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# ASPECTS OF PHASE CHANGES VISIBLE IN THE VERWEY TRANSITION[*]

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The Verwey phase transition in magnetite ($Fe_3O_4$) exhibits a variety of phenomena that are typical of phase transformations, but in a particularly striking and pronounced form. As these phenomena and their peculiarities can be easily overlooked in the observation of other phase transitions, observing the Verwey transition, where these peculiarities are clearly visible, can draw attention to them in other phase transition studies. Important and acute phenomena showing these peculiarities include: strong dependence on doping, non-stoichiometry and defects, which can even cause a change in the character of the phase transition; the complexity of the transition, which can be predicted and observed over a wide temperature range; strong electron–electron and electron–phonon coupling; and the ability to manipulate the electronic system using a magnetic field, hydrostatic pressure or uniaxial pressure. Since these properties are typical of all solids yet accentuated in this compound and the transition is easily observable using standard and sophisticated techniques, studying it may improve our understanding of any phase transformation.

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## 1. Introduction

The Verwey transition (VT) at $T_{\mathrm{V}} = 124$ K in magnetite is the phase transformation, where practically all physical characteristics have spectacular anomalies. The most well-known phenomenon, from which the term “metal–insulator transition” was coined, is the 2 orders increase of electrical resistance when the sample is cooled below *ca.* 120 K. However, there is also a change of structure, the huge peak in heat capacity confirming first-order character of the transition, the step in AC magnetic susceptibility $\chi_{\mathrm{AC}}$, despite non-magnetic character of the transition, the change of elastic constants [1], thermal diffusivity [2], and others. Each anomaly at $T_{\mathrm{V}}$

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is very well pronounced and mostly outstanding, and the transition is signaled already at high $T$, much exceeding $T_{\mathrm{V}}$, possibly already at 853 K, *i.e.* where ferrimagnetic $\mathrm{Fe_3O_4}$ turns to paramagnet upon heating. Finally, even a small number of dopants and non-stoichiometry changes the transition and in most reports less than 1/3% of dopants (of Zn, Ti) and non-stoichiometry unanimously drives the transition out of its discontinuous character.

Although VT was first noticed in 1913 by Karl Renger [3] and elaborated at lengt by Verwey [4] in the late 1930s and 1940s of the $20^{\mathrm{th}}$ century, a growing number of reports still widens our understanding of the transition *e.g.* [5–7]. This is due to the fact that the interaction of many subsystems drives the transition but also that all phenomena related with the transition are here very well seen. Therefore, magnetite and all the related problems started to be a test ground for new techniques, both experimental and theoretical. Here, we want to pay attention to some outstanding properties, measured in our group, that can help to study other phase transitions, where the related effects are much less obvious and can be shaded by other more apparent phenomena. In other words, we want to prove that, apart from being a test ground for techniques, magnetite is the material in which all aspects of electron–electron and electron–phonon interactions, which are present in many other phase transformations, can be studied as if through a magnifying glass.

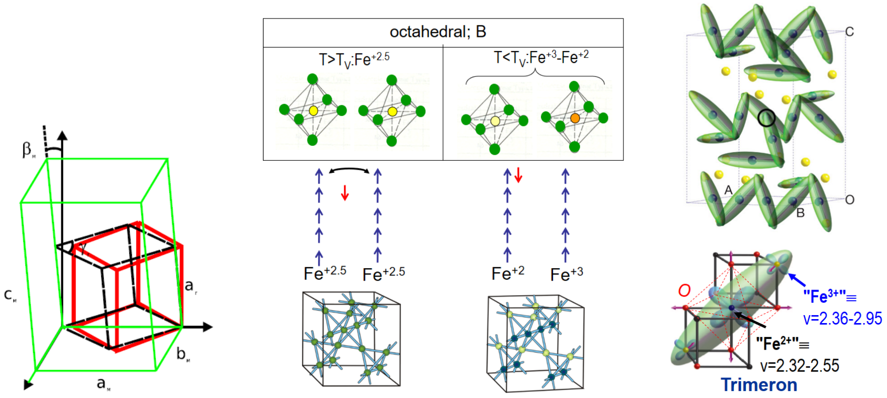
Below, some properties of magnetite are discussed that can have relevance to other phase transitions.

