice corresponding to granular assemblies.

First we consider a system of core/shell nanoparticles placed randomly on a hexagonal lattice coupled via dipolar forces. The particle concentration we consider is $p \approx 0.05$, well below the percolation threshold. In this case, exchange interparticle interactions can be neglected. Here we employ a six-spin model to describe each nanoparticle, namely, one spin for the FM core, one for the FM part of the interface, two spins for the AFM part of the interface (that interact with the one FM spin at the interface with exchange-coupling constants J_{IF1} and J_{IF2}), and two spins for the AFM shell and surface. We have calculated the hysteresis loops and ZFC magnetization of this system at different temperatures. Also we have calculated the hysteresis loops and ZFC magnetization of a random assembly of single-spin nanoparticles, each of which is modeled as a macrospin, at the same low concentration and for the same range of temperatures, for comparison. The results are given in Fig. 8.5a, where we have plotted the temperature dependence of the exchange bias field H_{ex} (triangles) and the coercive field H_{c} (squares) for the random assembly of composite nanoparticles together with the coercive field H_c (open circles) of the single-spin assembly of nanoparticles. We have plotted also the ZFC magnetization curves for composite nanoparticle assemblies (squares) and single-spin nanoparticle assemblies (circles) in Fig. 8.5b.

As we can see in Fig. 8.5a apart from the fact that H_c is lower for the single-spin assembly for the whole range of temperatures, in the case of composite nanoparticles H_c remains finite at higher temperatures. This is due to the extra anisotropy in composite nanoparticles induced by exchange coupling along the FM/AFM interface [18, 73, 74, 103]. In the case of composite nanoparticles we observe an exponential decay of H_c and H_{ex} with temperature, while in single-spin nanoparticles the decay is monotonic.

Also in Fig. 8.5b we observe that the blocking temperature $T_{\rm B}$ of the system (the maximum of ZFC) of the composite nanoparticle assembly is higher than in the single-spin ones, in agreement with experimental findings of Refs. [63, 103]. Namely, the blocking temperature increases in the case of composite nanoparticles due to the contribution of exchange anisotropy along the nanoparticle interface.



Figure 8.5 (a) Temperature dependence of H_c (squares) and H_{ex} (triangles) for the random assembly of composite nanoparticles and H_c (open circles) for the single-spin nanoparticle assembly. (b) ZFC curves for the random assembly of composite nanoparticles (squares) and for the single-spin nanoparticle assembly (circles).

Next we study the effect of the dipolar strength on the hysteresis behavior of a dilute assembly of FM/AFM nanoparticles dispersed in an sc lattice interacting via dipolar and exchange interparticle interactions. The core–shell interface leads to an exchange bias effect. The coercive field and the exchange bias field as a function of dipolar strength for FM/AFM nanoparticles with particle concentration 8% are presented in Fig. 8.6.


Figure 8.6 Coercive field (H_c) and exchange bias field (H_{ex}) as a function of dipolar strength (g) for the interparticle exchange-coupling constant $J_{out} = 2.5$, $K_c = K_{IF} = 1$, and $K_{SH} = 30$, $J_{IF1} = 10$, and $J_{IF2} = 5$ at T = 0.02 for a dilute random assembly of FM/AFM nanoparticles (p = 8%). Solid lines are guides to the eye.

In Fig. 8.6, we observe that the coercive field tends to increase, while the exchange bias field decreases with an increase of dipolar strength. We attribute this behavior to the competition between the dipolar and the anisotropy energy. The exchange interparticle interactions do not play an important role, because our sample is very dilute.

