The nature of the Werwey transition in magnetite

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We show that the low-temperature Werwey transition at 119 K in magnetite is not caused by electronic ordering of Fe^{2+} and Fe^{3+} ions in the octahedral sublattice. Our investigations of the longitudinal and transverse magnetoresistance of titanomagnetites lead us to assert that the Werwey transition in magnetite is rather the result of the formation of $Fe^{2+}-Fe^{2+}$ and $Fe^{3+} - Fe^{3+}$ pairs in the octahedral sublattice. © *1996 American Institute of Physics*. [S1063-7761(96)01601-5]

Despite the fact that magnetite has been studied comparatively often, recently it has once more become the object of close attention from both experimentalists and theoreticians. This interest in this ferrite is explained by the fact that low-temperature anomalies have been observed in it with various physical properties that are not addressed by existing theoretical models.

One of the characteristic features of magnetite that distinguish it from other simple ferrites is that it exhibits a low-temperature Werwey phase transition ($T_W = 119$ K), at which the electrical conductivity decreases abruptly[1] and the symmetry of the crystal structure is lowered. According to the model proposed by Werwey *et al.*, this transition takes place because of electronic ordering of the Fe^{2+} and Fe^{3+} ions in the octahedral sublattice. However, recently many papers have appeared that question the Werwey model.[2–7]

In this paper our task will be to clarify whether or not ordering of Fe^{2+} and Fe^{3+} ions is responsible for the Werwey transition in magnetite at 119 K. In order to address this problem, we will take two samples of the system $Fe_{3-x}Ti_xO_4$ with $x=0.5$ and $x=0.75$. The cation distributions $Fe^{3+}[Fe^{2+}_{1.5}Ti^{4+}_{0.5}]O^{2-}_4$ and $Fe^{2+}_{0.5}Fe^{3+}_{0.5}[Fe^{2+}_{1.25}Ti^{4+}_{0.75}]O^{2-}_4$ indicate that there are no Fe^{3+} at octahedral sites of these samples, which eliminates ordering of Fe^{2+} ions at the B-sites relative to Fe^{3+} ions as a possible reason for the transition, and also the appearance of intermediate valence at the iron atoms via the process $Fe^{3+}_B \rightleftarrows Fe^{2+}_B$.

We have studied the behavior of the electrical conductivity and linear thermal expansion of samples of these ferrites in the temperature interval (80–293 K). Information about such investigations in the literature is unavailable. We felt that we could more reliably compare the behavior of the electrical properties of our titanomagnetite samples with those of magnetite if we measured these properties in magnetite ourselves instead of using the results of other authors.

Polycrystalline samples of magnetite were synthesized at the Kiev Polytechnic Institute. A first sintering was carried out at a temperature of 1100 °C over a period of two hours, a second at a temperature of 1300 °C over a period of four hours. Both sinterings were carried out in a CO_2+H_2 atmosphere. Our analysis showed that the samples were single-phase spinels for which the lattice parameter at room temperature was $a = 8.392$ Å.

The titanomagnetites were prepared in the research laboratories of the Department of Natural Rock Magnetism at the Institute of Physics of the Russian Academy of Sciences (Siberian Region), using a thermal–vacuum apparatus and ceramic processing of the oxides FeO, TiO_2, and Fe_2O_3. The first sintering was carried out at a temperature of 800 °C over a period of six hours, the second at 1150 °C over a period of seven hours. The lattice parameters of the samples at room temperature were: $a = 8.458$ Å for $Fe_{2.5}Ti_{0.5}O_4$ and $a=8.496$ Å for $Fe_{2.25}Ti_{0.75}O_4$.

We measured the magnetoresistance in an electromagnet at fields up to 12 kOe, and the electrical resistance by the bridge method. Contacts to the sample were made using an indium–gallium paste. We measured the linear thermal expansion using strain gauges by the bridge method.

Figure 1 shows the results of measurements of the specific electrical conductivity. In the table we list the activation energy E over various temperature intervals. It turns out that for the titanomagnetites the dependence of log ρ on $1/T$ has the same form as for magnetite, with a jump in the activation energy for the titanomagnetites at almost the same temperatures as for magnetite. Especially interesting is the fact that for both samples the most abrupt change in activation energy takes place in the temperature interval where the Werwey transition is observed. For example, in the sample with $x=0.5$ it occurs at $T_t \approx 102$ K, while in the sample with $x=0.75$ it occurs at $T_t \approx 99$ K.

