Laser Ablated Iron oxide Thin films (Structural and Magnetic Properties)

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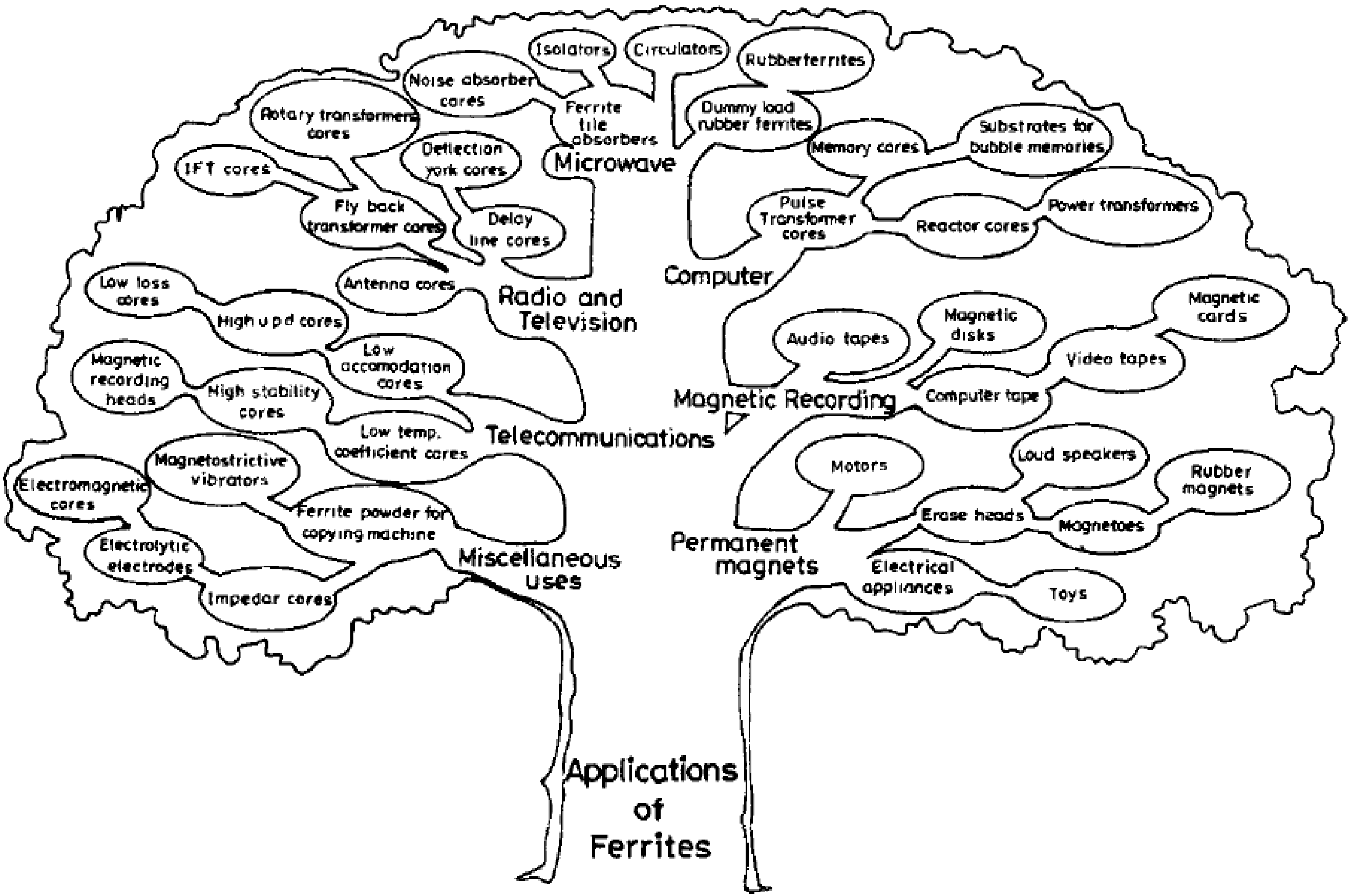
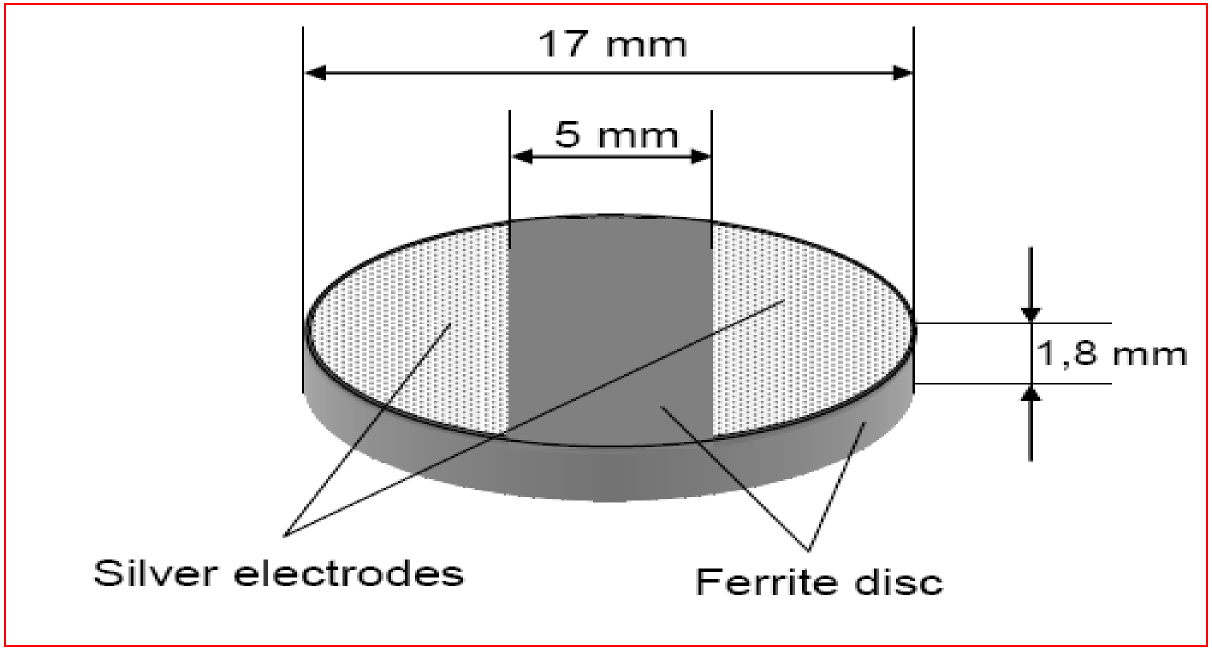
Layout

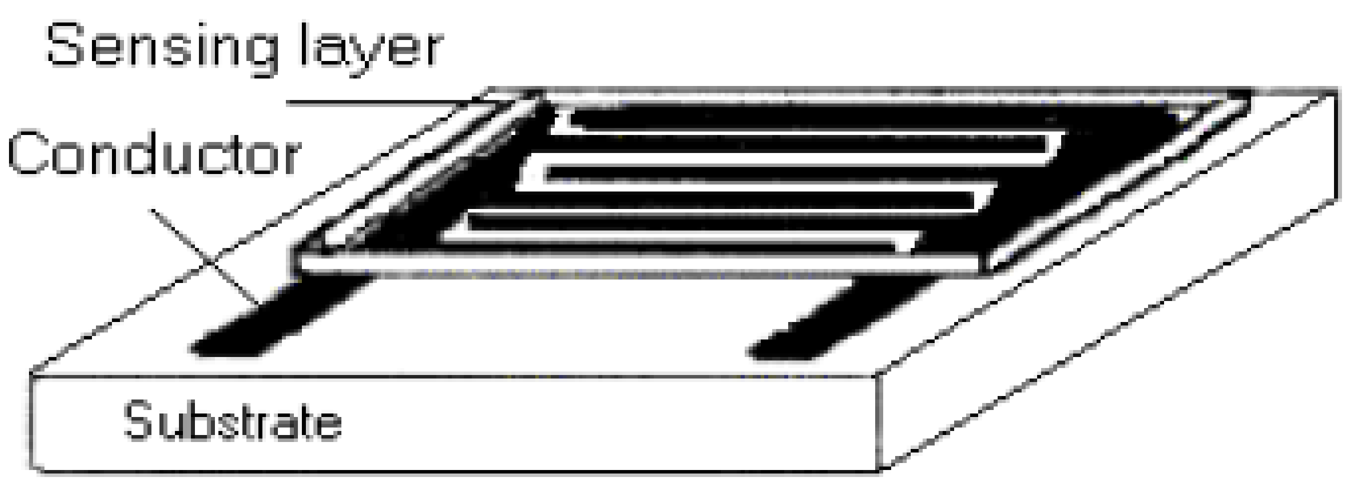
- **MOTIVATION**
- **INTRODUCTION**
- **EXPERIMENTAL METHODS**
  - **PREPARATION TECHNIQUES**
  - **CHARACTERIZATION TOOLS**
- **RESULTS & DISCUSSION**
- **CONCLUSION**
- **ACKNOWLEDGEMENT**