We proceed with the study of random assemblies of large concentrations, including interparticle interactions. We have developed a model to simulate large ensembles of bimagnetic core/ shell nanoparticles by reducing the number of spins inside the nanoparticles and introducing adequate anisotropy parameters and exchange parameters between them when they are in contact. Using this model we have demonstrated the effectiveness of our mesoscopic method based on an MC approach to satisfactorily represent their magnetic structure. Our MC simulation results on the effect of inter- and intraparticle exchange interactions on the exchange bias behavior of nanoparticles are in very good agreement with the experimental findings of the study of random assemblies of Co/CoO core/shell nanoparticles [87, 66]. Here we present our MC simulation results on disordered arrays of nanoparticles where *N* particles are placed, randomly, on the nodes of a 3D cubic lattice, with randomly oriented easy-axis directions. Each nanoparticle is described by three different effective spins: one for the FM core and two for the AFM shell with the appropriate anisotropy and exchange parameters extracted by experimental data. The shell thickness of the nanoparticles in our model is considered very small [66]. We introduce dipolar and exchange interparticle interactions between the neighboring shell–shell and core–shell spins.

We simulate the hysteresis loops (Fig. 8.7a) at T = 0.02 and the temperature dependence of the magnetization M(T) (Fig. 8.7b) of a 3D random assembly of Co/CoO core/shell nanoparticles with concentrations p = 0.15 and 0.63 and g = 1.0, $K_{\rm C} = 1$ and $K_{\rm SH} = 80$, $J_{\rm IF1} = 3.2$, and $J_{\rm IF2} = 3.0$.



Figure 8.7 (a) MC-normalized hysteresis loops of 3D random arrays of Co/ CoO core/shell nanoparticles with densities p = 0.15 and 0.63 at T = 0.02. (b) MC results for the temperature dependence of the normalized magnetization for the two densities.

The most prominent result of the simulation is the significant increase of both H_c and H_{ex} for the large concentration of nanoparticles, where while $H_{ex} > H_c$ for p = 0.63, it is opposite for p = 0.15. A simple explanation of this increase in H_c and H_{ex} as the number of particles increases is that when particles are in contact the "effective thickness" of the AFM layer increases. Namely, each core instead of "feeling" one shell "feels" two shells; thus the effective thickness leads to an enhancement of H_{ex} and H_c , similar to what is

observed for thin-film systems when the thickness of the AFM layer increases. Moreover, whereas the loop appears rather symmetrical for p = 0.15, it has an obvious asymmetry for p = 0.63.

Similarly, the results for ZFC/FC magnetization curves show that at higher densities the blocking temperature $T_{\rm B}$ increases dramatically, in agreement with experiments [87]. Importantly, the observed behavior is attributed to interparticle exchange interactions in the assembly.

Indeed, if we "switch off" the interparticle exchange interactions, (i.e., $J_{out} = 0$), but we retain the dipolar interactions, the behavior is completely different. Namely, in the pure dipolar case, an increase in nanoparticle concentration leads to a decrease in H_c and H_{ex} due to the competition between anisotropy and dipolar energy (Fig. 8.8a).



Figure 8.8 Normalized hysteresis loops with $H_{cool} = 0.05$ of 3D random arrays of Co/CoO core/shell nanoparticles calculated using MC simulations (a) for p = 0.15 and 0.63, by setting interparticle exchange interactions to zero ($J_{out} = 0$) and g = 1, and (b) for p = 0.63, by increasing the dipolar interaction parameter.

For the high-concentration case, p = 0.63, with interparticle exchange coupling present, if the dipolar coupling is artificially increased (increasing the parameter *g*) the main effect is a reduction of H_c and H_{ex} (Fig. 8.8b). The exchange interparticle interactions in dense assemblies change the overall energy profile, causing an increase in exchange and coercive fields and the blocking temperature. However, in this case a further increase of the dipolar

strength causes a decrease of the exchange bias field. Obviously, the interplay between interparticle and intraparticle energies produces a complex magnetic behavior, depending on the system.

8.4.2 Ordered Arrays of Core/Shell Nanoparticles

In this section, we examine the effects of core/shell morphology and dipolar interparticle interactions on the hysteresis characteristics of ordered arrays of composite nanoparticles: self-assembled arrays.

We present our results on composite nanoparticles with a FM core radius of five and an AFM shell radius of four lattice spacings placed in a 2D hexagonal ordered array. The effect of the interparticle distance (d_0) is examined for two different values of the dipolar coupling constant, which depends on the material. We plot the coercive field (Fig. 8.9a) and the exchange bias field (Fig. 8.9b) for various interparticle distances (d_0) . We show results for ordered nanoparticle arrays with weak (g = 1, squares) and strong (g = 6.5, circles)dipolar coupling strength.