Because the Werwey transition in magnetite is accompanied by a crystallographic distortion of the cubic lattice, it is interesting to test whether or not the linear thermal expansion of the titanomagnetites also exhibits anomalous behavior at low temperatures. It is clear that our data for the temperature dependence $(\Delta l/l)(T)$ shown in Fig. 2 are anomalous in character. This is especially evident from the temperature dependence of the coefficients of linear expansion $\alpha(T)$ (Fig. 3). When the samples are cooled, there is a jump in the coefficient α in the neighborhood of 260 K. However, as the temperature is further lowered, the functions $\alpha(T)$ begin to differ strongly for the two samples. For example, this coefficient decreases smoothly with temperature for the sample with $x=0.5$ starting at $T \approx 220$ K, and in the neighborhood of 115 K it changes sign from positive to negative. For the ferrite with $x=0.75$ the sign change from positive to negative takes place in the neighborhood of 220 K. Further cooling of this sample reveals that while the coefficient α re-
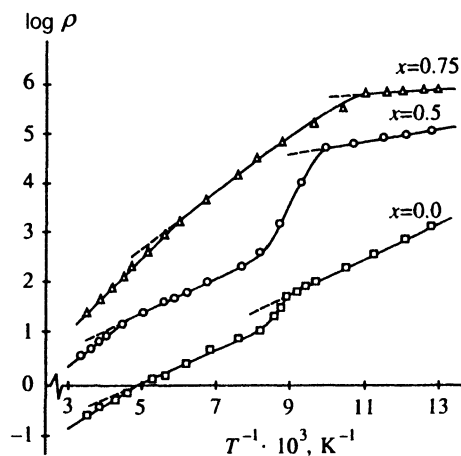
FIG. 1. Dependence of log ρ on $1/T$ for the samples $Fe_{2.5}Ti_{0.5}O_4$ and $Fe_{2.25}Ti_{0.75}O_4$.

mains a negative quantity, its absolute value reaches a maximum at 160 K and then decreases smoothly. The negative sign of the coefficient α implies that an anomalous phenomenon is taking place in the crystal lattice: the samples are expanding as the temperature decreases. Whereas for the sample with $x=0.5$ this anomalous behavior of the linear expansion occurs at $T\lesssim 115$ K, for the sample with $x=0.75$ it occurs at $T\lesssim 220$ K and continues down to 80 K.

Thus, our observations establish that the behavior of the electrical conductivity and thermal expansion of the titanomagnetites we have studied is anomalous in the neighborhood of the Werwey transition temperature. Based on these results we can conclude that a low-temperature transition occurs in both samples, just as in magnetite.

It is common knowledge that a number of other models have been proposed to explain the nature of the Werwey transition in magnetite. In our view, the model proposed by Buchenau[2] merits particular attention. This model asserts that formation of covalent cation B–cation B pairs in the octahedral sublattice is responsible for the Werwey transition in magnetite. These covalent pairs arise through overlap of t_{2g} orbitals of the octahedral $3d$ cations (i.e., the direct exchange interaction). On the basis of experimental results for the Mössbauer effect and NMR, Mizoguchi and Iida were led
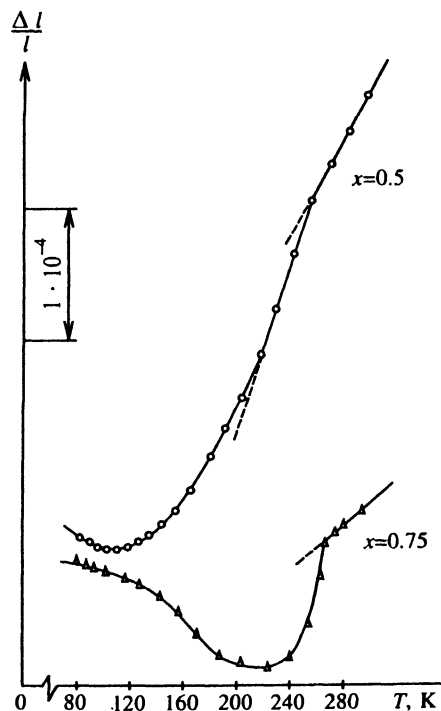

FIG. 2. Dependence of the linear expansion $\Delta l/l$ on temperature for the samples $Fe_{2.5}Ti_{0.5}O_4$ and $Fe_{2.25}Ti_{0.75}O_4$.

to an analogous conclusion.[4-6] They suggested that for $T<T_W$ the octahedral Fe^{2+} ions form pairs in the [110] direction in the (100) plane and they alternate with pairs of octahedral Fe^{3+} ions lying in the same plane along the same direction.

In Ref. 7, Belov et al. showed that if covalent cation B–cation B bonds are present in ferrite–spinels at low temperatures, an external magnetic field will compress the t_{2g} orbitals, leading to breaking of the bonds. As a result, delocalization of the $3d$ electrons from the $t_{2g}-t_{2g}$ bonds occurs, which leads to an anomalously high negative magnetoresis-

TABLE I.