## 2. Structure

At high temperatures, $T > T_{\mathrm{V}}$, magnetite crystallizes in cubic Fd $\bar{3}$m symmetry (Fig. 1 (a)), with Fe atoms in two O surroundings: tetrahedral, where iron atoms have +3 valance and octahedral, where the valence is mixed, 2.5. The simplest model of the transition, the Verwey model, states that below $T_{\mathrm{V}}$, electron–electron strong correlations drive magnetite to a monoclinic Cc structure, with simultaneous electron localization of one out of the possible two octahedral positions.

The low-temperature structure was fully resolved by Senn *et al.* [8] almost 100 years after the transition was discovered. It is Cc, but octahedral iron atoms have valences from 2.32–2.95, and they are arranged in 3-atom polarons dubbed trimerons (Fig. 1 (c)). Interestingly, this structure locally remains nearly unaltered at least up to room temperature or even up to the Curie temperature [9] within a global Fd $\bar{3}$m cubic structure.

Also, some other phenomena, such as diffuse scattering [10–13] and the temperature dependence of elastic constants show that the incoming transition is already envisaged from higher $T$. Although fluctuations do drive



(a) (b) (c)

Fig. 1. (a) The change of magnetite structure from high-$T$ Fd $\bar{3}$m (red) to monoclinic Cc (green). (b) The Verwey simplified model suggests that at $T > T_V$, one electron (red arrow shows the spin of this electron) jumps across all octahedral positions (+2.5 mean valence) that freezes below $T_V$ resulting in +2 and +3 Fe valence. (c) In reality, octahedrally coordinated Fe atoms are arranged in three-atom polarons (trimerons), with valences of 2.32–2.95 (adapted from [8]).

continuous phase transformation and it can be visible at $T$ higher than the actual phase transition temperature, the fact that it is seen in the case of a discontinuous Verwey transition adds to its complexity and needs attention.

These remnants of low-$T$ structure and a preparation for the transition at a temperature higher than the actual critical temperature are relatively well observed in magnetite, while being possibly present in many materials exhibiting phase transformation.

## 3. The role of doping/non-stoichiometry

One third of a percent of Zn and Ti dopants $x$ in $Fe_{3-x}O_4$ or non-stoichiometry $3\delta$ in $Fe_{3(1-\delta)}O_4$ linearly lowers the transition temperature and in this case, the $T_V$ *versus* $x = 3\delta$ relation has a break signaling the change of the transition character (see Fig. 2)[1].

The relationship remains valid even though the number of $Fe^{2+}$, which can be used to estimate the number of active electrons, increases (as in the case of Ti) or decreases (as in the case of Zn and non-stoichiometry), as shown in Fig. 2 (b). Therefore, purely electronic processes cannot be considered as a possible explanation for the $T_V$ *versus* $x = 3\delta$ relationship. Since this type of electron or hole doping is commonly used in many materials to

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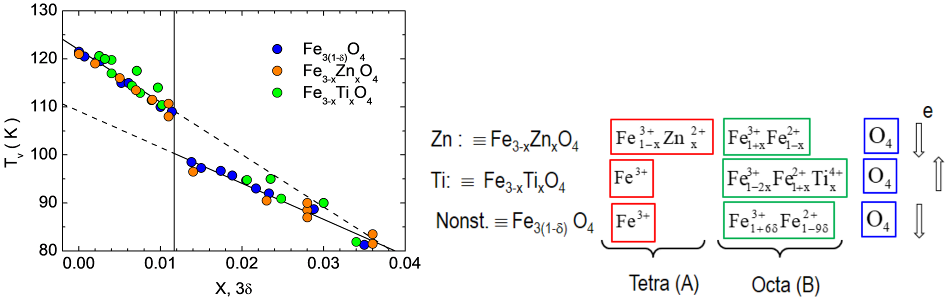
[1] Note that for other dopants, the universal relation does not seem to hold.