We observe that a reduction of the interparticle distance causes a reduction of coercivity due to the collective response of the magnetic moments, which leads to a reduction of the energy barrier for magnetization reversal. The reduction of H_c is more pronounced in strongly dipolar materials (g = 6.5). A decrease of the interparticle distance enhances the collective rotation of the magnetic moments in a strongly dipolar system. The exchange bias field is less affected by the increase in the interparticle distance (Fig. 8.9b). For weak dipolar materials H_{ex} is slightly increased with the decrease in d_0 , though for stronger ones it clearly increases. The dipole–dipole interactions enhance the exchange bias effect due to the competition between exchange anisotropy and dipolar interactions [104].

We continue our study of the effect of intraparticle characteristics on the magnetic behavior of an ordered array of FM/AFM nanoparticles. Since in this case the interparticle interactions are only the magnetostatic ones, we can use a two-spin model to describe each nanoparticle, one spin for the FM core and one for the AFM fully uncompensated interface assuming that the net magnetic moment of the shell is negligible [104]. We examine the role of the interface exchange coupling between the core and the shell in the nanoparticles by varying the exchange-coupling strength

($J_{\rm IF}$). In Fig. 8.10 we show data for three different 2D triangular arrays of composite nanoparticles with low ($J_{\rm IF} = 0.5$), moderate ($J_{\rm IF} = 1.0$), and strong ($J_{\rm IF} = 1.5$) interface exchange coupling for each nanoparticle in the assembly [104]. We observe that the coercive field is reduced (Fig. 8.10) as a function of the dipolar strength (g) due to the collective response of the magnetic moments, which leads to a reduction of the energy barrier for magnetization reversal. Our calculations indicate that this reduction of the coercive field with dipolar interactions is sensitive to the strength of the interface exchange. In particular, a weaker reduction of H_c is observed in systems with stronger interface exchange. This trend is anticipated as a strong $J_{\rm IF}$ leads to reduced H_c values for isolated nanoparticles [73, 105].



Figure 8.9 Dependence of H_c and H_{ex} on interparticle spacing (d_0) in a 2D hexagonal array of nanoparticles with a core radius of five and a shell thickness of four lattice spacings for (a) weakly dipolar (g = 1.0) material and (b) strongly dipolar (g = 6.5) material.

The behavior of the exchange field with increasing dipolar coupling strength appears more complex (Fig. 8.10). For strong interface coupling ($J_{IF} = 1.5$) H_{ex} drops linearly with increasing dipolar strength. In a strong dipolar limit (g >> 1, not shown here), the exchange field vanishes as the dominating dipolar forces restore the symmetry of the hysteresis loop around the zero field point.

However, a surprisingly different behavior is observed for weaker interface coupling (Fig. 8.11, $J_{\rm IF} = 1.0$) when the $H_{\rm ex}$ values go through a maximum at intermediate dipolar strength ($g \approx 0.2$) before decreasing to a constant value in the strong dipolar limit. The observed enhancement of $H_{\rm ex}$ due to weak dipolar interactions

is contrary to what would be expected on intuitive grounds, as interactions that lead to symmetric hysteresis loops with respect to field reversal loops, when competing with the random exchange anisotropy field lead to an increased loop shift. Therefore, we attribute the dipolar induced enhancement of H_{ex} to the interplay of dipolar interactions and exchange anisotropy. Finally, we mention that both for interacting and noninteracting arrays, increase of the interface exchange causes reduction of coercivity and increase of exchange field, as shown in Fig. 8.10. This behavior is in agreement with the behavior of single nanoparticles, as described by the atomic-scale models [73].



Figure 8.10 Dependence of coercivity (H_c) and the exchange bias field (H_{ex}) on dipolar strength (*g*) at low temperature (*T* = 0.01).