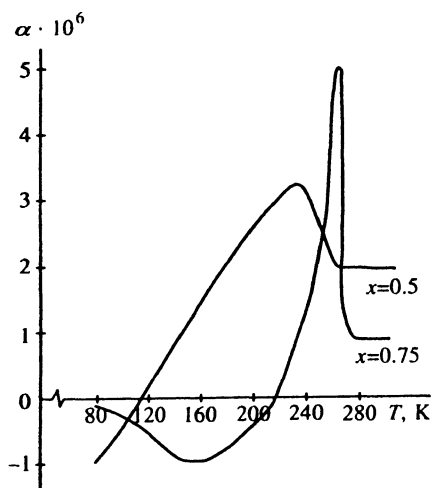| Ferrite composition	Activation energy E and temperature intervals		
Fe$_3$O$_4$	0.10 eV	0.08 eV	0.07 eV
	294–187 K	187–119 K	119–80 K
Fe$_{2.5}$Ti$_{0.5}$O$_4$	0.11 eV	0.08 eV	0.05 eV
	294–240 K	240–122 K	102–80 K
Fe$_{2.25}$Ti$_{0.75}$O$_4$	0.15 eV	0.10 eV	0.03 eV
	294–177 K	177–94 K	94–80 K

FIG. 3. Dependence of the coefficient of linear expansion α on temperature for the samples $Fe_{2.5}Ti_{0.5}O_4$ and $Fe_{2.25}Ti_{0.75}O_4$.
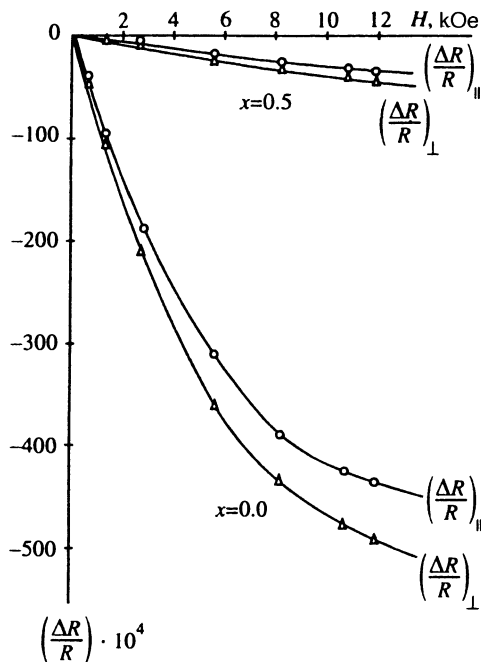
FIG. 4. Isotherms of the longitudinal $(\Delta R/R)_{\parallel}(H)$ and transverse $(\Delta R/R)_{\perp}(H)$ magnetoresistance for the samples $Fe_{2.5}Ti_{0.5}O_4$ and $Fe_{2.25}Ti_{0.75}O_4$.

tance ΔR. In this case, both magnetoresistances $\Delta R_{\parallel}$ and $\Delta R_{\perp}$ will acquire negative signs and be approximately equal in magnitude.

In magnetite, $Fe_B^{2+}-Fe_B^{2+}$ and $Fe_B^{3+}-Fe_B^{3+}$ pairs can form at the B-sites, whereas in the titanomagnetites we studied only $Fe_B^{2+}-Fe_B^{2+}$ pairs can form. In this case, we must take into account that whereas three half-filled t_{2g} orbitals participate in forming the pairs for the case of $Fe_B^{3+}(e_g^2 t_{2g}^3)$ ions, only two such orbitals are involved in $Fe_B^{2+}(e_g^2 t_{2g}^4)$

ions. Therefore, if the low-temperature transition for the titanomagnetites we studied is also due to formation of covalent cation B–cation B pairs, we should expect that the effects leading to negative $\Delta R_{\parallel}$ and $\Delta R_{\perp}$ at 80 K (i.e., for $T<T_t$) due to delocalization will be significantly smaller in these compounds than in magnetite.

Unfortunately, we were unable to measure the magnetoresistance of the sample with $x=0.75$ using our instruments, because the specific resistance in this sample was more than $10^7\Omega$ at 80 K.

Figure 4 shows isotherms of $(\Delta R/R)_{\parallel}(H)$ and $(\Delta R/R)_{\perp}(H)$ recorded at 80 K for magnetite and the sample with $x=0.5$. It is clear that for $Fe_{2.5}Ti_{0.5}O_4$ we also observe negative magnetoresistances $\Delta R_{\parallel}$ and $\Delta R_{\perp}$, which are almost equal in value. However, compared with magnetite the negative magnetoresistance for this sample is almost an order of magnitude smaller in absolute value.

On the basis of these results, we can conclude that the low-temperature transition in the ferrite $Fe_{2.5}Ti_{0.5}O_4$ results from the formation of the covalent $Fe_B^{2+}-Fe_B^{2+}$ pairs at the octahedral sites.

We argue that the results we have obtained for the titanomagnetites $Fe_{2.5}Ti_{0.5}O_4$ and $Fe_{2.25}Ti_{0.75}O_4$ indicate that the Werwey transition in magnetite is caused not by ordering of the Fe^{2+} and Fe^{3+} ions in the octahedral lattice, but rather has another origin.

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