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Ferrites – what is new?

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Abstract. Ferrites, combining insulating and ferrimagnetic properties, have long been used in technology. The aim of this paper is to focus on new features in these materials. In the classical theory of ferrimagnets, Néel had predicted the unusual thermal variation of the spontaneous magnetization, such as, the disappearance of the magnetization at a temperature which was not the Curie temperature but at a point where there was compensation of the spontaneous magnetization of the two sublattices. We show experimentally that temperature (T_K) in spinel oxide is different under the ZFC and FC magnetization method. To our knowledge, only limited attempt has been made to study T_K as very few systems exhibit such behavior. In general, some of the ferrites have specific semiconducting properties, e.g., a very low carrier mobility. We discuss the anomalies of the magneto-resistance in ferrites that occur at order–disorder and order–order magnetic phase transition along with our ac and dc conductivity data near the spin compensation temperature. Another notable feature of the ferrites is that, upon irradiation of heavy ions, one can tune the magnetic ordering on bulk sample without destructive effects, i.e., irradiation-induced magnetization. It is interesting to note that spinel ferrite (nano) particle is an ideal small particle magnetic system as the crystal chemistry issue can be controlled, unlike pure metal particle systems where the crystal chemistry issues are basically fixed. In relevance to this, we will also discuss the future prospects, namely, the effect of irradiation on small particle magnetism, as, so far, only a limited attempt has been made in this field.

Keywords. Ferrites; conductivity; magnetoresistance; spin compensation temperature; irradiation effect; nanoparticle.

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1. Introduction

Ferrites are widely used magnetic materials combining insulating and ferrimagnetic properties. Some of the ferrites have specific semiconducting properties (a very low carrier mobility), e.g., $MnFe_2O_4$ [1]. Focussing on nanoparticles of magnetic oxides, most of the reported work is based on ferrite nanoparticles. Recently, the possibility of CMR in ferrite systems has been shown, e.g., $FeCr_2S_4$, Co–Mn–O [2]. The purpose of this paper is to specify what are the new features still arising from the bulk and nanoparticle ferrite materials. Here we shall focus on: (1) The physical significance of the spin compensation temperature (T_K) in field-cooled (FC) and zero field-cooled (ZFC) measurements, (2) the changes in magneto-resistance (MR) in the region of magnetic compensation temperature of a typical ferrite and order–disorder transition, and (3) irradiation-induced magnetization of bulk sample and the prospects of such experimental work on spinel ferrite particles in view of its potential application in the development of bio-magnetic carrier.

2. Spin compensation temperature (T_K)

In a ferrimagnet, there are two sublattices of local dipoles, M_A and M_B, generally, with $M_A \# M_B$, for $T < T_C$, $M = M_A + M_B$. In most cases, at $T < T_C$, the contribution of one of the sublattices is larger in value, so that the resulting spontaneous magnetization increases as T is decreased. In a few cases, at a temperature between T_C and T_K (where T_K is the compensation temperature), $M_A = M_B$. Between T_C and T_K, the contribution of one of the sublattices dominates. In the classical theory of ferrimagnets, Néel had predicted the unusual thermal variation of such spontaneous magnetization [3]. In general, control of thermodynamics of magnetization is very difficult. In most magnetic materials, the magnetization increases monotonically with decreasing temperature. In order to search for a material with spin compensation temperature, the theoretical prediction of the magnetic properties of a material is required. However, in view of various types of exchange/superexchange interactions, such a prediction is difficult, particularly in metal or metal ion substitution. Even though Néel predicted the existence of T_K in 1948 [3], the first experimental observation was reported only in 1962 in certain metal oxides [4] and more recently in molecular magnets [5]. Recently, we have synthesized $Fe_2Mo_{1-x}Ti_xO_4$ ($x = 0.2$–0.6) where the spin compensation temperature T_K varies from ~160 K to 110 K and T_C varies from 345 K to 125 K, respectively [6]. The spin compensation temperature is achieved by making Fe_A–O–F_B interactions weaker with Fe^{3+} ions. We have observed T_K in this system under FC and ZFC conditions. Figure 1 shows that T_{K1}(ZFC) ~180 K and