So in an ordered array of magnetic nanoparticles with core/shell morphology, interparticle dipolar interactions cause suppression of the coercive field, while they produce a more complex behavior of the exchange field. In systems with high shell anisotropy and moderate interface coupling ($J_{\rm IF} \approx 1$), it is found that weak dipolar interactions ($g \approx 0.2$) could enhance the exchange bias effect. Our simulation results point to the possibility of increasing the exchange field by increasing the nanoparticle concentration.

8.5 Concluding Remarks

In this chapter we review our MC simulation results on the magnetic behavior of assemblies of composite nanoparticles with core/shell morphology. We start with a review of our study of the factors that influence the magnetic behavior of single (noninteracting) core/shell nanoparticles and lead to exchange bias effects. These factors include the number of uncompensated bonds rather than uncompensated spins along the interface, the exchange coupling strength that determines the strength of the exchange bias field, and the shell thickness. These results are in agreement with the experimental ones, indicating that MC simulations can shed light on the microscopic origin of the magnetic behavior of composite nanoparticles and provide conditions for optimized properties.

Taking into account the findings of our single-compositeparticle study we proceed with the study of assemblies of core/ shell nanoparticles, including both interparticle and intraparticle characteristics of the system. We introduced mesoscopic models to study the influence of these characteristics and their interplay in the magnetic behavior of structurally ordered and disordered arrays. In dilute random assemblies, where only dipolar interactions are present, magnetic behavior depends on the competition between anisotropy and dipolar energy. The inclusion of exchange interparticle interactions can play a dominant role in the exchange bias behavior, causing its increase, in addition to an increase of the coercive field and of the blocking temperature in agreement with experimental results. In the case of ordered arrays interparticle dipolar interactions cause suppression of the coercive field, while they produce a more complex behavior of the exchange field. Specifically, in systems with high shell anisotropy and moderate interface coupling, it is found that weak dipolar interactions could enhance the exchange bias effect. Our results show that our mesoscopic model reproduces properly the trends that are observed experimentally, but the exact behavior is very much system dependent.

References

- Piramanayagam, S. N., Srinivasan, K. (2009). J. Magn. Magn. Mater., 321, 485–494.
- Rostamnejadi, A., Venkatesan, M., Alaria, J., Boese, M., Kameli, P., Salamati, H., Coey, J. M. D. (2011). *J. Appl. Phys.*, **110**, 043905 (7pp).
- Bisero, D., Cremon, P., Madami, M., Sepioni, M., Tacchi, S., Gubbiotti, G., Carlotti, G., Adeyeye, A. O., Singh, N., Goolaup, S. J. (2011). *J. Nanopart. Res.*, 13, 5691.

