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Investigation of structural and magnetic properties of rare earth doped Co-Ferrite nanoparticles using X ray powder diffraction, Mossbauer effect spectroscopy and neutron diffraction measurements.

Mohammed Yehia Elbahrawy

Professor – Nuclear Solid State Physics

Egyptian Atomic Energy Authority

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M. Yehia
A. Hashhash
M. Kaiser

Joint Institute for Nuclear Research
Frank Laboratory of Neutron Physics

I. Bobrikov

Institute of Physics and Technology, Mongolian Academy of Sciences

E. Uyanga

Outline

1

Introduction

- Magnetism
- Ferrites

2

Experimental

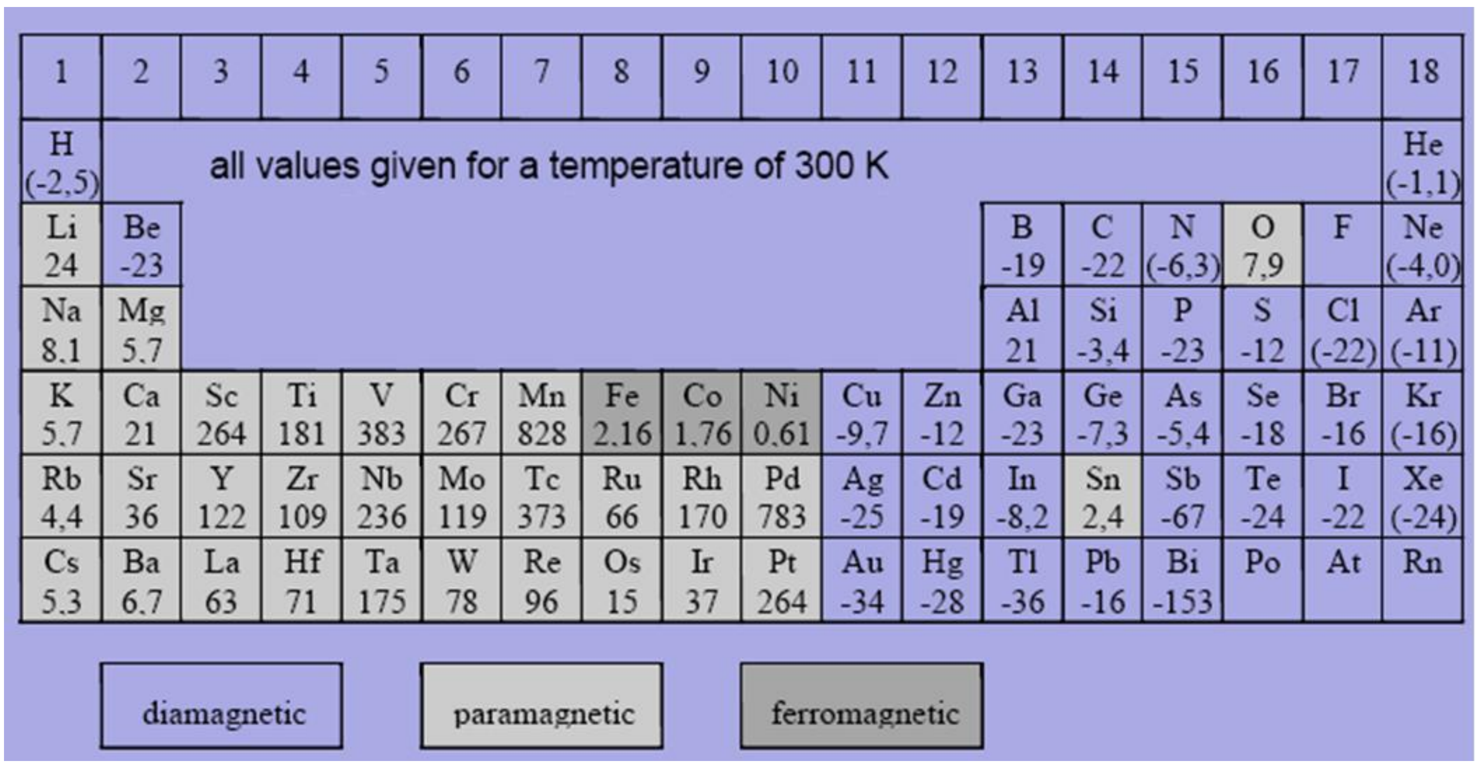
- Preparation
- Techniques

3

$CoFe_{2-x}Ce_xO_4$

- X-ray powder diffraction (XRD)
- Transmission Electron Microscopy (TEM)
- Vibrating Sample Magnetometer (VSM)
- Mössbauer Effect Spectroscopy
- Neutron Diffraction

- Magnetic moments originate from unpaired electrons which causes orbital and spin moment.



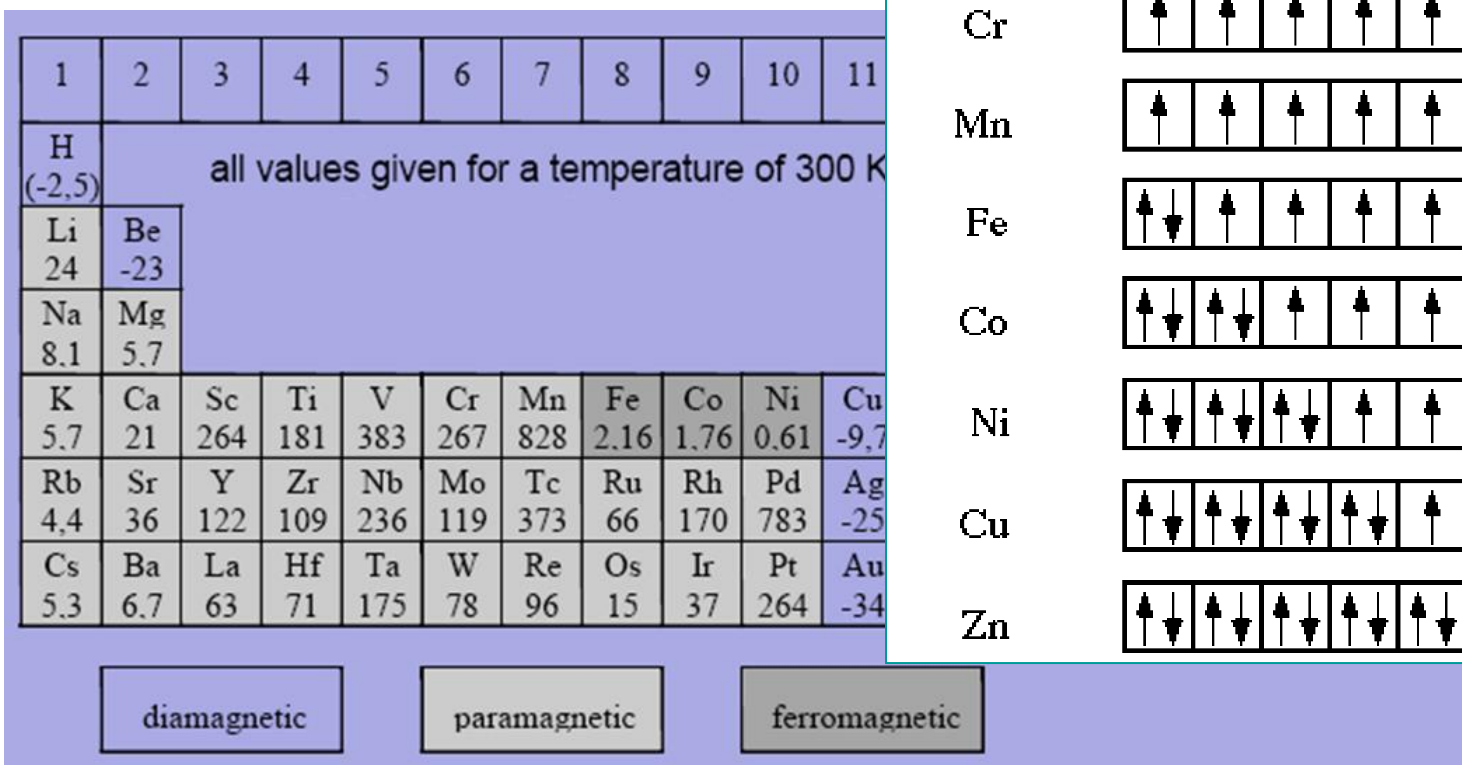
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H (-2,5)	all values given for a temperature of 300 K																He (-1,1)
Li 24	Be -23											B -19	C -22	N (-6,3)	O 7,9	F	Ne (-4,0)
Na 8.1	Mg 5.7											Al 21	Si -3,4	P -23	S -12	Cl (-22)	Ar (-11)
K 5.7	Ca 21	Sc 264	Ti 181	V 383	Cr 267	Mn 828	Fe 2.16	Co 1.76	Ni 0.61	Cu -9,7	Zn -12	Ga -23	Ge -7,3	As -5,4	Se -18	Br -16	Kr (-16)
Rb 4,4	Sr 36	Y 122	Zr 109	Nb 236	Mo 119	Tc 373	Ru 66	Rh 170	Pd 783	Ag -25	Cd -19	In -8,2	Sn 2,4	Sb -67	Te -24	I -22	Xe (-24)
Cs 5.3	Ba 6.7	La 63	Hf 71	Ta 175	W 78	Re 96	Os 15	Ir 37	Pt 264	Au -34	Hg -28	Tl -36	Pb -16	Bi -153	Po	At	Rn

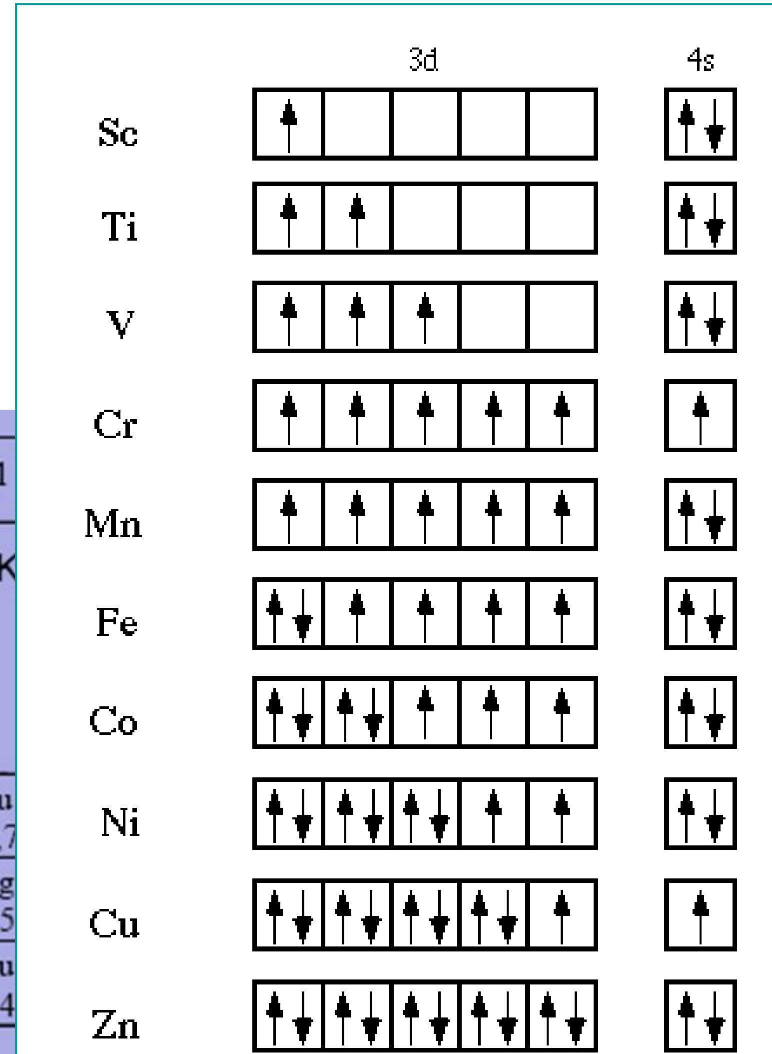
diamagnetic | paramagnetic | ferromagnetic

Introduction

Magnetism

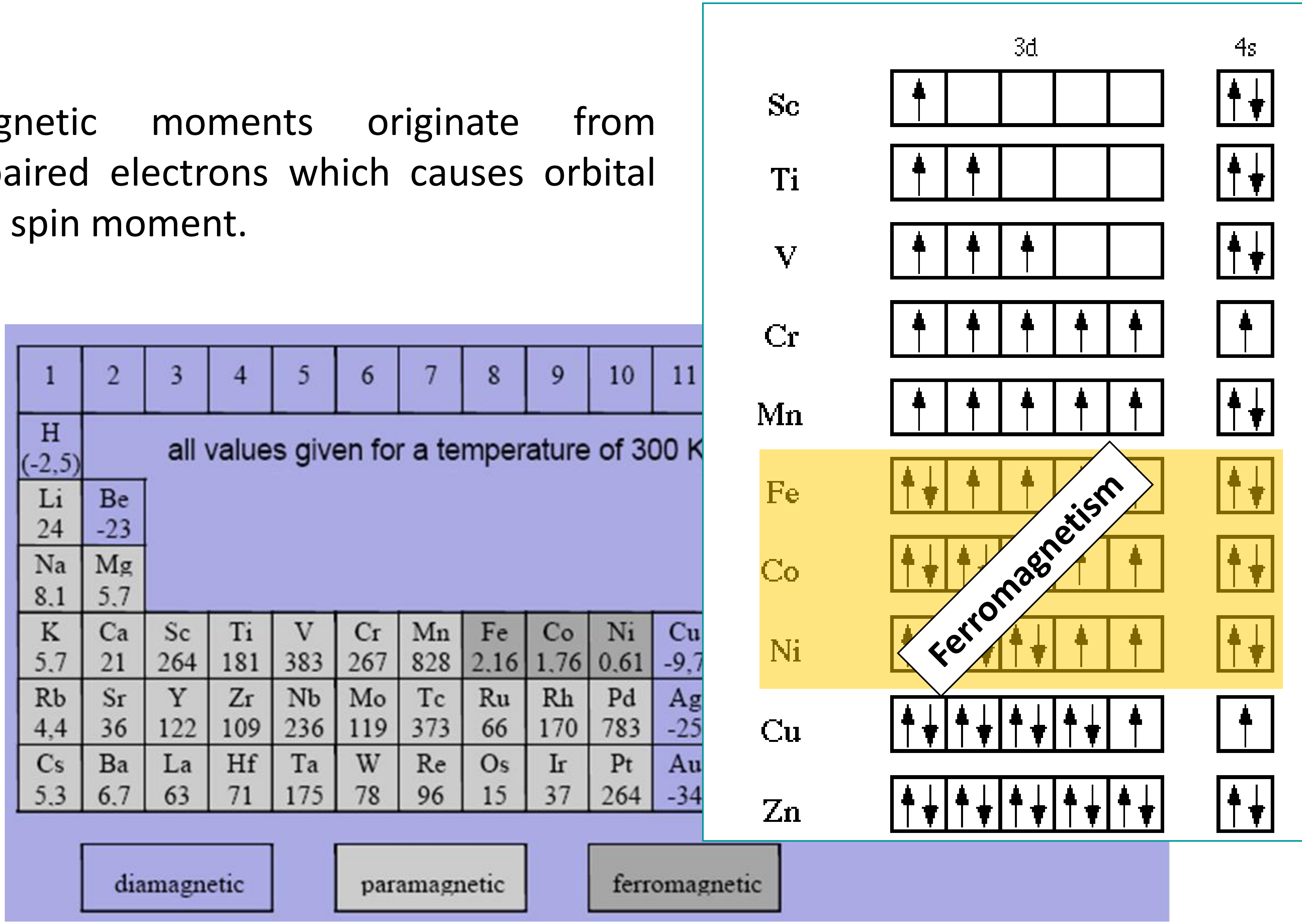
➢ Magnetic moments originate from unpaired electrons which causes orbital and spin moment.





