

Crystal Structure and Magnetic Interactions of Ferrites

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Abstract: Systematic study on chemical compositions and magnetic properties of various ferrites were reported by Hilpert in 1909. He successfully prepared spinel ferrites using manganese, copper, cobalt, magnesium and zinc. Ferrites can be divided into three groups based on their crystal structures: spinel ferrites, garnet ferrites and hexagonal ferrites. An ideal spinel structure consists of a cubic close-packed (fcc) array of oxygen anions, where one eighth of the tetrahedral (A) sites and one half of the octahedral (B) sites are filled with cations. Fundamental crystal structure of garnet is derived from the garnet mineral, $Mn_3Al_2Si_3O_{12}$, in which Si and Mn are substituted by Y and Al to form $Y_3Al_5O_{12}$. Hexagonal ferrites are a family of inter-related compounds with hexagonal and rhombohedral symmetries. Due to the specific electronic configurations of cations and the types of superexchange interactions among them, the magnetic properties of ferrites are strongly dependent on the occupancy and exchange of cations in the two sites.

Keywords: Spinel, garnet, hexagonal, superexchange interactions

1. Introduction

The meaning of Greek word 'magnet' is magnetite deposits in the district of Magnesia in Asia Minor [1]. The use of magnetite, a natural magnetic material, can be traced back to two millennia ago, when the ancient Chinese recognized its magnetic properties and started to use it as a mariner's compass. The first scientific book of magnetism titled *De Magnete* was published in 1600 by William Gilbert [2]. In 1825, the discovery of the origin of a magnetic field in relation to electrical currents by Oersted led to intensive studies and rapid development in magnetism [1]. Large variety of magnetic materials and their properties are related to the three ferromagnetic elements: iron, cobalt and nickel. Ferrites are a group of magnetic materials. They are defined as ceramic-based ferromagnetic materials, including iron oxides and complex iron oxides containing other metals such as a rare earth or an alkali earth [3]. As compared to their ferromagnetic alloys, ferrites have a lower saturation magnetization. They have several advantages, including applicability at higher frequencies, lower electrical conductivity, higher heat resistance and greater corrosion resistance [4].

Although the discovery and use of natural ferrites can be traced back to ancient time, the first systematic study on chemical compositions and magnetic properties of various ferrites were reported by Hilpert about one century ago in 1909, who successfully prepared spinel ferrites using manganese, copper, cobalt, magnesium and zinc [5]. Although commercialization of ferrites took place in the early twentieth century, they did not attract much attention until the 1950's, when the new applications, such as in electronics, computer circuitry and microwave devices, were rapidly expanding. The much progress of electronic and automobile industries has promoted the expansion of ferrite production all over the world. The rapid development of ferrite industry has lead to fundamental studies and understandings on the magnetic properties and structures of these materials. Polycrystalline soft ferrite prepared from metal oxides are magnetic semiconductor and have made important contribution both technological and conceptual

development of electronics and electronic industries. Up until today, soft ferrites remain the best magnetic materials which are irreplaceable by any other magnetic materials with respect to their very high frequency applications because they are inexpensive, more stable, easily manufactured. They have wide variety of technological applications in transformer core, inductors, high quality filters, radio frequency circuits, rod antennas, read write heads for high-speed digital tape and operating devices as well.

1) Crystal Structure

Ferrites can be divided into three groups based on their crystal structures: spinel ferrites, garnet ferrites and hexagonal ferrites [2].

2) Spinel Ferrites

The spinel structure is originated from the natural magnetic mineral $MgAl_2O_4$. There is a large group of ferrites possessing such a structure. An ideal spinel structure consists of a cubic close-packed (fcc) array of oxygen anions, where one eighth of the tetrahedral (A) sites and one half of the octahedral (B) sites are filled with cations. One unit cell consists of eight formula units AB_2O_4 , with 64 tetrahedral sites and 16 octahedral sites [6]. The general chemical formula for spinel ferrite is MFe_2O_4 where M is a divalent metal ion (like Mn, Zn, Fe, Ni, Mg, Co etc.). A diagram of the spinel crystal structure is illustrated in Fig.1