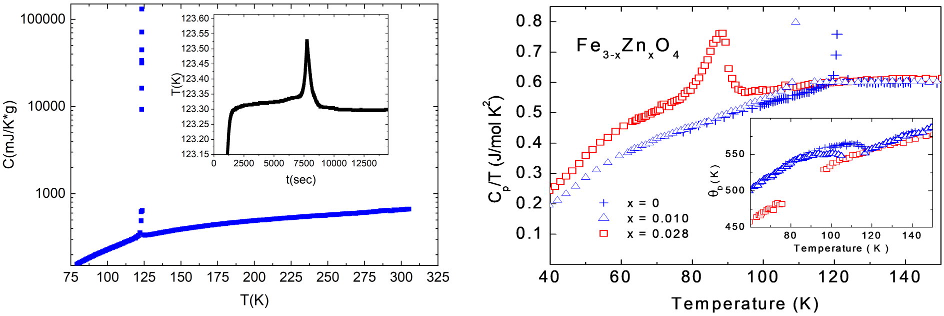
(a) (b)

Fig. 2. (a) $T_{\mathrm{V}}$ *versus* dopant content $x$ or non-stoichiometry $3\delta$; the vertical line delimits the discontinuous Verwey transition on the left from the continuous one on the right. (b) Apart from the fact that different dopants affect octahedral Fe positions differently, either by removing electrons (Zn doping and non-stoichiometry) or by adding them (Ti doping), the universality remains.

study other phase transformations, magnetite's resistance to such analysis should be considered. Relatively recent studies [6] suggest that these are point defects that are inevitable in doped/non-stoichiometric materials and that affect $T_{\mathrm{V}}$ linearly, causing no change in the character of the transition. Although structural defects may affect all phase transitions in all materials, the notion that they have a main impact on the critical temperature is, based on our experience, *e.g.* in heat capacity measurement results, an oversimplification.

Measurements of heat capacity proved that the transition in stoichiometric and slightly doped magnetite is discontinuous, as shown in Fig. 3. In the "second-order transition" regime, the transition occurs over a range of temperatures. However, the shape of the transition is not the only factor that differentiates between the two regimes. The heat capacity baseline below the transition temperature for a doping/non-stoichiometry level beyond $x = 3\delta = 0.012$ (in the case of Zn and Ti doping) is higher than that for the first-order discontinuous regime [14, 15]. As we demonstrated in [16], this universal effect is not due to a change in the phonon spectrum; therefore, the effects are likely caused by two distinct electronic arrangements in both classes of materials. Thus, both electronic processes and atomic disorder are probably responsible for lowering $T_{\mathrm{V}}$, in both gradual and step-like ways.

As already remarked, upon cooling, the Verwey transition is signaled already at much higher temperatures than $T_{\mathrm{V}}$. The observation of non-stoichiometric/doped magnetite of different orders reveals other related phenomena.



(a) (b)

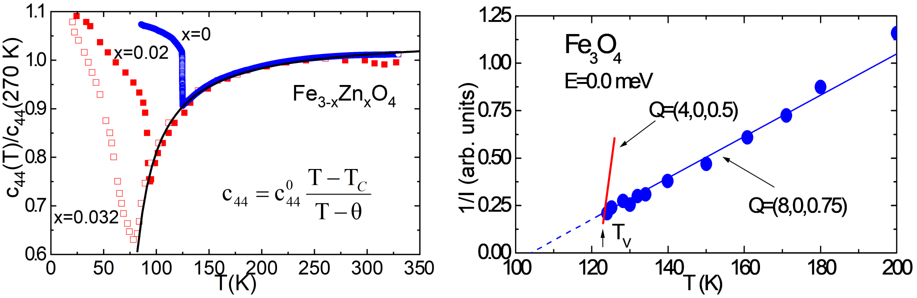
Fig. 3. Heat capacity of stoichiometric magnetite (a) with the inset proving the existence of latent heat (based on the results from [17]). In doped magnetite, the clear difference is seen between both the peak shape and the baseline below $T_V$ [14] (b). This difference extends at least down to 0.3 K [18].