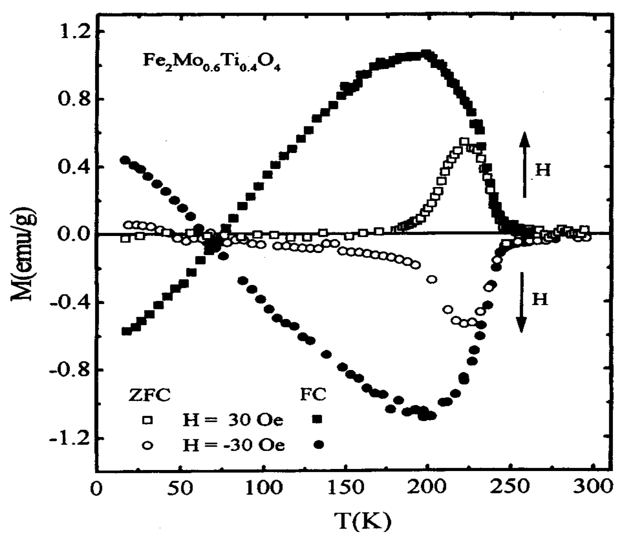

Figure 1. Temperature dependence of field-cooled (FC) and zero field-cooled (ZFC) magnetization of $Fe_2Mo_{0.6}Ti_{0.4}O_4$ measured at 30 Oe (positive and negative field).

T_{K2}(FC) ~75 K at 30 Oe, for $Fe_2Mo_{0.6}Ti_{0.4}O_4$ for $T < T_C$ (200 K). Application of negative magnetic field results mirror image of magnetization as shown in the figure. Figure 2 shows magnetization under FC and ZFC measured at 30 Oe and 1 kOe. It is interesting to note that T_K strongly depends upon field for ZFC condition whereas it is independent of field for FC condition. To our knowledge, only limited reports are available about such a field dependence. In some cases like molecular magnets (Prussian blue materials) this magnetic turn about with two reversal of magnetization, at 35 K and 55 K under FC condition, plays an important role in the design of a magnet [5]. However, the effect of magnetization in such systems under ZFC condition is not clear. It may be mentioned that the possibility of many compensation points in the total magnetization curve have been reported for different ferrimagnetic binary alloys, using standard mean-field theory and the effective field theory

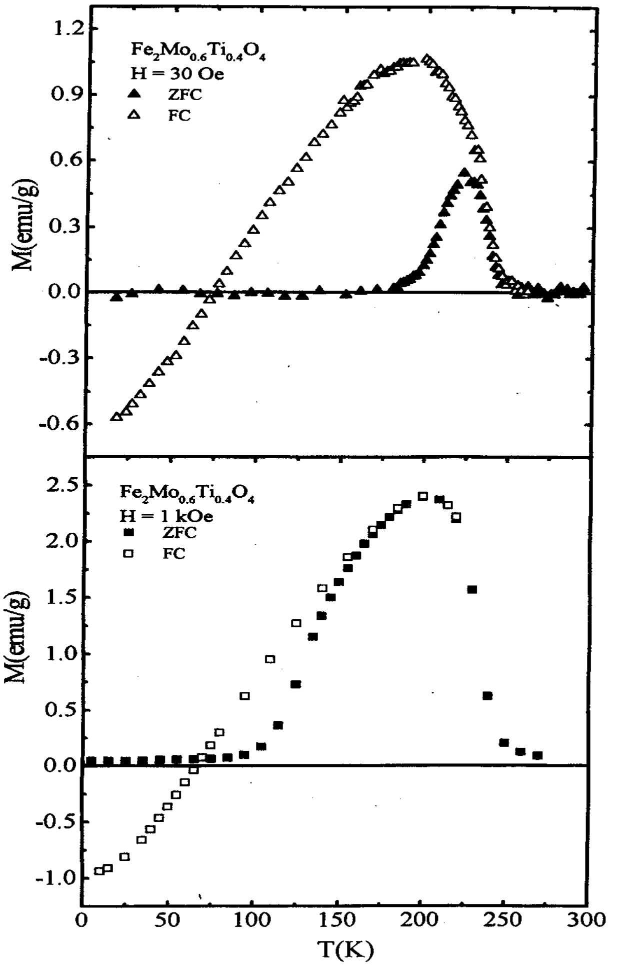

Figure 2. Temperature dependence of field-cooled (FC) and zero field-cooled (ZFC) magnetization of $Fe_2Mo_{0.6}Ti_{0.4}O_4$ measured at 1 kOe.

with correlations [7]. Magnetization curves not predicted in Néel theory of ferrimagnets, are also found. According to Belov [8] in the presence of field H the compensation point (T_K) indicates the occurrence of an order–order magnetic phase transition.

