# Electronic processes in magnetite (or, "Enigmas of magnetite")

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The properties of magnetite in the region of the low-temperature transformation $T_t = 100$–$120$ K are in many respects still unclear and even enigmatic, in spite of the enormous number of studies that have been undertaken over the years. In this review article a new model for the low-temperature transformation in magnetite is presented, based on an examination of the features of the temperature and field dependence of the spontaneous magnetization, magnetoresistance, and magnetocaloric effect and an analysis of the anomalies of electronic origin in the magnetic anisotropy and magnetostriction and the accompanying anomalies in the technical magnetization characteristics in the $T_t$ region. This "magnetic–electronic" model of the transition is consistent with experimental facts that do not fit into the well-known Verwey model of a "structural–electronic" transition.

## 1. INTRODUCTION. SOME PRELIMINARY INFORMATION

Magnetite, or lodestone, consists of the iron oxide $Fe_3O_4$ and is a principal component of iron ore, since it contains 70% iron. The strong magnetism of magnetite has been known since remote antiquity.

The magnetic properties of magnetite have been studied for over a century.[1] Among the earliest studies were those of P. Weiss.[1,2] In 1948 Néel showed in a famous paper[3] that magnetite is not a ferromagnet, as had long been assumed, but rather a ferrimagnet, i.e., the magnetic ordering in it is due to negative exchange interactions. Magnetite belongs to the family of spinel ferrites (iron ferrite $Fe^{2+}Fe_2^{3+}O_4$). Its magnetic cations $Fe^{2+}$ and $Fe^{3+}$ are located inside crystalline polyhedra, in the tetrahedral (A) or octahedral (B) sites of the cubic spinel lattice:

$$\underset{A}{(Fe^{3+})}\underset{B}{[Fe^{2+}Fe^{3+}]}O_4^{2-}.$$

The unit cell of magnetite contains 8 such molecules. The A and B cations form two magnetic sublattices with spontaneous magnetizations $(\vec{\sigma})_B$ and $(\vec{\sigma})_A$, oriented antiparallel (Fig. 1). This ferrimagnetic structure, known as the Néel structure, has been confirmed by neutron diffraction studies.[4,5] Magnetite has a high Curie temperature $\sim 850$ K, which indicates that the intersublattice (A–B) exchange interaction is large compared to the intrasublattice (A–A and B–B) exchange interactions, and this is the condition for the existence of the Néel magnetic structure.

Electrons move ("hop") between the $Fe^{2+}$ and $Fe^{3+}$ cations found in the octahedral sites:

$$Fe^{2+}(3d^6) \rightleftarrows Fe^{3+}(3d^5).$$

One of the difficulties in studying magnetite (and other ferrites as well) is the fact that, depending on the temperature and partial pressure in the surrounding medium, different physico-chemical changes occur in it, involving changes in the valences of the cations, breakdown of the stoichiometry of the compound with respect to oxygen, and the appearance or disappearance of defects,[6] which particularly affect its electrical and galvanomagnetic properties.

The study of the magnetic properties of magnetite is of interest for the physics of magnetism, mineralogy, and geophysics, particularly the study of paleomagnetism.[7]

In spite of the enormous number of studies that have been done on the magnetic properties of magnetite, especially the behavior of the spontaneous magnetization and the associated physical phenomena in the low-temperature region (below room temperature), much remains undiscovered and even mysterious.

In this review article the published data on the properties of magnetite in the region of the low-temperature transformation (100–120 K) are systematized and analyzed, and a summary of the research being done at Moscow University on the temperature and field dependences of the magnetization, electrical resistance, magnetoresistance, Hall effect, magnetic anisotropy, and characteristics of the technical magnetization is presented.

On the basis of this analysis a new concept of the low-temperature transformation in magnetite is proposed that is consistent with the experimental facts.

## 2. LOW-TEMPERATURE PHASE TRANSFORMATION. THE VERWEY MODEL OF A "STRUCTURAL–ELECTRONIC" TRANSITION

In the 1930s a low-temperature transformation in magnetite was identified[8–13] on the basis of the measurements of the temperature dependence of the specific heat, electrical resistance, magnetoresistance, and several other properties. Depending on the impurity and nonstoichiometry of the samples (measurements were made on both synthetic and naturally occurring crystals), this transformation occurred at temperatures lying in the interval 100–120 K.

