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Electrical and magnetic properties of $Fe_{3-z}Al_zO_4$ ($z<0.06$)

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Electrical resistivity and magnetization measurements have been carried out on synthetic single crystals of $Fe_{3-z}Al_zO_4$ in the range $0\leqslant z<0.06$. The samples were annealed to achieve the ideal 3:4 ratio of cations to anions. As has been previously reported for nonstoichiometric magnetite and for Zn- and Ti-doped magnetite, there is a change in the nature of the Verwey transition: with increasing z the transformation shifts from first to higher order and then disappears. Saturation magnetization measurements have been used to determine the possible distribution of divalent and trivalent iron and of trivalent aluminum among the tetrahedrally and octahedrally coordinated interstices. Differences in the present findings from those in Zn- and Ti-doped magnetite are pointed out and their implications are discussed. [S0163-1829(96)00821-1]

INTRODUCTION

Magnetite and other spinel ferrites, where iron is partially substituted for the transition-metal cations, have been extensively studied over the past 50 years. The reader is referred to Refs. 1–3 for representative literature reviews. One of the most interesting phenomena encountered in these materials is the Verwey phase transition, occurring near 121 K in stoichiometric Fe_3O_4, and at lower temperatures in nonstoichiometric and substituted compounds. Primarily, it was found that the nature of the Verwey transition changes from first to second or higher order with an increased degree of oxygen-metal nonstoichiometry 3δ in $Fe_{3(1-\delta)}O_4 \equiv (Fe^{3+})[Fe^{3+}_{1+6\delta}Fe^{2+}_{1-9\delta}]O_4$, and a similar change occurs upon substitution of iron by titanium in $Fe_{3-y}Ti_yO_4 \equiv (Fe^{3+})[Fe^{3+}_{1-2y}Fe^{2+}_{1+y}Ti^{4+}_{y}]O_4$ or zinc in $Fe_{3-x}Zn_xO_4 \equiv (Fe^{3+}_{1-x}Zn^{2+}_{x})[Fe^{3+}_{1+x}Fe^{2+}_{1-x}]O_4$.[4–6] Here parentheses ( ) denote tetrahedral lattice sites and brackets [ ], octahedral lattice sites; the number of Fe^{2+} and Fe^{3+} cations is determined by electroneutrality constraints. Quite recently, however, precise neutron[7] and x-ray investigations[8] showed that below T_v for the so-called ''II order transition'' systems long-range order is not attained. Nevertheless, throughout the rest of the paper we will retain the term ''II order transition'' in view of large thermodynamic anomalies observed in these materials, despite the complexity of this phenomenon.

For these compounds a universal relation exists for the dependence of the Verwey transition temperature T_v with composition; see Fig. 1. That is, the same level of substitution y of Ti or x of Zn, or iron vacancies 3δ produces the same effect on the transition temperature.

There is a long standing dispute as to the origin of the Verwey transition.[9] It is commonly accepted that below the transition temperature the distribution of Fe^{2+} and Fe^{3+} ions in octahedral sites changes from dynamic disorder (electrons resonating on octahedral sites) to long-range order (LRO); the electrons on the Fe^{2+} cations freeze out, causing a substantial rise in resistivity (about two orders of magnitude in pure Fe_3O_4). In considering charge ordering in Fe_3O_4, a condition pointed out by Anderson[10] is of great significance. This condition requires that in every tetrahedron formed by the nearest-neighbor (o) sites of the spinel structure there

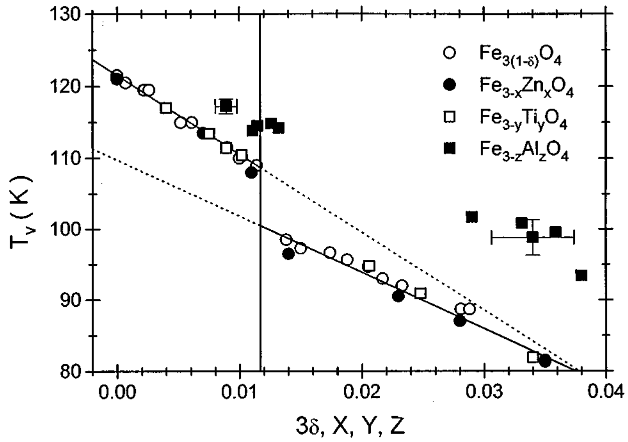

FIG. 1. Dependence of the Verwey transition temperature T_v on composition and on oxygen stoichiometry. The regions of first- and higher order are clearly delineated (data for nonstoichiometric or Zn- and Ti-doped magnetite cited after Ref. 5).