Introduction
Magnetism

- Magnetic moments originate from unpaired electrons which causes orbital and spin moment.



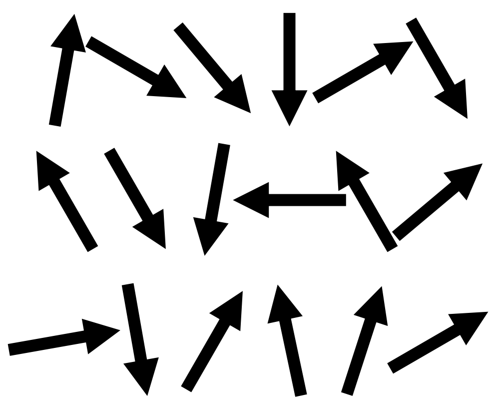
Exchange interaction vs thermal fluctuation

Heisenberg Hamiltonian

$$H = J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j$$

Randomizing thermal effects

$$\mathrm{K_B T}$$

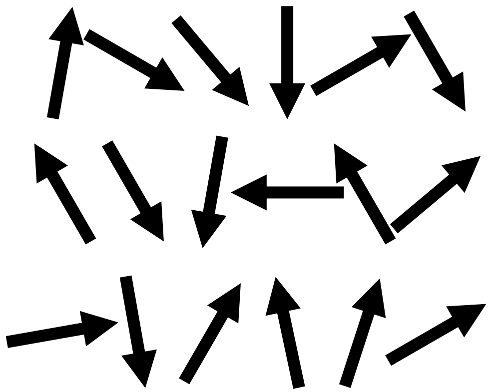


Paramagnet

thermal fluctuation higher than the exchange energy

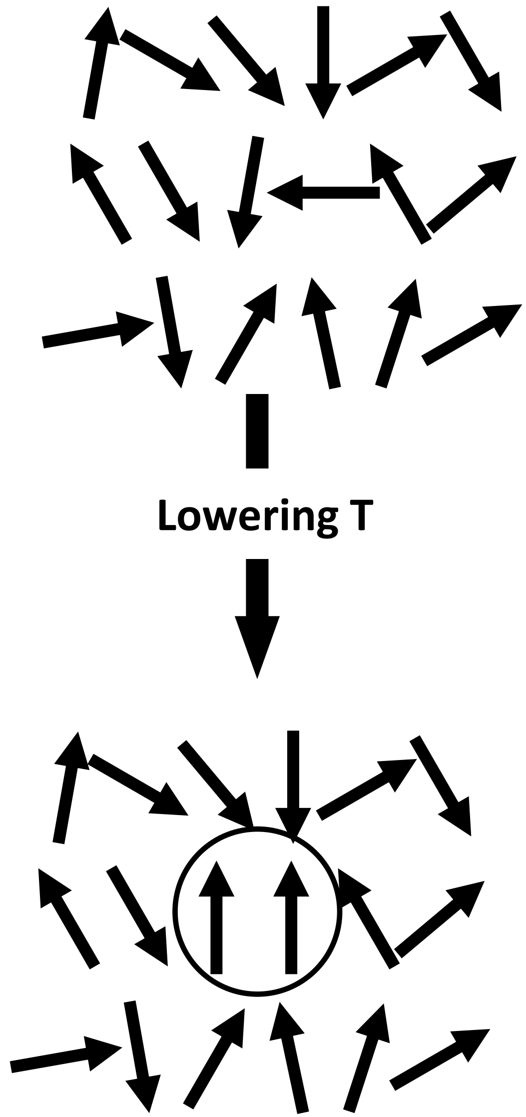
Introduction

Magnetism



Paramagnet

Thermal fluctuation stronger than the exchange energy



Paramagnet

Thermal fluctuation stronger than the exchange energy

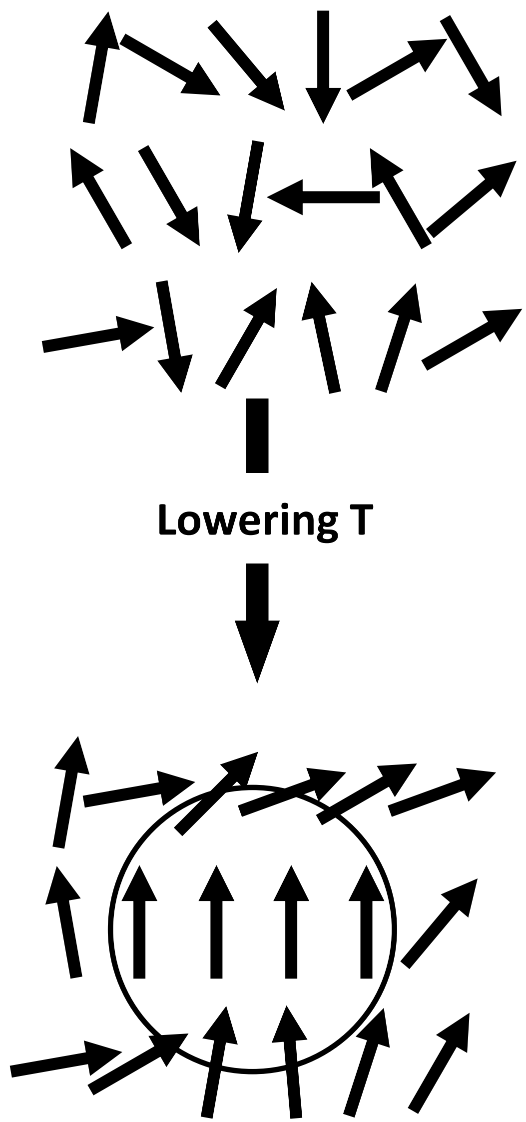
Thermal fluctuation weaker than the exchange energy

Growing magnetic correlation length
From short range to long range

Ferromagnetic
J -ve

Paramagnet

Thermal fluctuation stronger than the exchange energy



Thermal fluctuation weaker than the exchange energy

Ferromagnetic

J -ve

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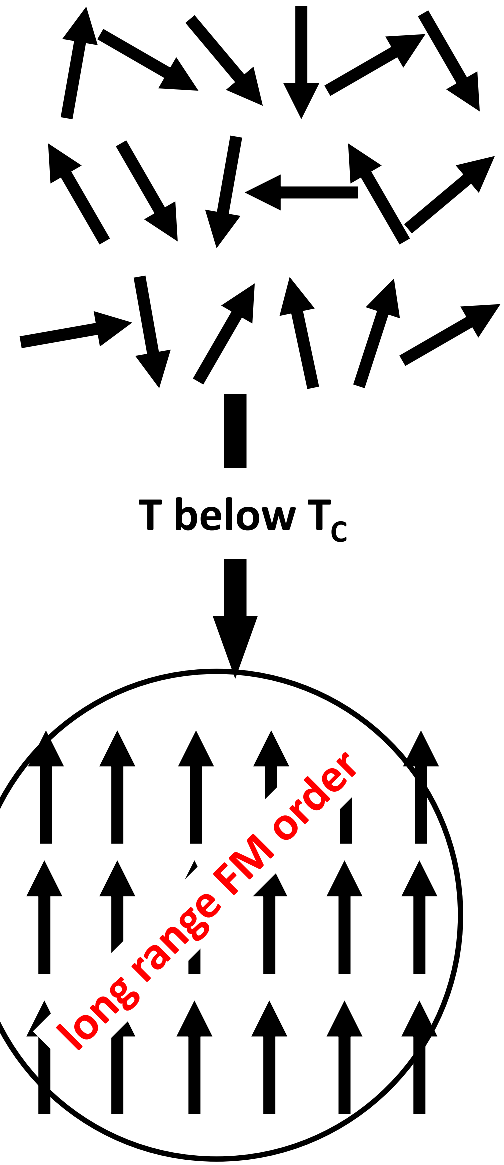

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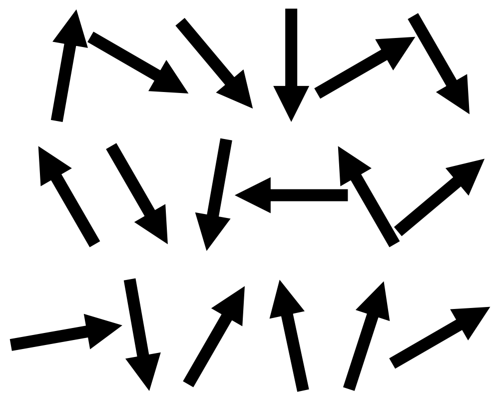
Introduction | Magnetism

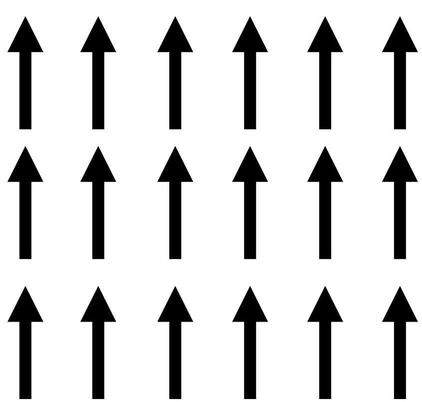


Paramagnet

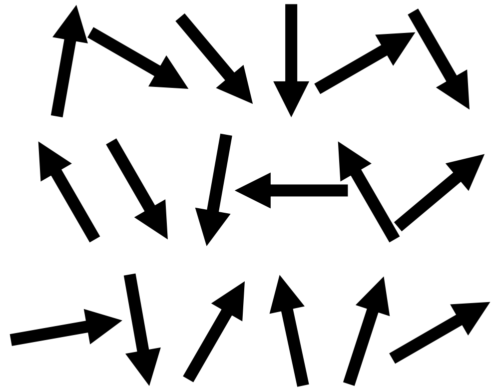
Thermal fluctuation stronger than the exchange energy

Lowering T below T_C or T_N

Thermal fluctuation weaker than the exchange energy



Introduction | Magnetism



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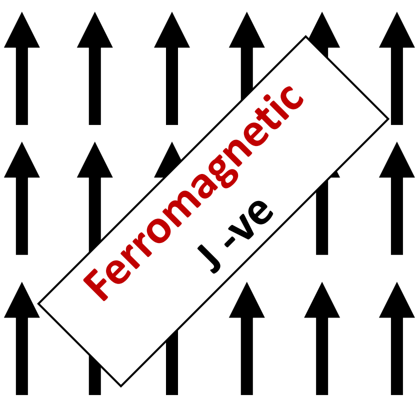

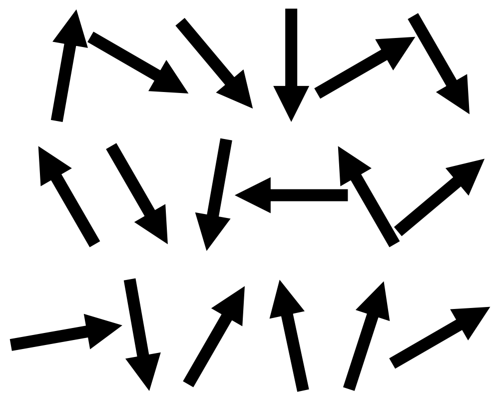

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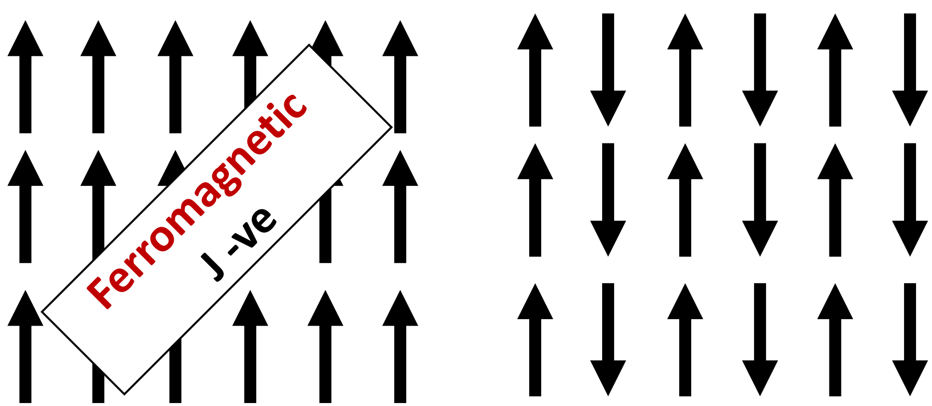
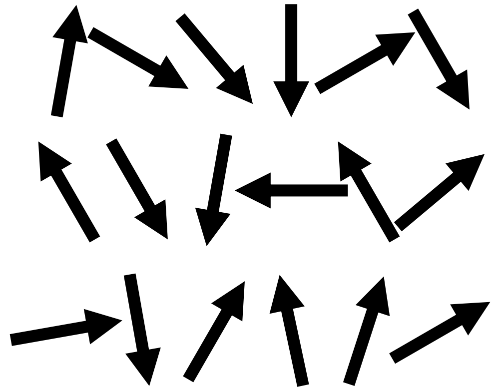


Introduction | Magnetism



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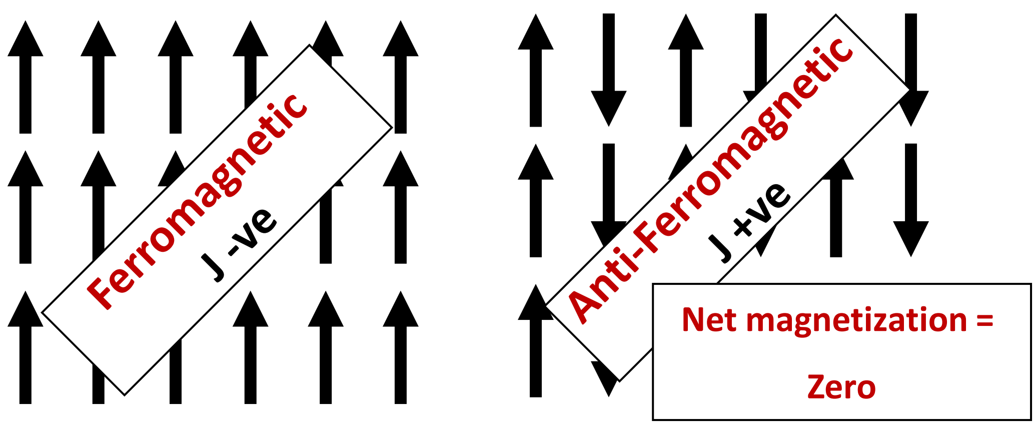