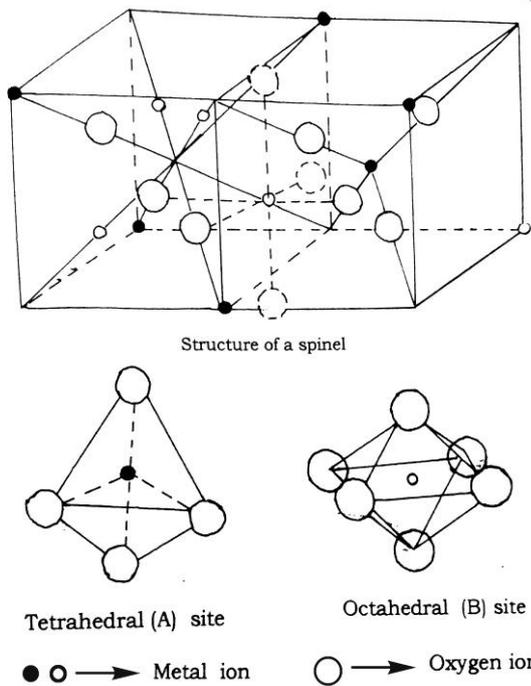


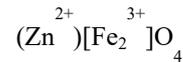
Figure 1: Spinal Structure

Actually, the oxygen anions in the spinel structure are located out of the ideal positions of the fcc array. This is because the presence of tetrahedral cations, where ionic sizes are always larger than the space of an ideal tetrahedral site, forcing oxygen anions to shift in the [111] direction. A deformation parameter, u , is used to reflect the adjustments in structure to accommodate the differences in ionic sizes of cations in the tetrahedral and octahedral sites [7] as shown in Fig.2. The ideal value of u is $3/8 (= 0.375)$ for the undeformed structure while most of the spinel ferrites possess a u value ranging between 0.375 and 0.385. The value of u can influence the cation distribution in different interstitial sites.

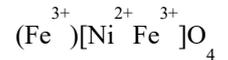
The u parameter increases linearly with $(r_A - r_B)/a$, where 'a' is the lattice parameter and r_A and r_B are the radii of ions in the tetrahedral (A) and octahedral [B] site respectively. The local symmetry of the cation sites is cubic in the A-position and trigonal in B. The trigonal symmetry is due to configuration of the neighboring cations and the distortion of the anion octahedron, if u is not equal to $3/8$. Each of the four diagonal belongs to one of the cations in the primitive cell. So that, these cations are nonequivalent, differing in their local symmetry axis. Each of them may be taken as representing on face centre cubic (Fcc) sub lattice with the lattice constant 'a'. But the local symmetry of the A-site remains cubic even if u is not equal to $3/8$, so that, both sub lattices represented by A-sites in the primitive cell are mutually equivalent.

Cation distributions in spinel ferrites are important because the physical properties are related to the types of cations in the structure and the cation distribution over the interstitial sites. There are two basic cation distributions in spinel ferrites: normal distribution and inverse distribution. In normal spinel ferrites, all divalent cations are located in tetrahedral sites, while all trivalent cations are located in octahedral sites. On the other hand, all divalent cations in the

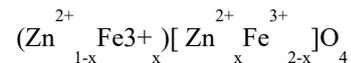
inverse spinel ferrites are located in octahedral sites, while trivalent cations are equally distributed in both tetrahedral and octahedral sites. For instance, one of the ferrite, zinc ferrite, has a normal spinel structure, which can be indicated as:



where the parentheses represent the tetrahedral site occupancy, and the octahedral sites are illustrated by the square brackets. Nickel ferrite, has an inverse spinel structure:



The above cation distributions are presented in ideal structures. Intermediate cation distribution exists in many ferrites. For example, the following distribution can occur in zinc ferrite:



where x indicates the degree of inversion, which can be strongly affected by the processing parameters as well as particle size. There are several factors that influence an individual cation

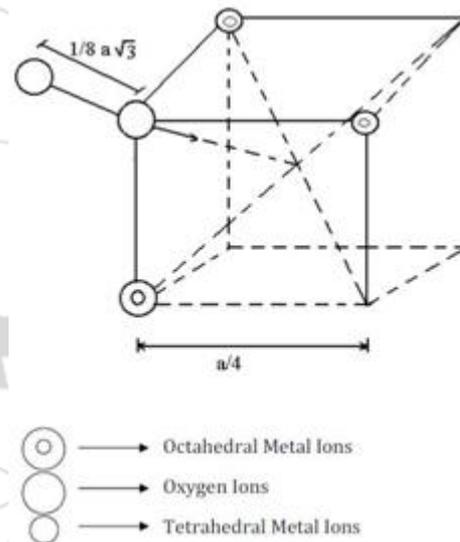


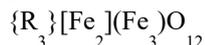
Figure 2: Surroundings of oxygen in spinel ferrite

occupying a particular site, including elastic energy, electrostatic energy, crystal field stabilization energy and polarization energy [8]. Among them, electrostatic energy is related to the deformation parameter u . For $u < 0.379$, the electrostatic energy favors the inverse arrangement, while for greater u values, the normal distribution is more stable.