In 1941, Verwey and Haayman[15] advanced the hypothesis that this transformation is a "structural–electronic" phase transition; this hypothesis stimulated a great deal of interest (see S. V. Vonsovskiĭ's commentary to the Russian translation (Mir, Moscow, 1949) of the book by J. L.

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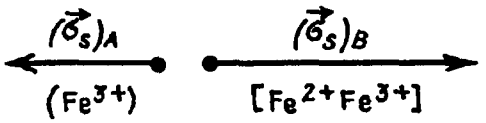


FIG. 1. Magnetic structure of magnetite.

Snoek, *New Developments in Ferromagnetic Materials* and also Vonsovskiĭ's own book, in Russian: *Modern Theory of Magnetism* (Nauka, Moscow 1952). At the phase transition temperature there arises an ordered (alternating) arrangement of the $Fe^{2+}$ and $Fe^{3+}$ cations in the octahedral positions of the spinel lattice of magnetite; this ordering occurs not through motion of the cations but by a change of their valences through a "hopping" of electrons between the $Fe^{2+}$ and $Fe^{3+}$ cations.

The hypothesis of Verwey and Haayman (which has come to be called the Verwey model in the literature) stimulated a torrent of research, including the application of Mössbauer spectroscopy[16–18] and NMR,[19,20] that continues to this day.

The experimental evidence cited for the validity of the Verwey model at the transition temperature $T_t$ (this notation was introduced by Domenicali;[21] the subscript "t" stands for "transition") is that the electrical conductivity $\sigma$ changes sharply, almost discontinuously, at this temperature. Figure 2 shows data[22] on the dependence $\sigma(1/T)$ for stoichiometric magnetite and, for comparison, for two samples of magnetite in which the concentration of the $Fe^{2+}$ cations was reduced through the introduction of $Ni^{2+}$ and $Zn^{2+}$ cations. It is seen that at temperatures below $T_t$ the electrical conductivity decreases by a factor of almost 100; according to Verwey and Haayman's idea, this is because the onset of ordering of the $Fe^{2+}$ and $Fe^{3+}$ cations below $T_t$ causes a strong increase in the activation energy required for hopping of the electrons, which in turn causes $\sigma$ to decrease sharply.

The argument for the "structural" nature of the low-temperature transformation in magnetite is based on the facts that peaks in the specific heat[8,13,23] and (very slight) changes in the symmetry of the crystal lattice[9,12–14] are observed at $T_t$. These facts are not very convincing, however, since they are observed at any phase transition, including magnetic ones.

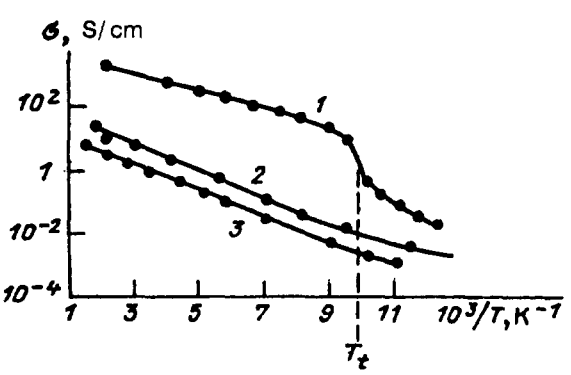


FIG. 2. Temperature dependence of the electrical conductivity of: *1*) $Fe_3O_4$, *2*) $Ni_{0.6}Fe^{2+}_{0.4}Fe_3O_4$, *3*) $Zn_{0.8}Fe^{2+}_{0.2}Fe_3O_4$.

The methods of Mössbauer spectroscopy and NMR enable one to determine $H_{hf}$ the hyperfine fields at the nuclei of the $Fe^{2+}$ and $Fe^{3+}$ cations [see the review by I. S. Lyubutin and T. V. Dmitriev, in: Itogi Nauki Tekh. Kristallokhim. **12**, 5 (1977)]. At temperatures $T > T_t$ the same value of $H_{hf}$ was found for the $Fe^{3+}$ and $Fe^{2+}$ cations in octahedral sites (this value was different from $H_{hf}$ for the $Fe^{3+}$ cation in the tetrahedral sites). This means that $Fe^{3+}$ and $Fe^{2+}$ are indistinguishable in terms of their electronic structure at $T > T_t$. Such a situation can arise if there exists a rapid hopping of electrons between them, i.e., a sort of "equalization" of their valence occurs. At temperatures $T < T_t$, however, the Mössbauer and NMR spectra for the $Fe^{2+}$ and $Fe^{3+}$ cations in the octahedral sites exhibit two groups of resonance lines, i.e., there are two different values of $H_{hf}$ for them. This, in turn, means that the $Fe^{3+}$ and $Fe^{2+}$ cations in the octahedral sites maintain their valences, since, according to the Verwey model the electron hopping is slowed, causing a sharp decrease in the electrical conductivity (see Fig. 2).