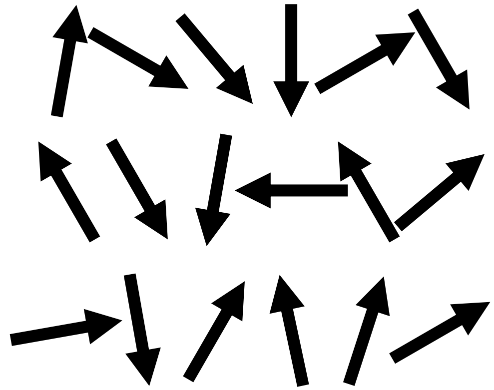

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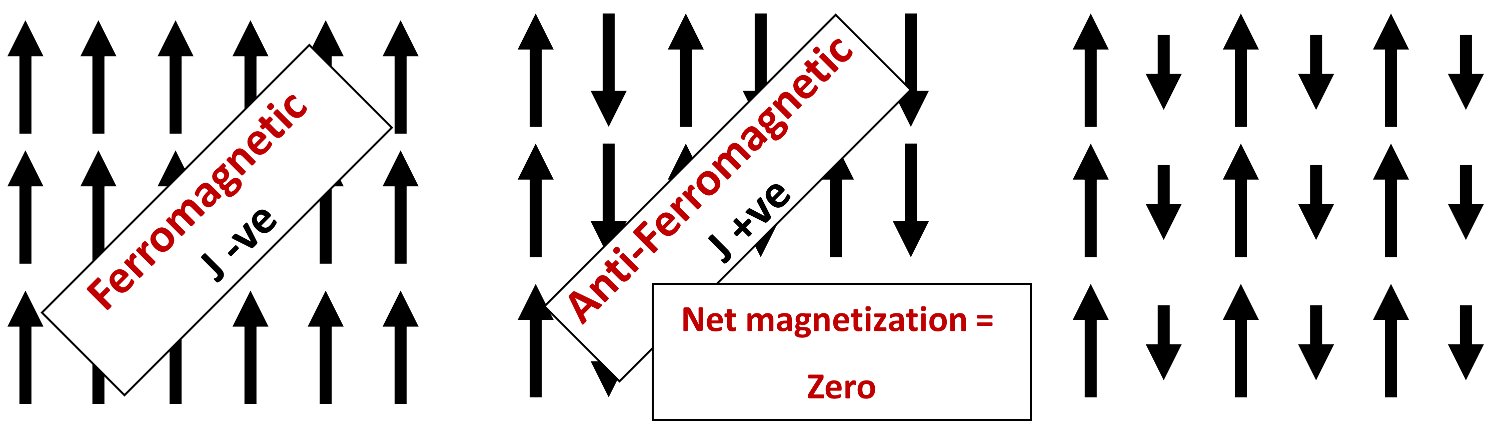
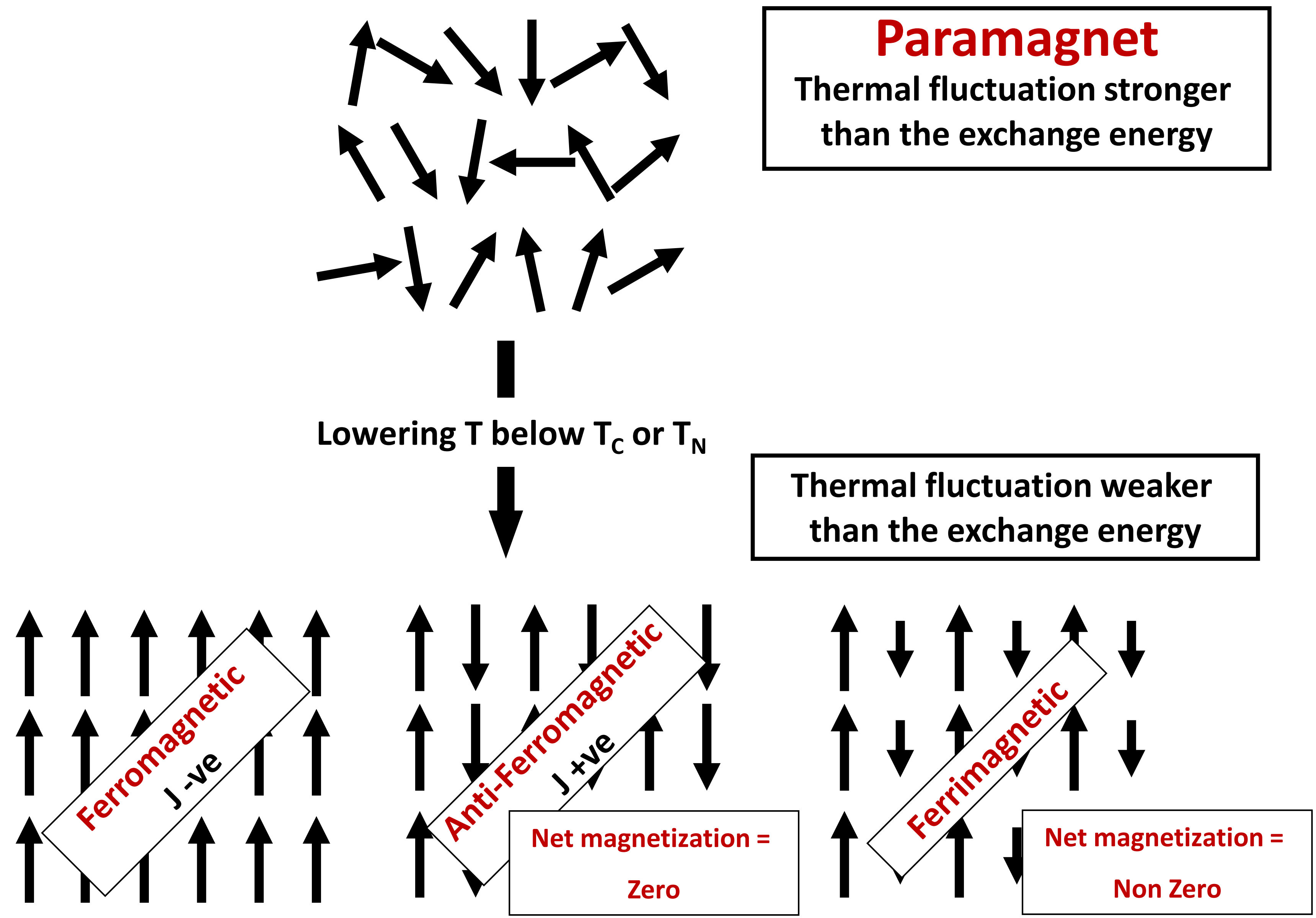


Introduction | Magnetism



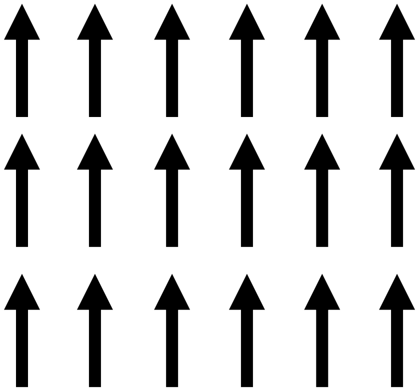
Landau theory for phase transition

Order Parameter

Landau theory for phase transition

Order Parameter

Ferromagnetic



Internal field

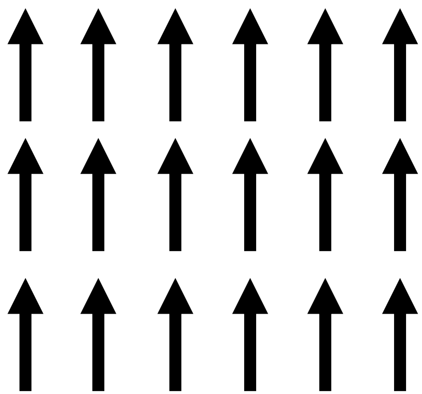
Introduction

Magnetism

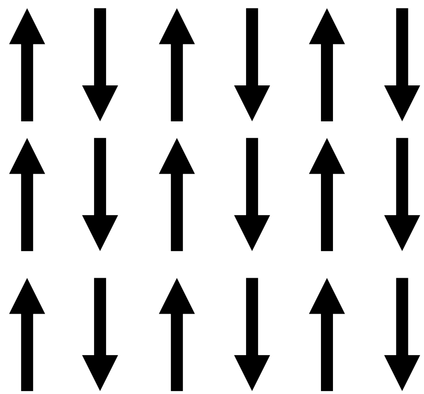
Landau theory for phase transition

Order Parameter

Ferromagnetic



Anti-Ferromagnetic



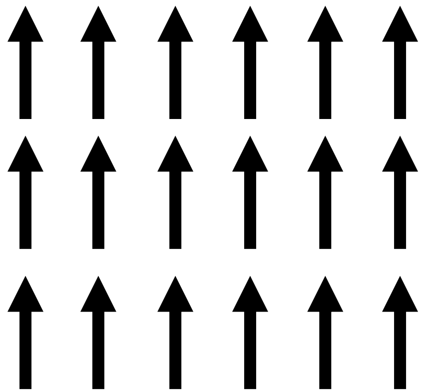
Internal field

Introduction Magnetism

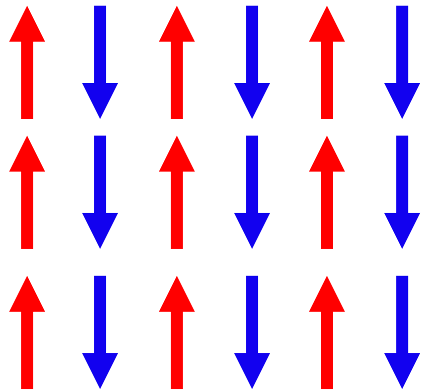
Landau theory for phase transition

Order Parameter

Ferromagnetic



Anti-Ferromagnetic



Internal field

Sub lattice magnetization

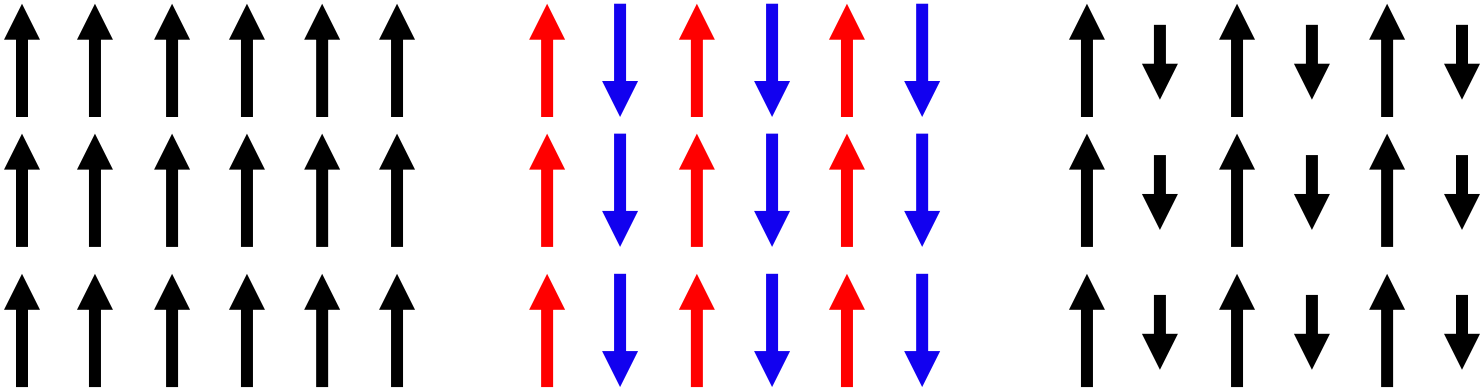
Landau theory for phase transition

Order Parameter

Ferromagnetic

Anti-Ferromagnetic

Ferrimagnetic



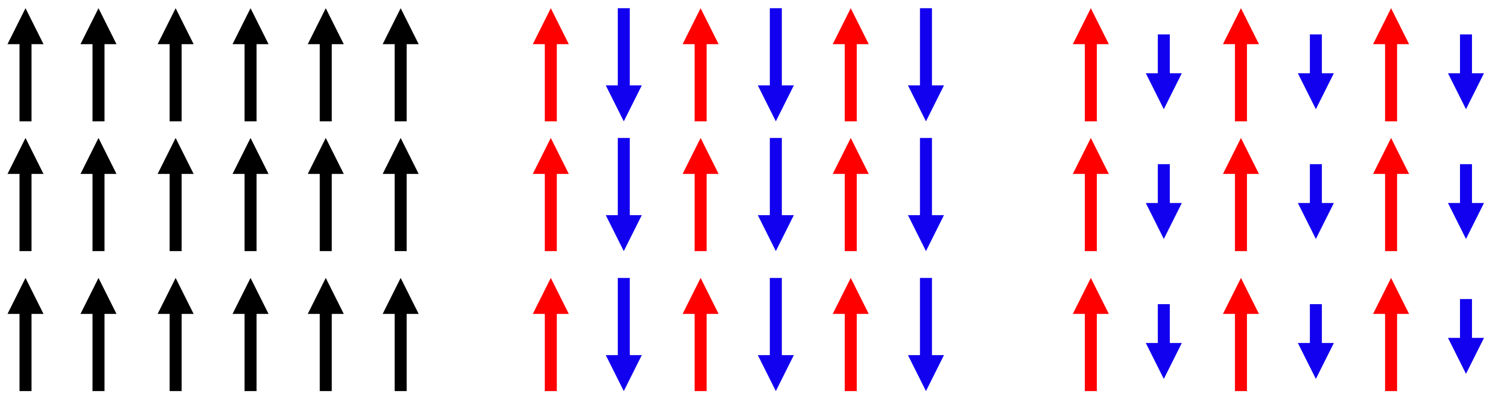
Internal field

Sub lattice magnetization

Introduction | Magnetism

Order Parameter

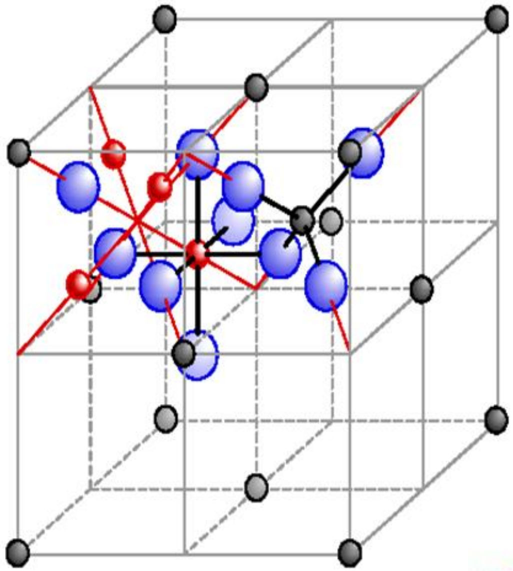
Ferromagnetic	Anti-Ferromagnetic	Ferrimagnetic



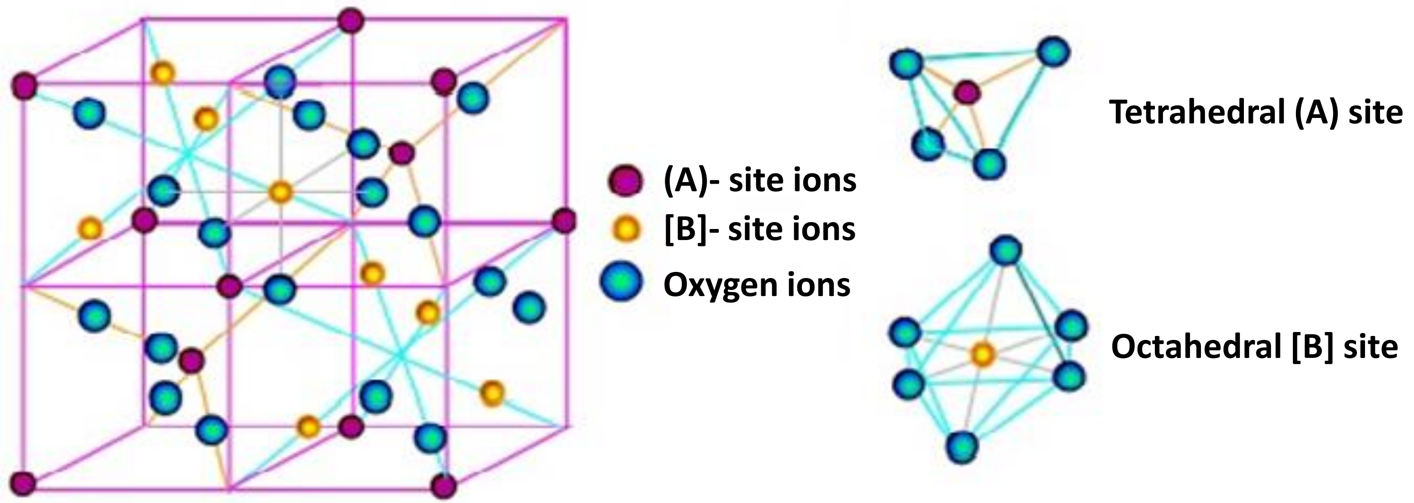
Internal field	Sub lattice magnetization	Sub lattice magnetization