Motivation

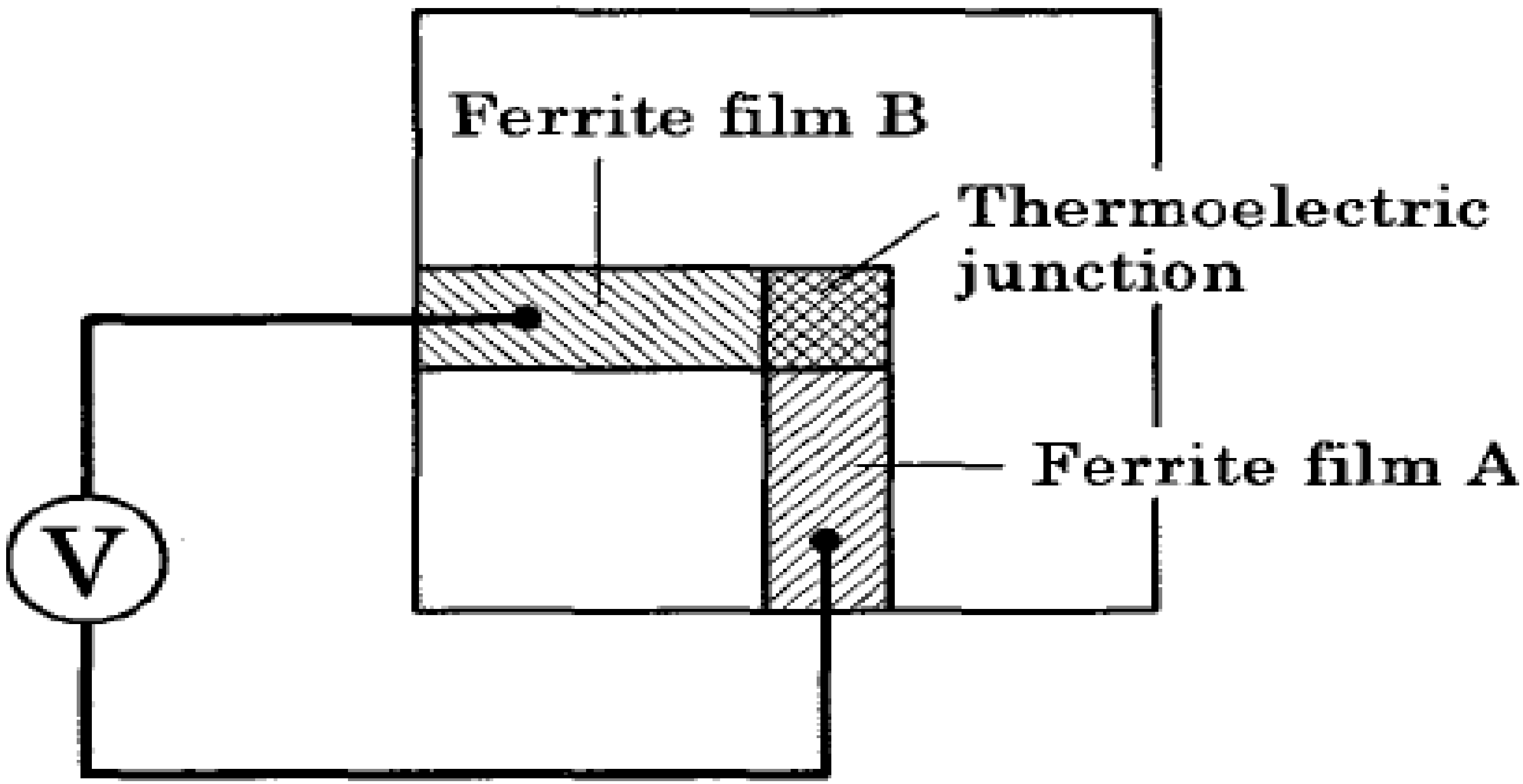


D. Bahadur, Bull. Mater. Sci., October, 1999





Ashok B. Gadkari, Ferrite Gas Sensors, IEEE SENSOR JOURNAL, 2011


Ferrite film B
Thermoelectric junction
Ferrite film A
V

Fundamentals of Electron Spin
1. Except for its mass and elementary charge, an electron has an intrinsic angular momentum, called spin.
2. Each spin has two arbitrary orientations, and its magnitudes are $\pm\hbar/2$ ($\hbar$ is Planck constant). When all electron spins in solid align along the same direction, a ferromagnet forms.
3. In a magnetic field, an electron has different energies when electron spin is parallel or anti-parallel with the field.
4. Directional motion of electrons circulates an electric charge. In a conventional electric circuit, electron spins of charge carriers are random, and the current does not exhibit spin properties.
5. Directional and coherent motion of electron spin circulates a spin current, which will carry or transport information and control quantum spin in an spintronic device.

Shun-Qing Shen, "Spintronics and Spin Current, AAPPS Bulletin, october, 2008

Spintronics

- **This term was proposed in 1998 in a joint press release of Bell Labs and Yale University (USA), which defined the problem of design of devices for information storage by manipulating atoms of matter using electron spin encoded bits.**

- **Researchers at the Defence Advance Research Project Agency (DARPA, USA) defined spintronics as "Spin-transport electronics".**

Flow of electrical charges as well as the flow of spin, manipulated and controlled together.

V.A. Ivanov et al "spintronics and spintronic materials", Russian chemical Bulletin, 2004

Major challenges in Spintronics

- Optimization of electron spin lifetimes (non-equilibrium polarization will decay over a timescale less than nanosecond)
- Detection of spin coherence in nanoscale structures
- Transport of spin-polarized carriers across relevant length scales
- Manipulation of both electron and nuclear spins on sufficiently fast time scales

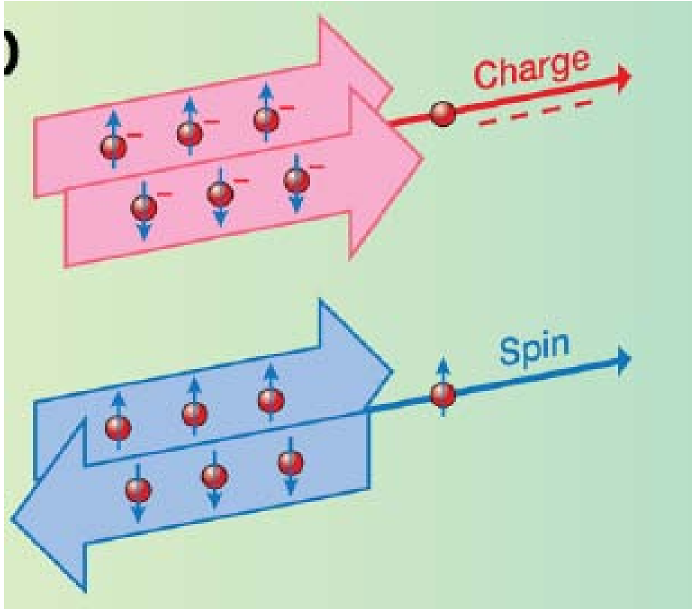
S.A. Wolf et al. "spintronics: A spin-Based Electronics Vision for the Future, Science, 294 1488, 2001.

Charge and Spin current

Spin Current differs from charge current in two important ways,

➢It is invariant under time reversal; if a clock ran backward, the spin current would still flow in the same direction

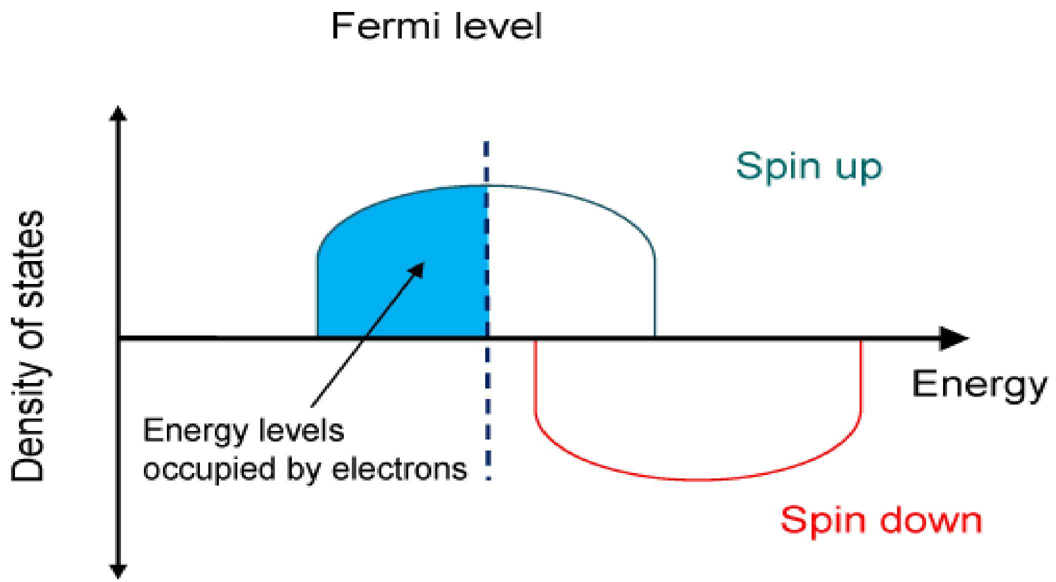
➢Spin current is associated with a flow of angular momentum, which is a vector quantity. This feature allows quantum information to be sent across semiconducting structures, just as quantum optics involves distribution of information across optical networks via polarization states of the photons.



1. P. Sharma, Science, Vol. 307, Jan. 2005
2. Pierce Coleman, Physics, 2, 6, 2009

- **Materials with high spin-polarization is now considered best for spintronic devices.**

- **In 1980, de Groot discovered new kind of materials called "Half metal ferromagnet" in which it shows the characteristics of a metal for one direction of spin and insulator for the other spin at the Fermi level.**



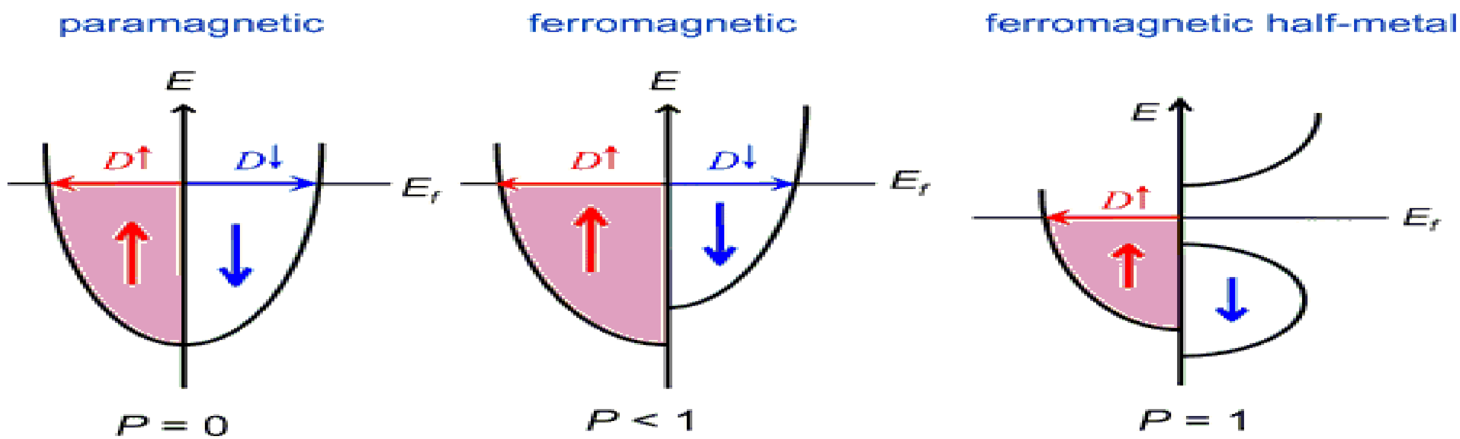
Combine “Half-metallicity” with “Spintronics”

↓

Magneto-electronic Devices

↓

Spin-polarization



$$P = \frac{D\uparrow(E_f) - D\downarrow(E_f)}{D\uparrow(E_f) + D\downarrow(E_f)}$$

P : electron spin polarization

Why Fe_3O_4???