The Verwey model has been criticized in a number of experimental and theoretical papers.[24–26]

It should be noted, however, that the key idea of the Verwey model is that a large role in the mechanism for the low-temperature transformation is assigned to the hopping of electrons between iron cations, i.e., to the participation of the conduction electrons in this phase transition. This is confirmed by the aforementioned experiments on the determination of the hyperfine fields in magnetite by the Mössbauer and NMR methods.

## 3. RESULTS ON THE ELECTRICAL RESISTANCE AND MAGNETORESISTANCE

Since an essential role in the mechanism of the low-temperature transformation is played by the conduction electrons, it is very important to examine the results on the electrical and (especially) galvanomagnetic properties of magnetite in order to obtain information about the nature of the electronic processes in this material.

In 1937, de Boer and Verwey[28] proposed a "hopping" mechanism for electrical conduction in magnetic oxides, including magnetite. This stimulated a large number of experimental and theoretical studies of the electrical conductivity of these materials to determine how well such a mechanism accords with the experimental facts. An alternative approach was to apply the band theory of electrical conduction to magnetite and other ferrites. In Ref. 29 it was shown on the basis of Hall effect measurements that band theory could be used to interpret the electrical conductivity of magnetite and other ferrites in the framework of a narrow conduction band. Here, however, it remained extremely puzzling why these materials have such an extraordinarily low mobility of the conduction electrons. The

applicability of the hopping and band mechanisms of electrical conduction to magnetite and other ferrites is analyzed in Ref. 22.

Most of the papers on the electrical properties of magnetite give preference to the hopping mechanism of electrical conductivity. The concentration $N$ of hopping electrons in magnetite can be estimated from the following considerations. There is one hopping electron per $Fe_3O_4$ molecule (or, equivalently, per pair of octahedral cations $Fe_B^{2+}$ and $Fe_B^{3+}$); consequently, there are 8 per unit cell. Since the lattice parameter of magnetite is $a=8.39\cdot 10^{-8}$ cm, we have

$$N=\frac{1\ \mathrm{cm}^3}{a^3}\,8\approx 1.35\cdot 10^{22}.$$

This value of $N$ is comparable to that which exists in metals and is much greater than the value of $N$ for ordinary semiconductors. These hopping electrons largely determine the electrical properties of magnetite. Electrons introduced by impurities and other defects give a small contribution to the electrical properties of magnetite.

The hopping mechanism of electrical conductivity is now widely used to interpret the electrical properties of disordered semiconducting systems such as heavily doped semiconductors. Magnetite can to some extent be included in this category (at temperatures $T>T_t$), since the $Fe_B^{2+}$ and $Fe_B^{3+}$ cations are distributed randomly over the B positions.

According to theory,[27] disordered systems are characterized by the onset of localized states of the conduction electrons (the latter have a so-called mobility threshold).

The reason for the low electron mobility in magnetite has been ascribed[22,30,31] to a strong electrostatic interaction with the cations, possibly accompanied by the formation of electric polaron states.

In magnetic semiconductors there is yet another factor that might bring about localized states of the conduction electrons. This is the s–d exchange interaction of Vonsovskiĭ.[34] Here there are two possibilities.

1) Positive s–d exchange. In ferromagnetic semiconductors this interaction gives rise to magnetopolaron (ferron) states.[33]

2) Negative (antiferromagnetic) s–d exchange. An analysis by Abrikosov[35] has shown that magnetically bound (localized) states of the conduction electrons can be formed in the case of the Kondo effect in impure magnetic systems. Unlike the positive s–d exchange, a negative s–d exchange leads not only to localization of the conduction electrons but also to a partial screening (decrease) of the magnetic moments of the atoms, since the spins of the conduction electrons are oriented antiparallel to these moments.

