
Proceedings of the XII National School "Correlated Electron Systems...", Ustroń 2006

Magnetite Fe_3O_4 : the Correlated Electron–Phonon System

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Dedicated to Professor Józef Spalek on the occasion of his 60th birthday

In the paper the influence of magnetic as well as electron–lattice interactions on the Verwey transition in magnetite related compounds is discussed based on the authors' experimental activity and available literature. While magnetism was proved to only reflect the transition, the results of nuclear inelastic scattering show that lattice dynamics actively participates in it. The studies of diffuse neutron scattering and heat capacity suggest also that the low temperature lattice properties of slightly doped magnetite are distinct from those with higher dopant concentration. Finally, recent theoretical results strongly suggest that the Verwey transition in magnetite cannot be understood and described without strong involvement of electron–lattice interactions.

PACS numbers: 64.70.Kb, 75.40.–s, 63.20.Kr, 71.30.+h, 75.30.Cr

1. Introduction

The spectacular first-order phase transformation in magnetite Fe_3O_4 at $T_V = 124$ K was discovered by Millar [1] and Verwey [2] and became known as the Verwey transition. The explanation of this phenomenon has been a challenge for generations of solid state physicists, since neither its mechanism occurred as simple as was believed initially, nor all the intervening interactions were known. The abundance of physical problems in such a relatively simple system caused magnetite to serve as a model for both experimental and theoretical techniques. The recent years, in particular starting from the commencement of a new Millennium, clearly prove that the Verwey transition is still the interesting subject,

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although in view of the recent works its explanation seems to be close as never before. The aim of this paper is to discuss two possible interactions that, potentially, can be vital for the understanding of the mechanism of this phenomenon, namely: magnetic and electron–lattice interactions. We will show, based on the experimental activity of our group, that although magnetism does not actively participate, the transition cannot be described without electron–lattice interactions and that the importance of this coupling was in fact long time ago evident from numerous experimental results.

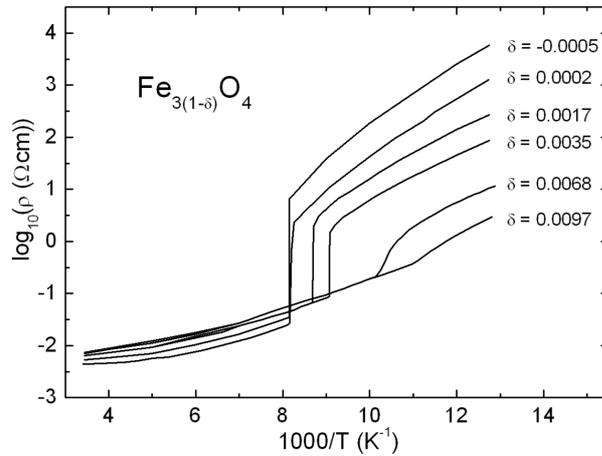


Fig. 1. Variation of resistivity ρ with temperature in magnetite $\text{Fe}_{3(1-\delta)}\text{O}_4$ for various δ values (after Ref. [3]), selected curves.

The Verwey transition is mainly known due to the drop of resistance by two orders of magnitude while heating above T_V (Fig. 1, [3]). Also the structure changes at the transition: at high temperatures magnetite crystallizes in the cubic inverse spinel structure of $Fd\bar{3}m$ type where iron cations in tetrahedral interstitial positions have valence 3+, while both Fe^{3+} and Fe^{2+} are present on octahedral sites. Verwey suggested that in its cubic phase the material could be viewed as a disordered electron system with Fe^{3+} ion core and “additional” electrons (forming Fe^{2+} ions) resonating between adjacent octahedral positions; with this explanation magnetite’s relatively large electric conductivity could be easily rationalized. Below T_V the structure turns to monoclinic Cc [4] with one of cubic $\langle 001 \rangle$ becoming monoclinic c axis. Let us note that free cooling inevitably leads to several structural domains since each cubic axis may become monoclinic c axis.