Spinel Ferrite

Introduction



Spinel structure MB_2O_4



64 tetrahedral sites ⇨ 8 occupied

32 octahedral sites ⇨ 16 occupied

Spinel Ferrite

Introduction

Regular spinel structure

Divalent metal ions in the tetrahedral (A)-site and trivalent metal ions in the octahedral [B]-site

$$(M^{2+})_A[Fe_2^{3+}]_B O_4$$

Inverse spinel structure

Half of the [B]-sites (8 sites) are occupied by divalent metal ions and the remaining half of the [B]-sites (8 sites) and all the (A)-sites are occupied by the trivalent metal ions

$$(Fe^{3+})_A[M^{2+}Fe^{3+}]_B O_4$$

Partial inverse spinel structure

$$(M_{1-\delta}^{2+}Fe_{\delta}^{3+})_A[M_{\delta}^{2+}Fe_{2-\delta}^{3+}]_B O_4$$

δ degree of inversion

Néel theory: $M = M_B - M_A$

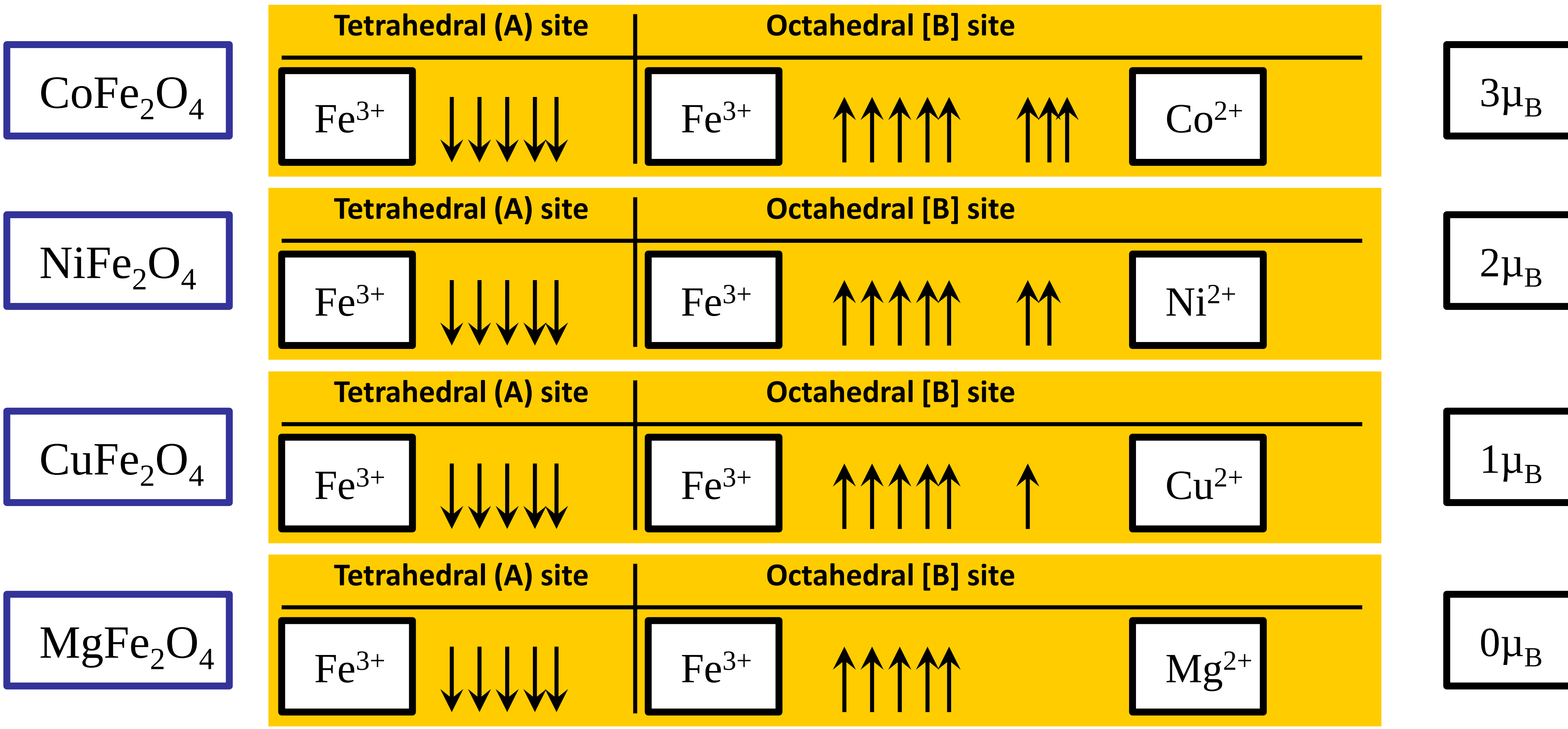
$$(Fe^{3+})_A[M^{2+}Fe^{3+}]_B O_4$$

Compound	Tetrahedral (A) site	Octahedral [B] site		Moment
$CoFe_2O_4$	Fe^{3+} ↓↓↓↓↓	Fe^{3+} ↑↑↑↑↑	↑↑↑ Co^{2+}	$3\mu_B$
$NiFe_2O_4$	Fe^{3+} ↓↓↓↓↓	Fe^{3+} ↑↑↑↑↑	↑↑ Ni^{2+}	$2\mu_B$
$CuFe_2O_4$	Fe^{3+} ↓↓↓↓↓	Fe^{3+} ↑↑↑↑↑	↑ Cu^{2+}	$1\mu_B$
$MgFe_2O_4$	Fe^{3+} ↓↓↓↓↓	Fe^{3+} ↑↑↑↑↑	Mg^{2+}	$0\mu_B$

Spinel Ferrite | Introduction

Néel theory: $M = M_B - M_A$

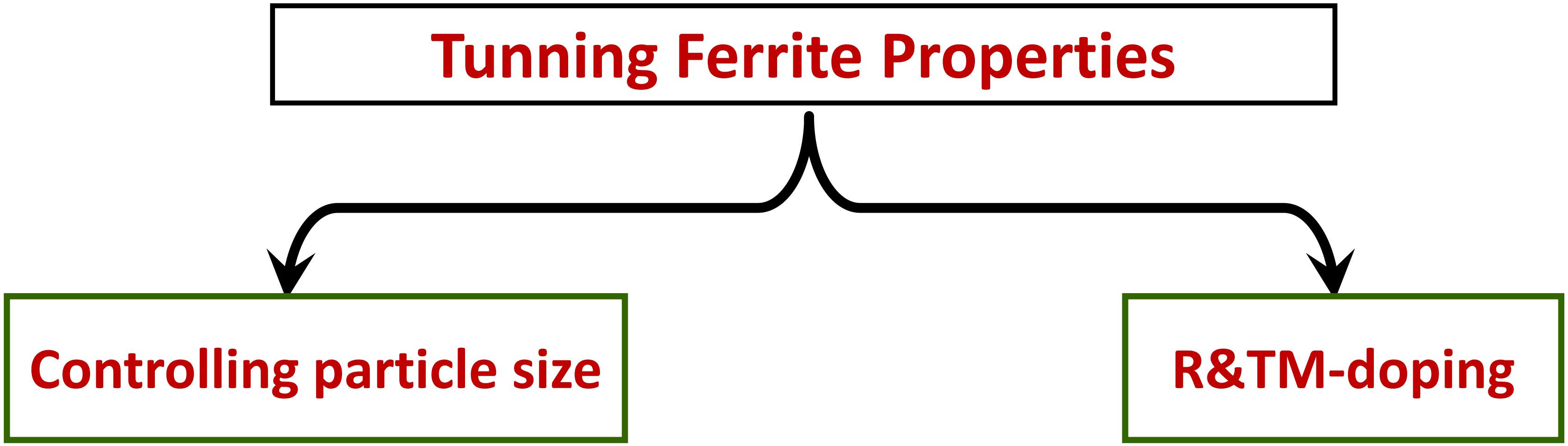
$(Fe^{3+})_A[M^{2+}Fe^{3+}]_B O_4$



1- Complex exchange interactions of the different cations between and within the A & B sites.
2- Effect of the reduced particle size.
3- Effect of defects and lattice deformation.

Applications of Ferrites

- **Ferrites have very wide rang of applications:**
  - In radio receivers to increase the sensitivity and selectivity of the receiver.
  - As cores in audio and TV transformer
  - In digital computers and data processing circuits.
  - To produce low frequency ultra sonic waves by magnetostriction principle.
  - In high-power microwave Components and Industrial Microwave Systems..
  - In the design of ferromagnetic amplifiers of microwave signals.
  - In instruments like galvanometers, ammeter, voltmeter, flex meters, speedometers, wattmeter, compasses and recorders
  - In high power circulators, isolators, couplers, phase shifters, filters, and loads for industrial, radar, medical and high energy physics applications.


Tunning Ferrite Properties
Controlling particle size
R&TM-doping

Spinel Ferrite

Introduction

Ion	A-site (Å)	B-site (Å)
r(Sm^{3+})	-	0.958
r(Gd^{3+})	-	0.938
r(Ce^{3+})	-	1.14

VS

Ion	A-site (Å)	B-site (Å)
r(Fe^{3+})	0.49	0.645
r(Ni^{2+})	0.55	0.69
r(Co^{2+})	0.38	0.745

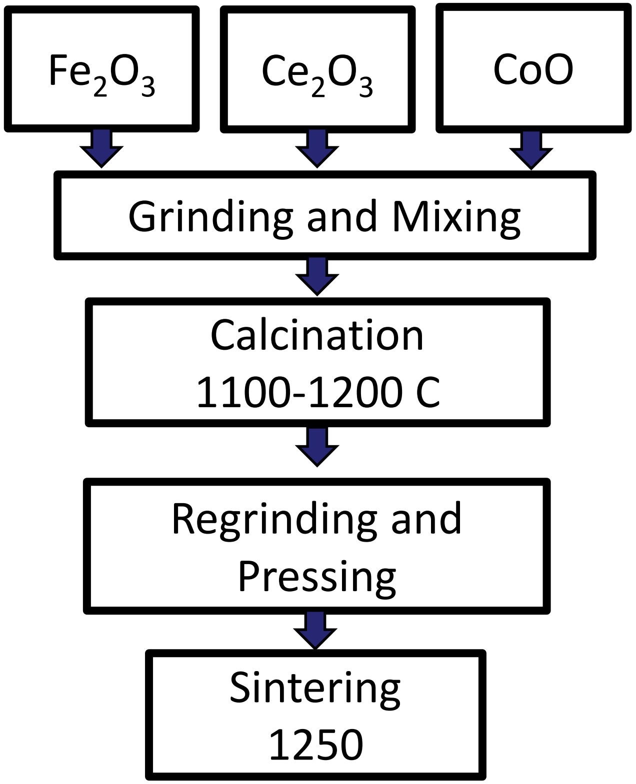
R^{3+} ions doping

- B-site
- Lattice distortion
- Diffuse to the grain boundaries
- Extra amorphous or crystalline phases
- Decrease the particle size