- 4. Lau J. W., Shaw, J. M. (2011). J. Phys. D: Appl. Phys., 44, 303001 (43pp).
- Reddy, L. H., Arias, J. L., Nicolas, J., Couvreur, P. (2012). *Chem. Rev.*, 112(11), 5818–5878.
- Stoner, E. C., Wolfarth, P. (1948). *Philos. Trans. R. Soc. London, A*, 240, 599.
- 7. Néel, L. (1949). Compt. Rend., 228, 664; Ann. Geophys., 5, 99.
- 8. Bean, C. P., Livingston, J. D. (1959). J. Appl. Phys., 30, 120.
- Bedanta, S., Kleemann, W. (2009). J. Phys. D: Appl. Phys., 42, 013001 (28pp).
- 10. Dormann, J. L., Fiorani, D. (eds.) (1992). *Magnetic Properties of Fine Particles*, North-Holland, Amsterdam.
- 11. Hassnain Jaffari, G. Ekiert, T., Unruh, K. M., Ismat Shah, S. (2012). *Mater. Sci. Eng. B*, **177**, 935–941.
- 12. Carrey, J., Mehdaoui, B., Respaud, M. (2011). J. Appl. Phys., 109, 083921.
- 13. Tamion, A., Bonet, E., Tournus, F., Raufast, C., Hillion, A., Gaier, O., Dupuis, V. (2012). *Phys. Rev. B*, **85**(1), 34430.
- 14. Tannous C., Gieraltowski, J. (2008). Physica B, 403, 3578-3584.
- 15. Sampaio da Silva, F. A., Castro, N. A., de Campos, M. F. (2013). *J. Magn. Magn. Mater.*, **328**, 53–57.
- Chuev, M. A., Hesse, J. (2007). J. Phys.: Condens. Matter, 19, 506201 (18pp).
- 17. Skumryev, V., Stoyanov, S., Zhang, Y., Hadjipanayis, G., Givord, D., Nogués, J. (2003). *Nature*, **423**, 850.
- Nogués, J., Sort, J., Langlais, V., Skumryev, V., Suriñach, S., Muñoz, J. S., Baró, M. D. (2005). *Phys. Rep.*, **422**, 65.
- 19. Fiorani, D., Del Bianco, L., Testa, A. M., Trohidou, K. N. (2006). *Phys. Rev. B*, **73**, 092403.
- 20. Skomski, R., Coey, J. M. D. (1993). Phys. Rev. B, 48, 15812.
- Salazar-Alvarez, G., Sort, J., Uheida, A., Muhammed, M., Suriñach, S., Baró, M. D., Nogués, J. (2007). *J. Mater. Chem.*, **17**, 322.
- 22. Chaubey, G. S., Nandwana, V., Poudyal, N., Rong, C. B., Liu, J. P. (2008). *Chem. Mater.*, **20**, 475.
- 23. Xi, L., Wang, Z., Zuo, Y., Shi, X. N. (2011). Nanotechnology, 22, 045707.
- 24. Lee, J. H., Jang, J. T., Choi, J. S., Moon, S. H., Noh, S. H., Kim, J. W., Kim, J. G., Kim, I. S., Park, K. I., Cheon, J., (2011). *Nat. Nanotechnol.*, **6**, 418.
- 25. Zeng, H., Sun, S. (2008). Adv. Funct. Mater., 18, 391.

- Costi, R., Saunders, A. E., Banin, U., (2010). Angew. Chem., Int. Ed., 49, 4878.
- 27. Carbone, L., Cozzoli, P. D. (2010). Nano Today, 5, 449.
- 28. Meiklejohn, W. H., Bean, C. P. (1957). Phys. Rev., 105, 904.
- 29. Nogués, J., Schuller, I. K. (1999). J. Magn. Magn. Mater., 192, 203.
- Giri, S., Patra, M., Majumdar, S. (2011). J. Phys.: Condens. Matter, 23, 073201 (23pp).
- O'Grady, K., Fernandez-Outon, L. E., Vallejo-Fernandez, G. (2010). J. Magn. Magn. Mater., 322, 883–899.
- 32. Malozemoff, A. P. (1987). Phys. Rev. B, 35, 3679.
- 33. Schulthess, T. C., Butler, W. H. (1998). Phys. Rev. Lett., 81, 4516.
- Nowak, U., Usadel, K. D., Keller, J., Miltenyi, P., Beschoten, B., Guntherodt, G. (2002). Phys. *Rev. B*, 66, 014430.
- 35. Zianni, X., Trohidou, K. N. (1998). J. Phys.: Condens. Matter, 10, 7475.
- Eftaxias, E., Vasilakaki, M., Trohidou, K. N. (2007). *Mod. Phys. Lett. B*, 21(21), 1169–1177.
- Passamani, E. C., Larica, C., Marques, C., Provetti, J. R., Takeuchi, A. Y., Sanchez, F. H. (2006). *J. Magn. Magn. Mater.*, 299, 11.
- Knobel, M., Nunes, W. C., Socolovsky, L. M., De Biasi, E., Vargas, J. M., Denardin, J. C. (2008). *J. Nanosci. Nanotechnol.*, 8, 2836–2857.
- Binns, C., Trohidou, K. N., Bansmann, J., Baker, S. H., Blackman, J. A., Bucher, J.-P., Kechrakos, D., Kleibert, A., Louch, S., Meiwes-Broer, K.-H., Pastor, G. M., Perez, A., Xie, Y. (2005). *J. Phys. D: Appl. Phys.*, 38, R357– R379.
- Martin, J. J., Nogués, J., Liu, K., Vicent, J. L., Schuller, I. (2003). J. Magn. Magn. Mater., 256, 449.
- Grzelczak, M., Vermant, J., Furst, E. M., Liz-Marzán, L. M. (2010). ACS Nano, 4(7), 3591–3605.
- 42. Dormann, J. L., Fiorani, D., Tronc, E. (1997). Adv. Chem. Phys., 98, 283.
- 43. Shtrikmann, S., Wohlfarth, E. P. (1981). Phys. Lett., 85A, 457.
- 44. Mørup, S., Tronc, E. (1994). Phys. Rev. Lett., 72, 3278.
- Allia, P., Coisson, M., Knobel, M., Tiberto, P., Vinai, F. (1999). *Phys. Rev. B*, 60, 12207.
- Allia, P., Coisson, M., Tiberto, P., Vinai, F., Knobel, M., Novak, M. A., Nunes, W. C. (2001). *Phys. Rev. B*, 64, 144420.
- Brandl, A. L., Socolovsky, L. M., Denardin, J. C., Knobel, M. (2005). J. Magn. Magn. Mater., 294, 127.