Our elastic constant studies of stoichiometric and Zn doped samples [1], also in the second-order transition regime, especially the $T$-dependence of the $c_{44}$ mode (Fig. 4 (a)), show increasing softening starting already at high temperatures. Despite the different character of the Verwey transition, $c_{44}$ for all measured samples is 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, $\theta (= 56$ K) is the temperature of the phase transition predicted by the Landau theory, and $T_c (= 66$ K) denotes the critical temperature resulting from the linear coupling of the order parameter to strain. Thus, not only the system prepares for a low-temperature transition in the same manner (this is represented by $\theta$), irrespective of its order, but also the coupling of the fluctuating entities to the elastic degrees of freedom is the same (represented by $T_c$). Apparently, high-temperature properties are not so susceptible to departures from stoichiometry or doping and do not differentiate between I and II order type materials. In fact, they signal the Verwey transition of continuous order, and those correlations that ultimately trigger the discontinuous transition occur just above $T_V$.

The same two-step character of the transition is also seen in neutron results from stoichiometric magnetite already mentioned and presented in Fig. 4 (b). The diffuse neutron scattering already started to change at a much higher temperature than $T_V$. The inverse of the intensity at a certain neutron momentum transfer is linear, as in the Curie–Weis law, signaling the



(a) (b)

Fig. 4. (a) The normalized $c_{44}$ elastic constant for stoichiometric (discontinuous transition) and Zn-doped magnetite (continuous transition), showing identical critical softening above $T_V$ [1]. (b) The Curie–Weiss law-like behaviour of the intensity of neutron diffuse scattering (blue dots), terminated by another feature occurring just above $T_V$ [11, 13].

incoming continuous transition that takes place 80 K below. Additionally, a different type of critical scattering, this time only a few K above $T_V$, was found, apparently triggering the transition.

Thus, the electronic states that are occupied at high $T$ and are responsible for the material's elastic properties and lattice vibrations prepare for the continuous type of transition. This process is interrupted by another process that ultimately causes a discontinuous transition in the case of low doping or non-stoichiometry. This process, probably triggered by fluctuations, results in the depopulation of some electronic states in stoichiometric and slightly doped magnetite, which is visible as a decrease in heat capacity for samples in the first-order regime.

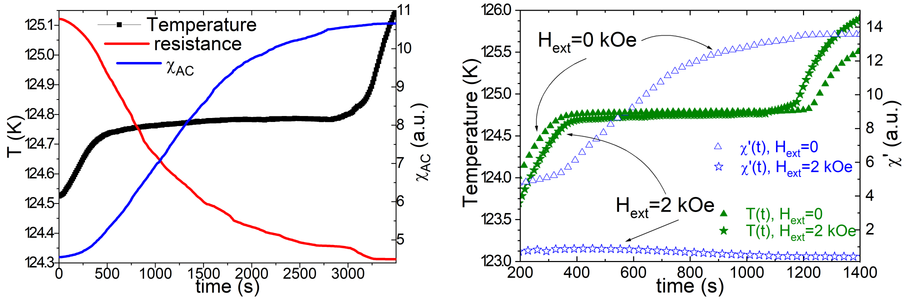
The depopulation and disordering of electronic states when the transition is observed upon heating across $T_V$ can be observed by taking advantage of the fact that a large amount of heat is required to alter magnetite at $T_V$; that is, the temperature remains constant while the transition occurs.

## 4. How the transition proceeds

The Verwey transition is also reflected in magnetic phenomena, both in magnetic domain movement and in magnetization that has 0.1% step at $T_V$. In fact, ferrimagnetism, which sets in already at 853 K, is frequently pointed out as the cause of the Verwey transition, see *e.g.* [7].

However, domain walls and their movement are governed by all coupled subsystems acting in the transition. Thus, observing magnetic domain wall movement (DWM) helps to see all these subsystems. This is done *e.g.* by means of AC magnetic susceptibility measurements, a simple technique, also commonly used for sample quality assertion.

Figure 5 (a) shows the temporal variations of AC susceptibility and resistance, while a very small amount of heat is added to the sample during the transition process, *i.e.* when the temperature remains almost constant (as checked by the thermometer attached to the sample).



(a) (b)

Fig. 5. (a) Temporal variation of the resistance and AC magnetic susceptibility during the process of Verwey transition, *i.e.* when temperature stays constant. (b) Although the signal from $\chi_{AC}$ may be switched off using an external magnetic field (blue stars), the transition still proceeds (green full stars) [19, 20].