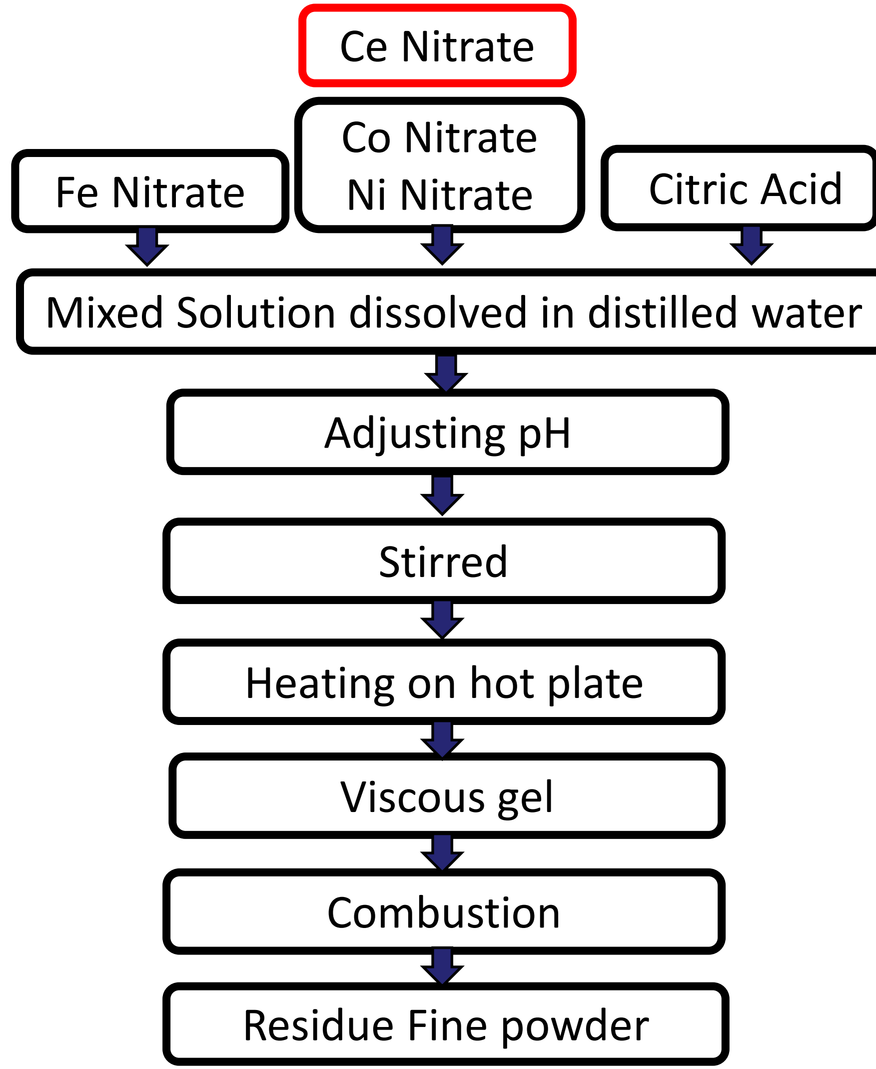
Experimental

Preparation

Standard Ceramic Method



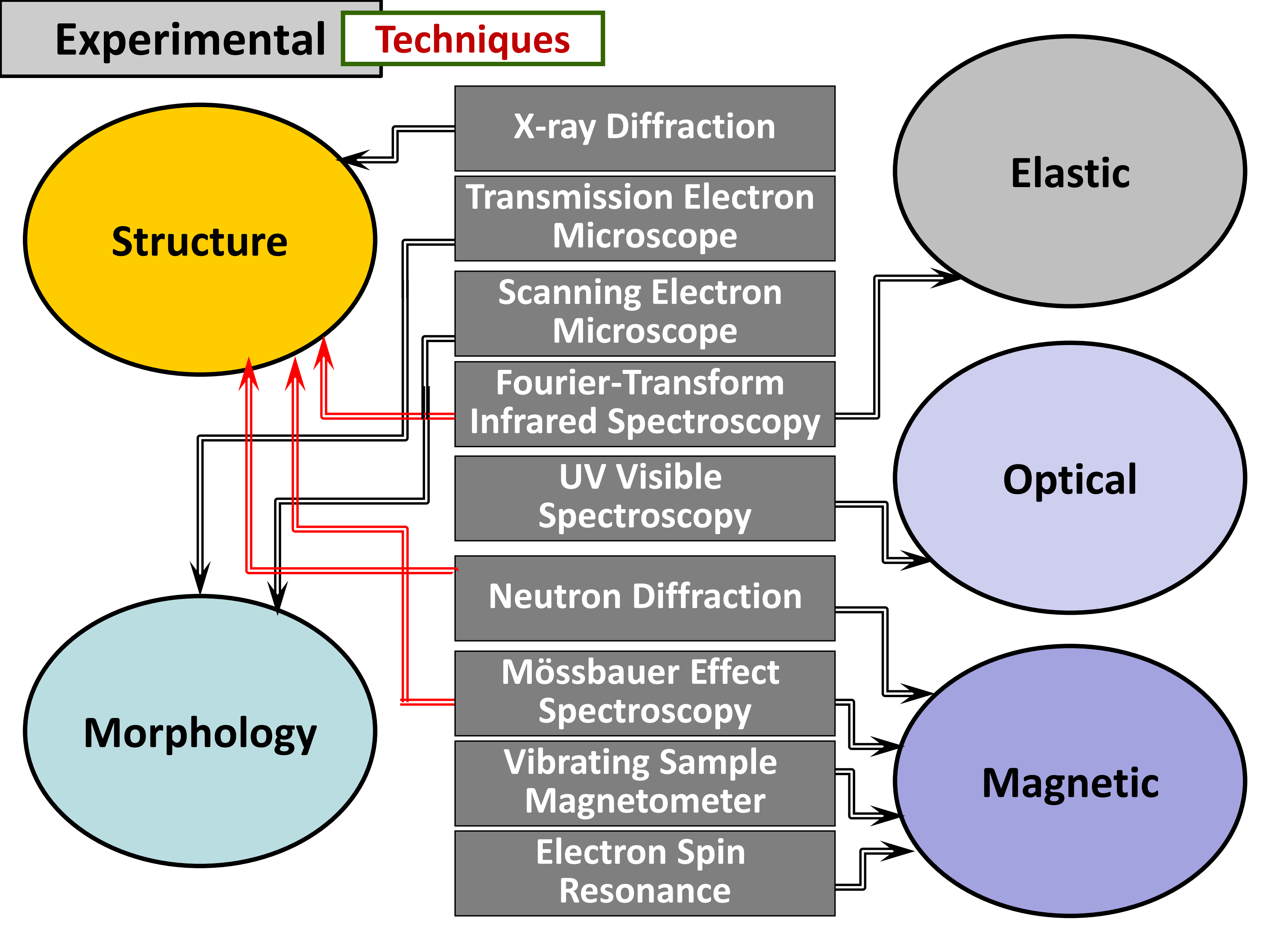
SOL-GEL Method



Experimental | Preparation

Preparation Methods

Solid State Reaction	Sol-gel
Transition metal-Rareearth Oxides	Transition metal-Rareearth Nitrates
Expensive	Reduced Cost
High Temperatures	Low Temperatures
Energy consuming	Energy saving
Bulk Material	Nano Material
Particle size - No control	Controlled Particle size



Experimental
Techniques
X-ray Diffraction
Transmission Electron Microscope
Scanning Electron Microscope
Fourier-Transform Infrared Spectroscopy
UV Visible Spectroscopy
Neutron Diffraction
Mössbauer Effect Spectroscopy
Vibrating Sample Magnetometer
Electron Spin Resonance
Structure
Morphology
Elastic
Optical
Magnetic

In this presentation

$CoFe_{2-x}Ce_xO_4$

x=0, 0.01, 0.03, 0.05, 0.07 and 0.1

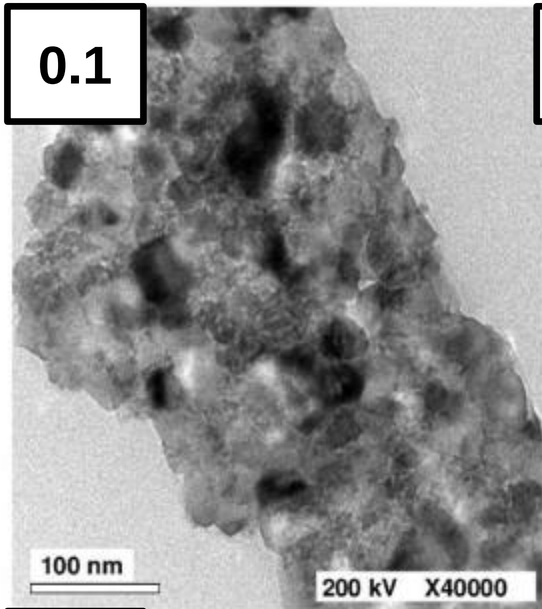
Sol-gel

- Transmission Electron Microscope
- X-ray Diffraction
- Vibrating Sample Magnetometer
- Neutron Diffraction
- Mössbauer Effect Spectroscopy

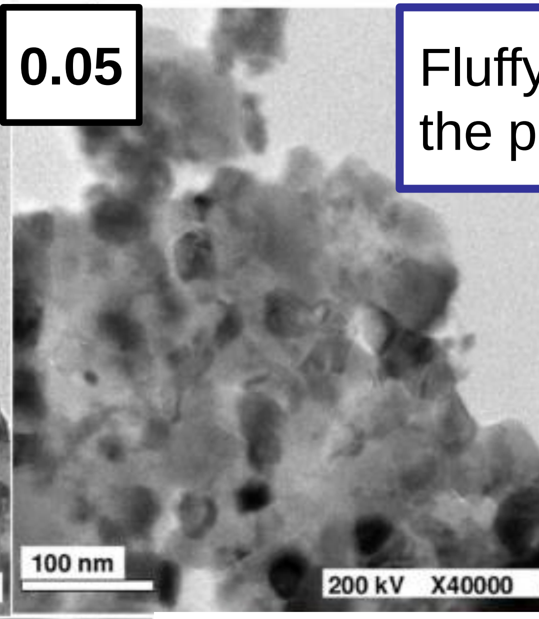
$CoFe_{2-x}Ce_xO_4$

TEM

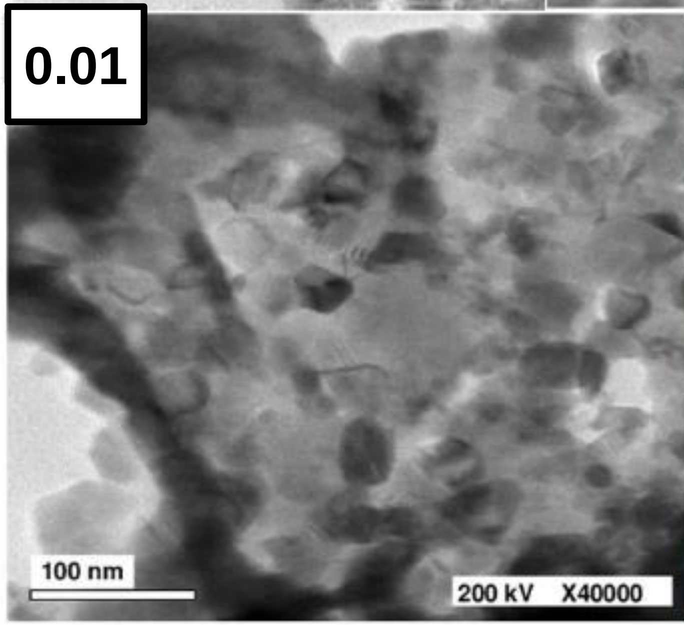
0.1



0.05



0.01

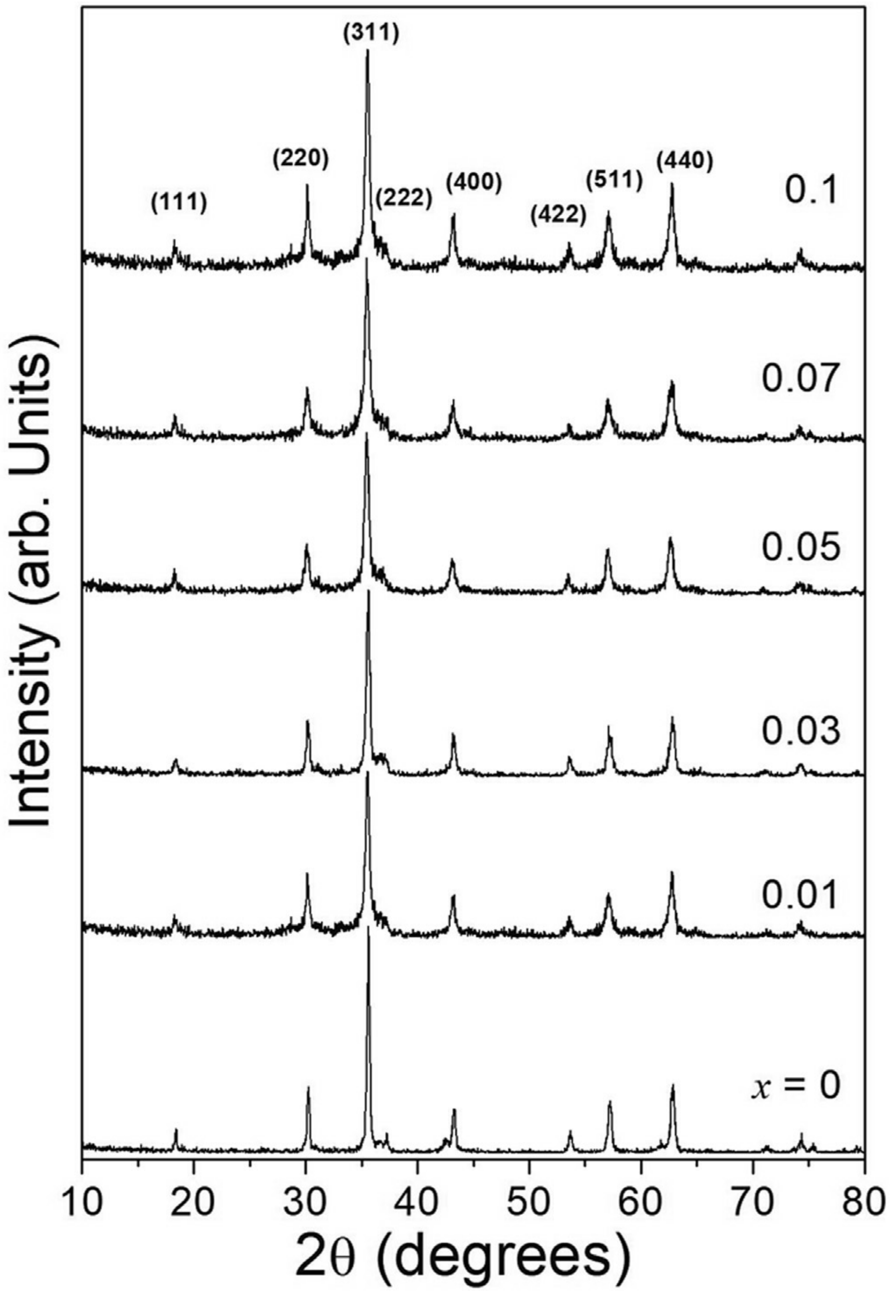


Fluffy final product for the prepared samples.