Half metals	Structure	Lattice parameter	Tc	μ_B/formula	Ms(MAm^{-1})
NiMnSb	Cubic (FCC)	5.92Å	728K	4.0	0.71
CrO_2	Tetragonal (rutile)	4.42Å;0.292nm	398K	2.0	0.40
$(La_{0.7}Sr_{0.3})MnO_3$	Rhombohedral	5.48Å;60.4°	380K	3.6	0.31
Fe_3O_4	Cubic (inverse spinel)	8.397Å	858K	4.0	0.48

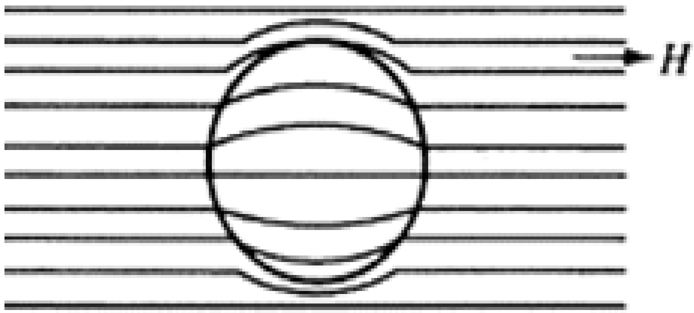
➢Operation temperature for magnetoresistive device is normally above 50 C

➢Magnetic materials having high Curie temperature are required for such devices

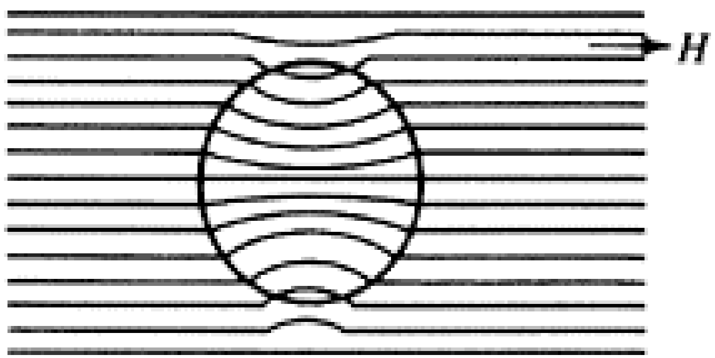
➢Fe_3O_4 is half-metallic and has the highest Curie temperature (860K), considered to the most promising choice for “Magneto-electronic Devices”.

Introduction

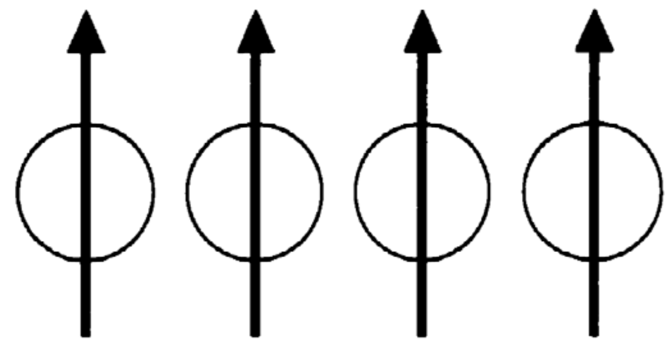
Classification of magnetic materials



Diamagnetic



Paramagnetic

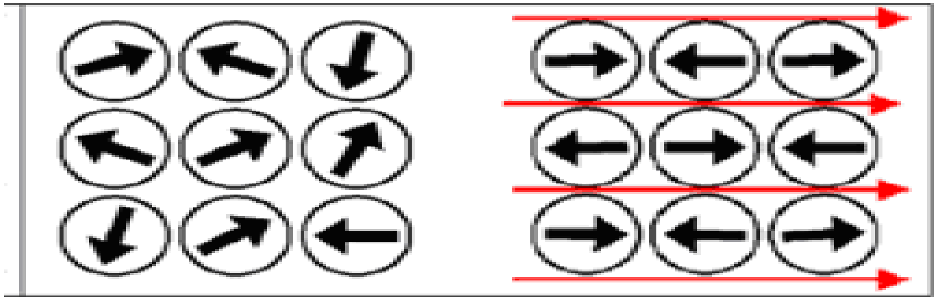


Ferromagnetic

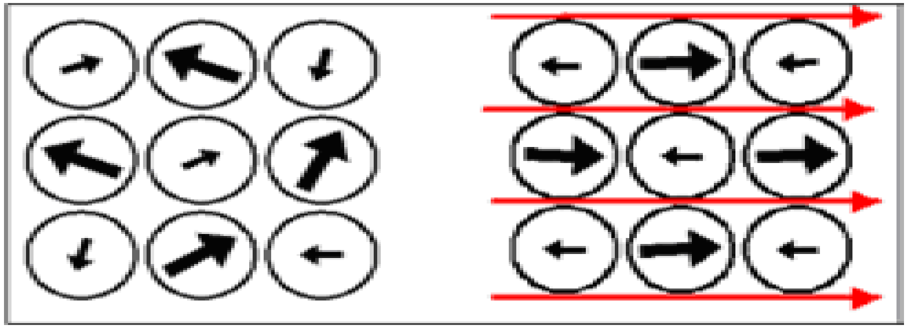
L.E. Smart, E.A. Moore, Solid State Chemistry (An introduction), 3rd. Ed. 2005

Introduction (continued..)

Antiferromagnetic and Ferrimagnetic Materials



Antiferromagnetic material with and without applied field (arrows represent atomic magnetic dipoles)

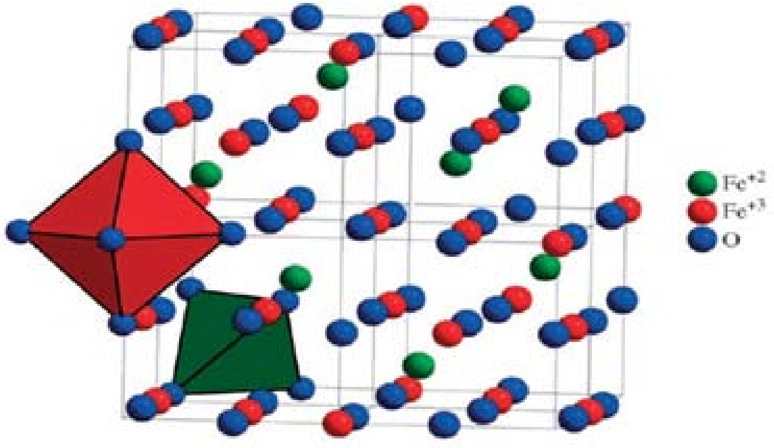


Ferrimagnetic material with and without applied field (arrows represent atomic magnetic dipoles)

Ferrites are ferrimagnetic transition-metal oxides, and are electrically insulators except Fe_3O_4 ($10^{-3}\Omega$-cm)

Spinel Structure

- Ionic, stable and is very amenable to large substitutional possibilities



- $A_8B_{16}O_{32}$ (8-formula unit)

- Total 96 interestial sites

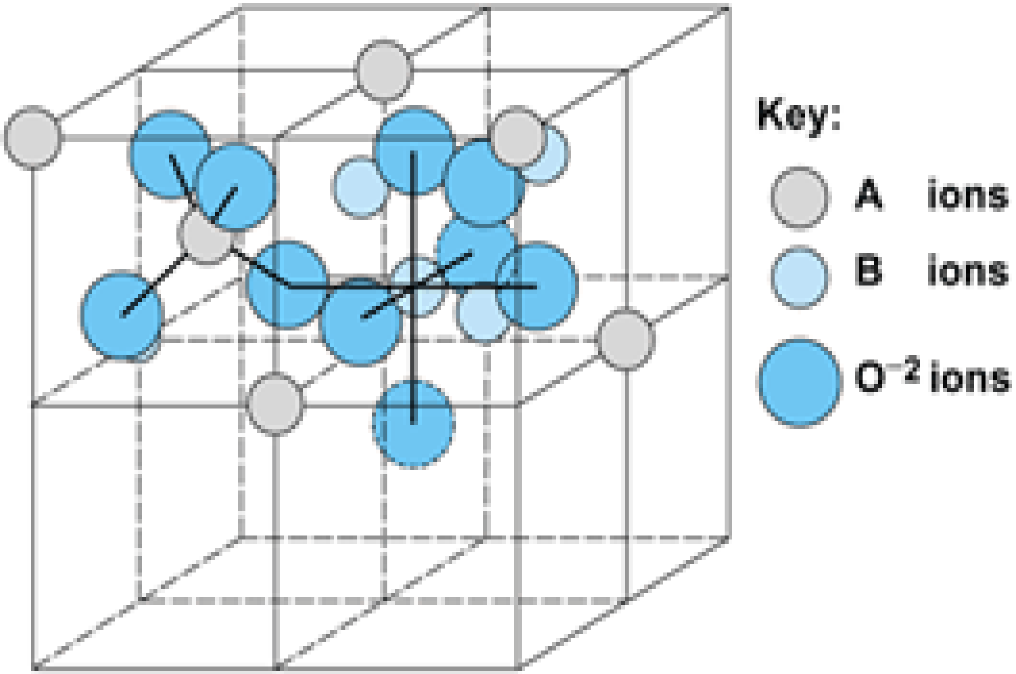
- 64 tetrahedral and 32 octahedral sites)

