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Impurity effects upon the Verwey transition in magnetite

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Magnetite single crystals Fe$_{3-x}$M$_x$O$_4$ doped with M = Ni, Co, Mg, Al, Ga, and Ti were grown and annealed under a controlled atmosphere to produce homogeneous and oxygen stoichiometric samples. The cation vacancy concentration of the samples was proved to be lower than $10^{-6}$ by means of magnetic disaccommodation spectroscopy. The Verwey temperature shift as function of the substituent concentration was determined from the temperature dependence of the resistivity. The systematics of the transition temperature shift as function of the concentration and nature of the substituents is indicative that the mechanism of the transition is related to the second-neighbor Coulomb interaction of the cations on the octahedral sites.

INTRODUCTION

Although magnetite (Fe$_3$O$_4$) is one of the most studied magnetic oxides, the investigation of the physical properties of this material is still an intriguing field of research. At room temperature, the crystal structure of Fe$_3$O$_4$ is the inverted spinel structure, in which the tetrahedral A sites are occupied by one-third of the Fe ions as Fe$^{3+}$ and the remaining Fe ions are located on the octahedral B sites as mixed-valent Fe ions with an average charge of 2.5+. Around 125 K, magnetite undergoes a first-order phase transition, which was already in the 1920’s and 1930’s probed by anomalies in the electrical conductivity of about two orders of magnitude, which is now known as the Verwey transition.

Verwey related this transition to an electronic ordering of Fe$^{2+}$ and Fe$^{3+}$ ions on the B sites, causing a decrease in the electrical conductivity of about two orders of magnitude, with which is now known as the Verwey transition.

Irrespective of the more and more refined structure models that have been developed to explain the low-temperature charge ordering in magnetite, some basic statements can be made concerning the driving forces of the ordering mechanisms at low temperatures.

(1) The Verwey transition in magnetite is not primarily induced by magnetic interactions, as follows from the small value of the magnetic anisotropy energy accompanying the magnetoelectric effect, the small change of the saturation magnetization at the transition temperature $T_v$ (Ref. 16), and the absence of anomalies of the magnetic anisotropy constants on passing the critical nonstoichiometry parameter $\delta_f$ for Fe$_{3-x}$O$_4$, above which the transition disappears.

(2) The Verwey transition is exceptional in the sense that the ordering mechanism is related to the Coulomb interactions according to which a transition temperature above $10^4$ K would be expected, whereas the real transition still occurs at low temperatures around 125 K. This apparent contradiction was cleared by Anderson by taking into account the particular geometry of the spinel lattice. The octahedral sites in the spinel structure are arranged in tetrahedra $B_4$, with each site belonging to two adjacent tetrahedra. In this arrangement, short-range order is imposed by the so-called Anderson condition: the charge of the individual tetrahedra must be constant, i.e., two Fe$^{2+}$ and two Fe$^{3+}$ ions per tetrahedron. If the interactions leading to the Verwey transition would be restricted to nearest-neighbor pairs, identical energies would be expected for all configurations fulfilling Anderson’s condition and no transition should occur. However, there is a transition, which means that the driving mechanism of the transition is achieved by next-nearest-neighbor Coulomb interactions.

(3) The discussion as to whether this short-range order persists above the Verwey transition has been decided positively by recent photoemission spectroscopy experiments on the (100) surface of Fe$_3$O$_4$.20,21

(4) Since the Verwey ordering mechanism originates from the Coulomb interactions, the effects of substitutions that alter the Fe$^{2+}$/Fe$^{3+}$ ratio on the octahedral sites can give more insight into this phase transition. Miyahara determined the shift of the transition temperature as a function of the concentration for a number of impurities. Unfortunately, the oxygen stoichiometry affects also the transition temperature. This may explain why no clear relations were found between the transition temperature shifts and the nature or concentration of the substituents.22 Aragon et al. reported two regimes in the nonstoichiometry dependence of the transition temperature on either side of a critical composition $\delta_c = 0.0117$ for Fe$_{3-x}$O$_4$, with a first-order transition for $\delta < \delta_c$ and a second-order transition for $\delta > \delta_c$. Similar results were reported for stoichiometric magnetite single crystals doped with Zn and Ti, Fe$_{3-x}$Zn$_x$O$_4$ and Fe$_{3-x}$Ti$_x$O$_4$.24