Based on an analysis of the results of measurements of the electrical resistance and magnetoresistance of magnetite (and certain other ferrites), it can be stated that the s–d exchange interaction (here the $s$ electrons are the $3d$ electrons, which hop between $Fe_B^{2+}$ and $Fe_B^{3+}$) should give rise to an effective mass of the electrons[32] and, hence, to their localization at the cations, not only near the Curie point[32] but also at low temperatures (far from the Curie point). Moreover, the conditions are more favorable for this in magnetite than in metallic alloys, since the hopping electrons have a low mobility.

Evidence that a negative s–d exchange interaction will give rise to localized (magnetically bound) states of the hopping electrons in magnetite (and in certain other ferrites below room temperature) is provided by the experimental data on the magnetoresistance effect in these materials.

Let us discuss the results of the magnetoresistance measurements in magnetite. It has long been established[21,36] that the dependence of the magnetoresistance on the field $H$ in magnetite is anomalous.

The normal manifestation of the magnetoresistance effect is when the longitudinal $(\Delta\rho/\rho)_\parallel$ and transverse $(\Delta\rho/\rho)_\perp$ magnetoresistances accompanying technical magnetization differ in magnitude and sign (anisotropic parity effects). Above technical saturation, i.e., in the region of the paraprocess, at a temperature of 300 K, small, negative effects $(\Delta\rho/\rho)_\parallel$ and $(\Delta\rho/\rho)_\perp$ of equal magnitude (isotropic parity effects) are observed. A typical example of the "normal" behavior of the magnetoresistances is shown by the curves of $(\Delta\rho/\rho)_\parallel$ and $(\Delta\rho/\rho)_\perp$ for nickel (Fig. 3a). As the temperature is lowered from 300 K the slope of the branches of the curves corresponding to the isotropic effects decreases as a result of the decrease in the paraprocess.

In magnetite, however, the curves of $(\Delta\rho/\rho)_\parallel$ and $(\Delta\rho/\rho)_\perp$ versus $H$ have a substantially different form from those for nickel. Figure 3b shows the data of Ref. 37 for the isotherms $(\Delta\rho/\rho)_\parallel(H)$ and $(\Delta\rho/\rho)_\perp(H)$ for the [100] axis of a magnetite crystal, taken at 300 K. The anisotropic effects $(\Delta\rho/\rho)_\parallel$ and $(\Delta\rho/\rho)_\perp$, i.e., those corresponding to the technical magnetization, can be determined here by extrapolating the linear branches of the curves in strong fields, i.e., the isotropic magnetoresistances, to the vertical axis. It is seen that these anisotropic effects are much smaller than the isotropic effects $(\Delta\rho/\rho)_\parallel$ and $(\Delta\rho/\rho)_\perp$, which have the same (negative) sign, and at low temperatures are completely masked by the isotropic branches of the magnetoresistances. Figure 4 shows as an example the isotherms of $(\Delta\rho/\rho)_\parallel$ and $(\Delta\rho/\rho)_\perp$ for magnetite at a temperature of 130 K. It is seen that the isotropic magnetoresistances $(\Delta\rho/\rho)_\parallel$ and $(\Delta\rho/\rho)_\perp$, measured in a field of 10 kOe, have increased above their values for 300 K (see Fig. 3) by a factor of 15–17 times.[38]

The question arises: What is the mechanism responsible for such a strong increase in the isotropic negative magnetoresistances as the temperature is lowered? The usual mechanism, viz., a decrease in the scattering of the electrons on the magnetic disorder on account of the paraprocess, does not operate here, since the paraprocess in magnetite at room temperatures is very small, and its intensity decreases still further as the temperature is lowered.

The strong growth of the isotropic magnetoresistance in magnetite as the temperature is lowered is due to delocalization of the conduction electrons by the magnetic