56-atoms/unit cell O^{-2} + octa + tetra

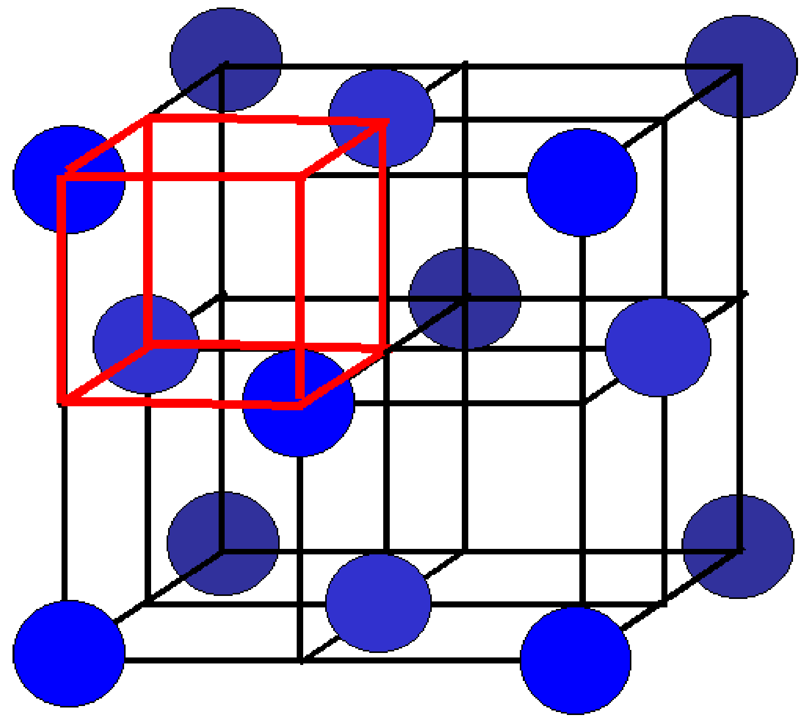
32 + ½ 32 + 1/8 64

32 + 16 (occupied) + 8 (occupied) = 56

Spinel Structure



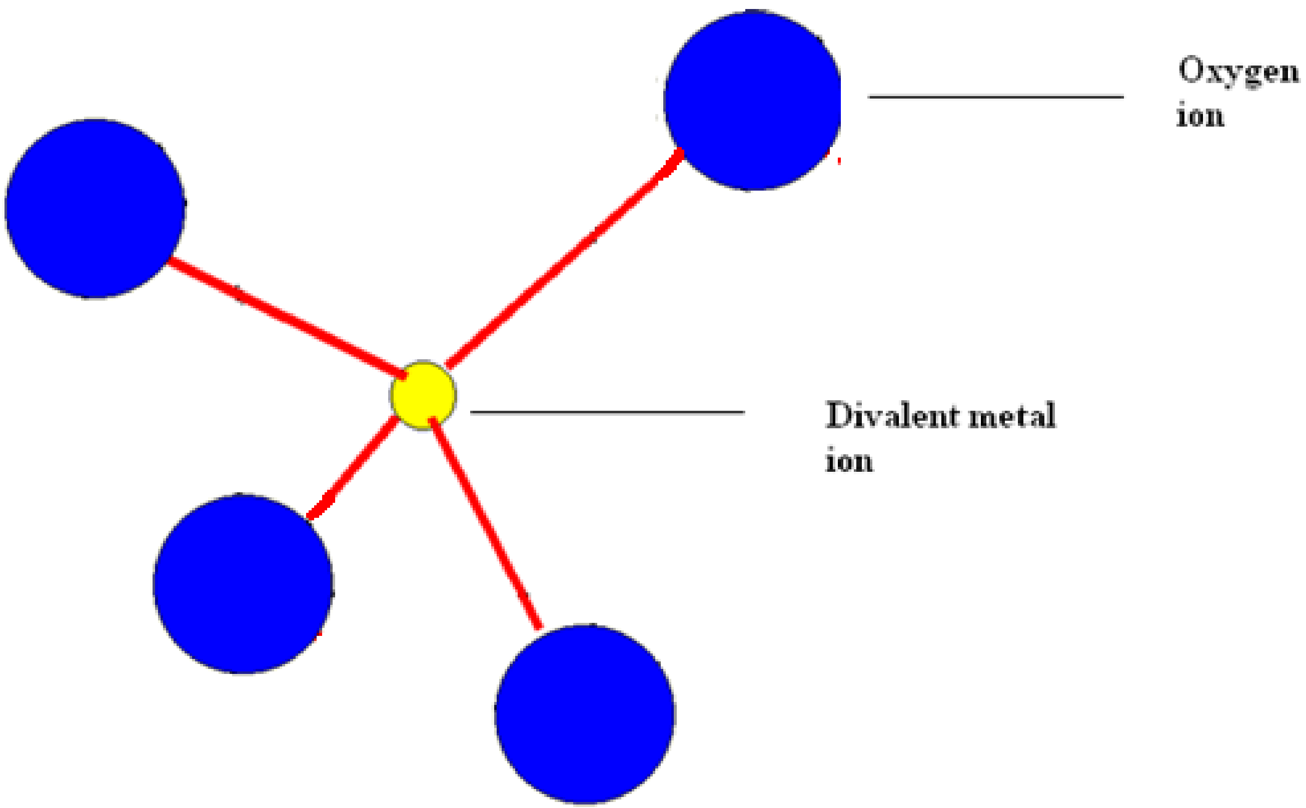
Tetrahedral and Octahedral sites in adjacent mini cubes