For Al-substituted magnetite a relative weak dependence of the $T_v$ shift as a function of the substituent concentration was reported, which was partially attributed to a mixed distribution of Al over the A and B sites.25

So far it remains still an open question if there is a general universal dependence of $T_v$ upon the dope concentration, irrespective of the nature of the substituent, which is the
To study the effects of impurities on the Verwey transition and to separate the impurity from the oxygen stoichiometry effects, we prepared a number of single crystals Fe$_{3-x}M_x$O$_4$ with $M$ = Co, Ni, Mg, Al, Ga, and Ti by means of a floating-zone technique.

After crystallization, the single crystals were additionally heat treated for at least 48 h at temperatures between 1150 and 1300 °C in adjusted mixtures of CO$_2$ and H$_2$ to obtain the highest oxygen stoichiometry. With this technique, homogeneous and stoichiometric single crystals with a predetermined impurity composition could be prepared. Because the standard chemical analysis of the oxygen stoichiometry is not accurate enough for our purpose, we used a high-sensitivity magnetic disaccommodation technique, allowing us to resolve deviations in the oxygen stoichiometry smaller than 1 ppm. The pronounced vacancy-mediated peak near 300 K in the disaccommodation (DA) spectrum of magnetite serves as probe for the detection of octahedral vacancies (cf. Fig. 1).

To determine the DA spectra and to separate the impurity from the oxygen stoichiometry, we prepared a number of single crystals Fe$_{3-x}M_x$O$_4$ with $M$ = Co, Ni, Mg, Al, Ga, and Ti by means of a floating-zone technique.

The substituent concentration is much higher than that of the first impurity, and the transition seems to be of first order and the transition from first to second order lies between 0.01 and 0.02, comparable with the value of 0.012 for the Zn or Ti substitutions.

As an example, we show in Fig. 1 the vacancy-induced 300-K relaxation of polycrystalline Fe$_{3-x}O_4$ as reported by Kozłowski et al. For $x=0.005$ and $x=0.01$ a sharp first-order transition was observed, whereas for $x=0.02$ and 0.03 a gradual change was observed pointing to a second-order transition. The critical Al concentration for the transition from first to second order lies between 0.01 and 0.02, comparable with the value of 0.012 for the Zn or Ti substitutions.

The weaker composition dependence of the transition temperature upon the concentration $x$ may be explained by their different preparation technique that resulted in less perfect Al homogeneity. Figure 3 presents the resistivity measurements of Fe$_{3-x}$Ga$_x$O$_4$ with $x=0.05$ and 0.1 and stoichiometric Fe$_3$O$_4$. The substituent concentration is much higher than that of the Al system; the transition seems to be of first order and the transition from first to second order lies between 0.01 and 0.02, comparable with the value of 0.012 for the Zn or Ti substitutions.

The DA spectra are presented by the isochronal curves, displaying the relative reluctivity at different time intervals $(t_1,t_2)$:

$$\frac{\Delta r}{r_1} = \frac{r(t_2,T) - r(t_1,T)}{r(t_1,T)}. \quad (1)$$

As an example, we show in Fig. 1 the vacancy-induced 300-K relaxation of polycrystalline Fe$_{3-x}O_4$, with $\delta=10^{-4}$ together with its strength dependence on the inherent vacancy content, cf. inset (a). In all our substituted samples the relaxations due to electronic processes are distinctly present in the temperature range below 150 K, whereas the vacancy induced 300-K peak is completely absent, thus indicating a vacancy concentration of lower than $10^{-6}$; cf. inset (b) of Fig. 1 representing as a typical example the disaccommodation spectra of Fe$_{2.93}$Ni$_{0.07}$O$_4$. The Verwey temperature of the samples was determined from the temperature dependence of the electrical conductivity being measured by a four-probe technique.