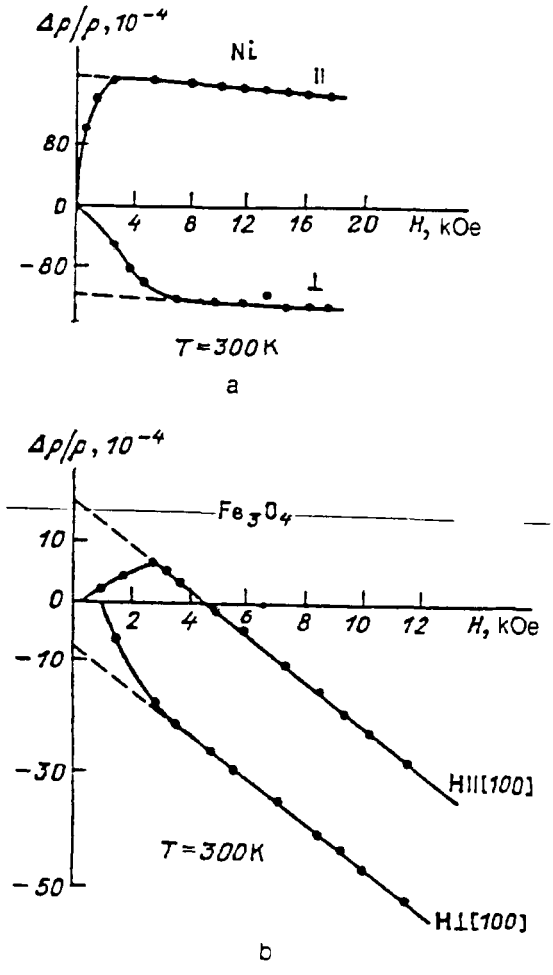


FIG. 3. Dependence of the magnetoresistances $(\Delta\rho/\rho)_{\parallel}$ and $(\Delta\rho/\rho)_{\perp}$ on the magnetic field in nickel (a) and in a magnetite crystal in the [100] direction (b).

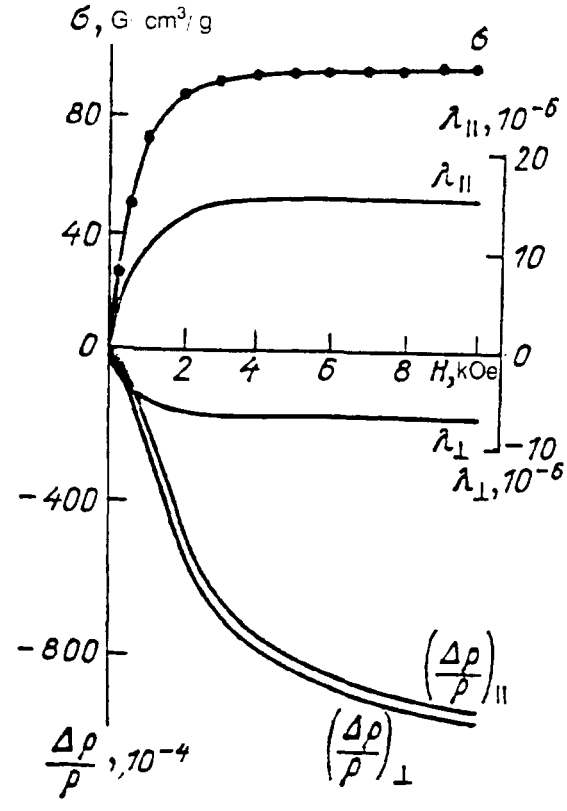


FIG. 4. Isotherms of the specific magnetization $\sigma$, longitudinal and transverse magnetoresistances $(\Delta\rho/\rho)_{\parallel}$ and $(\Delta\rho/\rho)_{\perp}$, and magnetostrictions $(\lambda)_{\parallel}$ and $(\lambda)_{\perp}$ of magnetite, taken at 130 K.

field. The latter, by polarizing the spins of these electrons, increases their kinetic energy and thereby delocalizes them, thus introducing a substantial contribution to the isotropic negative magnetoresistance.

Since at low temperatures the number of localized conduction electrons is large, the number of electrons delocalized by the field $H$ will also be large, and this gives rise to very large isotropic magnetoresistances $(\Delta\rho/\rho)_{\parallel}$ and $(\Delta\rho/\rho)_{\perp}$. Here the delocalization process is very intense and leads to rapid depletion of the localized electrons. As a result, the isotherms of $(\Delta\rho/\rho)_{\parallel}$ and $(\Delta\rho/\rho)_{\perp}$ have a tendency to saturate (see Fig. 4).

We note that this delocalization does not materially influence the other parity effect in magnetite—the magnetostriction. As follows from Fig. 4, on going to low temperatures it maintains its anisotropic properties; $(\lambda)_{\parallel}$ and $(\lambda)_{\perp}$ retain different signs, and the "rule of two" is well satisfied. This is because the effect is governed mainly by the character of the interaction of the cations, and the contribution of the conduction electrons to the magnetostriction is negligible.