Divide the f.c.c. unit cell into 8 ‘minicubes

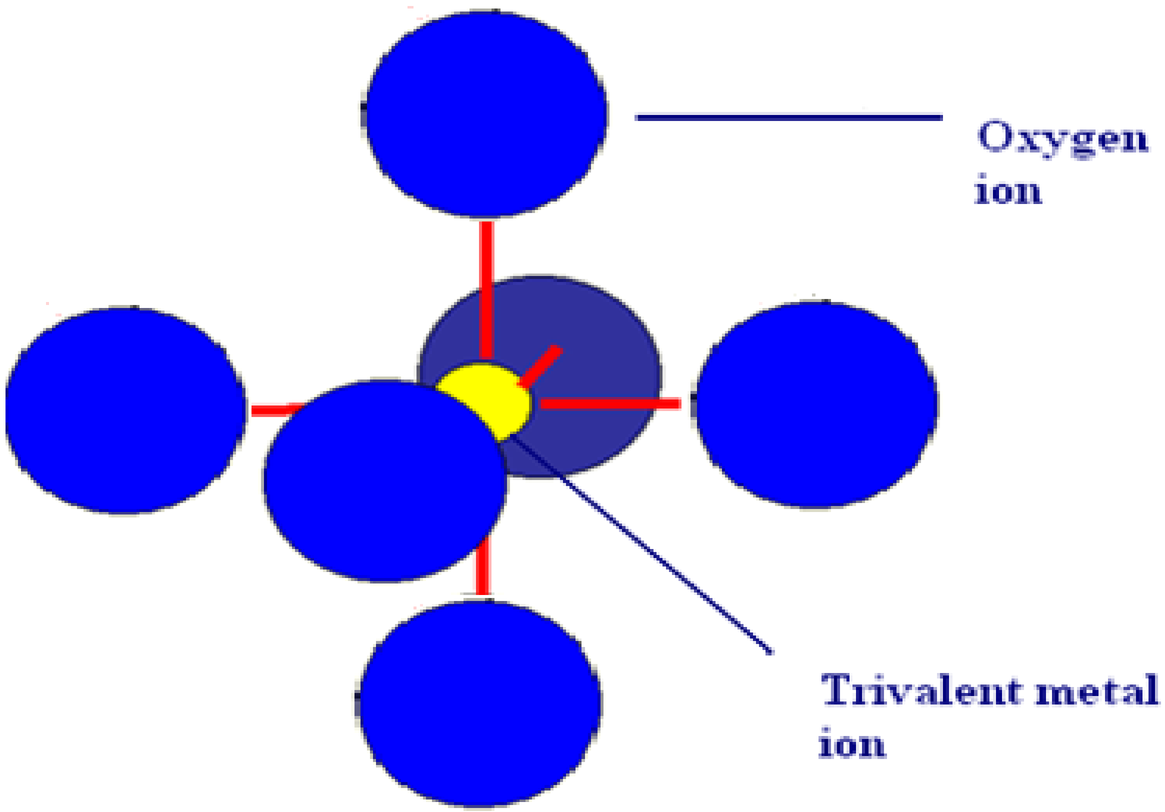
Spinel Structure

Tetrahedral Site

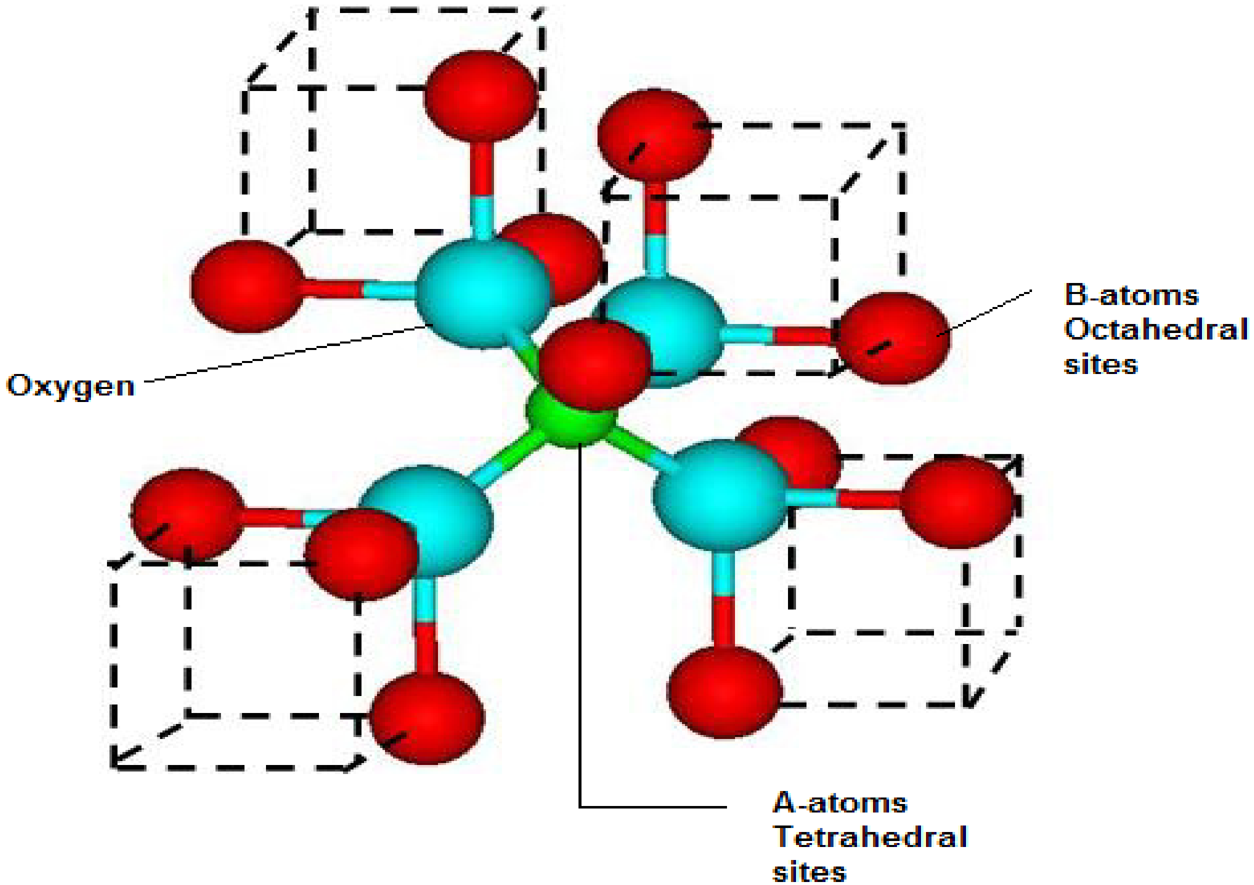


Spinel Structure

Octahedral Site

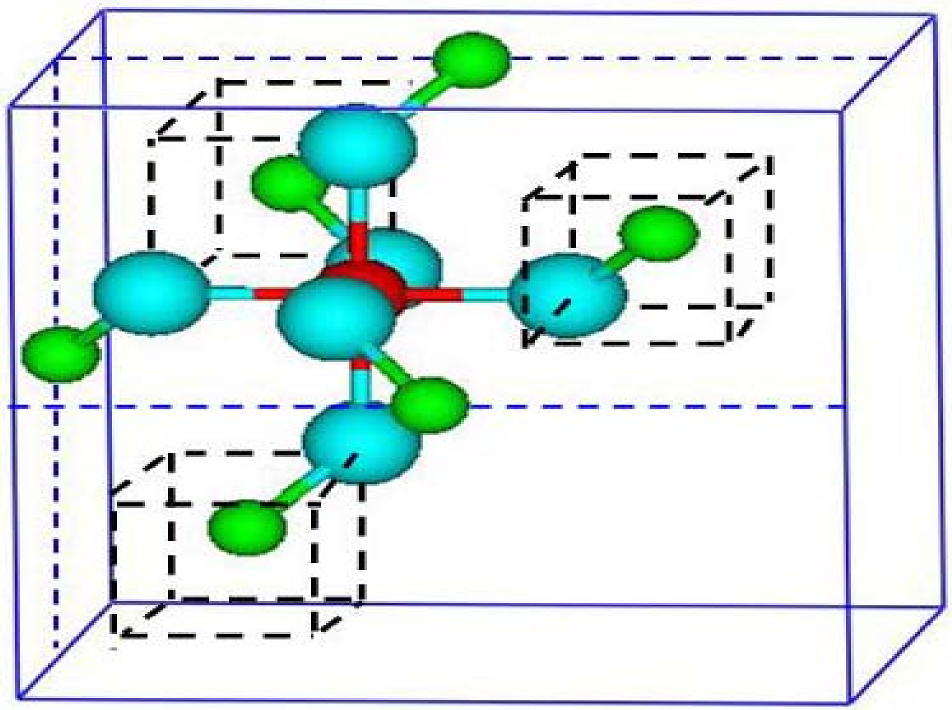


Local atomic arrangement for tetrahedral site in spinel structure



Tetrahedral site has 12 nearest (B) atoms)

Local atomic arrangement for octahedral site in spinel structure



Each B-atom in an octahedral site has 6 nearest A-atoms

When divalent and trivalent atoms are both magnetic elements, exchange interaction exist between them.

Classification of Spinels

1. **Normal Spinel structure**

   Where all Me^{2+} ions occupy A sites; structural formula of such ferrites is $Me^{2+}[Fe_2^{3+}]O_4^{2-}$

2. **Inverse Spinel structure**

   Where all Me^{2+} ions are in B-position and Fe^{3+} ions are equally distributed between A and B sites

3. **Mixed Spinel structure**

   When cation Me^{2+} and Fe^{3+} occupy both A and B positions, structural formula of this ferrite is as follow

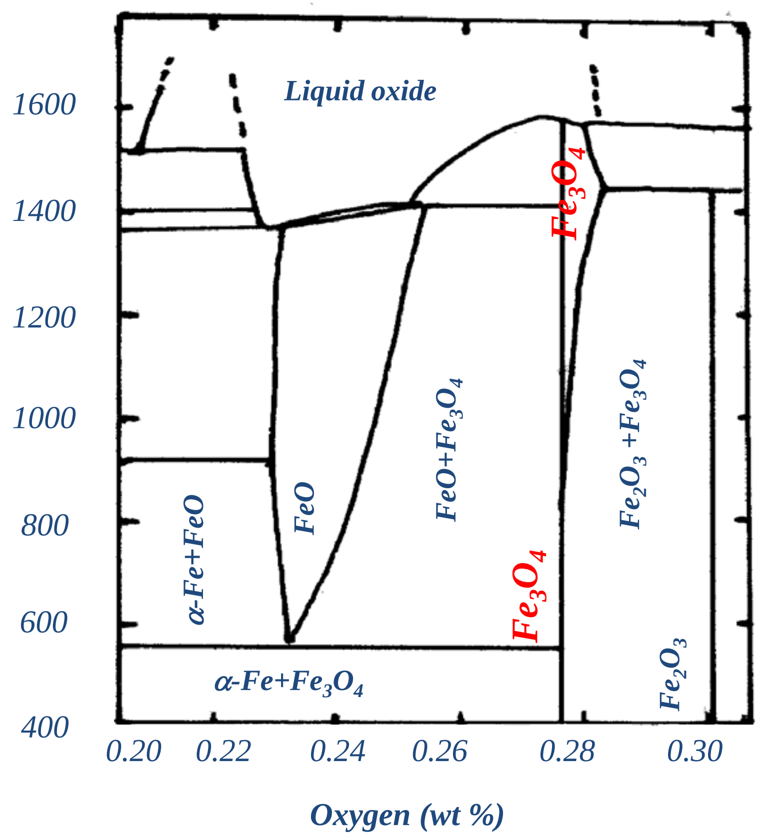
$$Me_{1-\delta}^{2+}Fe_{\delta}^{3+}[Me_{\delta}^{2+}Fe_{2-\delta}^{3+}]O_4^{2-}$$

Here δ is the degree of inversion, mostly it depends on the preparation technique, especially on the cooling rate after sintering.

Fe_3O_4
Thin films
(Pulsed Laser Deposition)

Common Phases of Iron oxide

1- FeO (Wustite)------------- Antiferromagnetic
2- α-Fe_2O_3 (Hematite)------- Antiferromagnetic
3-ɣ-Fe_2O_3 (Maghemite)----- Ferrimagnetic
4-Fe_3O_4 (Magnetite)--------- Ferrimagnetic



Landolt-Bornstein 2000 Non-Tetrahedrally Bonded Binary compounds-II (Berlin: Springer) Vol. 41D pp 1-4

Advantages of Fe_3O_4

- Half-metal with highest curie temperature (860K)
- Low electrical resistivity at room temperature (10^{-3} Ω-cm)
- Structure changes from cubic to monoclinic at 120 K (order-disorder transition)
- Preferred over DMS due to half metallicty and highest Curie temperature

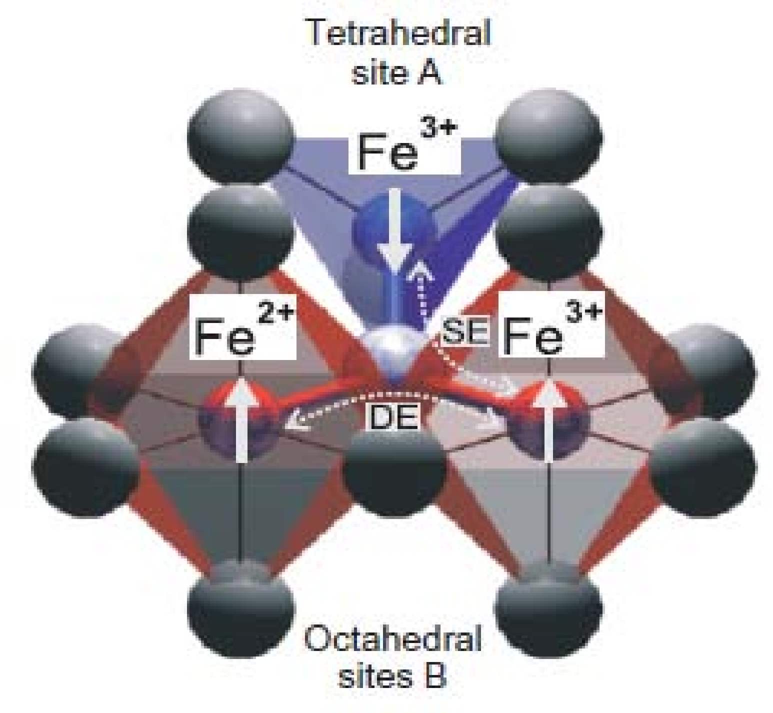
J. Kikkawa and D.D Awschalom, Nature (London) 397, 139 (1999)

R. Fiederling, M. Keim, G. Reusher, W. Osau, G.Schmidt, Nature(London) 402, 787 (1999)

Y. Ohno, D.K. Young, B. Beschoten, F. Matsukura, H. Ohno, and D.D. Awschalorn, Nature (London) 402, 790 (1999)

How Fe_3O_4 – a ferrimagnet?