FIG. 1. Disaccommodation spectrum of polycrystalline, vacancy-doped Fe$_{3-x}O_4$ ($\Delta = 10^{-4}$), as obtained in the temperature range 4–450 K for the measuring times $t_1 = 1$ s and $t_2 = 180$ s. Inset (a) shows the strength of the 300-K relaxation as a function of the vacancy concentration; inset (b) represents the disaccommodation spectrum for oxygen-stoichiometric Fe$_{2.93}$Ni$_{0.07}$O$_4$.

FIG. 2. The resistivity of stoichiometric Fe$_{3-x}$Al$_x$O$_4$ single crystals with $x=0.005, 0.01, 0.02$, and $0.03$ as function of temperature at each temperature using an automated LC oscillator technique. The DA spectra are presented by the isochronal curves, displaying the relative reluctivity at different time intervals $(t_1,t_2)$:

$$\frac{\Delta r}{r_1} = \frac{r(t_2,T) - r(t_1,T)}{r(t_1,T)}. \quad (1)$$

As an example, we show in Fig. 1 the vacancy-induced 300-K relaxation of polycrystalline Fe$_{3-x}O_4$, with $\delta=10^{-4}$ together with its strength dependence on the inherent vacancy content, cf. inset (a). In all our substituted samples the relaxations due to electronic processes are distinctly present in the temperature range below 150 K, whereas the vacancy induced 300-K peak is completely absent, thus indicating a vacancy concentration of lower than $10^{-6}$; cf. inset (b) of Fig. 1 representing as a typical example the disaccommodation spectra of Fe$_{2.93}$Ni$_{0.07}$O$_4$. The Verwey temperature of the samples was determined from the temperature dependence of the electrical conductivity being measured by a four-probe technique.
transition temperatures of 116.9 and 110.6 K for \( x = 0.05 \) and \( x = 0.10 \), respectively, are shifted in a less pronounced way. For pure magnetite, a transition temperature of 123.9 K is found.

Doping magnetite with Ni, Co, or Mg yields a transition temperature shift that is in between that of Ga and Al as can be seen from the \( \Delta T_v \) plot versus concentration in Fig. 4. For all the measured concentrations, sharp transitions were observed, thus suggesting that for all these samples the transition is still of first order. Additionally, some data for Ti substitution in stoichiometric magnetite are plotted in Fig. 4.\(^{26,31}\) Despite some qualitative agreement with the data reported by Miyahara,\(^{22}\) in particular concerning the weak influence of the Ga substitution, there remain substantial differences with our numerical data that are supposed to have their origin in the nonstoichiometry of Miyahara’s specimens.

The \( T_v \) shift versus the substituent concentration reveals specific effects of the various substituents, which were up until now not so evident. Ni, Co, and Mg are all bivalent ionic substituents in magnetite. All three metals give similar stoichiometric single crystals \( \text{Fe}_3\text{O}_4 \) with \( x = 0.05 \) and \( x = 0.10 \) as a function of the reciprocal temperature.

For pure magnetite, a transition temperature of 123.9 K is observed. Further, if magnetic interactions were involved in the mechanism of the Verwey ordering, one would expect a substantial difference between the doping with magnetic (Ni\(^{2+}\), Co\(^{2+}\), and Fe\(^{3+}\)), i.e., 5–20\% of the Mg or Co ions are located on \( A \) sites, whereas Ni will remain at the \( B \) sites. Since these cations are valent, the ratio of \( B \)-sited bi- and trivalent cations is for Ni exactly 2, which is a stipulation for perfect Verwey ordering, whereas for Co and Mg this ratio deviates weakly from 2.

