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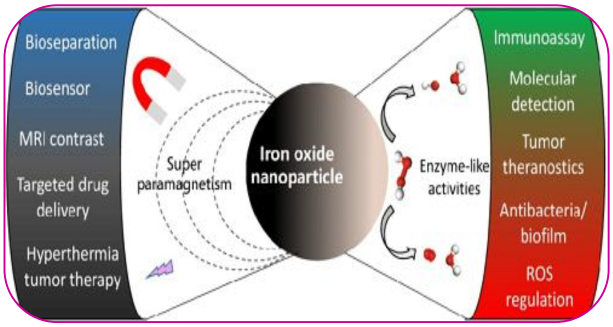

AN INTRODUCTION AND REVIEW ON IRON OXIDES AND MAGNETISM

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ABSTRACT:
Brief crystallographic and magnetic properties of different iron oxides have been discussed. Structural and magnetic properties of different iron oxides vary with temperatures are also illustrated.

KEYWORDS: *Magnetic properties, iron oxides, spinel, Mössbauer spectroscopy.*

1. INTRODUCTION AND REVIEW ON IRON OXIDES:

1.1 Ferrimagnetism: A substance composed of two sublattices with the magnetic moments of one sublattice tending to be antiparallel to those of the other [1]. A ferrimagnetic material may be defined as one, which below a certain temperature possesses a spontaneous magnetization that arises from a nonparallel arrangement of the strongly coupled atomic dipoles. There will be a net magnetic moment, when the sublattice magnetizations are not equal. The concept of ferrimagnetism has been broadened to include materials with more than two sublattices and with other spin configurations, such as spiral or triangular arrangements.

Ferrimagnetism was first found in materials with the spinel system structure [2-3]. Their chemical formula is PQ_2X_4, in which often $X = O^{2-}$, $Q = Fe^{3+}$, and P is some divalent cations, other more general combination of cations also are possible. Spinel was originally the name of a naturally occurring mineral with the chemical formula $MgAl_2O_4$. Ferrimagnetic spinels have the same crystal structure as the mineral but the cations are replaced by ions of transition elements. The oxygen ions, which are large compared to the cations, form essentially a face centered cubic lattice. The smallest cubic unit cell consists of eight molecules of PQ_2X_4, i.e., 32 oxygen ions. The cations occupy interstitial positions, of which there are two distinctly different types. In one the magnetic ion is surrounded by four oxygen ions located at the corners of a tetrahedron. Such an interstice is called tetrahedral, or A, site. In the other the magnetic ion is surrounded by six oxygen ions placed at the vertices of an octahedron; this is called as octahedral, or B, site. Eight A sites and 16 B sites are occupied per unit cell. Tetrahedral and octahedral sites are indicated in the diagram of a unit cell of the spinel lattice as shown in the fig. 1.1.

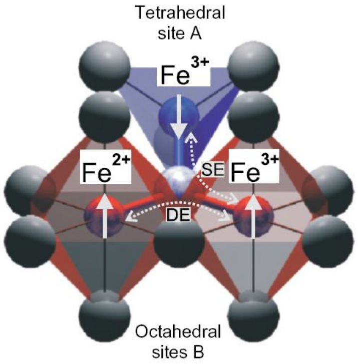

Fig.1.1 Crystallographic and magnetic structure in magnetite, Fe_3O_4, near tetrahedrally (site A) and octahedrally (site B) coordinated Fe atoms.

The length of an edge of the unit cell is approximately 8 Å. If the eight divalent (P) ions occupy the "A" sites and the 16 trivalent (Q) ions occupy the "B" sites, the structure is said to be a normal spinel. If on the other hand, "B" sites are occupied half by the divalent and half by trivalent ions, generally distributed at random, and the "A" sites by trivalent ions, the structure is said to be an inverse spinel. In the early days of the development of the subject such materials were called ferrites.