3. Magneto-resistance in the region of spin compensation temperature

The magnetic field and temperature dependence of the magneto-resistance of ferrites, including ferrimagnets, are complex due to the influence of inter-sublattice structure of ferrites and the specific nature of the electronic processes which occur in these materials. Figure 3 shows the isotropic magneto-resistance $H > H_s$ where H_s is the saturation field of lithium chromite ferrite in the region near T_K [8]. The sign of the isotropic MR is reversed from negative to positive. Similar changes of the sign of the MR have been observed for the metallic ferrimagnet $MnGe_2$. At temperature $T < T_K$, where the ferrite magnetization is due to the octahedral sublattice exhibiting a strong low temperature paraprocess, an external field H orders the magnetic moments of the cation and this leads to negative MR. In the region $T < T_K$, the magnetization of the octahedral sublattice is reversal to H and the paraprocess is of the antiferromagnetic type (flipping the magnetic moments of the cation). This enhances the scattering of carriers and gives rise to a positive MR.

The ac and dc conductivity results of $Fe_2Mo_{1-x}Ti_xO_4$ are shown in figures 4 and 5. It is seen that the resistivity increases by a factor of 10^5. The increase is more or less raising in

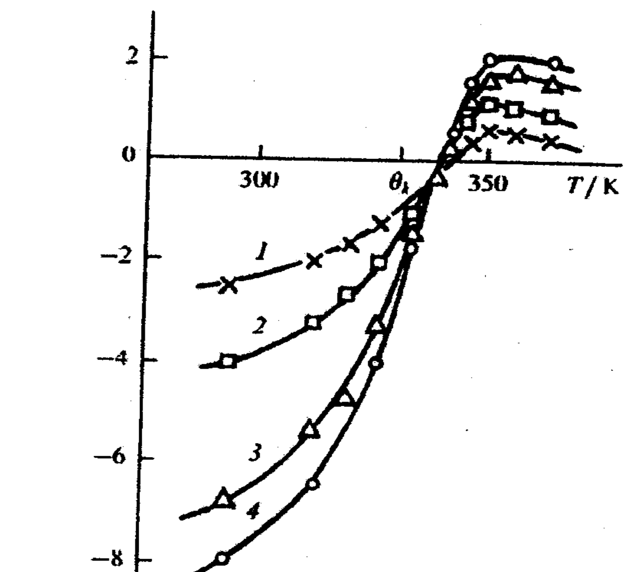

Figure 3. Isotropic magneto-resistance in the region of spin compensation temperature for $Li_2O{\cdot}2.5Fe_2O_3{\cdot}2.5Cr_2O_3$ for the fields: (1) 2260 Oe, (2) 4500 Oe, (3) 9030 Oe (4) 1170 Oe (from [8]).

a monotonic way below T_C. For example, for $x = 0.4$, R(42 K)/R(300 K) $\sim$ 10.7 $\times$ 10^6, R(160 K)/R(300 K) $\sim$ 12 and R(40 K)/R(160 K) $\sim$ 8 $\times$ 10^5. ac Conductivity (G) results show that there is no appreciable change in the region of T_K. $G \sim B\omega^n$ where ω is the angular frequency dependence and B and n are composition, temperature dependent parameters. n decreases while B increases as the temperature increases. There is no systematic variation of B with concentration.

Experimental results on $MnFe_2O_4$ show that in magnetic field in excess of the technical saturation and at temperatures below the Curie point, these ferrites have two physically different components of the isotropic negative MR. The first is due to the mechanism of the