HR-TEM Micrographs

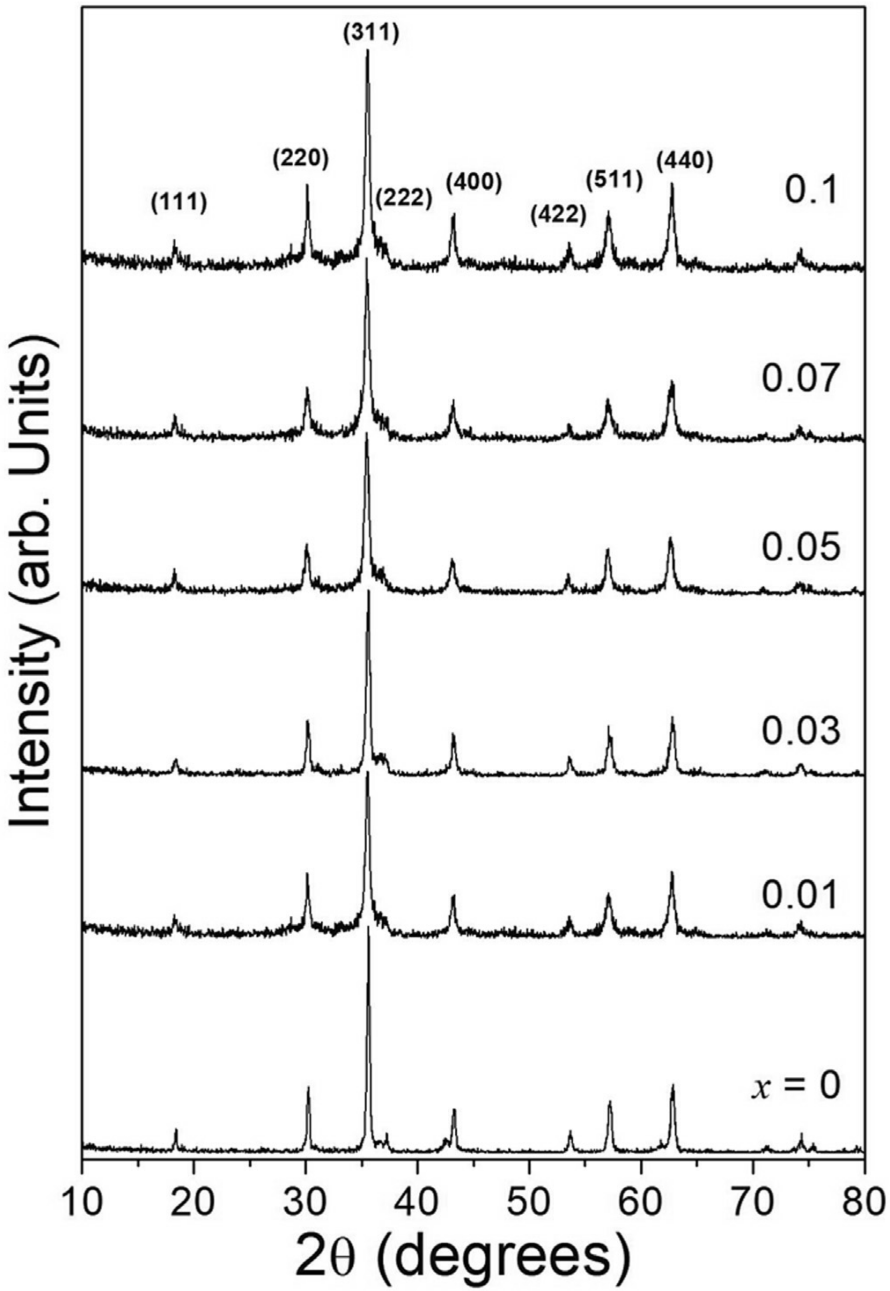
- Nano size
- Spherical shape

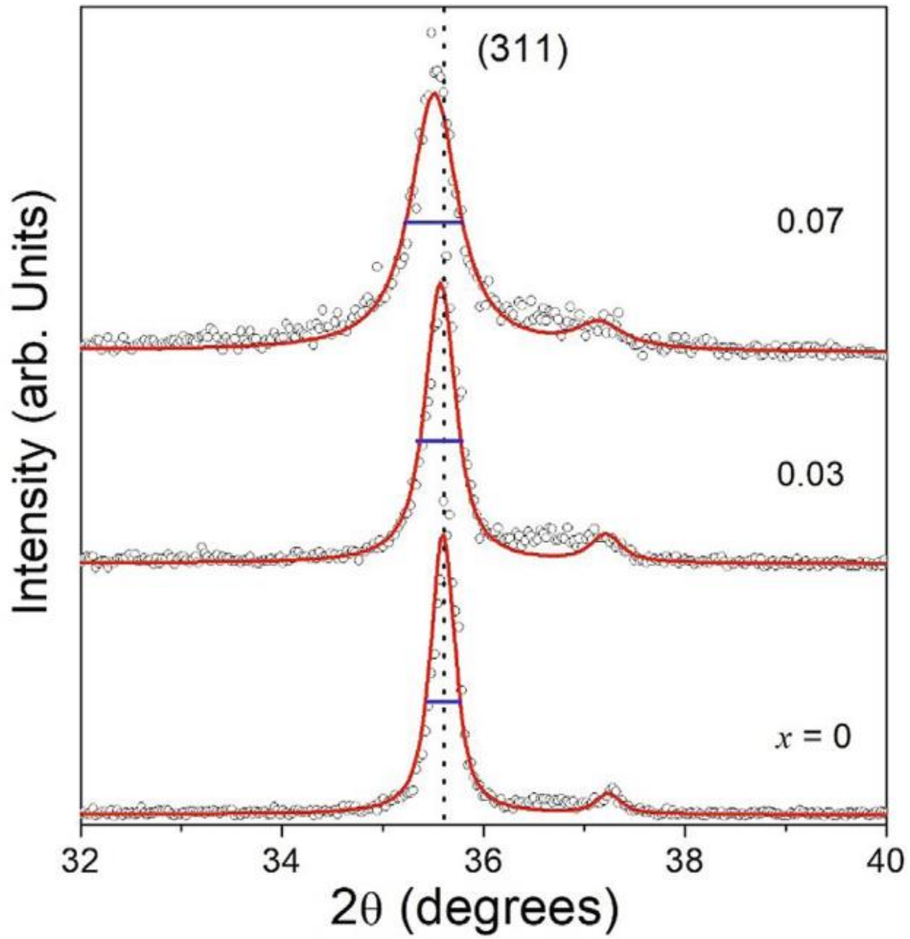
$CoFe_{2-x}Ce_xO_4$ XRD



$CoFe_{2-x}Ce_xO_4$

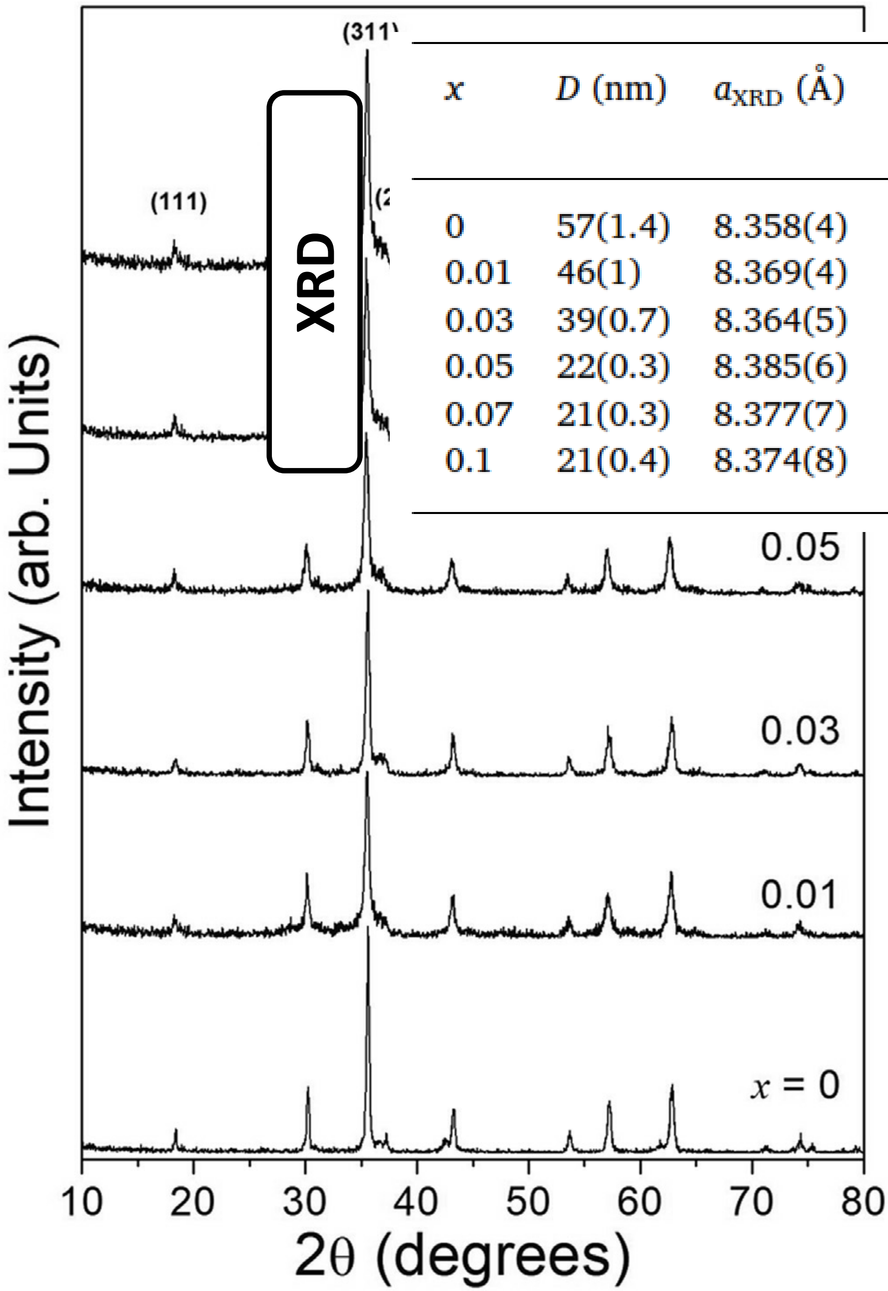
XRD





$CoFe_{2-x}Ce_xO_4$

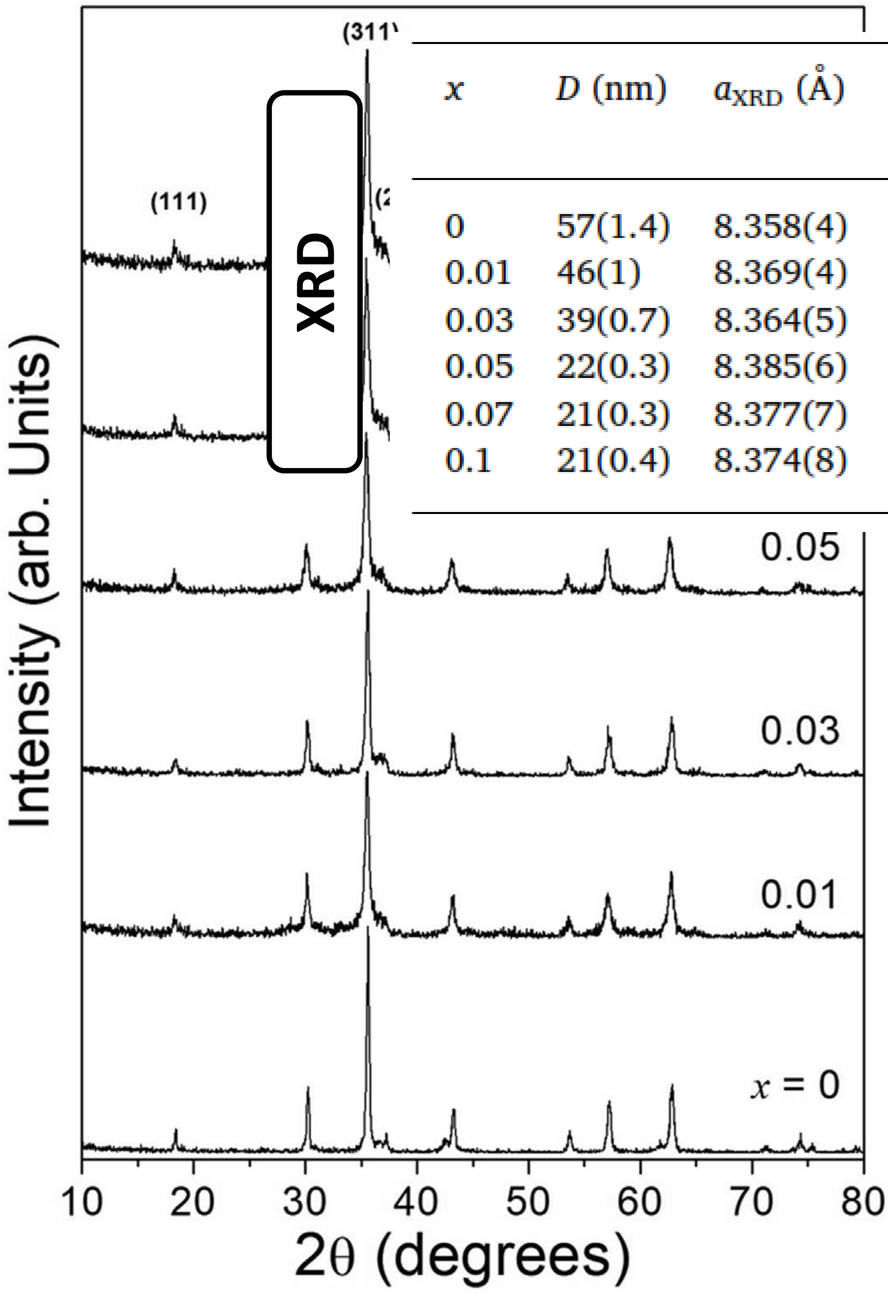
XRD



x	D (nm)	a_{XRD} (Å)	a_{th} (Å)	A-O cal. (Å)	B-O cal. (Å)	u^{3m} (Å)	u^{43m} (Å)
0	57(1.4)	8.358(4)	8.367	1.859	2.064	0.272	0.397
0.01	46(1)	8.369(4)	8.346	1.849	2.062	0.273	0.398
0.03	39(0.7)	8.364(5)	8.348	1.846	2.064	0.273	0.398
0.05	22(0.3)	8.385(6)	8.33	1.836	2.064	0.274	0.399
0.07	21(0.3)	8.377(7)	8.321	1.829	2.064	0.274	0.399
0.1	21(0.4)	8.374(8)	8.328	1.826	2.068	0.274	0.399

$CoFe_{2-x}Ce_xO_4$

XRD



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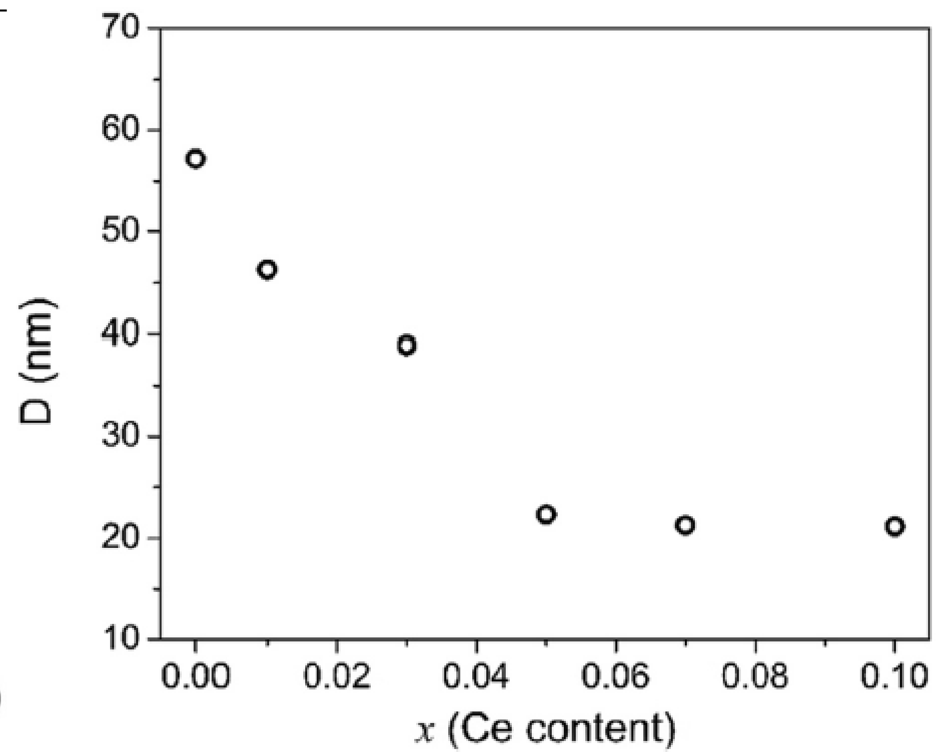
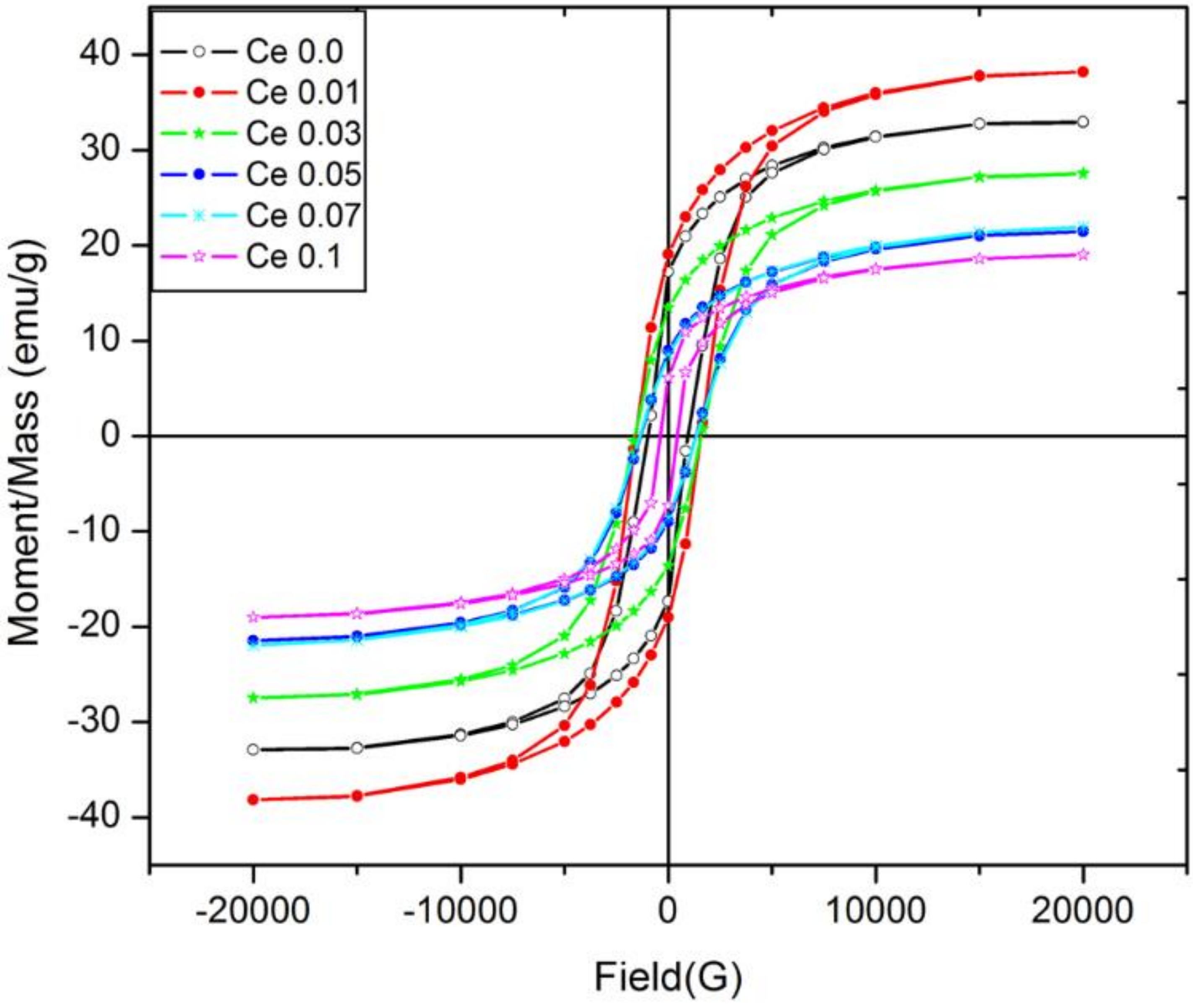