Delocalization of the electrons can also occur when the sample is heated in the absence of magnetic field. In this case it is due to a decrease in the exchange field created by the $Fe^{2+}$ and $Fe^{3+}$ cations. This accounts for the extraordinarily sharp drop in the resistivity of magnetite with increasing temperature. Figure 5a shows the curve of the temperature dependence of the resistivity[22] for magnetite. It is seen that from $T_t$ all the way up to room temperatures this curve has a sharp (almost vertical) drop in the resistivity $\rho$, which is explained by an intense delocalization of the conduction electrons owing to a decrease in the exchange field created by the $Fe_B^{2+}$ and $Fe_B^{3+}$ cations. In the investigated temperature region the mobility of the electrons contributes insignificantly to the conductivity. At room temperatures the number of localized electrons is depleted, and the $\rho(T)$ curve has a broad bottom (at 300–500 K). After this there is a slight increase in $\rho$ up to $T_c$. In this temperature region the change in $\rho$ is due to the slight decrease in the electron mobility, since practically no delocalization of the electrons occurs here. This is confirmed by measurements of the normal Hall constant $R_0$. Figure 5b shows the curves of $\ln R_0(1/T)$ for magnetite and, for comparison, several other ferrites.[29] It is seen that, in agreement with what we have said, in the interval from 350 K to $T_c$ the density of conduction electrons $N$ $(R_0 \sim 1/n)$ remains constant.

Finally, we note that the extremely low mobility of the conduction electrons in magnetite and other ferrites (less than 1 $cm^2/V \cdot s$) is explained not only by their strong

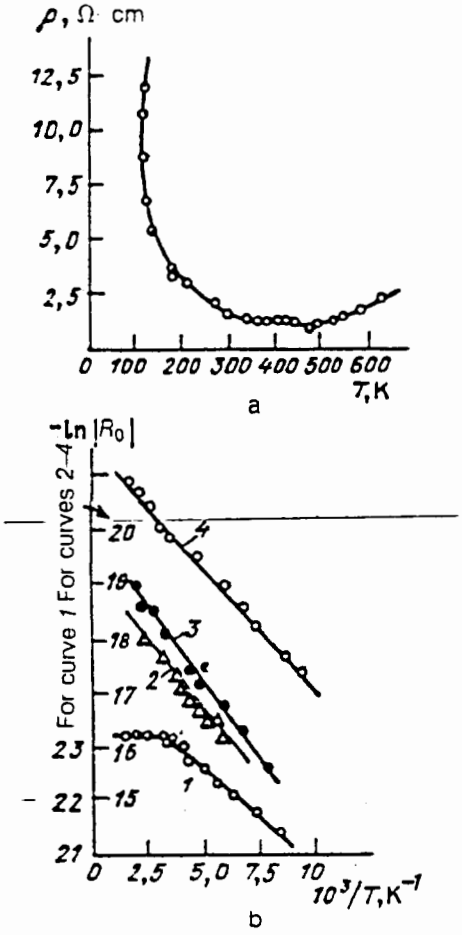


FIG. 5. Temperature dependence of the electrical resistivity $\rho$ (a) and of the logarithm of the normal Hall constant $R_0$ (b) *1*) $Fe_3O_4$, *2*) $NiFe_2O_4$, *3*) $Ni_{0.7}Fe_{2.3}O_4$, *4*) $Mn_{0.8}Fe_{2.2}O_4$.