Concomitantly with the high T description, the Verwey idea was that the transition is the freezing of the resonating electrons, or a charge ordering (CO) of Fe^{2+} and Fe^{3+} cations on certain octahedral positions of the spinel structure. The driving force of this CO was supposed to originate from the Coulomb repulsion between resonating electrons. This strong electronic correlation was described by

the well known Anderson criterion [5] stating that at low, but also, in statistical meaning, at high temperatures, only those electronic configurations are possible where exactly two Fe^{2+} and two Fe^{3+} reside on each tetrahedron of octahedral iron positions.

Up to the early eighties considerable conflicting experimental data about the Verwey transition were accumulated. Most of these controversies were rationalized when it was found, based on heat capacity data [6], that even very small departures from the ideal 3:4 cation to anion ratio may greatly alter the nature of the transition, see Fig. 1, and the same is valid when iron is replaced with Ti (as in $Fe_{3-x}Ti_xO_4$) or Zn (in $Fe_{3-x}Zn_xO_4$) [7]. Namely, it was shown that the $Fe_{3(1-\delta)}O_4$ nonstoichiometry of the level $3\delta = x < 0.012$ linearly lowers the transition temperature and with a still larger number of vacancies 3δ or doped atoms x the nature of the Verwey transition is changed from first to second order, as was verified by the disappearance of latent heat of transition. The study of Ti and Zn doped materials was designed to take advantage of the fact that Ti^{4+} and Zn^{2+} are magnetically and electrically inactive dopants that enter octahedral (Ti) or tetrahedral (Zn) interstices, thus providing a means for introducing an independent perturbation on different types of structural sites.

Even though the number of “additional” electrons (i.e. Fe^{2+} cations on octahedral sites) created by nonstoichiometry and doping is different, a striking universal compositional correspondence $x \Leftrightarrow 3\delta$ was found [7] for all these materials with respect to the transition temperature T_V . The attribution of the Verwey transition temperature changes to the number of defects is, however, not justified, since other dopants do not follow such a clear universal dependence [8]. No universal explanation for the disturbing effect of extraneous elements on the Verwey transition was suggested so far.

The picture of strongly correlated electrons freezing at T_V was partly supported by the existing literature data. First, the entropy released at the transition was $R \ln 2$ [6], instead of $2R \ln 2$ in case of no order at all was present above T_V . Second, in the older NMR results [9] two frequencies observed below T_V coalesced into one above in accordance with the Verwey model. The theoretical models based on strongly correlated electron concept could describe the transition and the band models for strongly correlated electrons were quite successful in explaining some experimental facts, e.g. the temperature dependence of resistivity [10]. Finally, the experimentally determined total magnetic moment of magnetite formula unit agreed well with that calculated from this model [11].

However, despite the success of this simple ionic picture, some other measurements started to show that the real mechanism is much more complicated and the orthodox meaning of Fe^{2+} and Fe^{3+} is highly questionable (we will return to this point further on in Sect. 4); even the Coulomb correlations as a driving force of the transition were questioned [12, 13] and no high T electron hopping slower than 10^{-16} s could be found [14]. Together with these controversies, some

older problems remained valid since it was obvious from the very beginning that additional interactions apart from electron–electron must be involved. This was because any low temperature cationic pattern satisfying the Anderson condition is degenerate: almost identical Coulomb energy of either ordered or disordered ionic configurations require additional interactions to stabilize long range atomic order [5]. The energy needed to do this is only a small fraction of the dominant Coulomb repulsion energy and since clear anomalies at T_V were observed in lattice and some magnetic characteristics (e.g. the jump in AC magnetic susceptibility), the origin of those additional driving forces was sought in electron–lattice and magnetic interactions. In what follows, the experimental efforts of the authors to clarify the role of those interactions will be presented and it will finally be shown that, contrary to magnetism which does not actively participate in the transition, the role of electron–lattice coupling is vital.