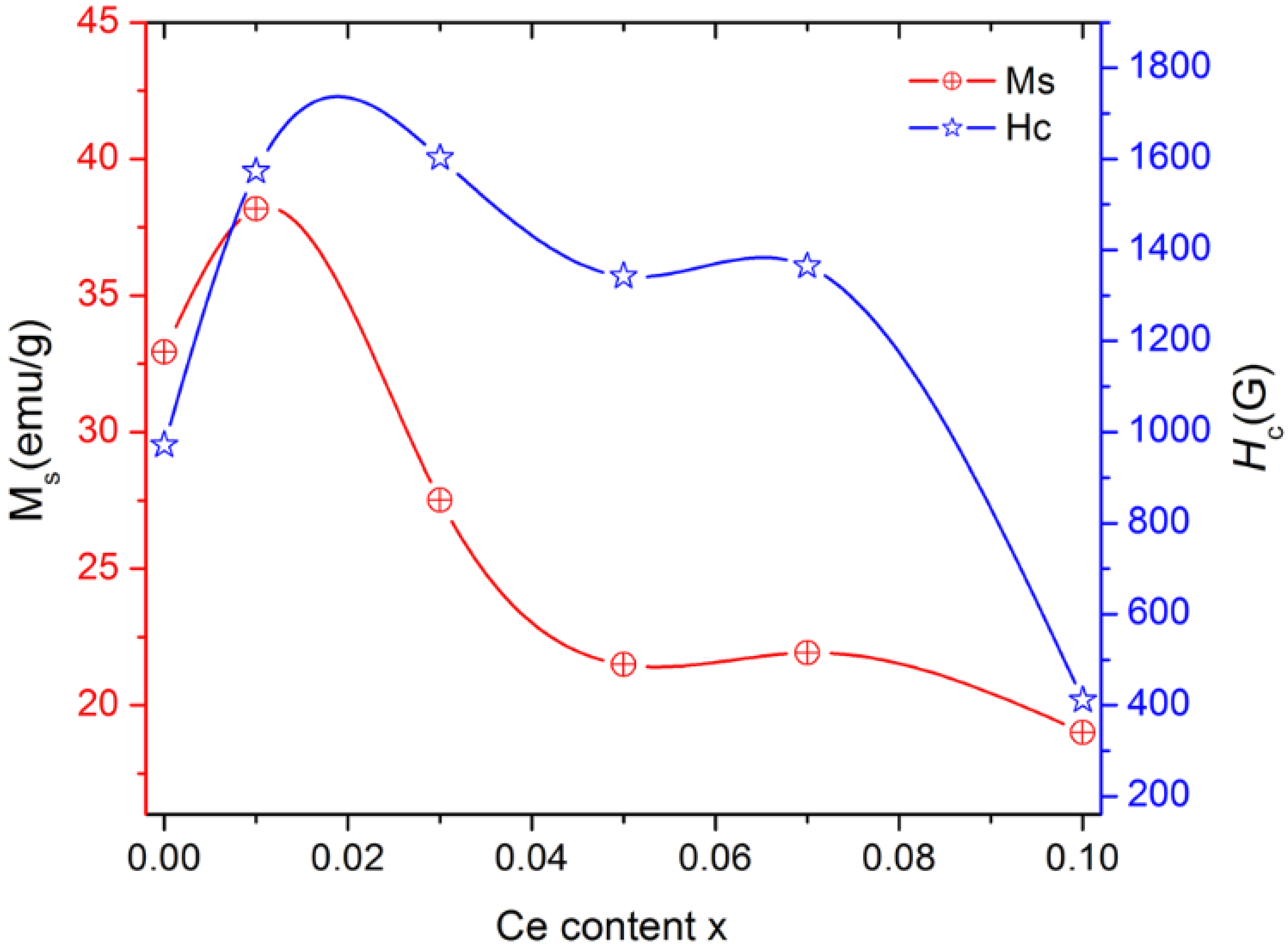
$CoFe_{2-x}Ce_xO_4$

VSM



$CoFe_{2-x}Ce_xO_4$

VSM



$CoFe_{2-x}Ce_xO_4$

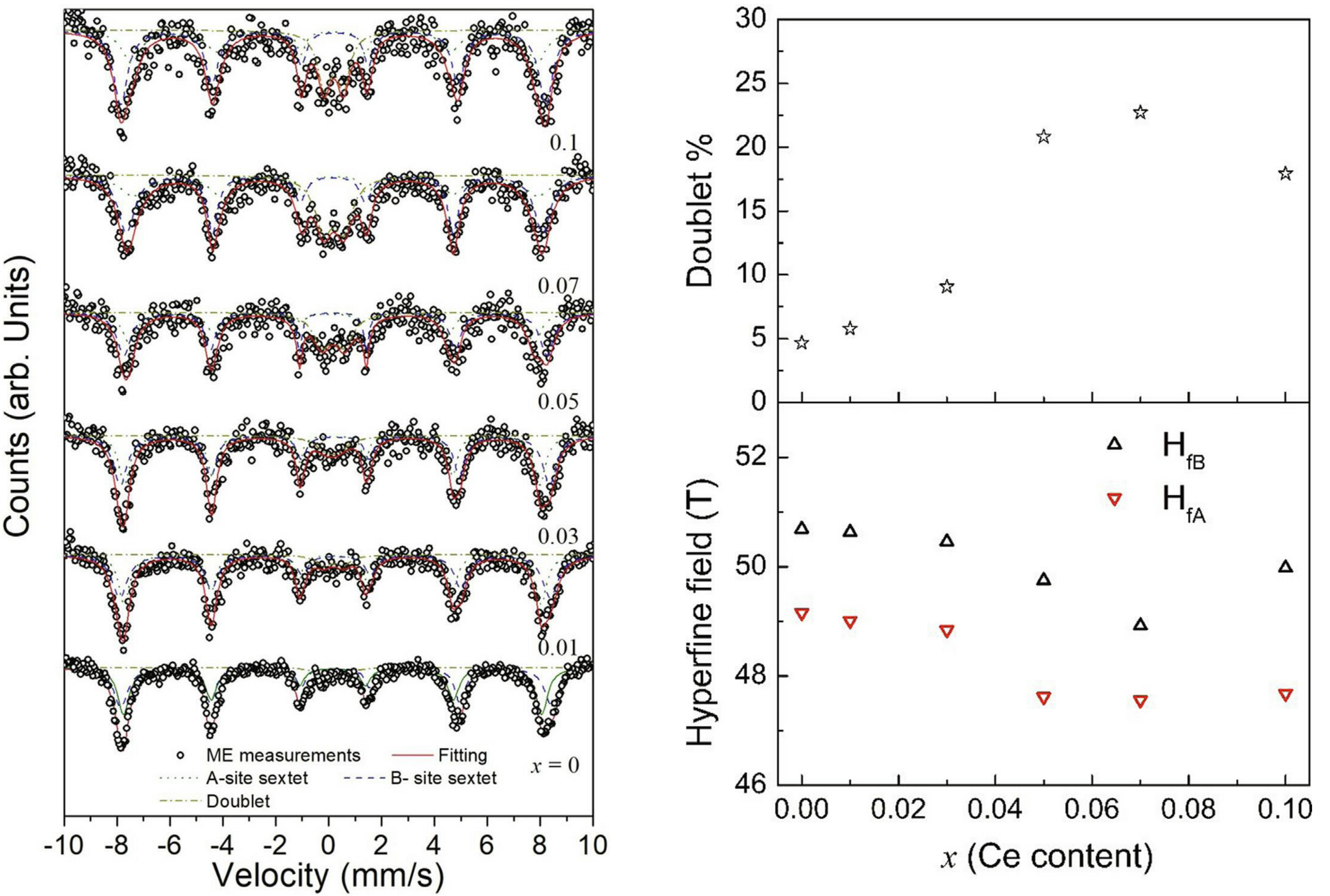
VSM

x	Saturation magnetization M_S (emu/g)	Coercivity H_c (G)	Remanent magnetization M_r (emu/g)	Magnetic moment n_B (μ_B)
0.0	32.9	972	17.3	1.38
0.01	38.2	1573	19.0	1.61
0.03	27.5	1603	13.6	1.17
0.05	21.5	1342	9.0	0.92
0.07	21.9	1364	8.6	0.94
0.1	19.0	411	6.7	0.83

Decreasing D ⟹ Ms & Hc

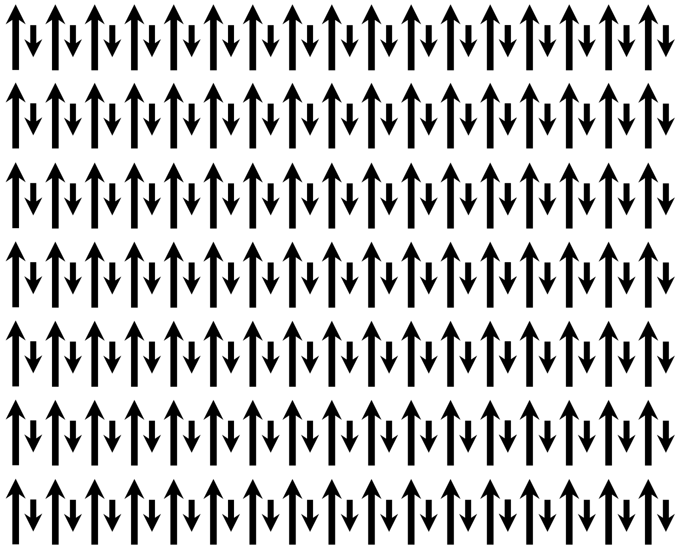
$CoFe_{2-x}Ce_xO_4$

ME



$CoFe_{2-x}Ce_xO_4$

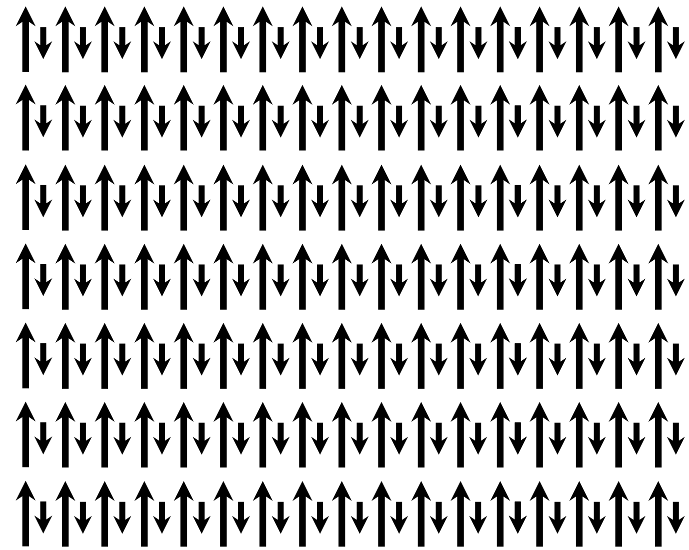
ME



Typical long range ferrimagnetic order

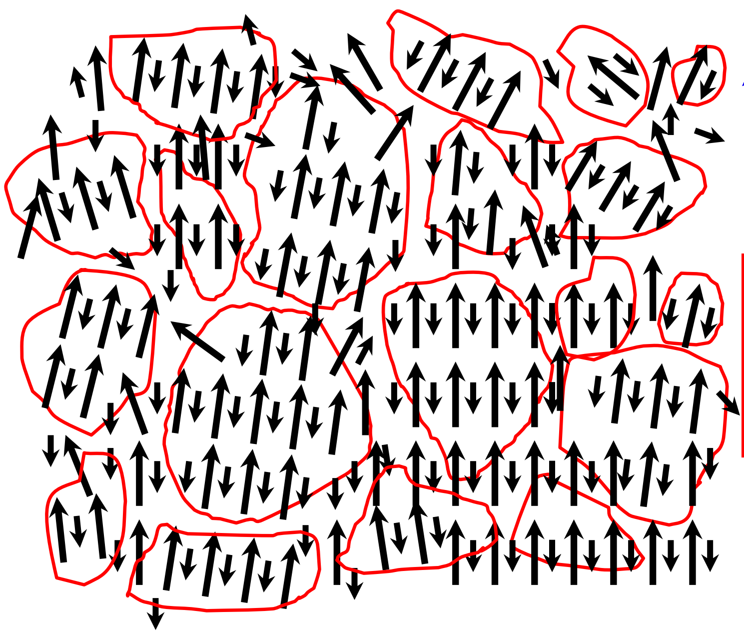
$CoFe_{2-x}Ce_xO_4$

ME



Typical long range ferrimagnetic order

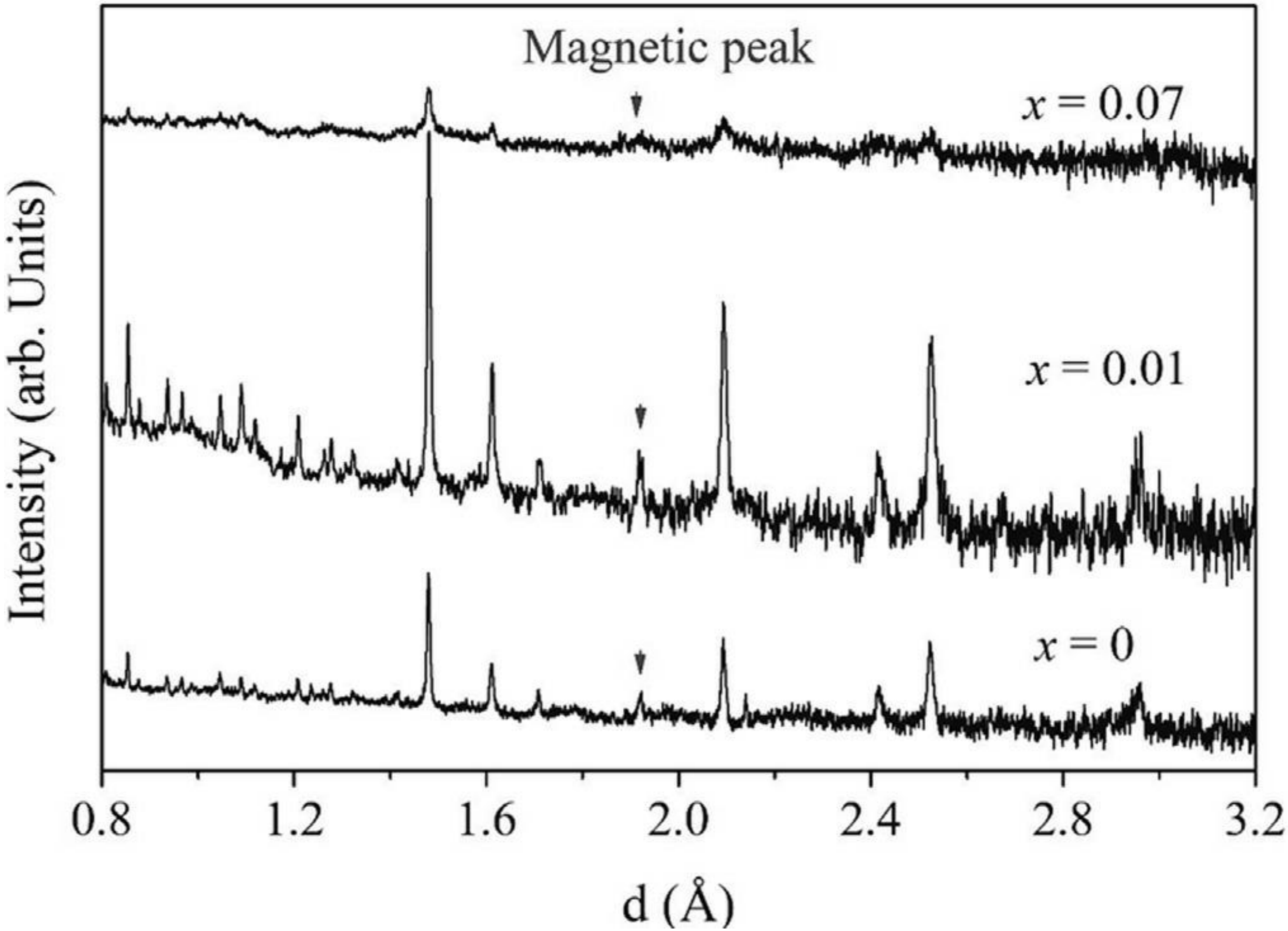
Nano Scale: Small grain sizes (D) with short range magnetic order