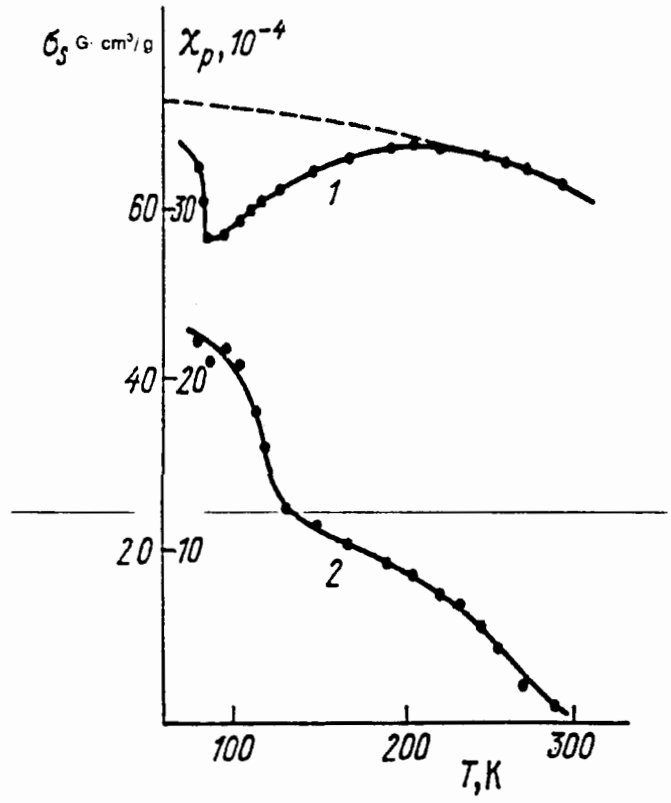


FIG. 6. Temperature dependence of the specific spontaneous magnetization $\sigma_s$ (*1*) and paraprocess susceptibility $\chi_p$ (*2*) near the low-temperature transition $T_t$.

electrostatic interaction with the cations but also by their magnetic (spin) interaction with the cations.

The ideas about the magnetic localization and delocalization of conduction electrons in magnetite set forth in this Section are the key to understanding the mechanism for the low-temperature transformation in this material, which entails a new concept (see Sec. 4).

## 4. EXPERIMENTAL FACTS THAT ARE INCONSISTENT WITH THE VERWEY MODEL. A NEW MODEL OF THE LOW-TEMPERATURE TRANSFORMATION IN MAGNETITE: A "MAGNETIC–ELECTRONIC" TRANSITION

In this section we will adduce the experimental facts that do not fit into the Verwey model and which, moreover, appear puzzling from the standpoint of this model.

1) In Ref. 39 it was shown that as $T_t$ is approached from above, the specific spontaneous magnetization $\sigma_s$ decreases, and right at $T_t$ the function $\sigma_s(T)$ takes on the character of a negative jump (Fig. 6a). It was also found[39] that the paraprocess susceptibility $\chi_p$ increases strongly on approach to $T_t$ (Fig. 6b). The value of $\sigma_s$ was determined by extrapolating the branches of the magnetization isotherms corresponding to fields above technical saturation to $H=0$, and $\chi_p$ was found from the slope of the $\sigma(H)$ isotherms in these fields. The $\sigma(H)$ isotherms of magnetite measured at helium temperature[56] and at 80 K and 300 K[39] do not have a slope in strong fields (magnetic saturation sets in fields $H\sim 2$ kOe). However, near $T_t$ magnetic saturation does not occur even in fields of 10 kOe, since here the paraprocess arises. These experimental facts, as we shall see, are of fundamental importance for interpreting the mechanism of the low-temperature transformation $T_t$ in magnetite.

2) In 1960, Krasovskiĭ and Fakidov[41] detected a sharp peak in the magnetocaloric effect at $T_t$, with an anomalous sign (negative when the magnetic field $H$ was turned on). This result was confirmed in Ref. 42 (Fig. 7). It is seen in Fig. 7 that far from $T_t$ on the high-temperature side the sign of the $\Delta T$ effect in magnetite is normal (positive).

The anomalous sign of the $\Delta T$ effect in the $T_t$ region has remained unexplained for 30 years. Attempts[42] to explain it as an effect of a spin-flip transition occurring at 130 K, i.e., near $T_t$, are too hypothetical and "strained" and are therefore doubtful.

3) There have been several papers[11,43–45] devoted to the study of the magnetoresistance in magnetite in the region of the transformation temperature $T_t$. Figure 7 shows the data of Ref. 42 and temperature dependence of $(\Delta\rho/\rho)_{\parallel}$ measured in a field of $10^4$ kOe. It is seen that the transition $T_t=120$ K corresponds to the maximum of the negative magnetoresistance and that there is also an anomaly in the