- Nunes, W. C., Socolovsky, L. M., Denardin, J. C., Cebollada, F., Brandl, A. L., Knobel, M. (2005). Phys. *Rev. B*, **72**, 212413.
- Knobel, M., Nunes, W. C., Winnischofer, H., Rocha, T. C. R., Socolovsky, L. M., Mayorga, C. L., Zanchet, D., (2007). *J. Non-Cryst. Solids*, **353**, 743– 747.
- 50. Bertram, H. N., Bhatia, A. K. (1973). IEEE Trans. Magn., 9, 127.
- 51. Stamps, R. L., Camley, R. E. (1999). Phys. Rev. B, 60, 11694.
- 52. Russier, V. (2001). J. Appl. Phys., 89, 1287.
- 53. Figueiredo, W., Schwarzacher, W. (2008). Phys. Rev. B, 77, 104419.
- 54. Tran, N. L., Tran, H. H., (2011). J. Non-Cryst. Solids, 357, 996–999.
- Kechrakos, D., Trohidou, K. N. (1998). Phys. Rev. B, 58(18), 12169– 12177.
- 56. Kechrakos, D., Trohidou, K. N. (2004). Appl. Surface Sci., 226, 261–264.
- Buján-Núñez, M. C., Fontaiña-Troitiño, N., Vázquez-Vázquez, C., López-Quintela, M. A., Piñeiro, Y., Serantes, D., Baldomir, D., Rivas, J. (2008). *J. Non-Cryst. Solids* 354, 5222–5223.
- 58. Politi, P., Pini, M. G. (2002). Phys. Rev. B, 66, 214414.
- 59. Kechrakos, D., Trohidou, K. N., (2002). Appl. Phys. Lett., 81, 4574.
- 60. Jensen, P. J., Pastor, G. M. (2003). New J. Phys., 5, 68.
- 61. Kechrakos, D., and Trohidou, K. N., (2003). *J. Magn. Magn. Mater.*, **262**, 107–110.
- 62. Skomski, R. (2011). J. Appl. Phys., 109, 07E149.
- Binns, C., Domingo, N., Testa, A. M., Fiorani, D., Trohidou, K. N., Vasilakaki, M., Blackman, J. A., Asaduzzaman, A. M., Baker, S., Roy, M., Peddis, D. (2010). *J. Phys.: Condens. Matter*, 22, 436005 (6pp).
- 64. Bi, H., Li, S., Jiang, X., Du, Y., Yang, C. (2003). Phys. Lett. A, 307, 69.
- Girgis, E., Portugal, R. D., Loosvelt, H., Bael, M. J. V., Gordon, I., Malfait, M., Temst, K., Haesendonck, C. V., Leunissen, L. H. A., Jonckheere, R. (2003). *Phys. Rev. Lett.*, **91**, 187202.
- Margaris, G., Trohidou, K. N., Nogués, J. (2012). Adv. Mater., 24(31), 4331.
- Metropolis, N., Rosenbluth, A., Rosenbluth, M., Teller, A., Teller, E. (1953). *J. Chem. Phys.*, **21**(6), 1087–1092.
- 68. Binder, K. (1987). *Applications of the Monte-Carlo Method in Statistical Physics*, Springer-Verlag, New York.
- 69. Landau, D. P., Binder, K. (2000). *A Guide to Monte Carlo Simulations in Statistical Physics*, Cambridge University Press, U.K.