Finite size effects lead to a reduction in magnetism and the appearance of superparamagnetic phase in ultrasmall particles

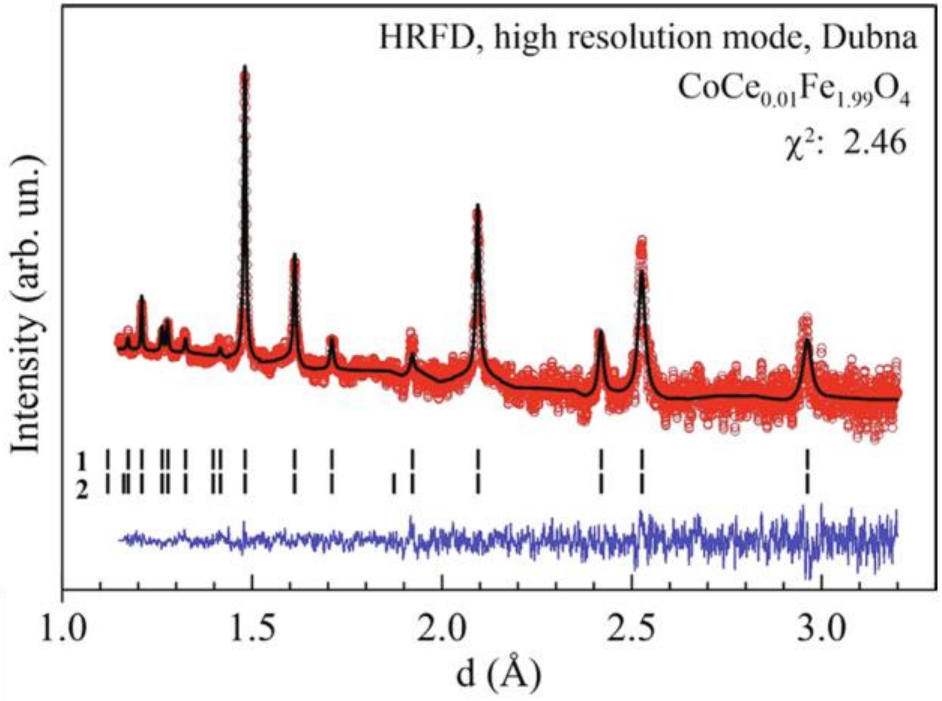
$CoFe_{2-x}Ce_xO_4$

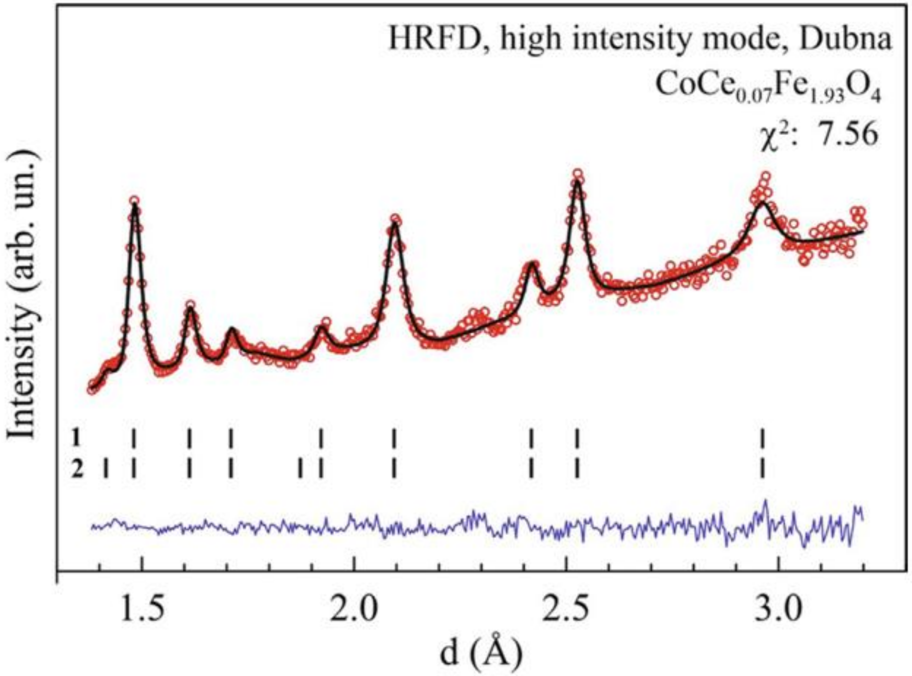
ND



$CoFe_{2-x}Ce_xO_4$

ND





$CoFe_{2-x}Ce_xO_4$

ND

XRD

x	D (nm)	a_{XRD} (Å)	a_{th} (Å)	A-O cal. (Å)	B-O cal. (Å)	u^{3m} (Å)	u^{43m} (Å)
0	57(1.4)	8.358(4)	8.367	1.859	2.064	0.272	0.397
0.01	46(1)	8.369(4)	8.346	1.849	2.062	0.273	0.398
0.03	39(0.7)	8.364(5)	8.348	1.846	2.064	0.273	0.398
0.05	22(0.3)	8.385(6)	8.33	1.836	2.064	0.274	0.399
0.07	21(0.3)	8.377(7)	8.321	1.829	2.064	0.274	0.399
0.1	21(0.4)	8.374(8)	8.328	1.826	2.068	0.274	0.399

Neutron Diff.

Parameter	$x = 0.0$	$x = 0.01$	$x = 0.07$
a_{cub}, Å	8.375	8.380	8.378
x (O)	0.249(1)	0.256(1)	0.252(1)
$n_{(A)}$ (Fe)	0.99(8)	0.95(9)	0.97(9)
$\mu_{(A)}/\mu_{(B)}$, μ_B	5.9/3.94(12)	5.9/2.68(13)	5.9/2.95(17)
A-O, Å	1.807(5)	1.900(3)	1.84(1)
B-O, Å	2.097(5)	2.047(3)	2.08(1)
L, Å	767	530	274

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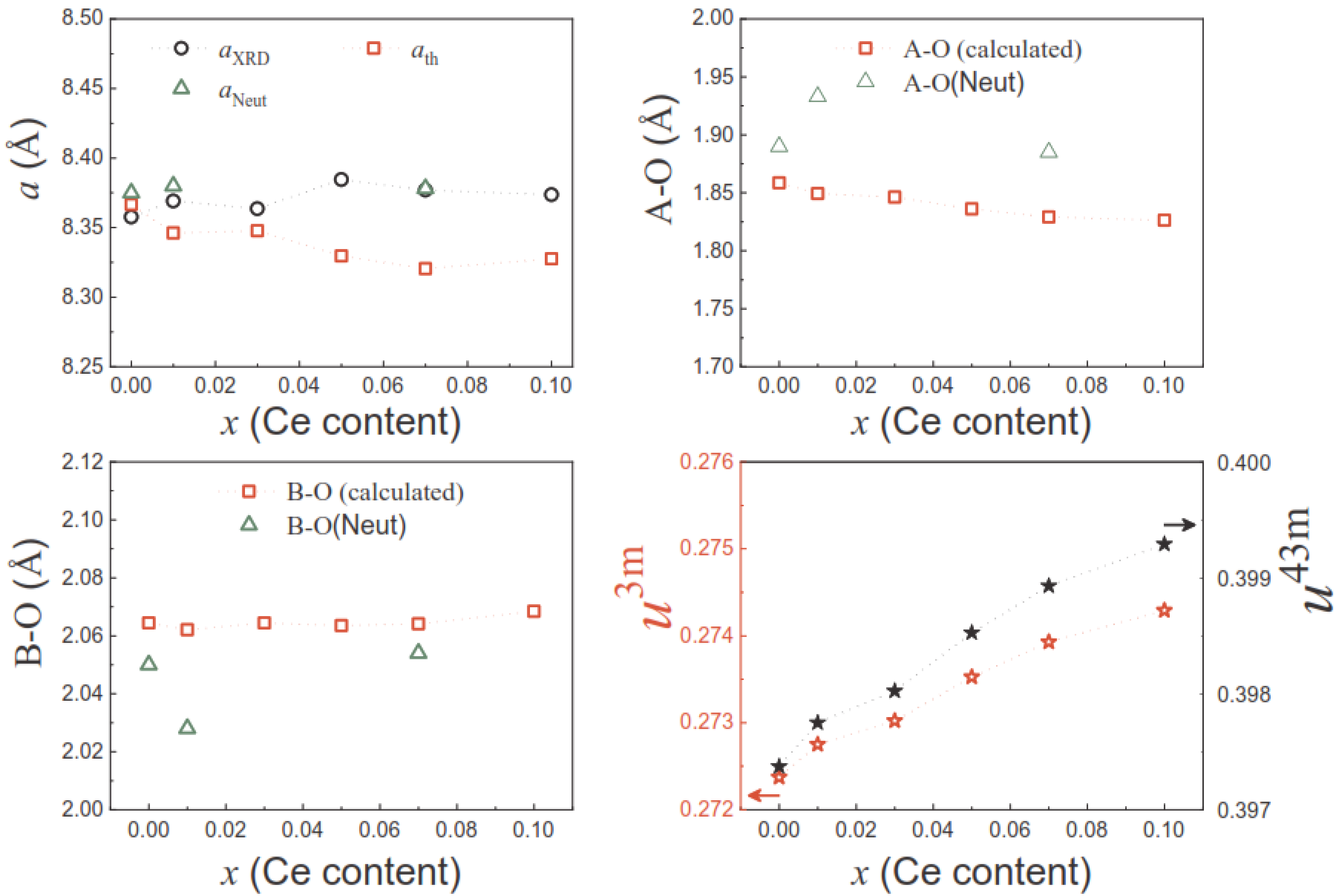
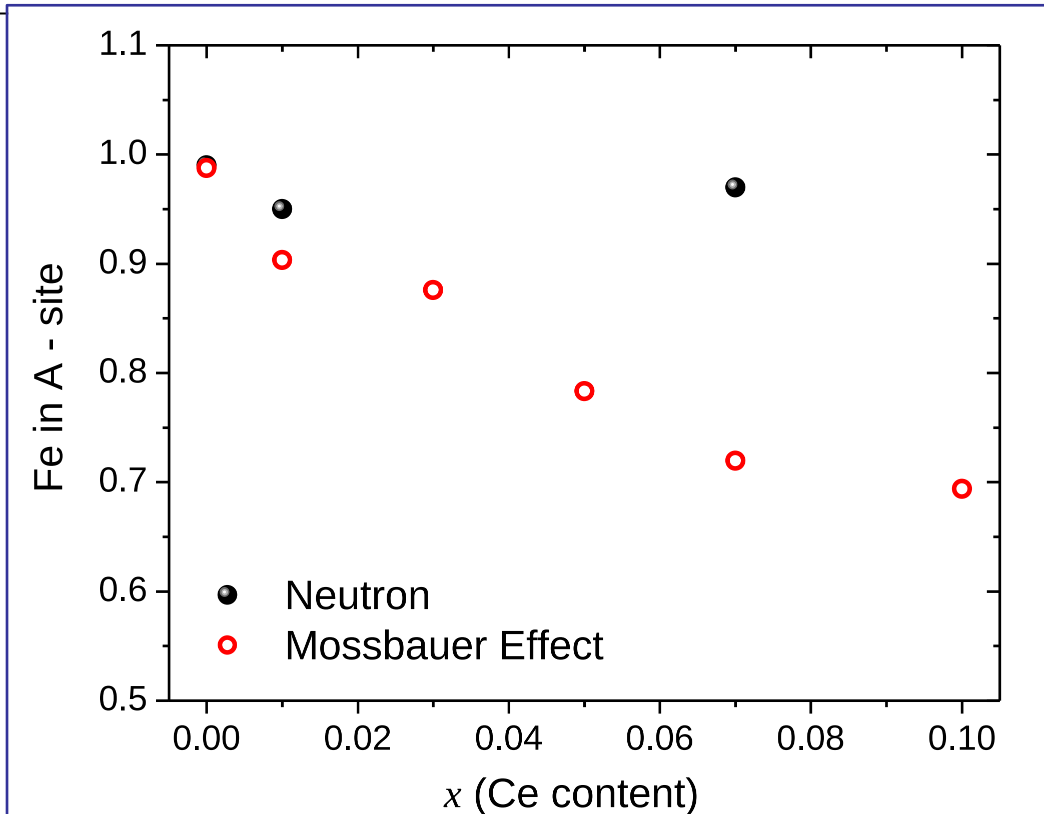


$CoFe_{2-x}Ce_xO_4$ ND

x	Cation Distribution (Mössbauer Effect)	Cation Distribution (Neutron Diffraction)	δ Mössbauer Effect)	δ Neutron Diffraction
0	$(Fe_{0.988}Co_{0.012})[Fe_{1.012}Co_{0.988}]O_4$	$(Fe_{0.99}Co_{0.01})[Fe_{1.01}Co_{0.99}]O_4$	0.988	0.99
0.01	$(Fe_{0.903}Co_{0.097})[Fe_{1.087}Co_{0.903}Ce_{0.01}]O_4$	$(Fe_{0.95}Co_{0.05})[Fe_{1.04}Co_{0.95}Ce_{0.01}]O_4$	0.903	0.95
0.03	$(Fe_{0.876}Co_{0.124})[Fe_{1.094}Co_{0.876}Ce_{0.03}]O_4$		0.876	
0.05	$(Fe_{0.783}Co_{0.217})[Fe_{1.167}Co_{0.783}Ce_{0.05}]O_4$		0.783	
0.07	$(Fe_{0.72}Co_{0.28})[Fe_{1.21}Co_{0.72}Ce_{0.07}]O_4$	$(Fe_{0.97}Co_{0.03})[Fe_{0.96}Co_{0.97}Ce_{0.07}]O_4$	0.72	0.97
0.1	$(Fe_{0.694}Co_{0.306})[Fe_{1.206}Co_{0.694}Ce_{0.1}]O_4$		0.694	



Conclusion

- Ce^{3+} doping decreases the particle size of the prepared samples.
- TEM measurements confirm the formation of nano sized – spherical shaped particles.
- XRD illustrates a single spinel phase for all the prepared samples and a gradual decrease of D with increasing Ce content was observed.
- VSM measurements spot a gradual decrease in the saturation magnetization with decreasing D.
- Mössbauer effect spectroscopy suggests the coexistence of the magnetic order for large particle sizes and superparamagnetic behavior for ultrasmall particles.
- Neutron diffraction measurements capture the reduced particle size and the magnetic order.

Thanks for your attention!