The spinels comprise an important class of compound with a large variety of electronic properties; some spinels are superconductors with a relatively high transition temperature [4-5], other exhibit magnetic properties which make these systems interesting for magnetic storage devices and other technological applications [6]. Nearly all spinels belong to the space group Fd3m (O_h^7) though some spinels also exist with lower symmetry [6]. The spinel structure is characterized by two parameters, the lattice constant "a" and the oxygen parameter "u" [7-8]. In the ideal spinel structure, the oxygen anions form a cubic close packed sublattice with $u = 3/8 = 0.375$. However in most spinels $u \neq 0.375$ which leads to a trigonal distortion of the octahedron of oxygens surrounding the "B" site along [111] while the "A" site remains in cubic symmetry. The spinel $ZnFe_2O_4$ belongs to the normal spinel structure with $\mathrm{a} = 0.84599$ Å and $u = 0.3845$. The Fe ions, which carry a magnetic moment due to partially filled 3d shell, are expected to occupy the "B" sites only. However, depending on the procedure under which the compound is prepared, partial inversion has been claimed to occur [9-13].

1.2 Iron oxide particles: The structures of iron oxides have been determined physically by single crystal x-ray diffraction or neutron diffraction. A crystallographic data for few iron oxides are given in the table 1.1.

Table 1.1: Crystallographic data for few iron oxides

Compound	Crystallographic system	Space group	Stacking of closed packed anions	A	b	C	Formula unit per unit cell, Z
Hematite	Hexagonal (Rhombohedral)	$R\bar{3}c$	ABAB[001]	0.5034	-	1.3752	6
Magnetite	Cubic	Fd3m	ABCABC[111]	0.8396	-	-	8
Maghemite	Cubic	$P4_332$	ABCABC[111]	0.83474	-	-	8

Iron oxides consist of arrays of Fe ions and O^{2-} ions. As the anions are much larger than the cations (the radius of the O^{2-} ion is 0.14 nm, whereas those of Fe^{3+} and Fe^{2+} are 0.065 nm and 0.082 nm respectively), the arrangement of the anions governs the crystal structure. There are two basic ways of representing the crystal structures of iron oxides – either in terms of the anion arrangement (packing) or a linkage of octahedra and/or tetrahedra formed from a central cation and its nearest anion neighbors. Iron oxides are made up of closed packed arrays of anions. The commonest arrangements of these sheets of anions in the third dimension are hexagonal close packing (hcp). The sheets of anions are stacked along some particular crystallographic direction with an average distance between anion layers of 0.23-0.25 nm for all iron oxides. The structural types of a few iron oxides are given in the table 1.2.

Hematite is isostructural with corundum. The unit cell is hexagonal with a=0.5034 nm and c=1.375 nm [14-17]. There are six formula units per unit cell. Hematite may also be indexed in the rhombohedral system. For the rhombohedral unit cell a_{rh}= 0.5427 nm and ⍰= 55.3^0 and there are two formula units per cell. The structure of hematite can be des0cribed as consisting of hcp arrays of oxygen ions stacked along the [001] direction, i.e. planes of anions are parallel to the (001) plane as given in fig. 1.2.

Table 1.2: Structural types of a few iron oxides

Structural type	Fe Oxide
Corundum	Hematite
Inverse spinel	Magnetite
Defect spinel	Maghemite

Two thirds of the sites are filled with Fe^{III} ions which are arranged regularly with two filled sites being followed by one vacant site in the (001) plane thereby forming six fold rings as shown in the fig. 1.3.

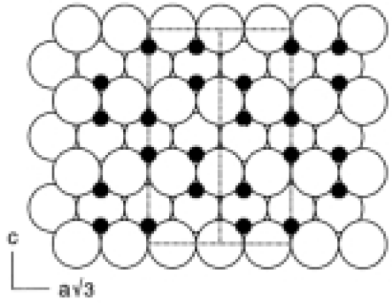

Fig. 1.2Structure of hematite; hexagonal closed packing of oxygens with cations distributed in the octahedral interstices, unit cell outlined.

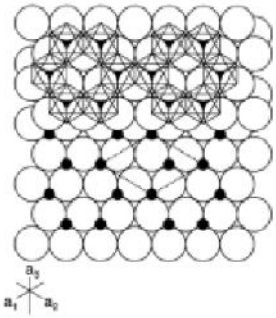

Fig. 1.3 View down the c-axis showing the distribution of Fe ions over a given oxygen layer and the hexagonal arrangement of octahedra, unit cell outlined.