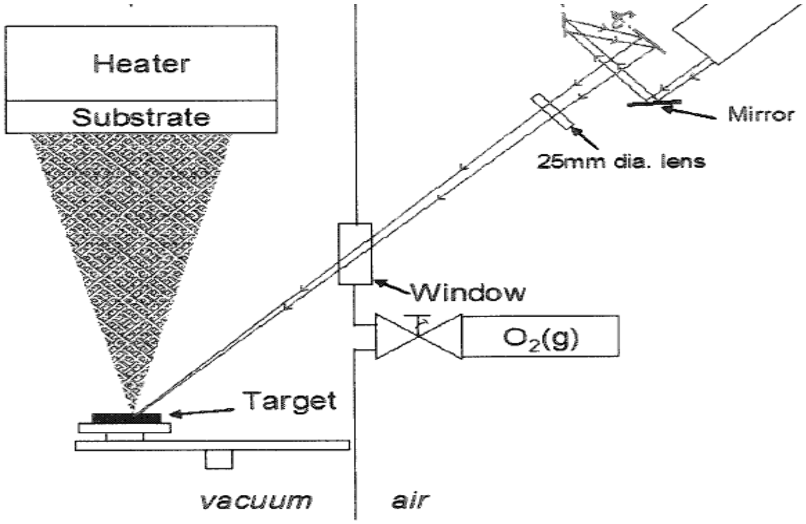
- Two Fe^{3+} ions in tetra-octa sites are anti- ferromagnetically coupled and their moments cancel each other.
- Spins of ions of the same element of two different valences simultaneously exchange electrons through the oxygen ion thereby changing the valences of both
  - Fe^{+2}- O^{-2}- Fe^{+3} ↔ Fe^{+3}- O^{-2}- Fe^{+2}



J. Stohr, H.C. Siegmann, "Magnetism" from fundamental to nanoscale dynamics, Springer, 2006

Process of laser ablation and interaction with target

Nd:YAG LASER (EKSPLA)



Primary mechanisms are;

1. **Collisional sputtering:** interaction of laser beam with the target
2. **Thermal sputtering:** boiling from the target
3. **Electronic sputtering:** sputter from electronic phenomena
4. **Exfoliation sputtering:** ejection of material resulting from thermal stress
5. **Hydrodynamic sputtering:** thermal expansion of droplets known as asperites

In PLD, formation of oxides is favored by the presence of small amount of O_2 inside the deposition chamber . The oxygen while interacting with the ablation plume promotes incorporation into the growing film.

Problems in depositing Fe_3O_4 thin films

- Fe_3O_4 is unstable in various oxygen pressure
- Fe_3O_4 likes vacuum and does not like oxygen

Advantages of PLD

PLD is Advantageous

- Lasers are clean thermal sources that introduce minimal contamination
- Multilayer films can be grown
- Stoichiometry in the film can be maintained
- Possibility of getting thin films of almost any kind of material

Draw back

- Occurrence of droplets (0.5-0.2μm) results in roughness of the film
- depositing small area.

D.B. Chrisey and G.K. Hubler, "PLD of thin films", Wiley 1994

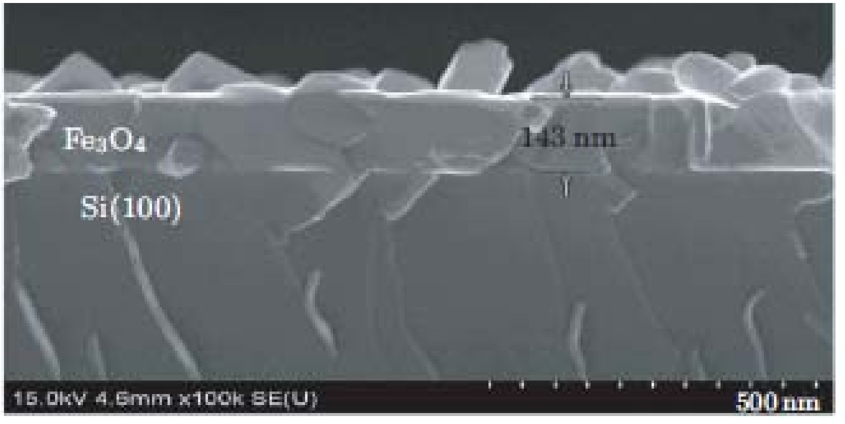
Preparation of Fe_3O_4

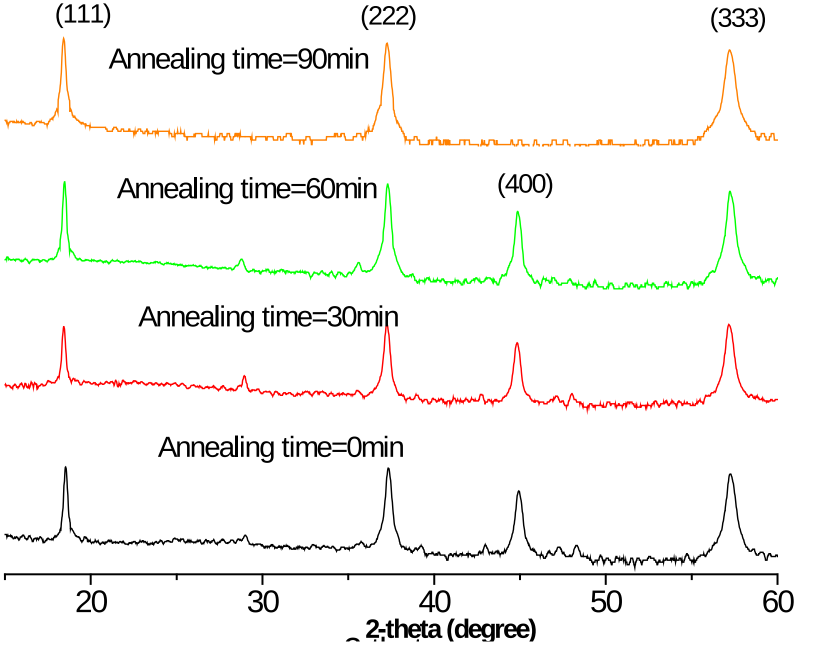
Before deposition, Si(100) substrates were subjected to chemical cleaning using acetone and isopropanol in an ultrasound bath. The cleaned substrates were then pre-heated in the deposition chamber (10^{-7} torr) at 500 °C for 30 minutes.

Deposition Conditions

- **Target = Fe_3O_4 (99.9 % purchased from Japan)**
- **Base Pressure = 10^{-7} torr**
- **O_2 flow rate = 0.3 sccm**
- **Working Pressure = 10^{-6} torr**
- **Substrate temp. = 450 °C**
- **Deposition time = 20 min.**
- **Pulsed Energy at 266 nm = 80 mJ**
- **Repetition Rate = 10 Hz**
- **Target to substrate distance = 36 mm**
- **Annealing temp. = 450°C**
- **Annealing time = 0 min, 30 min, 60 min, 90 min.**

Effect of annealing time on the structural properties of Fe_3O_4 thin films

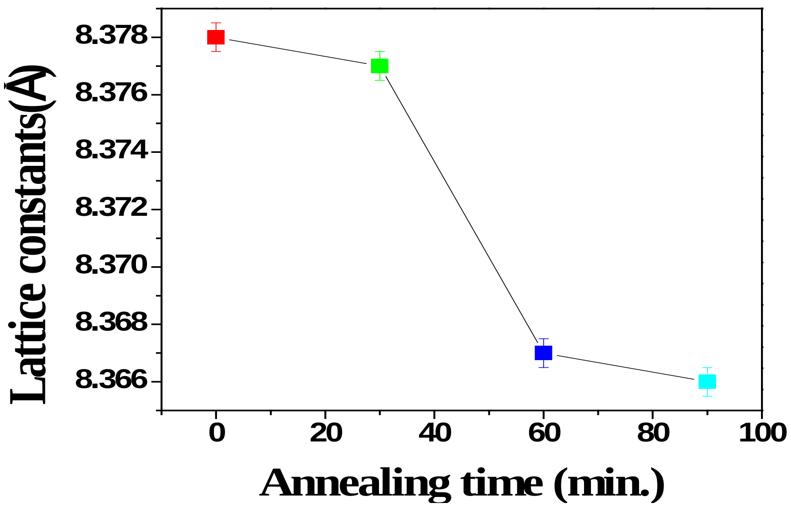


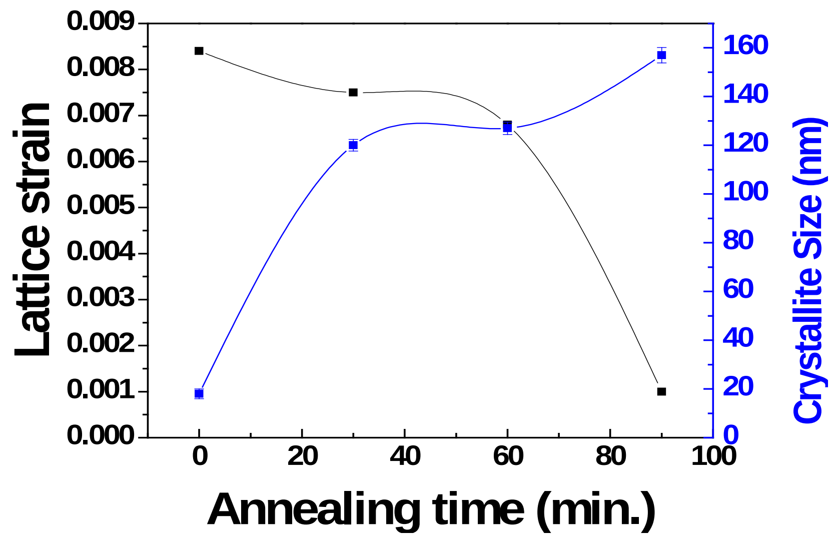


XRD patterns of Fe_3O_4 deposited on Si(100) at 450 °C for different annealing time.
Compared with JCPD S= 19-0629

- **<111> oriented Fe_3O_4 surface is most energetically favorable and has the highest atomic density.**
- **When lattice mismatch is very large, the substrate control over the film is weak and growth orientation is determined by thermodynamically stable state having minimum internal energy.**

Structural Properties

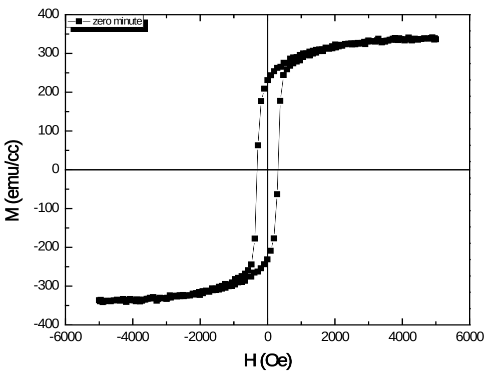




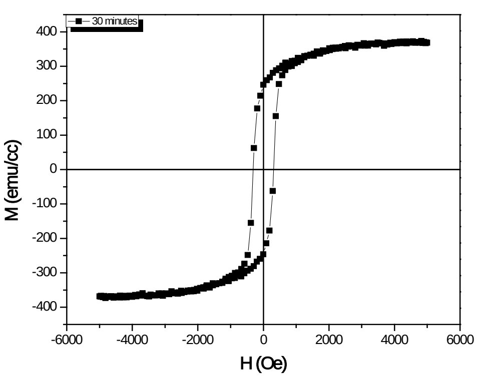
- **Increasing annealing time the lattice parameters deviated from bulk material (8.396 Å),this may be due to the substrate induced strain in the film.**

- **The size of the crystallite with annealing time increases due to the increase in surface mobility**

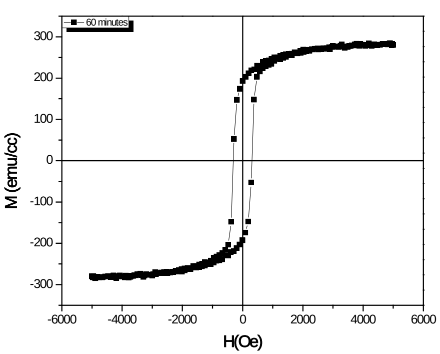
Magnetic Properties



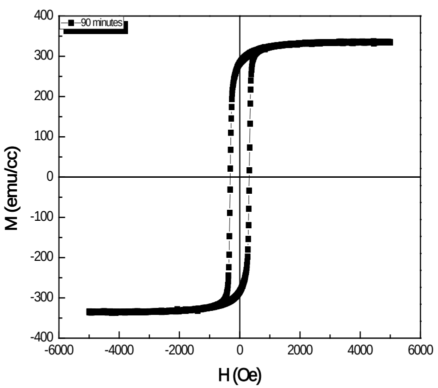
Zero min.