should be two Fe^{2+} and two Fe^{3+} ions, due to the strong Coulombic interaction between electrons. This strong nearest-neighbor Coulomb interaction U_1 stabilizes the short-range order (SRO). Furthermore, Anderson pointed out that LRO can be produced without affecting the ordering of the nearest neighbors, and that additional interactions stabilize LRO. The energy U_2 needed to do this is only a small fraction of the energy U_1, and its origin is still a subject of dispute.

It is of interest to determine whether these additional interactions are responsible for the change of the Verwey transition (and its temperature) with doping. The other possibility connects these changes with the alteration of SRO. This, however, seems to be less probable, because the population of octahedral sites, and therefore the SRO, changes in a different manner by doping for the investigated systems, while the character of changes of the Verwey transition is similar for all examined materials.

Several mechanisms have been proposed as a possible source for these interactions. Here we discuss the recent suggestion[11] that magnetic interactions can serve as a basis for the universal T_v vs x, y, δ behavior. In this scheme[11] the change of T_v with dopant concentration scales with the difference in population of Fe^{3+} cations on the tetrahedral and octahedral sublattices, ΔFe^{+3}. For magnetite and the Ti or Zn substituted compounds, the values of $\Delta Fe^{+3} = Fe^{3+}{}_{(tetra)} - Fe^{3+}{}_{(octa)}$ are

$$Fe_{3-3\delta}O_4, \quad \Delta Fe^{+3} = -6\delta,$$

$$Fe_{3-x}Zn_xO_4, \quad \Delta Fe^{+3} = -2x,$$

$$Fe_{3-y}Ti_yO_4, \quad \Delta Fe^{+3} = +2y.$$

This could account for the experimentally observed 3δ, x, y universality relation involving T_v, provided that only the relative number of Fe^{3+} cations is considered.

Magnetic interactions have already been considered as being responsible for the Verwey transition. Fe_3O_4 is a ferrimagnetic material, with spin-only magnetic moments correlated through oxygen-mediated superexchange interactions. The intersublattice coupling J_{ab} is stronger than the intrasublattice one, so the resultant magnetic order is ferromagnetic within a given sublattice and antiferromagnetic between the sublattices. For magnetite and spinels with low dopant concentrations, the Curie temperature is relatively high (~850 K); therefore, the magnetic order is nearly perfect at temperatures near the Verwey transition. Although no significant (higher than 0.1%) change in magnetization was observed at the transition temperature, the magnetic anisotropy is strongly affected.[11–14] In a recent analysis[14] of anisotropy and magnetization vs T dependence, both T_v and the Curie temperature have been simultaneously calculated from the derived J_{ab} exchange integral. This would suggest an intimate connection between magnetic interactions and the Verwey transition with, possibly, magnetic interactions as the driving force of the transition. Also, Rosencwaig[15] pointed to possible double-exchange interactions between octahedral cations as an explanation for both the transport properties and Mössbauer effect data; however, in his explanation the driving force for the Verwey transition is of structural, rather than magnetic origin. Clearly, the problem of the relation of the Verwey transition to magnetic properties is still unresolved and deserves further investigation.

The aim of this paper is to discuss further the character of the additional interactions leading to the Verwey transition. Specifically, we would like to check for possible correlations between changes in resistivity in the vicinity of the transition, and the transition temperature, as a function of sample composition. In particular, we intend to test the suggestion that the change in the Verwey transition temperature with dopant concentration is related to the difference in Fe^{3+} population of the octahedral and tetrahedral sublattices (ΔFe^{3+}).

As an extension to the series of materials already mentioned we have grown and examined single-crystal aluminum ferrites $Fe_{3-z}Al_zO_4$ with low Al concentration, $z<0.06$. In this material, the difference in the number of Fe^{3+} cations in the sublattices should differ from that in Zn- and Ti-doped or nonstoichiometric magnetite, thus providing the means for an independent test of the hypothesis cited above.