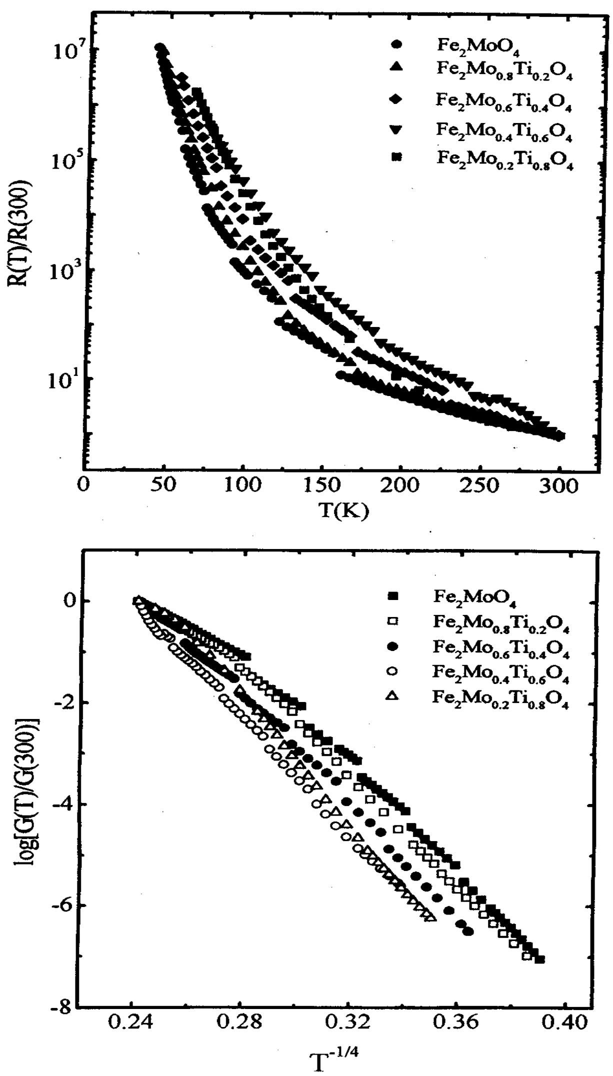

Figure 4. Temperature dependence of resistivity for $Fe_2Mo_{1-x}Ti_xO_4$.

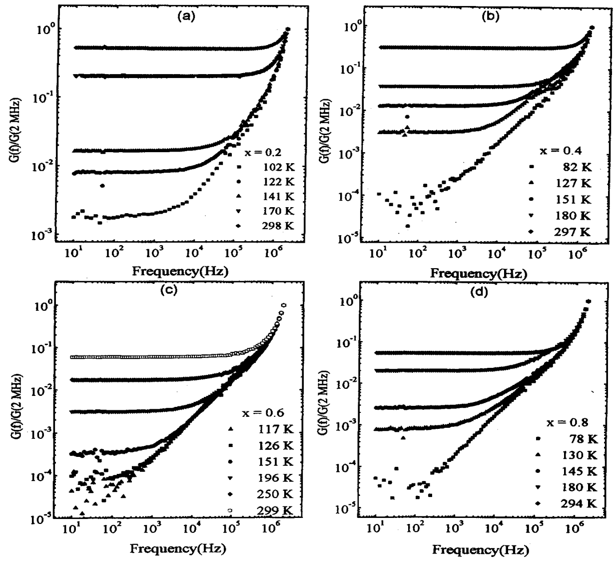

Figure 5. ac Conductivity vs. frequency at different temperatures for $Fe_2Mo_{1-x}Ti_xO_4$.

scattering of conduction electrons by the changes in the magnetic ordering caused by external field. This MR component increases on approach to T_C and reaches its maximum at temperature T_C itself. Second component of MR increases away from T_C and reaches high value at low temperatures. This is explained on the basis of magneto-electron sublattice model [8]. According to this model, the hopping electrons are in a magnetically localized state. The application of an external magnetic field H delocalizes these electrons which is the cause of negative isotropic MR. Such a delocalization occurs also as a result of change in temperature and it becomes stronger at higher temperatures, leading to the experimentally observed dependence of the second component of the negative MR. However, more experimental work is required to confirm the model.

The behavior of resistivity for $Fe_2Mo_{0.6}Ti_{0.4}O_4$ under the application of small magnetic filed is interesting. The resistivity keeps decreasing while sweeping magnetic field (figure 6). A very similar behavior (figure 7) has been observed in the case of the perovskite $Nd_{0.6}Sr_{0.4}CoO_3$ [9]. The origin of such peculiar behaviour is not yet clear.