30 min.



60 min



90 min

Annealing time (min.)	Saturation Magnetization (emu/cc)	Coercivity H_c (Oe)
0.0	330.34	303
30	366.30	306
60	276.14	272
90	335.00	315

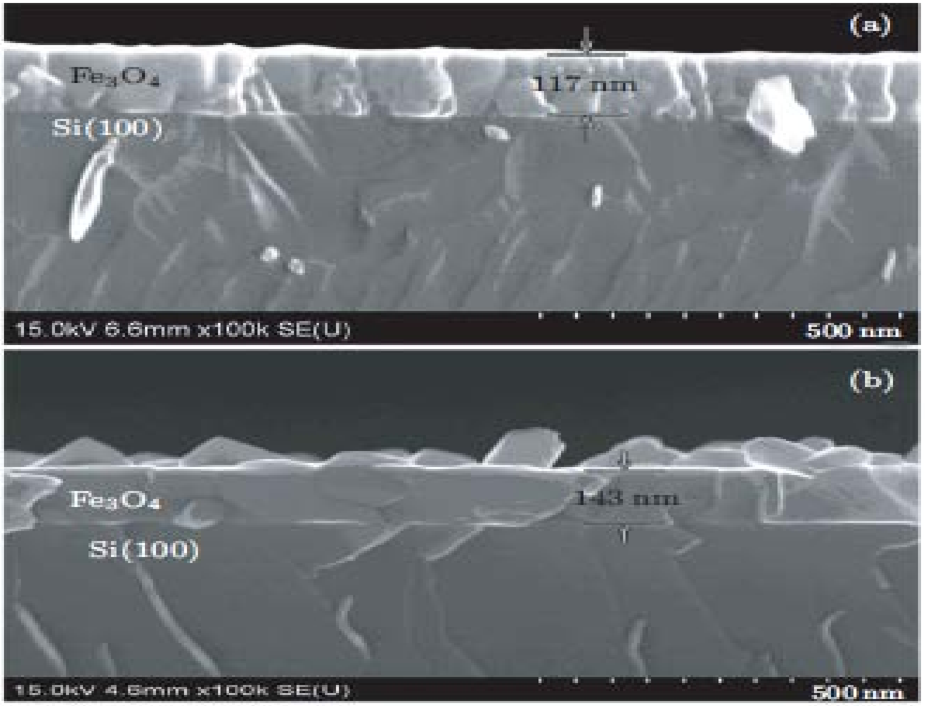
- Lowering of saturation magnetization due to the presence of antiphase boundaries between the films and substrates.

- Antiphase boundaries even in epitaxial Fe_3O_4 films come from the nucleation of islands when the films are deposited on substrates.

Effect of temperature on the structural and magnetic properties of Fe_3O_4 thin films

Pulse repetition rate = 10Hz
Energy density = 1.3 J/cm^2
Target to substrate distance = 35 mm
Laser wavelength = 266 nm
Working pressure = 1x 10^{-6} torr
Oxygen flow rate = 0.2 sccm

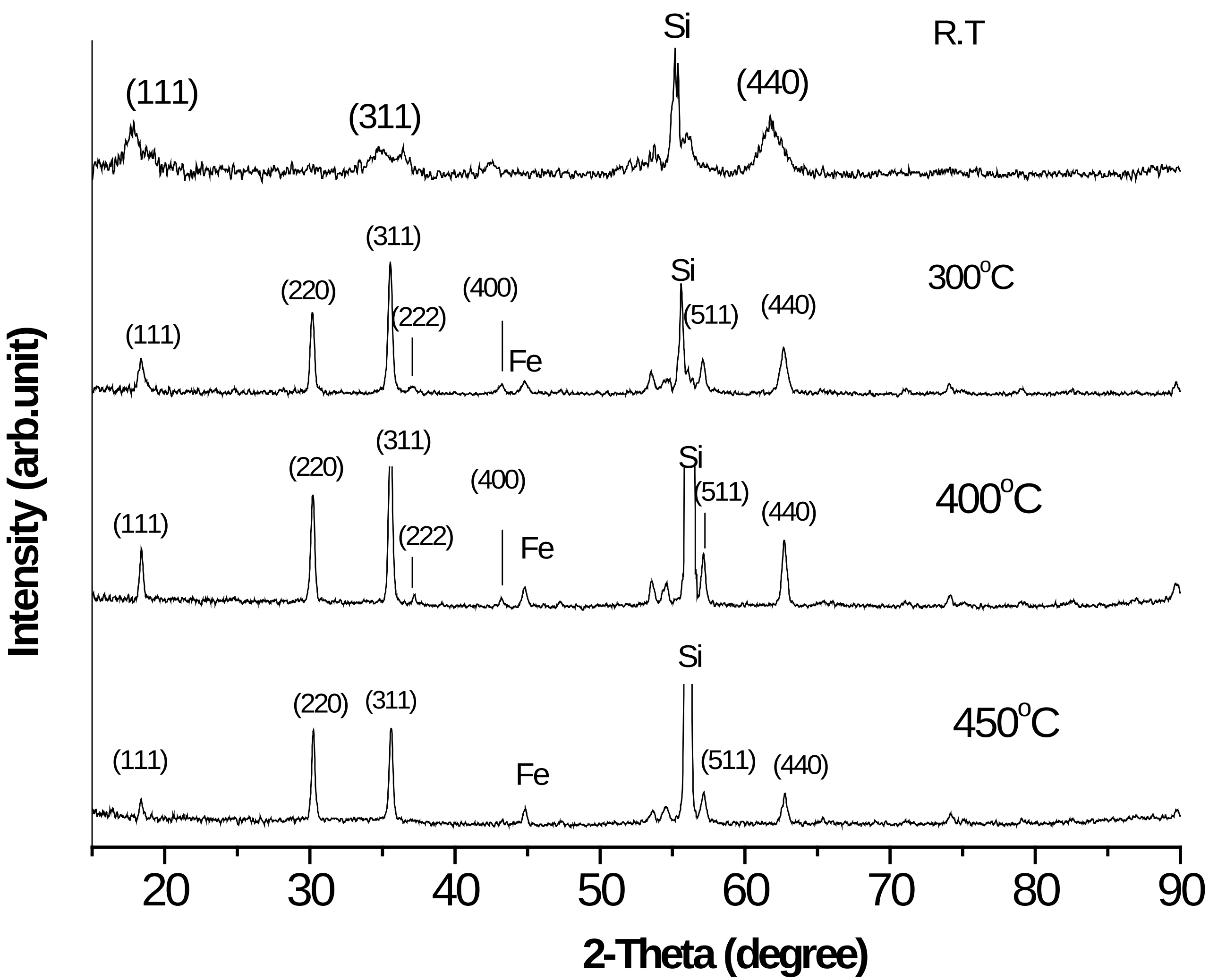
i) Deposition temperature = R. T
ii) Deposition temperature = 350, 400, 450°C
iii) Annealing temperature = 300, 400, 450°C for 1hr



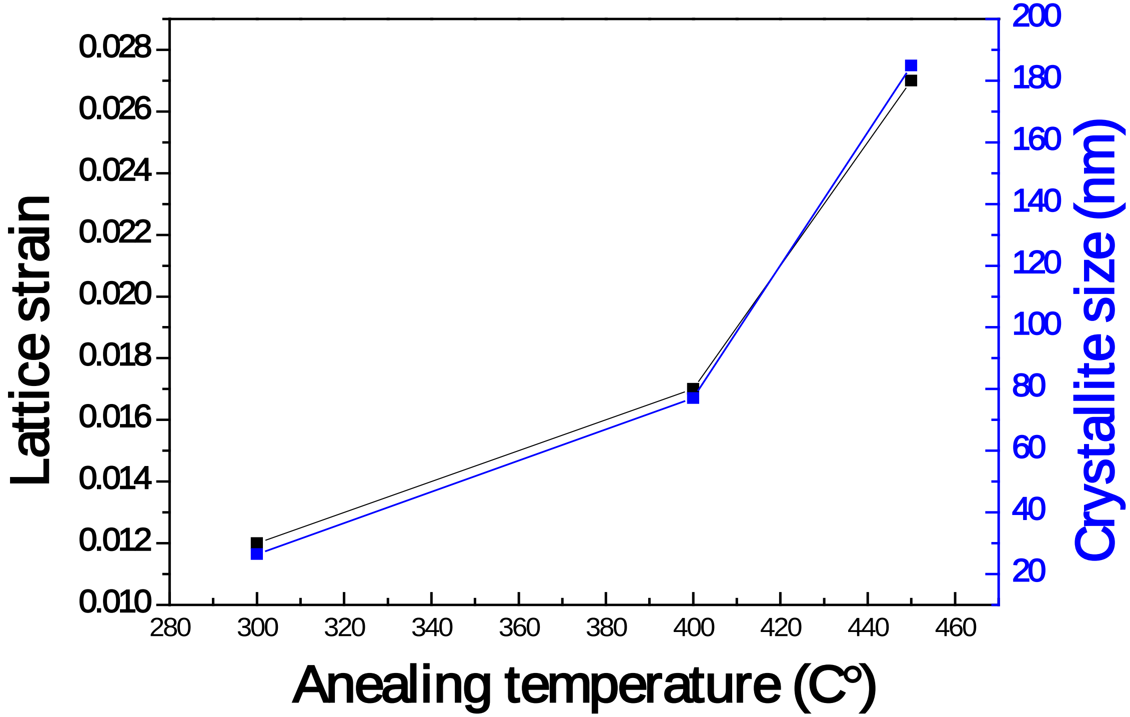
SEM images of (a) Fe_3O_4 thin film annealed at 450 °C and (b) as-deposited film at 450 °C.