There are conflicting reports concerning the cation distribution in $Fe_{3-z}Al_zO_4$. Gillot and Jemmali[16] and Mason and Bowen[17] suggest that, for low concentrations, aluminum cations occupy only octahedral sites. This leads to the formula for the distribution

$$(Fe^{3+})[Fe^{3+}_{1-z}Fe^{2+}Al^{3+}_z]O_4. \tag{1}$$

On the other hand, based on Mössbauer effect measurements, Dehe *et al.*[18] have proposed, that both Al^{3+} and Fe^{2+} enter tetrahedral as well as octahedral positions, leading to the distribution:

$$(Fe^{3+}_{1-0.5z}Fe^{2+}_{0.385z}Al^{3+}_{0.115z})[Fe^{3+}_{1-0.5z}Fe^{2+}_{1-0.385z}Al^{3+}_{0.885z}]O_4. \tag{2}$$

Additional results of magnetic measurements on polycrystalline samples[19,20] support the conclusion that the cation distribution may be more complicated than that given by Eq. (1). Therefore, the problem of cation distribution for small Al concentrations ($z<0.06$) is unresolved and requires further study. Treating the above two formulas as limiting cases, the difference in the number of Fe^{3+} ions $\Delta Fe^{3+}=z$ for distribution (1) and $\Delta Fe^{3+}=0$ for distribution (2). For either case, the change in T_v with composition should be smaller than that for the Zn and Ti doped or nonstoichiometric materials, if it is directly related to ΔFe^{3+}. Namely, T_v should vary with concentration as $3\delta = x = y = z/2$ for distribution (1) and should be independent of Al concentration for distribution (2).

The dependence of the Verwey transition temperature with concentration in aluminum-substituted magnetite is also the subject of conflicting results. From the resistivity of polycrystalline samples with $z=0.10$, Gillot[16] reports a transition temperature of 99 K. Results of measurements on monocrystals with composition $z=0.03$ and $z=0.10$,[21] show transitions at 90 and 45 K, respectively. Though inconsistent, these data support the suggestion that the decrease in T_v with

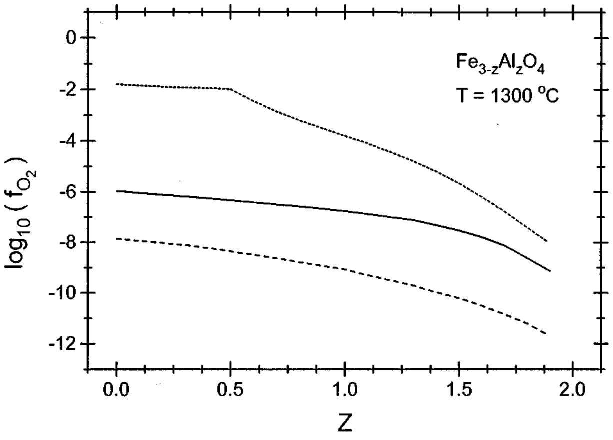

FIG. 2. Experimentally determined (Ref. 25) stability field at 1300 °C for $Fe_{3-z}Al_zO_4$ (dashed lines) and intrinsic oxygen fugacity of stoichiometric aluminum ferrites calculated after Eq. (3) (solid line).

composition for aluminum ferrites is less pronounced than that for titanomagnetites, zinc ferrites, and nonstoichiometric magnetite.

EXPERIMENT

$Fe_{3-z}Al_zO_4$ single crystals were grown under a CO_2 atmosphere using the cold crucible skull-melter technique, discussed in detail elsewhere.[22,23] The starting materials were 99.999% purity Fe_2O_3 and 99.99 purity Al_2O_3. Single crystals (typically 15 mm×5 mm×5 mm) were isolated from the boules, analyzed for Al and Fe content by the electron microprobe technique, and checked by Laue back scattering, and x-ray powder diffraction. All the peaks observed in the powder diffraction patterns could be attributed to the aluminum spinel ferrite.[24]

For samples with low substitutions, vacancies produced during crystal growth and subsequent annealing may greatly alter the physical properties, as has been shown in numerous publications. For this reason, proper annealing conditions must be determined to ensure the ideal cation to oxygen ratio of 3:4. The treatment of this problem for $Fe_{3-y}Ti_yO_4$ was discussed by Aragón and McCallister;[25] our calculations closely follow this procedure. The assumption is made that the nonstoichiometry arises from cationic point defects of the Frenkel type, affecting only the magnetite component in the $Fe_{3-z}Al_zO_4$ system; that is, a stability field of zero width is assumed for $FeAl_2O_4$. Applying the procedure of Ref. 25 and using this assumption, the following formula may be derived:

$$\log_{10}(f_{O_2}) = \log_{10}(f_{O_2}Fe_3O_4) + 2.5\ \log_{10}[(2-z)/2], \quad (3)$$

where $\log_{10}(f_{O_2}Fe_3O_4)$ is the intrinsic oxygen fugacity for stoichiometric magnetite[26] and $\log_{10}(f_{O_2})$ specifies the oxygen fugacity at which stoichiometric $Fe_{3-z}Al_zO_4$ can be obtained. We believe that formula (3) yields a reasonable approximation for the low dopant concentrations used in our investigations. The result of the calculations is shown in Fig. 2, together with the stability field for $Fe_{3-z}Al_zO_4$.[27] All anneals were carried out under the conditions specified by the above formula, using a furnace with a controlled atmosphere that contained an oxygen sensor.[28]

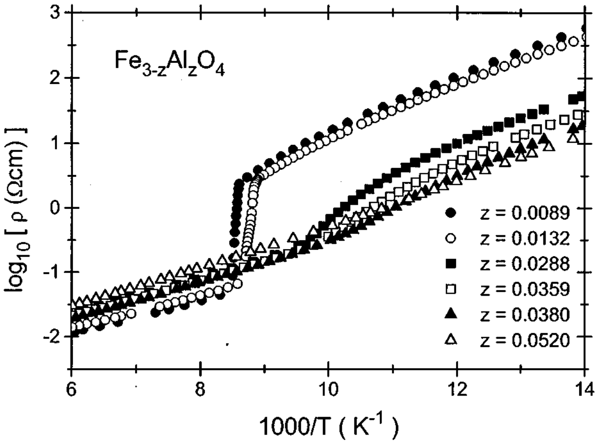

FIG. 3. Variation of resistivity ρ with temperature for selected samples in the vicinity of the Verwey transition.

Samples for the resistivity measurements were bars, typically of dimensions 8 mm×1 mm×1 mm, cut from unoriented single crystals. Current and voltage contacts for resistivity measurements were soldered ultrasonically in the standard dc four-probe arrangement; these conditions lead to an uncertainty of about 10% in the absolute value of the resistivity. Saturation magnetic moment measurements were carried out on spherical samples (2–3 mm in diameter), with a vibrating sample magnetometer at a temperature of 4.2 K, and in a magnetic field of 13 kOe applied along the easy magnetic direction. The unique easy axis, for the low-temperature phase, was established through the appropriate procedure of cooling in a magnetic field, described in detail elsewhere.[12]

After the measurements the composition of the samples was checked again by the electron microprobe technique. The inhomogeneity of Al concentration within the samples used for resistivity measurements was typically less than 12%, while samples used for magnetic measurements were more homogeneous (<5%).

The details of preparation of Ti and Zn doped, and nonstoichiometric single magnetite crystals are similar and are presented in detail in relevant papers.

RESULTS AND DISCUSSION

Typical results of resistivity ρ measurements in the temperature region near the Verwey transition are presented in Fig. 3 (as $\log_{10}\rho$ vs $1/T$). A clear change in the nature of the transition with increased Al concentration is observed, presumably from first to second order. The dependence of T_v versus Al concentration is shown in Fig. 1. The Verwey transition temperature was chosen as the inflection point in a plot of $\log_{10}\rho$ versus $1/T$ (peak in the derivative of $\log_{10}\rho$ vs $1/T$), in accordance with previous publications.[5] Although no apparent transition was seen for the sample with aluminum concentration of $z = 0.052$, a plot of the derivative indicated a change in slope at $T \sim 86$ K.

The overall variation of the transition with sample composition is similar, irrespective of the particular dopant; how-

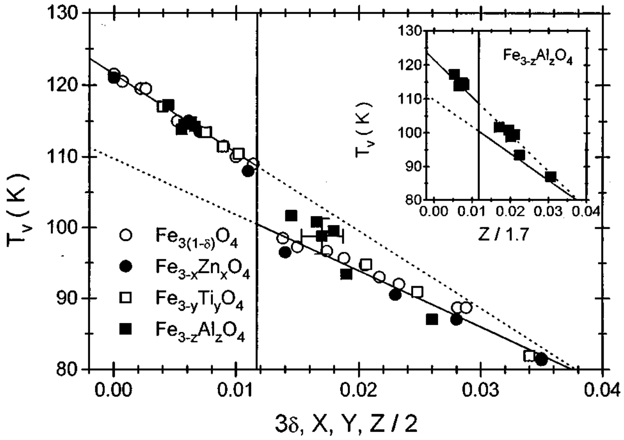

FIG. 4. Dependence of the Verwey transition temperature with composition, with $z/2$ scaling for aluminum ferrites. The inset shows yet another scaling for $Fe_{3-z}Al_zO_4$ with the results for other ferrites marked as a solid line.