2. Magnetic anomalies at the Verwey transition

Magnetite is a ferrimagnet with the Néel temperature as high as ≈ 850 K; therefore, the magnetic order is nearly perfect at the Verwey transition temperature. Since the same d electrons from octahedral iron cations seem to participate in the Verwey transition and convey magnetic interactions, it was tempting to look for drastic changes in magnetic properties at T_V . Surprisingly, no significant, higher than 0.1% [15], change in magnetization was observed at the transition temperature. By contrast, the sharp jump in AC susceptibility at T_V and a drastic drop of magnetic anisotropy energy (resulting in isotropy point just above T_V) were interpreted as a proof of the intimate connection with magnetic degrees of freedom and the Verwey transition [15]. On the other hand, if magnetic interactions were strongly involved in the Verwey transition we would expect a substantial difference between the doping with magnetic (Ni, Co) and non-magnetic (Mg) ions, while all three ions change T_V in a very similar manner [8]. Thus, the prevailing point of view was that the magnetic degrees of freedom are frozen in the vicinity of T_V . The controversy, however, remained and we have undertaken the systematic studies of the AC magnetic susceptibility temperature dependence of Zn doped magnetite crystals to clarify this point.

Some results of our studies [16], the behavior of AC susceptibility for stoichiometric magnetite crystal under several heat/magnetic field treatment is presented in Fig. 2. The main experimental conclusion was that the χ_{AC} jump at T_V may largely be diminished when the sample was field (2 kOe) cooled across the transition and measured on heating with the DC field removed. Since field cooling partly prevents breaking the cubic material into structural domains, it becomes clear that those structural domains actively participate in the χ_{AC} jump formation. In the next experiment, the sample was not only field cooled but also the measurements on heating was performed under the external DC field. This time both the signal at all temperatures as well as the jump at T_V were greatly lowered.

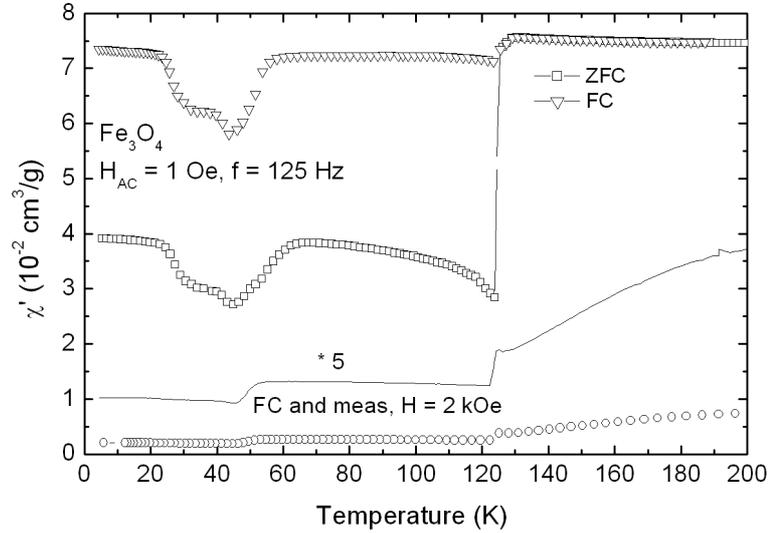


Fig. 2. Results of AC susceptibility measurements on stoichiometric single crystalline magnetite under different field and heat treatment (after Ref. [16]).

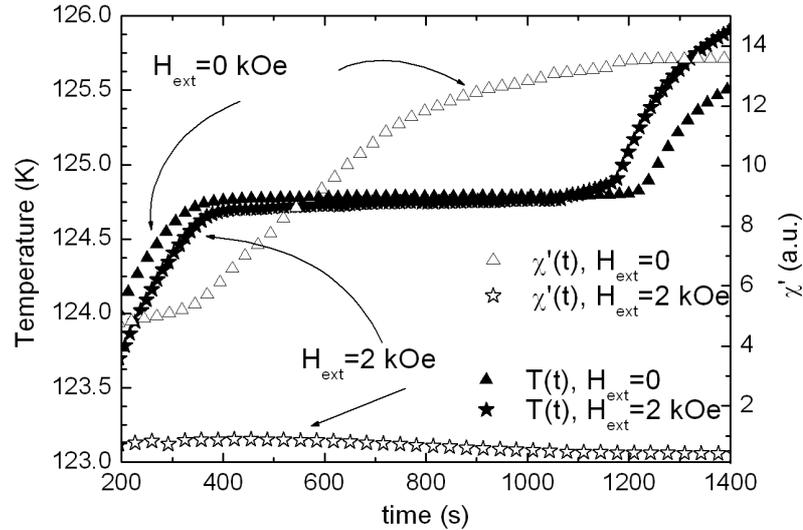


Fig. 3. Temperature changes profile (bold symbols) and respective AC susceptibility changes at the Verwey transition under external magnetic field (stars) and without (triangles) (after Ref. [17]).

