

Contents

1	Introduction	1
2	Theoretical Background	5
2.1	Superparamagnetism	6
2.2	Scattering methods applied to magnetic nanoparticles	9
2.2.1	Structural correlations on the atomic scale	10
2.2.1.1	Bragg scattering	11
2.2.1.2	Total scattering and the Pair Distribution Function	14
2.2.1.3	X-ray absorption techniques	17
2.2.2	Nanoparticle Morphology: Small-Angle Scattering	19
2.2.2.1	Form factors	21
2.2.2.2	Structure factors	23
2.2.2.3	Size distribution	24
2.2.2.4	Instrumental resolution	26
2.2.2.5	Asymptotic behavior	27
2.2.2.6	Anomalous Small-Angle Scattering	28
2.2.3	Nanoparticle assemblies: Scattering under grazing incidence	29
2.2.3.1	Specular reflectivity	30
2.2.3.2	Off-specular reflectivity	32
2.2.3.3	Grazing Incidence Small-Angle Scattering	33
2.2.4	Nanoparticle magnetization: polarized neutron scattering	35
2.2.4.1	Scattering cross sections	36
2.2.4.2	Polarization analysis	38
2.2.4.3	SANSPOL	39
3	Instruments	41
3.1	Small-angle Scattering	42
3.1.1	B1 - JUSIFA	42
3.1.2	SWING	43
3.1.3	ID01	44

3.1.4	KWS2	45
3.1.5	D22	45
3.2	Reflectivity	46
3.2.1	TREFF	46
3.3	Wide angle scattering	47
3.3.1	6-ID-D	47
3.4	Absorption Spectroscopy	48
3.4.1	SAMBA	48
3.5	Polarization Analysis	48
3.5.1	DNS	48
3.5.2	J-NSE	49
3.5.3	IN12	51
4	Cobalt Nanoparticles	53
4.1	Nanoparticle Synthesis	54
4.2	Methods	59
4.2.1	Sample preparation	59
4.2.1.1	Co(AOT) ₂	59
4.2.1.2	Cobalt nanoparticles standard synthesis route	62
4.2.1.3	Particle extraction	63
4.2.1.4	Concentration variation	64
4.2.1.5	Temperature variation	64
4.2.1.6	Addition of nonionic and anionic surfactants	65
4.2.1.7	Microemulsion	68
4.2.1.8	Variation of the reducing agent	69
4.2.1.9	Decomposition of dicobalt octacarbonyl	72
4.2.2	Characterization and data treatment	72
4.2.2.1	Magnetization measurements	72
4.2.2.2	SAXS	74
4.2.2.3	ASAXS	76
4.2.2.4	SANS	76
4.2.2.5	XAS	77
4.2.2.6	UV-VIS spectroscopy	78
4.3	Results and Discussion	78
4.3.1	Preparation and Characterization of Cobalt nanoparticles	78
4.3.1.1	Nanoparticle preparation	78
4.3.1.2	Magnetization measurements	82

4.3.1.3	Partial and full oxidation	85
4.3.1.4	Small-angle X-ray scattering	89
4.3.1.5	Anomalous small-angle X-ray scattering	95
4.3.1.6	Particle extraction	96
4.3.1.7	Small-angle neutron scattering	100
4.3.1.8	Summary: Results of the primary characterization	104
4.3.2	Possible Routes to Size Variation	106
4.3.2.1	Concentration Variation	106
4.3.2.2	Temperature Variation	107
4.3.2.3	Addition of nonionic and anionic surfactants	111
4.3.2.4	Microemulsion	119
4.3.2.5	Variation of the reducing agent	125
4.3.2.6	Nanoparticle growth by decomposition of dicobalt octacarbonyl	134
4.4	Summary	136
5	Iron Oxide Nanoparticles	139
5.1	Morphological and Magnetic Characterization	140
5.1.1	Introduction of the samples	140
5.1.2	Methods	143
5.1.2.1	Sample preparation and data treatment	143
5.1.2.2	Oleic acid	145
5.1.2.3	Development of the cubic form factors	148
5.1.3	Results and Discussion	152
5.1.3.1	SAXS: size and size distribution	152
5.1.3.2	SANS: core shell structure	156
5.1.3.3	Magnetization measurements	162
5.1.4	Summary	165
5.2	Local Structure	167
5.2.1	Introduction	167
5.2.2	Methods	168
5.2.2.1	Wide Angle Scattering	168
5.2.2.2	XAS	170
5.2.2.3	The magnetite/maghemite structure	171
5.2.3	Results and Discussion	172
5.2.3.1	Selection of samples for evaluation	172
5.2.3.2	Particle size	179

5.2.3.3	Lattice constant	179
5.2.3.4	Oxidation state	184
5.2.3.5	Local structural distortions	186
5.2.4	Summary	192
5.3	Magnetic Structure	195
5.3.1	Introduction	195
5.3.2	Methods	196
5.3.2.1	Sample preparation and data treatment	196
5.3.2.2	Development of the magnetic form factor model	197
5.3.2.3	Determination of the magnetization density	200
5.3.3	Results and Discussion	201
5.3.3.1	Approaching the magnetic form factor	201
5.3.3.2	Magnetic interparticle correlations	220
5.3.4	Summary	229
5.4	Superlattices	231
5.4.1	Introduction	231
5.4.2	Methods	233
5.4.2.1	Deposition Techniques	233
5.4.2.2	Data treatment	235
5.4.2.3	GISAXS evaluation	237
5.4.2.4	Reflectivity evaluation	240
5.4.3	Results and Discussion	241
5.4.3.1	lateral order in magnetic nanoparticle assemblies	241
5.4.3.2	Into the third dimension: determination of the nanocubes superstructure	245
5.4.3.3	Supercrystals of nanospheres	252
5.4.3.4	Nanocubes revisited	257
5.4.3.5	Routes to a long range ordered nanoparticle monolayer	266
5.4.3.6	Magnetization measurements	268
5.4.4	Summary	270
6	Not So Small Angle Neutron Scattering with Polarization Analysis	273
6.1	Introduction	274
6.2	Methods	275
6.2.1	Sample preparation and data treatment	275
6.2.1.1	DNS	275
6.2.1.2	J-NSE	275

6.2.1.3	IN12	275
6.2.2	Correction of imperfect polarization	276
6.2.3	Multiple scattering correction	279
6.3	Results and Discussion	283
6.3.1	DNS	283
6.3.2	J-NSE	286
6.3.3	IN12	292
6.3.4	Comparison of the results	295
6.4	Summary	296
7	Conclusive Remarks	299
	Appendices	307
A	Abbreviations & Physical Constants	308
B	Chemical reagents	310
C	Sample holders	311
C.1	PPMS sample holder	311
C.2	MPMS sample holder	312
D	Form factors used for small-angle scattering	313
D.1	Truncated cube	313
D.2	Truncated cube with truncated cubic shell	315
D.3	Truncated cube with spherical shell	316
D.4	Magnetic contrast variation	318
D.5	Magnetic-nuclear cross term	323
E	Refinement parameters	329
E.1	Diffraction	329
E.2	PDF	330
E.3	EXAFS	330
F	Neutron PDF	332
	Bibliography	334