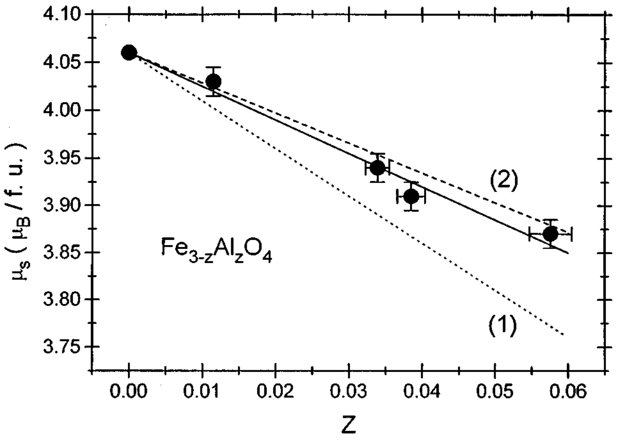

FIG. 5. Variation of saturation moment at 4.2 K with composition parameter z for various models of cationic distribution cited in the literature (line 1, Refs. 14 and 15, line 2, Ref. 16); solid circles represent measured data points, while solid line is the best fit to these data.

ever, some quantitative differences are observed. Namely, T_v decreases with increasing aluminum concentration more slowly than for Ti, Zn-doped or nonstoichiometric magnetite (see Fig. 1). Also, the transition switches to second order for z probably higher than 0.012, the value characteristic for x, y, and 3δ, although the lack of data for z between 0.013 and 0.028 does not allow any firm conclusions to be drawn. These facts suggest that the same mechanism is responsible for both the order of the transition and for the transition itself.

If formula (1) for the cation distribution were correct, then the difference in Fe^{3+} cations (ΔFe^{3+}) would be equal to z. Thus, in agreement with the hypothesis cited above,[11] aluminum substitution should produce an effect half as large on T_v as does Ti, Zn doping or nonstoichiometry (for which the ΔFe^{3+} parameter is $2y$, $2x$, and 6δ, respectively) at the same level of doping. In other words, T_v should scale with concentration as $3\delta = x = y = z/2$. On the other hand, for cation distribution (2), increasing the Al concentration should not affect T_v at all. The T_v versus concentration relation in $z/2$ coordinates is presented in Fig. 4, showing much better agreement with the universal curve. Actually, the data could be represented by a single line in Fig. 4 that is continuous across the range of first- and second-order transitions. If we try to match T_v vs $z/\mathbf{a}$ (**a** represents a scaling factor) for first-order samples (where the transition temperature can be determined with high accuracy) with the universal curve we obtain scaling factor $\mathbf{a} = 1.7$. This scaling is presented in the inset of Fig. 4.

The above analysis is subject to uncertainties in the Al cation concentration. We found it very difficult to obtain a homogeneous Al distribution over large regions of the sample. Even in the best of samples, there is still a standard deviation of 12% in composition for the larger samples used in resistivity measurements (for magnetization experiments the samples were smaller and more homogeneous: here the standard deviation was below 5%). The question then arises, to what extent this inhomogeneity of the Al distribution can affect the above and future conclusions.

The inhomogeneity problem was analyzed by Koenitzer,[29] who found that nonuniformity in Zn and Ti distribution affects mainly the T_v vs composition curve; in particular, the characteristic break in this curve may not be seen when inhomogeneities in doping concentrations become severe.

To clarify this point, we carried out a computer simulation of resistivity vs T for an inhomogeneous sample composed of two regions, with Zn concentrations $x_1 = 0.023$ and $x_2 = 0.035$, for which the amount of each phase was varied. For this case, the resultant ρ versus T plot is a superposition of the two relevant relations for each composition, with the one with the lower Zn content exhibiting a much more pronounced break at T_v than the other one. Thus, T_v for such a composite sample, calculated from the derivative of the $\log_{10}\rho$ vs $1/T$ dependence, is representative for the lower x phase, whereas the concentration is a mean weighted value of both dopant contents.