In Fig. 5 (b), the magnetic susceptibility $\chi_{AC}$ *versus* time measured in a zero static field (blue triangles) and in a static field of 2 kOe is presented. Even in case when magnetic domains are absent due to the external magnetic field (blue stars in Fig. 5 (a)), *i.e.* no signal comes from DWM, the transition still proceeds, which is signaled by a constant temperature (green stars in Fig. 5 (a)).

The results of similar studies, but aimed to observe the emergence of low-$T$ monoclinic (1 3/2 2) reflection (or its disappearance upon heating), are presented in Fig. 6 and described in [21].

The phase transition *in statu nascendi*, as described above, was also observed in [22] in magnetite and in [23] in freezing water.

Usually, several subsystems are engaged in any phase transformation and to observe them separately for a long time, like here in magnetite (more than 1 hour, like in the inset of Fig. 3 (a)), is both fascinating and can be used to understand the transition. In case this observation is performed upon heating across a critical temperature, the system completes its transformation from the lower energy configuration to the excited one. However, the phenomena that precede the transition and are related to it are sometimes visible already below the critical temperature. In magnetite, such phenomena are trimeron excitations visible either by optical excitation [24] or by the change of monoclinic c-axis triggered by an external magnetic field; this last process is called the Axis Switching and was noticed for the first time by Calhoun [25].

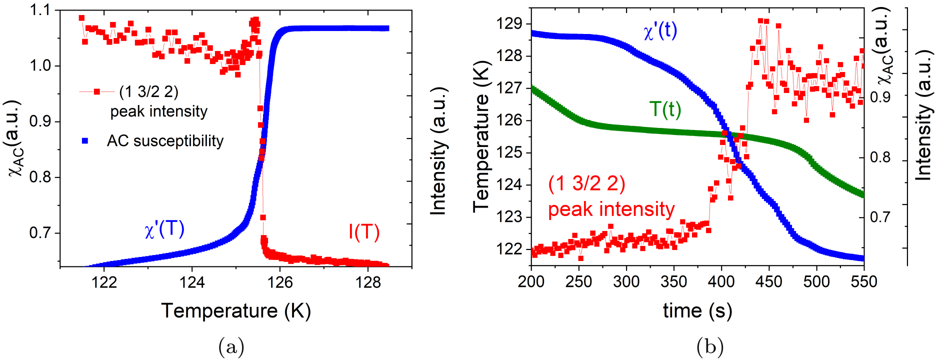


Fig. 6. (a) The temperature dependence of the AC magnetic susceptibility and the (1 3/2 2) superstructure peak intensity that were simultaneously measured in a stoichiometric magnetite single crystal [21]. The same results are shown in panel (b), but *versus* time, while the temperature remained nearly constant.

## 5. Monoclinic c-axis switching

The low-$T$ structure of magnetite is monoclinic Cc, with the well-defined c-axis, one of three cubic $\langle 100\rangle$ axes at high temperature. Therefore, when the sample is cooled across $T_V$ from higher temperatures, the sample breaks into several structural domains (Fig. 7; actually 24 [26]) unless some precautions are taken on cooling. These are either cooling in a magnetic field inclined along one of $\langle 100\rangle$ directions (in this case, this particular direction will become the c-axis), or uniaxial stress application, or both. In any case, it is possible to achieve a system with basically one c-axis throughout the whole sample but some other kinds of structural domains are inevitably present, despite the fact that it was cooled below $T_V$ from an ideal cubic single crystal.

Since the monoclinic c-axis is simultaneously an easy magnetic axis, the energy rises once an external magnetic field is applied at $T < T_V$ in the direction perpendicular to the c-axis along the other cube edge (Fig. 7, the lower central panel). At sufficiently high $T$, still below $T_V$, the c-axis switches to the field position [25], the phenomenon easily seen in magnetic moment *versus* $B$ experiments, but also when crystal structure is observed (Fig. 8). In other words, the magnetic field can change the crystal structure direction. Since the structure turns to cubic at $T_V$ (with elements of low-$T$ structure surviving [27]), it may mean that by observing AS, we are manipulating with the same elements, crystal and electronic, that disorient at $T_V$.