4. Irradiation dependence of small particle magnetism

The crystallographic and magnetic changes in bulk samples induced by irradiation are known for various kinds of radiation, such as fast neutron, low energy ions, high energy ions and for different kinds of ferrite structures, such as, spinels, garnets and hexa-ferrites [10]. The observed effects depend on the mechanism of interaction of the irradiating particle with the ions of the material with context to the structure. For example, it has been found that irradiation of bulk sample of $ZnFe_2O_4$ (which is known to order antiferromagnetically at 10 K) using Kr, Xe ions, results in the appearance of ferrimagnetic ordering with $T_N \sim 600$ K. It is presumed that irradiation induces distribution of ferric ions over

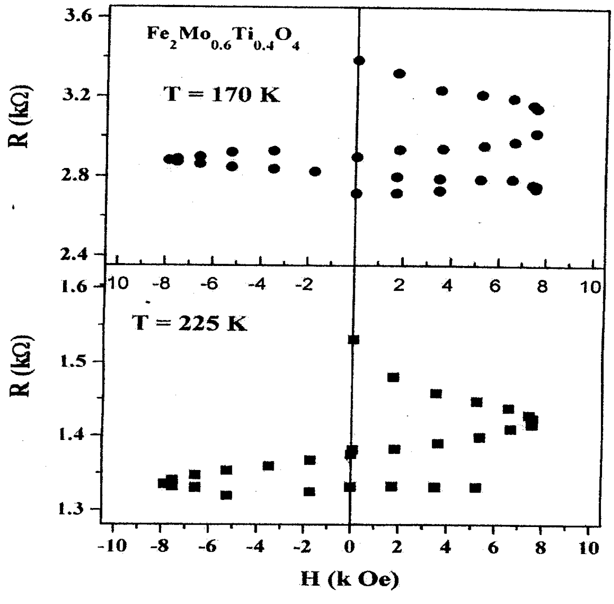

Figure 6. Evolution of the electrical resistivity of the $Fe_2Mo_{0.6}Ti_{0.4}O_4$ under the influence of magnetic field. Arrow shows the history of the applied field.

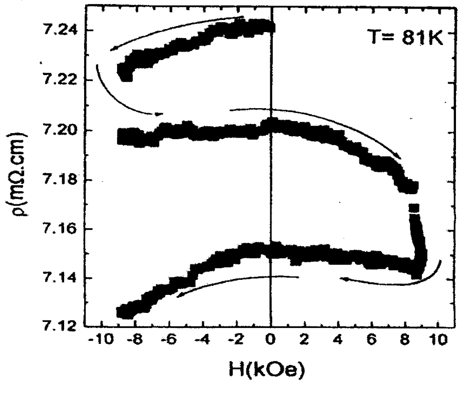

Figure 7. Electrical resistivity of $Nd_{0.6}Sr_{0.4}CoO_3$ with field (from [9]).

tetrahedral and octahedral sites in zones extending around the trajectories. The question arises as to how the energy transfer to target electron gets converted into large atomic displacements and cause drastic changes of magnetic properties. Ferrites in general is an ideal system as the effect of irradiation does not cause any destructive effects on the structure. In relevance to the above, the scenario on nanoparticle systems and the scope for such studies is discussed in §5.

5. Small particle magnetism and superparamagnetic state

Superparamagnetic (SP) state is usually observed in metal particles within a few nanometer size ranges [11]. SP properties of materials are determined by magnetic anisotropy, which comes from electron spin-orbital angular momentum coupling at lattice site in the crystal structure. The major factors that control the strength of magnetic couplings are the magnitude of magnetic moment on each coupling component, the distance between them, and the symmetry of the lattice site. These factors correspond to the crystal chemistry issues of chemical composition, lattice constant, and coordination environment at the lattice sites. In pure metal systems, these crystal chemistry issues are basically fixed. Apart from size, little variation can be chemically applied to change the crystal chemistry of pure metal nanoparticles to vary and control their SP properties. On the other hand, the crystal chemistry issues can be controlled in metal oxide such as spinel ferrite. At SP state, the collective behavior of the magnetic particles is the same as that of paramagnetic atom. Each particle behaves like a paramagnetic atom but with giant magnetic moment. There is a well-defined magnetic order within each nanoparticle. Spinel ferrite nanoparticles provide excellent experimental systems in which one can study the correlation between the crystal symmetry and SP properties on nanoparticles. It is to be noted that in spite of considerable work on bulk irradiated samples, to our knowledge, no attempt has been made so far to investigate the effect of irradiation on small particles of these systems. Such studies will be useful in many ways – e.g., in the development of bio-magnetic carriers.

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