For $Fe_{3-z}Al_zO_4$ samples the overall error in T_v can be estimated as a product of standard deviation of z (12%) and the T_v vs z slope. The representative error bars are presented in Figs. 1 and 4; the corresponding error in **a** equals ±0.1. This simulation procedure does not account for the lack of a break in the resultant T_v vs composition curve.

To check on the actual cation distribution in $Fe_{3-z}Al_zO_4$ the saturation magnetization $\mu_s(z)$ (in Bohr magnetons) measurements are compared with those calculated for the cation distributions (1) and (2) in Fig. 5. Despite the scatter of data, model (1) may be clearly rejected; model (2) provides much better agreement with experiment. The experimental data fit well to the linear relation $\mu_s = (4.06 - 3.50z)\mu_B$, which is similar to the previously reported dependence for Al-doped magnetite, $\mu_s = (4.06 - 3.16z)\mu_B$,[19,20] or $\mu_s = (4.06 - 3.13z)\mu_B$, that results from distribution (2). However, it is not possible to determine the cation distribution in a unique way from magnetization data without additional assumptions. Postulating that Al cations enter both octahedral and tetrahedral positions, but keeping Fe^{2+} cations only on octahedral places, we end up with the following distribution:

$$(Fe^{3+}_{1-0.15z}Al^{3+}_{0.15z})[Fe^{3+}_{1-0.85z}Fe^{2+}Al^{3+}_{0.85z}]O_4. \tag{4}$$

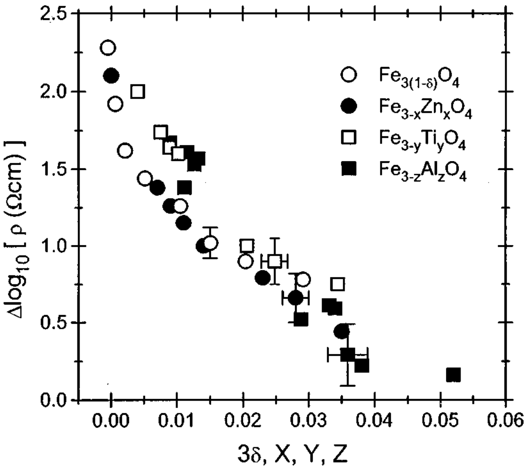

FIG. 6. Resistivity drop near the Verwey transition, $\Delta \log_{10} \rho$ vs dopant concentration and nonstoichiometry.

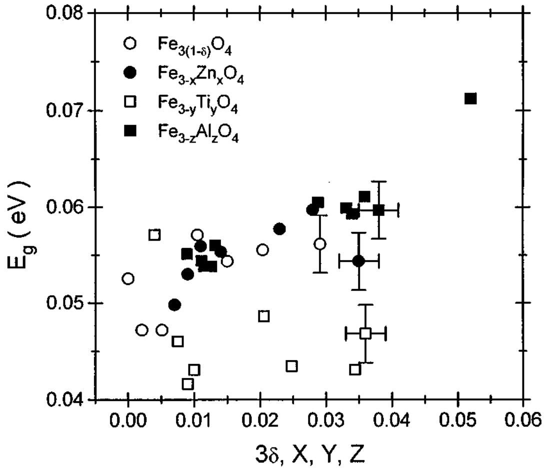

FIG. 7. Plot of activation energy as a function of concentration (or nonstoichiometry) for some weakly doped magnetite-based compounds.

The assumption that Al^{3+} cations occupy only octahedral positions, but that Fe^{2+} ions may be present on both sites leads to

$$(\mathrm{Fe}^{2+}_{0.75z}\mathrm{Fe}^{3+}_{1-0.75z})[\mathrm{Fe}^{2+}_{1-0.75z}\mathrm{Fe}^{3+}_{1-0.25z}\mathrm{Al}^{3+}_{z}]\mathrm{O}_4, \qquad (5)$$

as a cation distribution. This latter distribution is less probable, because the Fe^{2+} ions have a strong preference for octahedral positions.[17]