We have made many measurements observing AS, both with macroscopic techniques, such as magnetic moment *versus* magnetic field, XRD and Resonant X-ray Diffraction [28, 29], and also with microscopic techniques, such as Mössbauer spectroscopy [28] and NMR [30]. We have also measured AS

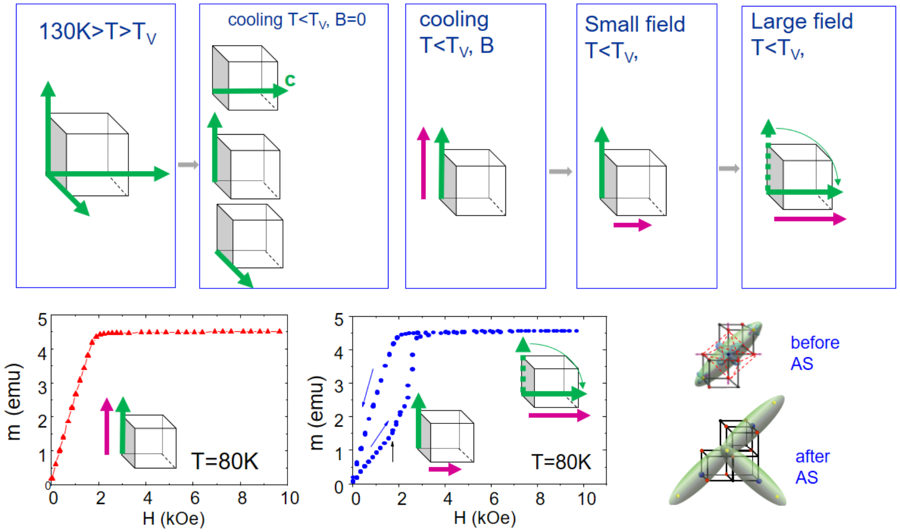


Fig. 7. When magnetite with 3 easy axes (green) is cooled without an external magnetic field, each of the easy axes can become a c monoclinic axis: three kinds of “c domains” are formed. An external field along one of the easy axis forces c along the field (purple arrow). Once $B$ is later applied perpendicular to the c-axis, this eventually switches into the field direction (dashed curved arrow) that can easily be seen in the magnetic moment $m$ *versus* $B$ and results in some reorganization of the trimeron lattice (shown symbolically here).

upon hydrostatic pressure [31]. All the results for stoichiometric and doped magnetite samples suggest that although all samples change in the process of AS, the more ideal systems, like stoichiometric magnetite, are more vulnerable to AS than doped/non-stoichiometric samples, that contrasts with $T_\mathrm{V}$ behaviour. This is presented in Fig. 9 as the intrinsic field $B_{\mathrm{i\_SW}}$ needed to switch the c-axis *versus* temperature (after [31]). Thus, further studies are needed to link the changing structure by magnetic field with the processes occurring at the Verwey transition, although it is obvious that some trimeron excitations, different than that described in [24], are taking place here and the processes in trimerons are crucial to the understanding of the transition.

Thus, although the link between the axis switching and the Verwey transition is more subtle, the phenomena like AS that precede any transition frequently occur. They are usually in the form of fluctuations to the high-temperature phase with the simultaneous adjustment of this phase, finally culminating in the phase transformation. Therefore, the study of AS, which is a similar process occurring prior to the transition, has a universal character.