Honig and co-workers\(^{24,26}\) reported the concentration dependence of the \( T_v \) shift in Zn-substituted magnetite to be about two times larger, as we observed for the Ni\(^{2+}\) magnetites. \( \text{Zn}^{2+} \) is known to occupy \( A \) sites, thereby changing the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratio on the \( B \) sites which, evidently, proves to be more effective in disturbing the Verwey order than the replacement of an equal number of octahedral \( \text{Fe}^{2+} \) ions by other two-valent ions \( \text{M}^{2+} \). This becomes plausible by considering that such \( B \)-site-substituted \( \text{M}^{2+} \) ions—within a low-enough concentration range where they cannot hurt the Anderson criterion—in contrast to \( \text{Fe}^{2+} \) sites are immobile and thereby may even contribute to a stabilization of the ordered phase. The order-disturbing effect of \( \text{Zn}^{2+} \) substitutions, on the other hand, results from the fact that an equal amount of octahedral \( \text{Fe}^{2+} \) has to be replaced by \( \text{Fe}^{3+} \), which means that \( x \text{B}_4 \) units have a charge of \( 11^+ \) instead of \( 10^+ \), thereby destroying the equivalency of the \( B_4 \) units. This elucidates why Zn, though not entering the \( B \) lattice, has a larger effect upon the Verwey ordering. In contrast to \( \text{Fe}^{3+} \) sites are immobile—within a concentration range where they cannot hurt the Anderson criterion—this effect upon \( T_v \) than the two-valent substitutions on the octahedral lattice. Furthermore, it is an interesting observation that trivalent \( \text{Ga}^{3+} \), which, at least for low concentrations, enters preferentially on the tetrahedral sites,\(^{33,34}\) reveals a lower composition dependence of \( \Delta T_v \). If we estimate that only \( \frac{1}{3} \) of the Ga ions enter the octahedral sites,\(^{34}\) the \( T_v \) shift corresponding to the octahedral \( \text{Ga}^{3+} \) concentration would be identical to that of the \( \text{Ni}^{2+} \) concentration, thus indicating comparable charge-order perturbations for both fixed \( \text{M}^{3+} \) and \( \text{M}^{2+} \) ions on \( B \) sites. However, the \( \text{Al}^{3+} \) substitutions show a much stronger effect, which does not fit into the picture discussed above. This incompatibility may be explained in terms of the ionic radii of \( \text{Al}^{3+} (0.535 \text{ Å}) \) and \( \text{Ga}^{3+} (0.620 \text{ Å}) \) of which the latter one is much closer to that of the octahedral \( \text{Fe}^{3+} (0.645 \text{ Å}) \). The geometry of a \( B_4 \) unit containing one small \( \text{Al}^{3+} \) ion will be more deformed, resulting in a variation of the Coulomb energy and, consequently, a larger effect upon the Verwey ordering. In contrast to \( \text{Al}^{3+} \), the ionic radii of the bivalent ions \( \text{Ni}^{2+}, \text{Co}^{2+}, \text{Mg}^{2+} (0.69, 0.745, 0.720 \text{ Å})—though being smaller than that of \( \text{Fe}^{2+} (0.78 \text{ Å})—range in between the radii of \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) and thus, evidently, are disturbing to a smaller extent the ionic packing that governs the Verwey transition.\(^{35}\)

Recently, it has also been suggested that magnetic interactions could explain a universal \( T_v \) shift versus the concentration of respective substituents, this shift being proportional to the population difference, \( \Delta \text{Fe}^{3+} \) of the \( \text{Fe}^{3+} \) cations on the tetrahedral and octahedral sublattices.\(^{25}\) However, the results obtained on the bivalent substitutions, for which \( \Delta \text{Fe}^{3+} = 0 \), do not support this suggestion. Moreover, \( \text{Al}^{3+} \) substitutes for low concentrations only on \( B \) sites,\(^{34}\) which would imply \( \Delta \text{Fe}^{3+} = x \), thereby inducing—in terms of the proposed scaling—a much smaller \( T_v \) shift than observed. Further, if magnetic interactions were involved in the mechanism of the Verwey ordering, one would expect a substantial difference between the doping with magnetic (Ni\(^{2+}\),
Co\(^{2+}\)) and nonmagnetic (Mg\(^{2+}\)) ions, which is not observed. Since the magnetic interactions in magnetite, leading to the magnetically ordered state, are nearest-neighbor interactions, where the octahedral nearest-neighbor configurations are controlled by the Anderson criterion, it is unlikely that magnetic interactions play a dominant role in the Verwey ordering mechanism. In contrast, the systematics in the \(T_c\) shifts, in dependence of varying concentrations of specific substituents as we have found, are in favor of the next-nearest-neighbor Coulomb interactions as driving forces for the Verwey ordering.

\[\text{References} \]