The measurements in field strong enough to saturate the sample prevent magnetic domain walls formation, so the small χ_{AC} strongly suggests that magnetic domain walls movement is the dominant source of the observed dynamic susceptibility. Since these magnetic domains move freely under the action of AC magnetic field

in cubic magnetite, where no structural domains are present, and in monoclinic phase with number of structural domains lessened, we concluded that the jump in χ_{AC} was caused by the interplay between structural and magnetic domain walls. Namely, the magnetic domain walls may be blocked by the structural domains. Summarizing, the jump in AC susceptibility is not an indication of a magnetic participation in the mechanism of the Verwey transition.

The additional argument in favor to this conclusion came from our efforts [17] to observe the proliferation of a new phase exactly at the Verwey transition. We have simultaneously measured χ_{AC} , electrical resistivity, and the temperature of a stoichiometric magnetite. For many hours we could observe the development of a new phase while the latent heat was slowly delivered to (or removed from) the sample, i.e. while the sample temperature was almost constant. The same experiment was done in external magnetic field saturating the sample and the same temperature profile, i.e. the same latent heat, was observed as shown in Fig. 3. Thus, the drop in χ_{AC} can be switched off by the external magnetic field, even though the transition still proceeds. We consider it as a final proof that magnetic phenomena do not drive the Verwey transition, but, due to dependence of magnetic domains on the changing phase, can be used to observe the details of the transition.

3. Experimental evidence of electron–lattice interactions

Since the Verwey transition is accompanied by a change in crystal symmetry, the vital role that the lattice plays in the mechanism of the transition was quite obvious from the very beginning. The question, however, was if the structural transition causes the gap opening, or if the special electronic and phonon states acting together make the transition possible. This last conjecture was suggested by the fact that the substitution of 43% of normal ^{16}O by the heavier ^{18}O resulted in a considerable increase in the Verwey temperature by *ca.* 5 K [18]. In addition to that, in the middle seventies two types of critical scattering were found in the results of neutron scattering [19] on stoichiometric magnetite. First, diffuse scattering increased critically on cooling already 80 K above T_V , in the manner similar to the second-order phase transition. Second type of critical scattering was observed only a few K above T_V . Therefore, not only the lattice vibrations are connected to the transition, but the lattice fluctuates already at high T preparing to the continuous type of the transition, but this process is somehow interrupted by yet another process that ultimately causes the transition of discontinuous type.

Neutron experiments were continued in nineties by Aragón et al. [20], who showed that the lattice dynamics, reflected in the diffuse scattering, is different for first- and second-order magnetite. In some later experiments of resonant X-ray diffuse scattering [21], the authors found the arguments to claim that already at high T the changing lattice dynamics is linked to the emerging charge ordering.

Additional arguments of magnetite lattice high temperature fluctuations can be drawn from the results of our elastic constant studies [22], where we have

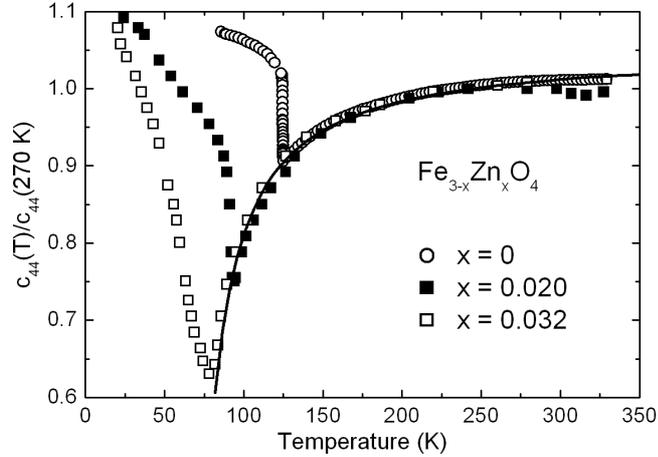


Fig. 4. Temperature dependence of c_{44} for $Fe_{3-x}Zn_xO_4$ with the line representing the fitted Landau relation (after Ref. [22]).