The main details of the structure of magnetite were established in 1915 [18-19]. The structure is that of an inverse spinel [20], Magnetite has face centered cubic unit cell based on 32 O^{2-} ions which are regularly cubic closed packed along the [111]. The unit cell edge length is a = 0.839 nm. There are eight formula units per unit cell. Magnetite differs from most other iron oxides in that it contains both divalent and trivalent iron. The structure consists of octahedral and mixed tetrahedral/octahedral layers stacked along [111]. Magnetite is frequently non stoichiometric in which case it has a cation deficient Fe^{III} sublattice. In stoichiometric magnetite Fe^{II}/Fe^{III} =0.5, the divalent iron may also be partly or fully replaced by other divalent ions (eg. Mg^{II}, Co^{II}, Zn^{II}). Fitting of guest ions into the structure is assisted by the flexibility of the oxygen framework, which can expand or contract to accommodate cations, which differ in size from Fe^{II}. Cation substitution is accompanied by changes in the unit cell edge length.

Maghemite has a structure similar to that of magnetite. It differs from magnetite in that all or most Fe ions are in the trivalent state. Cation vacancies compensated for the oxidation of Fe^{II}. Maghemite has a cubic unit cell and Hägg first determined the value of which in 1935. The currently accepted value of ‘a’ is 0.834 nm. Eight cations occupy tetrahedral sites and the remaining cations are randomly distributed over the octahedral sites [21]. The vacancies are confined to the octahedral sites. Each cell of maghemite contains 32 O^{2-} ions and total 13.33 Fe^{II} ions and 2.67 vacancies and this gives the formula $Fe_8[Fe_{13..33}\square_{2.67}]O_{32}$ (□≡ vacant sites) and the space group Fd3m.

The main type of magnetic interaction between Fe ions and adjacent sites in a solid is the electrostatic exchange interaction; this tends to cause parallel or antiparallel alignment of the spins. In iron oxides, the Fe^{3+} ions are surrounded by O^{2-} or OH^- ions, so the exchange reaction proceeds via the intervening ligand. This process is termed super-exchange. Unpaired electron in the e_g orbitals of the Fe^{3+} ions interact magnetically with electrons on the p orbitals of the O^{2-} ions and, provided the cation and the ligand are close enough to permit coupling of their electrons, a chain coupling effect which passes through the crystal takes place. The exchange constants for these processes have been measured and found to depend on the Fe-O bond length and, above all, on the bond angle. Exchange interactions are strong when the Fe^{3+} bond angles are 120-180° and much weaker when these angles are 90°. The types of exchange interactions in iron oxides are listed in the table 1.3.

Table 1.3: Exchange interactions in some iron oxides.

Ion pair	Fe-O-Fe bond angle	Type of interaction
Fe^{3+}- Fe^{3+}	90^o 120^o	weak antiferromagnetic strong antiferromagnetic
Fe^{2+}- Fe^{2+}	90^o $120\text{-}180^o$	weak antiferromagnetic strong antiferromagnetic

The magnetic properties of iron oxides can be determined using Mössbauer spectroscopy, neutron powder diffraction and magnetometry. The characteristic parameters are the magnetic constants, the permeability, the saturation magnetization, the magnetic anisotropy constants and the B_{hf} as given in the table 1.4 [22];

The origin of the magnetic hyperfine field (B_{hf}) in iron oxides is the polarization of the inner "s" electrons by the atom's own 3d electrons. Minor contributions also come from the polarization of the s electrons by the 3d electrons of neighboring cations and from the spin dipolar moment of the 3d electrons themselves. Below T_N or T_C, iron oxides undergo spontaneous magnetization.

Table 1.4: Magnetic properties of some iron oxides.

Oxide	Temperature (K)	Magnetic structure	Saturation magnetization σ_s at 300 K ($Am^2\ kg^{-1}$)	Anisotropy Constants K_{eff} (Jm^{-3})	Magnetic hyperfine field B_{hf} (T)	
					295 K	4 K
Hematite	956 T_C 260 T_M	weakly ferromagnetic antiferromagnetic	0.3	$1\text{-}6.10^4$	51.8	54.2
Magnetite	850 T_C	ferrimagnetic	92-100	$10^4\text{-}10^5$	49.2	-
	120 Verwey Transition					
Maghemite	820-986 T_C	ferrimagnetic	60-80	10^5	50	52.6

The B_{hf} increases rapidly as the temperature falls below that of the ordering temperature and at low enough temperatures approaches the saturation value, i.e. the maximum value obtainable at 0 K. The magnitude of the saturation hyperfine field can provide an estimate of the degree of covalent character in the solid [23]. B_{hf} decreases as diamagnetic cations, such as Al, enter the structure.