- Binder, K. (1986). Topics in Current Physics, Monte Carlo Methods in Statistical Physics, Springer-Verlag, Berlin, Heidelberg, New York, and Tokyo.
- Garcia-Otero, J., Porto, M., Rivas, J., Bunde, A. (1999). J. Appl. Phys., 85(4), 2287–2292.
- 72. Dimitrov, D. A., Wysin, G. M. (1996). Phys. Rev. B, 54(13), 9237-9241.
- 73. Eftaxias, E., Trohidou, K. N. (2005). Phys. Rev. B, 71(13), 134406.
- 74. Vasilakaki, M., Trohidou, K. N. (2009). *Phys. Rev. B*, **79**(14), 144402–144408.
- 75. Chui, S. T., De-Cheng, T. (1995). J. Appl. Phys., 78, 3965.
- 76. Kaneyoshi, T. (1991). J Phys.: Condens. Matter, 3, 4497.
- Respaud, M., Broto, J. M., Rakoto, H., Fert, A. R., Thomas, L., Barbara, B., Verelst, M., Snoeck, E., Lecante, P., Mosset, A., Osuna, J., Ould Ely, T., Amiens, C., Chaudret, B. (1998). *Phys. Rev. B*, 57, 2925.
- 78. Coey, J. M. D. (1971). Phys. Rev. Lett., 27, 1140.
- 79. Schulthess, T. C., Butler, W. H. (1998). Phys. Rev. Lett., 81, 4516.
- 80. Berkowitz, A. E., Takano, K. (1999). J. Magn. Magn. Mater., 200, 552.
- 81. Wood, D. W., Dalton, N. W. (1967). Phys. Rev., 159, 384.
- Trohidou, K. N. (2005). In Surface Effects in Magnetic Nanoparticles (Fiorani, D., ed.), pp. 45–74, Springer, New York.
- 83. Kachkachi, H., Ezzir, A., Nogués, M., Tronc, E., (2000). *Eur. Phys. J. B*, **14**, 681.
- 84. Trohidou, K. N., Blackman, J. A. (1995). Phys. Rev. B, 51, 11521.
- 85. Mao, Z., Chen, D., He, Z. (2008). J. Magn. Magn. Mater., 320, 2335-2338.
- 86. Fernández, J. F., Alonso, J. J. (2009). Phys. Rev. B, 79, 214424.
- Nogués, J., Skumryev, V., Sort, J., Givord, D. (2006). *Phys. Rev. Lett.*, 97, 157203.
- Frandsen, C., Ostenfeld, C. W., Xu, M., Jacobsen, C. S., Keller, K., Lefmann, K., Mørup, S. (2004). *Phys. Rev. B*, **70**, 134416.
- De Toro, J. A., Andrés, J. P., González, J. A., Riveiro, J. M., Estarder, M., López-Ortega, A., Tsiaoussis, I., Frangis, N., Nogués, J., (2011). *J. Nanopart. Res.*, 13, 4583.
- Imre, A., Csaba, G., Ji, L., Orlov, A., Bernstein, G. H., Porod, W. (2006). Science, 311, 205.
- Binns, C., Maher, M. J., Pankhurst, Q. A., Kechrakos, D., Trohidou, K. N. (2002). *Phys. Rev. B*, 66, 184413.