found that the c_{44} mode for magnetite, but also for any Zn doping, shows increasing softening starting already at high temperatures, see Fig. 4. Whatever the transition order, c_{44} for all measured samples are very well fitted by the formula $c_{44} = c_{44}^0 \frac{T-T_c}{T-\theta}$ based on the Landau theory of continuous phase transitions. Here θ ($= 56$ K) is the temperature of the phase transition predicted by Landau theory, and T_c ($= 66$ K) denotes the critical temperature resulting from the linear coupling of the order parameter to the strain. Thus not only the system prepares for some low temperature transition in the same manner, irrespective of its order (this is represented by θ), but also the coupling to the elastic degrees of freedom is the same (represented by T_c). Apparently, high temperature properties are not so susceptible to doping as the Verwey transition and do not differentiate between I and II order type materials. In fact, they signal the transition of continuous order, and those correlations that ultimately trigger the Verwey transition set in just above T_V , as also neutron data suggested.

In contrast to high temperature lattice dynamics, those processes that drive the transition do differentiate between magnetite of first and second order. This is shown in Fig. 5, where the drop of heat capacity [23] background below T_V for the first-order samples is seen, while this background remains constant for second-order one. This is even better seen in the temperature dependence of the Debye temperature θ_D extracted from heat capacity data: for first-order samples the 50 K jump of θ_D is present, while θ_D goes smoothly across transition for $x = 0.028$ (second order). Apparently, the lattice gets more rigid below T_V for the first-order magnetite while it does not show any particular change for second order.

Magnetite lattice dynamics and its change with temperature was measured [24] directly for stoichiometric single crystalline magnetite film by means of resonant nuclear inelastic scattering (NIS). Based on the experimental results, shown

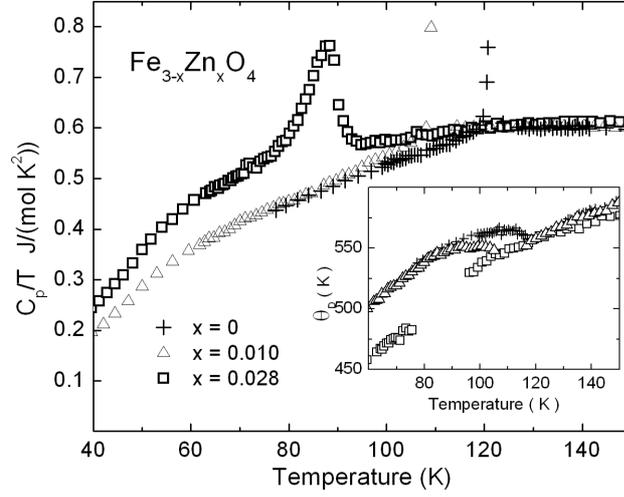


Fig. 5. $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$ heat capacity temperature dependence showing first ($x = 0, 0.010$) and second transition order. The inset shows Debye temperature θ_D extracted from heat capacity data (after Ref. [23]).