Ramay *et. al*, Chinese Physics Letters 26 (2009) 117504

Annealed Films



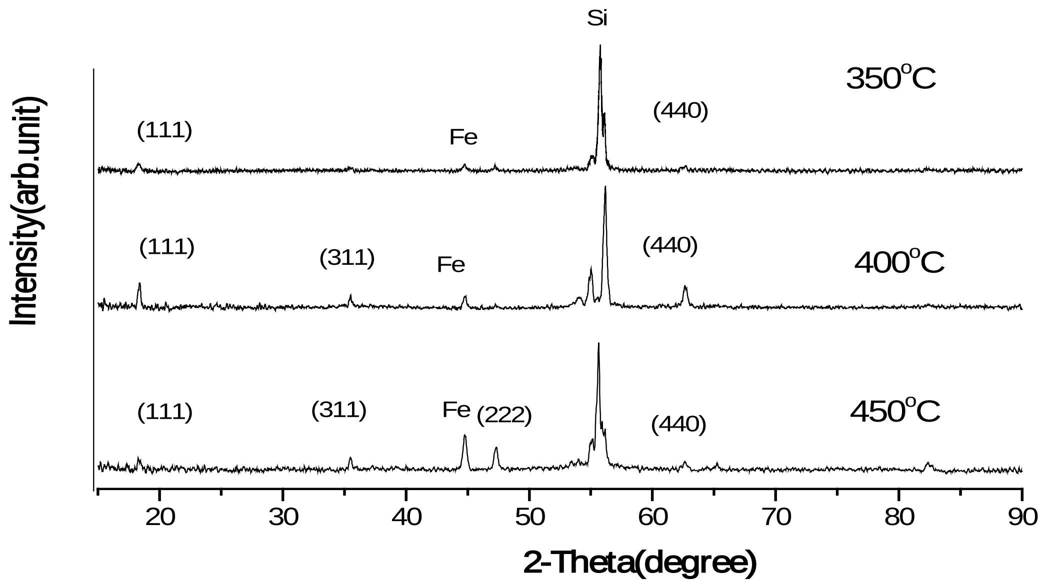
X-ray diffraction patterns of Fe_3O_4 thin films on Si(100) substrates deposited at room temperature and annealed at the shown temperatures



- Peak positions shifts to higher angles as compared to bulk Fe_3O_4
- Shifting is related to uniform lattice strains in the plane of the films
- FeO is stable only at a temperature greater than 570 ° C and is decomposed into Fe and inverse spinel Fe_3O_4 below 570 ° C.

Ramay *et. al*, Chinese Physics Letters 26 (2009) 117504

As deposited Films



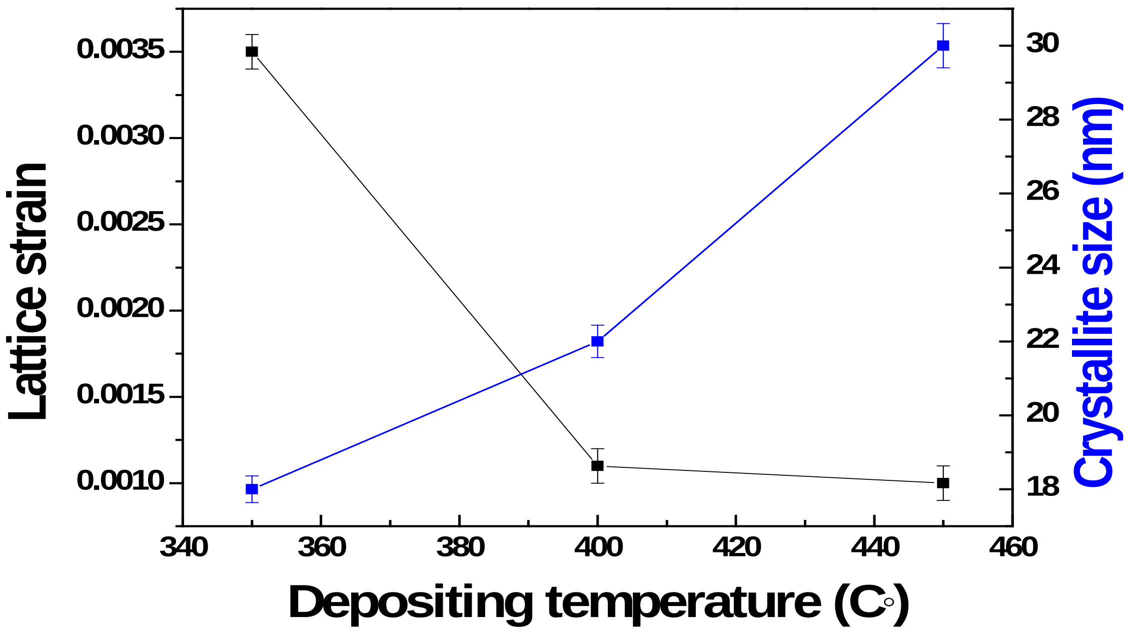
XRD diffraction patterns of as deposited thin films

- Smaller lattice strains as compared to annealed films due to larger film thickness

- The trends in the unit cell and crystallite size are identical in the annealed and as-deposited films.

Ramay *et. al*, Chinese Physics Letters 26 (2009) 117504

As deposited Films



- ➢Smaller lattice strains as compared to annealed films due to larger film thickness

- ➢The trends in the unit cell and crystallite size are identical in the annealed and as-deposited films.

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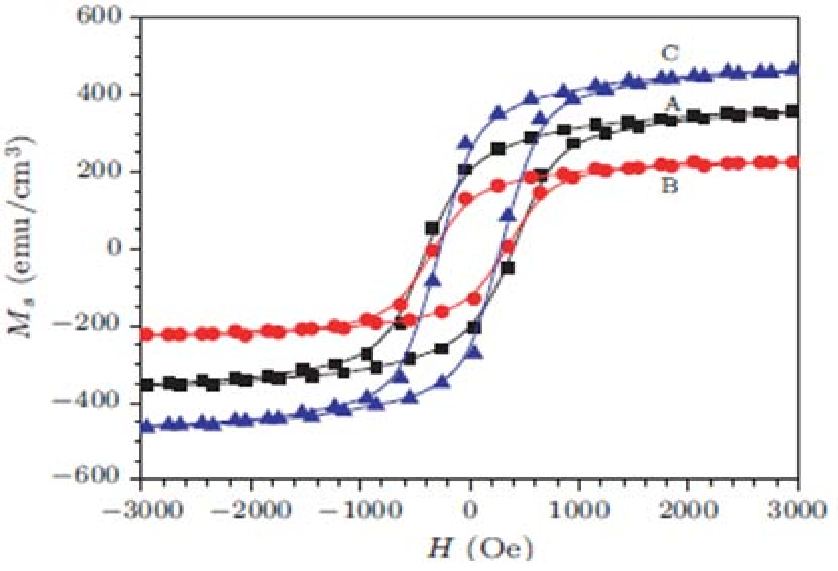
Effect of substrate temperature on the magnetic properties of Fe_3O_4 thin films

Annealed Films

Annealing temperature (°C)	M_s (emu/cc)	Hc (Oe)
300	431	422
400	649	390
450	854	325



In-plane magnetization curves of annealed thin films with A, B and C representing the samples annealed at 300, 400 and 450∘C.

- Coercivity decreased with increasing annealing
- Increased saturation magnetization could be due to the increased Fe content in the thin films

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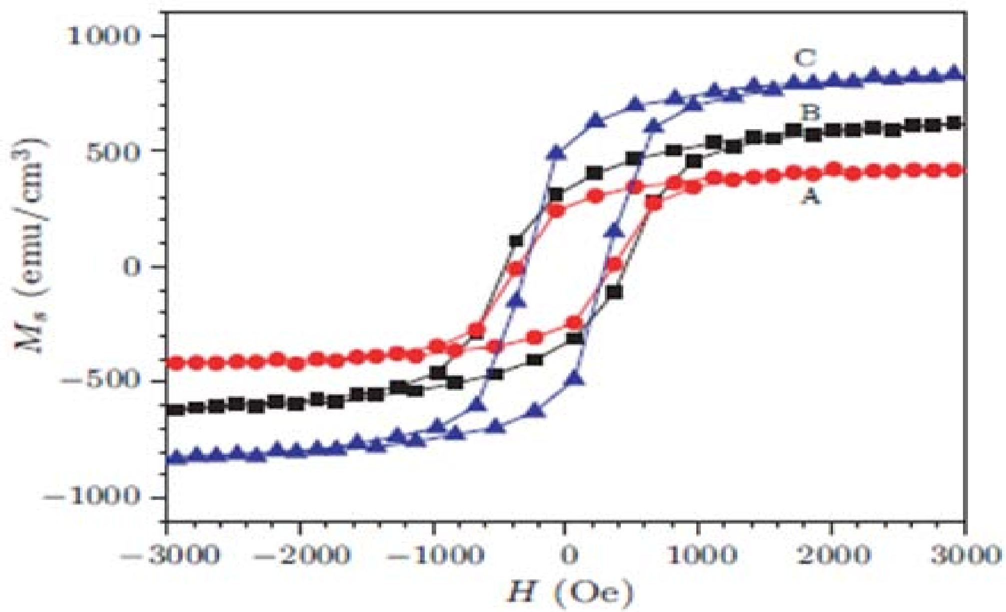
As-deposited Films

As-deposited temp. (°C)	M_s (emu/cc)	Hc (Oe)
300	374	449
400	231	318
450	477	274



Inplane magnetization curves of as-deposited thin films with A, B and C representing deposition temperatures of 350, 400 and 450 C respectively

- **Hysteresis loop indicate a single phase magnetic material but it is possible that the coercivity of Fe is too small as compared to M-H loop step size, so it is difficult to distinguish it.**

Kennedy R J and Stampe P A 1999 J. Phys. D: Appl. Phys. 32 16

Ramay *et. al*, Chinese Physics Letters **26** (2009) 117504

Acknowledgement

Prof. Dr. Sung Chull Shin
Director
Centre of Nanospinics of Spintronic Materials (KAIST, South Korea)

Prof. Dr. Saadat Anwar Siddiqi, Centre of Excellence in Solid State Physics

Dr. Sabieh Anwar
LUMS

Thanks

with

Good Energy!