The above relations represent the simplest formulas for which the saturation magnetization relations $\mu_s = (4.06 - 3.50z)\mu_B$ is satisfied. We could also assume that both Fe^{2+} and Al^{3+} cations enter the tetrahedral sublattice, as in distribution (2); however, this leads to a two-parameter distribution that, as mentioned, cannot be resolved solely by magnetization data. Nevertheless, we checked all the possible cation distributions (i.e., those which agree with magnetization data) and found that for all of them the relevant parameter $\Delta\mathrm{Fe}^{3+}$ is smaller than z [note that $\Delta\mathrm{Fe}^{3+} = +0.70z$ for distribution (4) and $-0.50z$ for distribution (5)]. Thus, in each case, the influence of aluminum concentration on the transition temperature should be smaller than is observed. So, although the Verwey transition temperature versus $z/2$ shows reasonable agreement with the proposed universal curve, the magnetization measurement results are not consistent with distribution (1) from which $\Delta\mathrm{Fe}^{3+} = z$ is derived. Therefore, the relative number of Fe^{3+} cations on the sublattices is not directly related to the observed variation of T_v with aluminum concentration. The data presented above do not, however, imply that magnetic interactions play no role in the Verwey transition. In fact, experimental observations show that there are significant differences in the temperature variation of the anisotropy constants in the second-order samples, as compared to the first-order specimens in the temperature range below T_v.[30,11]

The rapid change in resistivity is another characteristic of the Verwey transition. Data for $\mathrm{Fe}_{3-z}\mathrm{Al}_z\mathrm{O}_4$ is presented in Fig. 6, together with relevant data for other materials discussed,[5] showing reasonable agreement. In this case, the $z/2$ scaling produces results at odds with the universal behavior. This may mean that the mechanism leading to the transition (and to the change of its character) and the one responsible for the resistivity drop are not the same. This is not unreasonable since conduction characteristics involve electron exchange between octahedrally coordinated cations, whereas the factors governing the Verwey transition include the participation of tetrahedrally coordinated cations.

As for Ti and Zn-doped magnetite,[31] there is a small linear region in plots of $\log_{10} \rho$ versus $1/T$ in the temperature range immediately above the transition. In this region, the resistivity can be fitted to the formula $\rho = \rho_0 \exp(-E_g/kT)$. The E_g vs concentration data for low dopant content are shown in Fig. 7. Although the Ti data are well detached from the rest, E_g for $\mathrm{Fe}_{3-z}\mathrm{Al}_z\mathrm{O}_4$ increases with z, while the scatter of data points for $\mathrm{Fe}_{3-y}\mathrm{Ti}_y\mathrm{O}_4$ and $\mathrm{Fe}_{3-x}\mathrm{Zn}_x\mathrm{O}_4$ does not permit firm conclusions to be drawn. However, the data presented in Ref. 31 clearly show that for $\mathrm{Fe}_{3-y}\mathrm{Ti}_y\mathrm{O}_4$ E_g increases with $y > 0.1$, whereas for $\mathrm{Fe}_{3-x}\mathrm{Zn}_x\mathrm{O}_4$ E_g diminishes with increasing $x > 0.1$. The arguments presented in Ref. 31 attributed the variation in E_g with dopant concentration to the changes of Coulomb interactions between carriers. The increasing carrier concentration gives rise to a higher Coulomb energy, as manifested by an increase of activation energy (the carrier concentration for $\mathrm{Fe}_{3-z}\mathrm{Al}_z\mathrm{O}_4$ should rise slightly with z if distribution (2) were correct). It is clearly seen that T_v changes gradually with dopant concentration, whereas E_g does not. Therefore, the factor that determines E_g may not be the same as the interactions leading to the Verwey transition.

In conclusion, we have shown that aluminum doping influences the Verwey transition to a smaller extent than Ti and Zn doping or oxygen nonstoichiometry, although the overall shape of the transition, and the change of its character from first to second order remains the same. The scaling of T_v versus Al concentration must be chosen close to $z/2$, to match the universal T_v versus composition curve. The cation distribution derived from the magnetization measurements for Al-doped magnetite does not conform to the recent suggestion[11] that the Verwey transition temperature in $Fe_{3(1-\delta)}O_4$, $Fe_{3-x}Zn_xO_4$, or $Fe_{3-y}Ti_yO_4$ scales with the difference in the number of Fe^{3+} cations on octahedral and tetrahedral positions in the spinel lattice. The simplest explanation of this fact is that in the case of $Fe_{3-z}Al_zO_4$ the Al cations locate in both octahedral and tetrahedral positions, in contrast to Ti- and Zn-doped materials.

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