1.3 SUMMARY OF REVIEWS AND CONCLUSION:

The above review briefly discussed the basics structures and magnetic properties of iron oxides. The variations in structural and magnetic properties of different types of iron oxide particles with the variation of temperature have been discussed.

1.4 REFERENCES:

[1] L. Néel, Ann. Phys. (Paris) **3, 137**, 1948.
[2] C. Kittel, *Introduction to solid state physics,* John Wiley & Sons, Inc., New York, 7th Ed., 1996.
[3] A.H. Morrish, *The physical principles of magnetism,* IEEE Press, New York, 2001.
[4] D.C. Johnston, J. Low. Temp. Phys. **25**, 145, 1976.
[5] R.W. McCallum, D.C. Johnston, C.A. Luengo, and M.B. Maples, J. Low. Temp. Phys. **25**, 177, 1976.
[6] R.E. Vanden berghe and E.De Grave, in *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, edited by G.J. Long and F. Grandjean, Vol.3, Plenum, New York, 1989.
[7] E.W. Gorter, Philips Res. Rep. **9**, 295, 1954.
[8] R.J. Hill, J.R. Graig, and G.V. Gibbs, Phys. Chem. Miner., **4**, 317, 1979.
[9] F.K. Lotgering, J. Phys. Chem. Solids **37**, 139, 1966.
[10] S. Ligenza, Phys. Status Solidi **75**, 315, 1976.
[11] T. Sato, K. Haneda, T. Iijima, and M. Seki, in *Ferrites*, Proceedings of the ICF6, Tokyo, 1992, edited by T. Yamaguchi and m. Abe (The Japan Society of Powder and Powder Metallurgy, Tokyo, 1992), p. 984.
[12] T. Sato, K. Haneda, M. Seki and T. Iijima, *Proceedings of the International Symposium on the Physics of Magnetic materials* (World Scientific, Singapore, 1987), p. 210.
[13] T. Kamiyama, K. Haneda T. Sato, S. Ikeda, and H. Asano, Solid State Commun. **81**, 563, 1992.
[14] W.H. Bragg and W.L. Bragg; *X-rays and crystal structure,3rd Ed.* G. Bell and Sons, London, 1918.
[15] L. Pauling and S.B. Hendricks; *The crystal structures of hematite and corundum,* J. Am. Chem. Soc., **47**, 781-790,1925.
[16] R. L. Blake, R. E. Hessevick, T. Zoltai, L. W. Finger; *Refinement of hematite structure,* Am. Min. 51, 123-129, 1966.
[17] Y. Sata, S. Akimoto; *Hydrostatic compression of four corundum type compounds:* ⍰-Al_2O_3, V_2O_3, Cr_2O_3; and ⍰-Fe_2O_3, J Appl. Physics **50,** 5285-5291, 1979.
[18] W.H. Bragg, *The structure of magnetite and spinels*, Nature, **95**, 561, 1915.
[19] S. Nishikawa, The structure of some crystals of spinel group, Proc. Math. Phys. Soc., Tokyo, 8, 199-209, 1915.
[20] R. J. Hill, J. R. Craig and G.V. Gibbs, Systematics of the spinel structure type, Phys. Chem. Min., **4**, 317-339,1979.
[21] G. A. Waychunas, Crystal chemistry of oxides and oxyhydrides, In: Lindsley, D. H. (ed.) Oxide minerals petrolic and magnetic significance. Reviews in Mineralogy **25,** Min. Soc. Am., 11-68, 1991.
[22] J.M.D. Coey Magentic properties of iron in soil iron oxides and clay minerals. In: J.W. Stucki, B.A. Goodman and U. Schwertmann (eds.) Iron in soils and clay minerals. D. Reidel Publ. Co., 397-466, 1988.
[23] E. Murad and J.H. Johnston, *Iron oxides and oxyhydroxides.* In. G. Long (ed.) Mössbauer spectroscopy applied to inorganic chemistry. Plenum Publ. Corp. **2**, 507-582,1987.

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