- 92. Domingo, N., Fiorani, D., Testa, A. M., Binns, C., Baker, S., Tejada, J., (2008). *J. Phys. D, Appl. Phys.*, **41**, 134009.
- 93. Murray, C. B., Sun, S., Duyle, H., Betley, T. (2001). MRS Bull., 26, 985.
- 94. Kretschmer, R., Binder, K. (1979). Z. Phys. B, 34(4), 375-392.
- Grzybowski, A., Gwoźdź, E., Brodka, A. (2000). *Phys. Rev. B*, 61(10), 6706–6712.
- Bahiana, M., Pereira Nunes, J. P., Altbir, D., Vargas, P., Knobel, M. (2004). J. Magn. Magn. Mater., 81(2–3), 372–377.
- Feygenson, M., Yiu, Y., Kou, A., Kim, K., Aronson, M. C. (2010). *Phys. Rev.* B, 81, 195445.
- 98. Morel, R., Brenac, A., Portemont, C. (2004). J. Appl. Phys., 95, 3757.
- 99. Kodama, R. H., Berkowitz, A. E. (1999). Phys. Rev. B, 59, 6321.
- 100. Iglesias, O., Labarta, A. (2001). Phys. Rev. B, 63, 184416.
- 101. van Lierop, J., Schofield, M. A., Lewis, L. H., Gambino, R. J. (2003). *J. Magn. Magn. Mater.*, **264**, 146.
- 102. Vasilakaki, M., Eftaxias, E., Trohidou, K. N. (2008). *Phys. Status Solidi A*, 205, 1865.
- 103. Domingo, N., Testa, A. M., Fiorani, D., Binns, C., Baker, S., Tehada, J. (2007). *J. Magn. Magn. Mater.*, **316**, 155.
- Kechrakos, D., Trohidou, K. N., (2008). J. Nanosc. Nanotech., 8, 2929– 2943.
- 105. Kechrakos, D., Trohidou, K. N., Vasilakaki, M. (2007). J. Magn. Magn. Mater., 316, e291–e294.

"A compendium of contemporary experimental and computational research on magnetic phenomena, Magnetic Nanoparticle Assemblies provides excellent insight into the compelling issues at the forefront of the discipline. The breadth of topics that are addressed in this text, contributed by some of the leading researchers within the field, will be of useful reference to students, scientists, and engineers working at the frontier of magnetism within nanoparticle ensembles."

Prof. James H. Dickerson Brown University, USA

"This book is a well-balanced collection of review articles, by well-known specialists in the field, on intrinsic and collective effects on the equilibrium and time-dependent properties of assemblies of magnetic nanoparticles. It covers a great deal of experimental and numerical work together with some of the most promising applications. It is a valuable addition to the series of textbooks on the interplay between intrinsic and collective behaviour in nanostructures."

> **Prof. Hamid Kachkachi** University of Perpignan, France

Magnetic nanoparticles with diameters in the range of a few nanometers are today at the cutting edge of modern technology and innovation because of their use in numerous applications ranging from engineering to biomedicine. A great deal of scientific interest has been focused on the functionalization of magnetic nanoparticle assemblies. The understanding of interparticle interactions is necessary to clarify the physics of these assemblies and their use in the development of high-performance magnetic materials.

This book reviews prominent research studies on the static and dynamic magnetic properties of nanoparticle assemblies, gathering together experimental and computational techniques in an effort to reveal their optimized magnetic properties for biomedical use and as ultra-high magnetic recording media.



Kalliopi N. Trohidou received her PhD from the University of Athens in 1988 with funding from the Greek Atomic Energy Agency, the British Council, and the Rutherford Appleton Laboratory. She worked in Great Britain as research fellow at the Rutherford Appleton Laboratory (1988–1989) and the University of Reading (1989–1990). From 1991 to 1993 she was research fellow at the Institute of Materials Science in NCSR Demokritos in Athens and then professor in the Department of Physics, Chemistry and Materials Technology at the Technical University of Piraeus (1993–1995). Her current research interests are theoretical studies and computational modeling of nanostructured materials. Dr. Trohidou has published more than 80 articles in scientific journals and several chapters in books. At present she is deputy director of the Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems and head of the Computational Materials Science group.