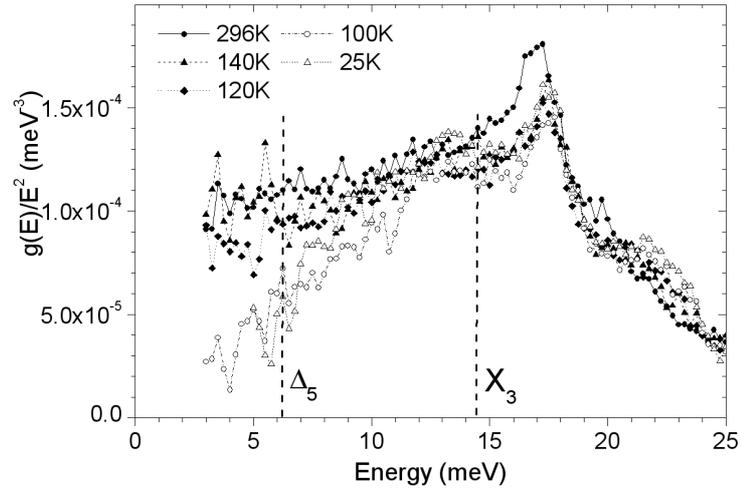


Fig. 6. Low T phononic density of states $g(E)/E^2$ for magnetite thin film (after Ref. [24]). Dashed lines mark the energy positions of Δ_5 and X_3 phonons related to the two primary order parameters, as suggested in [30].

in the form of normalized density of states in Fig. 6, and their comparison with the calculated phonon density of states the conclusion was drawn that the octahedral iron vibration spectrum changes discontinuously at T_V .

4. Discussion

The problem of what interactions play an important role in the Verwey transition usually emerged in the discussion of experiments that were planned to confirm or reject the original Verwey model. The first result questioning charge order came from NMR studies by Novak et al. [25], the other one from X-ray resonant scattering experiments made by Garcia and coworkers (see e.g. [14]).

On the other hand, the concept of charge ordering was supported by the combined X-ray and neutron scattering experiments made on powder magnetite [13]. It was proposed how ions are arranged in low T magnetite and it was found that octahedral iron ions have different charge, however with the difference not exceeding 0.2 (in contrast to 1 as for Fe^{2+} and Fe^{3+}). The charge order has major periodicity of cubic lattice constant, but the minor atomic order substantiating observed doubling of cubic lattice constant in c direction was also found.

Quite recently, the existence of charge ordering was supported by another results of resonant X-ray diffraction studies of magnetite on Fe K (either on powder sample [26] or on single crystal [27]), Fe L [28], or even on O L edge [29]. In all of them not only charge ordering on octahedral iron positions was found but also iron orbital states were proved to be ordered.

The experimental studies were accompanied by even more vast theoretical considerations based on band structure calculations. The general conclusion from these studies are that only if strong Coulomb correlations are included (by LSDA+U, or GGA+U approaches) and within realistic low temperature structure (generally easier $P2/c$ [30], but also real Cc [31]) then charge ordered insulating phase with the gap was obtained. Therefore, both crystal symmetry and Coulomb repulsion are vital for magnetite to undergo the Verwey transition. Also, the charge difference of *ca.* 0.7 between octahedral “ Fe^{3+} ” and “ Fe^{2+} ” is observed [32] on t_{2g} orbitals, but since this charge is screened by e_g orbitals (forming strong bonds with $2p$ oxygen orbitals that give substantial contribution to the occupied states in the valence band) the resultant total $3d$ charge difference is only *ca.* 0.2, as found experimentally. This screening and the fact that the elastic energy plus the Coulomb energy rather than the sole Coulomb energy should be minimized to find the most suitable electronic pattern explain why the Anderson criterion is violated in all recent, either theoretical or found experimentally, atomic arrangements.

All basic experimental facts were finally taken into account in the quite recent paper [30] where two order parameters that drive the Verwey transition, Δ_5 and X_3 , were suggested. They are both characterized by the strong electron-phonon coupling and the mechanism is that above T_V strong Coulomb electronic correlations reduce electron mobility so as they start to respond to the Δ_5 and X_3 lattice deformations, finally leading to the simultaneous transition to another structure and the insulating state. Both phononic states were observed in our NIS studies and the Δ_5 certainly changed discontinuously at the transition, as shown in

Fig. 6. Thus, electron–electron and electron–lattice interactions drive the Verwey transition.

In conclusion, we have shown that the magnetism does not actively participate in the mechanism of the Verwey transition, even though some magnetic characteristics behave anomalously at T_V . In contrast, electron–lattice interaction, observed clearly in several experiments, is indispensable factor driving the transition.

Acknowledgments

This project is financially supported by Polish Ministry of Education and Science grant for the years 2006–2008.

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