2) Garnet Ferrites

Garnet ferrites can be represented by the general formula $R_3Fe_5O_{12}$, where R is rare earth trivalent cation or yttrium cation [2]. Their fundamental crystal structure is derived from the garnet mineral, $Mn_3Al_2Si_3O_{12}$, in which Si and Mn can be substituted by Y and Al to form $Y_3Al_5O_{12}$. For magnetic garnets, Al is further substituted by Fe. A unit cell of garnet therefore consists of eight formula units, where the oxygen sublattice has a polyhedra combination with three types of interstitial sites: dodecahedral (eight-fold), octahedral (six-fold) and tetrahedral (four-fold) sites. All the

polyhedra are distorted, where the cation distributions can be represented as follows:



where { }, [] and () represent dodecahedral, octahedral and tetrahedral sites, respectively.

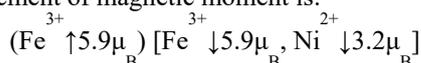
3) Hexagonal ferrites

Hexagonal ferrites are a family of inter-related compounds with hexagonal and rhombohedral symmetries [2,9]. Their compositions is the combinations of three oxides MeO, Fe₂O₃ and BaO, where Me is a divalent metal. In crystal structure, all the related compounds can be understood as a stacking of three basic block units, S, R and T, where S unit is formed by two formula units MeFe₂O₄, R unit has the stoichiometry (BaFe₆O₁₁)²⁻ and T unit has four layers with formula Ba₂Fe₈O₁₄. Unlike spinel and garnet ferrites, hexagonal ferrites has more than one types of crystal structure. Different stackings of block units give rise to a remarkable variety of compounds.

4) Magnetic Interactions

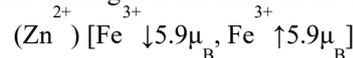
In ferrites, the metallic ions occupy two crystallographically different sites, i.e. octahedral [B] and the tetrahedral (A) site. Three kind of magnetic interactions are possible, between the metallic ions, through the intermediate O²⁻ ions, by super-exchange mechanism, namely, A-A interaction, B-B interaction and A-B interaction. It has been established experimentally that these interaction energies are negative, and hence induce an anti-parallel orientation.

As mentioned earlier, spinel ferrites exhibit cubic close-packed (fcc) arrays of O anions, where the tetrahedral (A) and octahedral (B) sites are partially occupied by metal cations. Due to the specific electronic configurations of cations and the types of superexchange interactions among them, the magnetic properties of ferrites are strongly dependent on the occupancy and exchange of cations in the two sites. In spinel ferrites, direct interactions are negligible, due to the large distance between cations. Superexchange interaction occurs between two metal cations through the existence of a bridging oxygen ion. It involves the temporary transfer of one oxygen 2p electron to a neighboring metal ion. The A-B interaction is the strongest superexchange interaction in the spinel structure, followed by B-B interaction, and then A-A interaction [10]. The magnetic moment can be calculated based on the magnetic moment of the cations and the interactions between them. For example, in nickel ferrite with an inverse spinel structure, Fe³⁺ cations on A sites are aligned with those on B sites in an antiparallel fashion through A-B interaction. Since Fe³⁺ has a magnetic moment of 5.9μ_B and Ni²⁺ has a magnetic moment of 3.2μ_B, the arrangement of magnetic moment is:

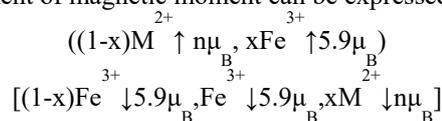


The antiparallel arrangement cancels the moments of Fe³⁺ on octahedral and tetrahedral sites. The net moment therefore only comes from the magnetic moment of Ni²⁺, which is parallel to Fe³⁺ on octahedral sites. In contrast, as Fe³⁺ on octahedral sites are in antiparallel order through B-B interaction and Zn has zero magnetic moment, zinc ferrite

with normal spinel structure has zero net magnetic moment. The arrangement of magnetic moment on the two sites is:



In general, for a spinel ferrite with a degree of inversion “x” and a magnetic moment of nμ_B for divalent cation “M²⁺”, the arrangement of magnetic moment can be expressed as:



The net moment is therefore:

$$\{11.8[1-x]-n[1-2x]\}\mu_B$$

where x = 0 and 1 for the normal and inverse cation distributions, respectively, while 0<x<1 for the partially inverted spinel ferrites.

2. Conclusions

- 1) Ferrites are divided into three groups depending on the crystal structures: spinel ferrites, garnet ferrites and hexagonal ferrites.
- 2) The spinel structure is originated from the natural magnetic mineral MgAl₂O₄
- 3) Fundamental crystal structure of garnet is derived from the garnet mineral, Mn₃Al₂Si₃O₁₂
- 4) Hexagonal ferrites are inter-related compounds with hexagonal and rhombohedral symmetries.
- 5) Three kind of magnetic interactions are possible, between the metallic ions, through the intermediate O²⁻ ions, by super-exchange mechanism, namely, A-A interaction, B-B interaction and A-B interaction.

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