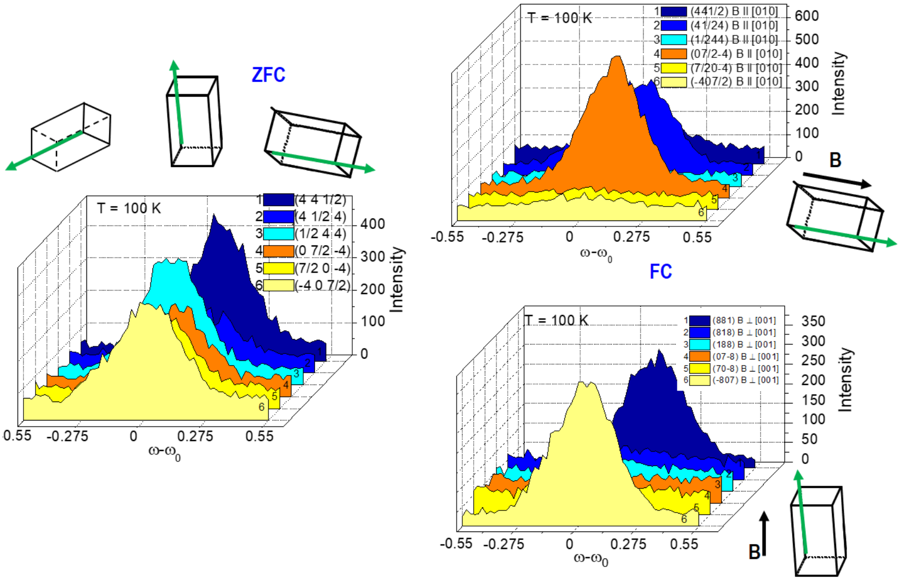


Fig. 8. The c-axis switching can also be seen in the change of superlattice reflections (here (4 4 1/2) and (7/2 0 4)) from the sample with domains (left) to a quasi one-domain state when the field $B$ was applied [29].

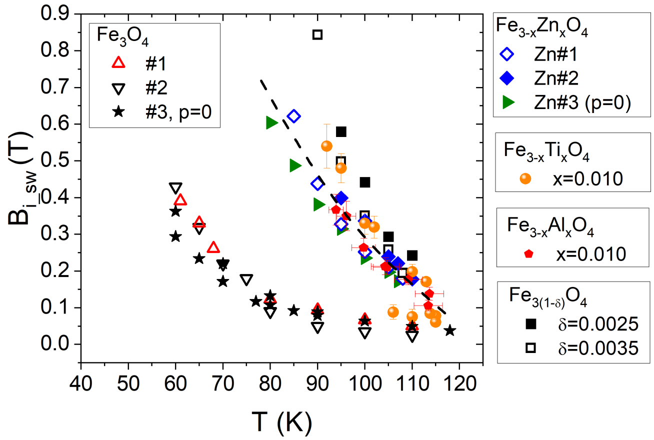


Fig. 9. Intrinsic magnetic field $B_{\mathrm{i\_sw}}$ required to switch the axis for stoichiometric $Fe_3O_4$ and doped/non-stoichiometric magnetite single crystals (based on [31]).

## 6. Mechanism of the Verwey transition

The Verwey transition is a result of strong electron–electron and electron–phonon correlations, as shown in numerous papers, recently by Piekarz

[32–34]. Here, a strong coupling at $T < T_{\mathrm{V}}$ between electrons in orbitally ordered trimerons and phonons allowed for the perfect agreement between DFT calculated phononic density of states with experiment. The same charge-orbital 3-atom arrangement is required to get the agreement with experimental phonon density of states at $T > T_{\mathrm{V}}$, where the structure is nominally cubic [34]. Thus, electron–electron, charge-orbital, and electron–phonon interactions are essential both in low-$T$ magnetite structure as well as in high $T$, possibly up to the Curie temperature.

Although the main mechanisms of the Verwey transition are known, the details are still being discussed despite over 100 years of study.

In particular, the ground state of stoichiometric magnetite and that of doped/non-stoichiometric materials with a continuous Verwey transition, as evidenced by the difference in heat capacity baseline, are still unknown. Also, recently, an electronic configuration resembling nematic order above the Verwey transition was discovered and proposed as universal in correlated materials [5].

The leading mechanism, as well as its consequence in the form of nematic order, which is possibly present in magnetite, is probably universal for the majority of phase transitions, and studying magnetite may help to understand the others.

## 7. Conclusions

We intended to demonstrate that the Verwey transition in magnetite at $T_{\mathrm{V}} = 124$ K is not only a testing ground for theoretical and experimental techniques, but also a means of studying other phase transformations. This is because the main interactions that govern this transition — *i.e.*, electron–phonon interactions — and their consequences, such as nematic order, are present in many other phase transitions. However, in magnetite, all of these properties are pronounced and easily observable.

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