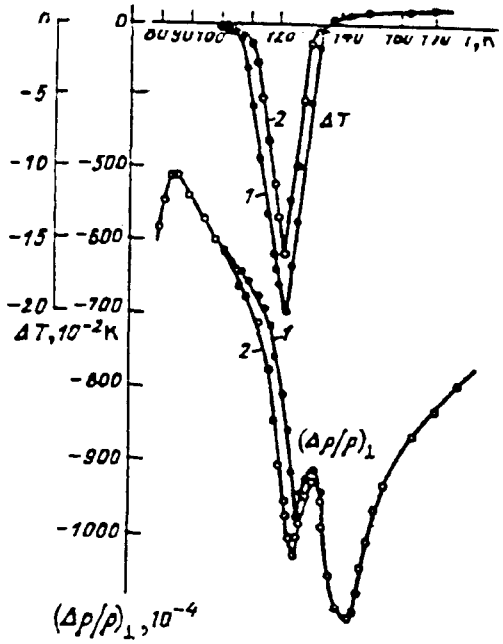


FIG. 7. Temperature dependence of the magnetocaloric effect $\Delta T$ and magnetoresistance $(\Delta\rho/\rho)$ of magnetite in the region of the low-temperature transformation, according to the data of Ref. 42. Both curves were taken in a field of 10 kOe: 1) first measurement, 2) repeat measurement.

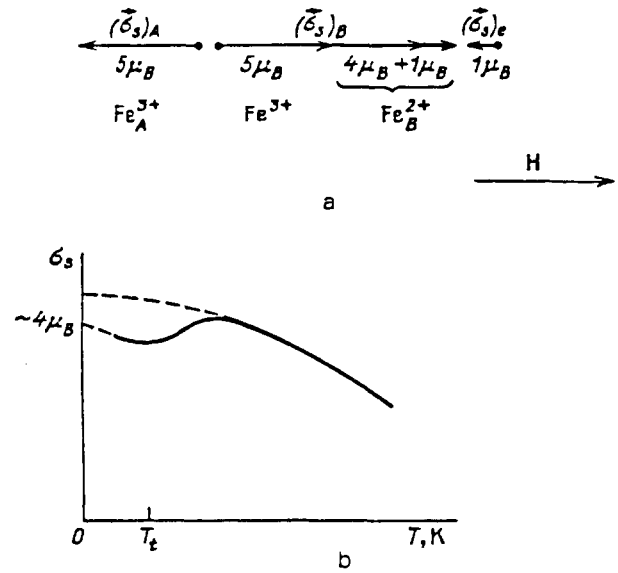


FIG. 8. Magnetic structure of magnetite near $T_t$ (illustrating the new model for the low-temperature transformation in magnetite).

temperature dependence of the magnetoresistance at a temperature somewhat above $T_t$ (at $T \sim 145$ K).

The measurements of $\Delta\rho/\rho$ and the $\Delta T$ effect exhibit relaxation effects (see Fig. 7) in that the values of these effects are slightly different the first time the field $H$ is applied and in subsequent runs (see Sec. 5 for more details).

All of these experimental facts, which are related to magnetic ordering, remain unexplained in the framework of the Verwey model of a "structural–electronic" transition. They can, however, be interpreted with the aid of the following magnetic model.

The magnetic and electrical properties of magnetite below room temperatures can be interpreted in a model wherein this material consists of two subsystems: the subsystem of the octahedral cations $Fe^{2+}$ and $Fe^{3+}$, and the subsystem of conduction electrons, the role of which is played by the $3d$ electrons hopping between the $Fe^{2+}$ and $Fe^{3+}$ cations.

As the temperature is lowered from room temperature to $T_t$, these electrons, under the influence of the exchange field created by the $Fe^{2+}$ and $Fe^{3+}$ cations in octahedral sites, are localized at these cations in ever greater numbers, and, simultaneously, this exchange field orients the spins of the electrons antiparallel to the magnetic moments of the iron cations, giving rise at first to short-range order in the electronic subsystem (possibly with the formation of magnetopolarons) and then, when $T_t$ is reached, to long-range magnetic order. Thus a magnetic phase transition of the induced type arises at $T_t$.

The magnetic structure of magnetite near $T_t$ can be represented in the form of three magnetic sublattices (Fig. 8a), similar to the magnetic structure of rare-earth iron garnets. The role of the rare-earth sublattice is played by the electron subsystem with magnetization $(\sigma_s)_e$.

1) The sublattice magnetization $(\sigma_s)_e$ sharply reduces the magnetization $\sigma_s$ of magnetite at $T_t$ and also at $T < T_t$, including the saturation magnetization $\sigma_0$ at 0 K. The magnetization $\sigma_s$ increases somewhat on approach to 0 K, but the increase (according to the Brillouin function) is insignificant (Fig. 8b).

In making a numerical estimate of the negative peak in $\sigma_s$ at $T_t$ it is necessary to take into account that the $Fe^{2+}$ cation has, in addition to the spin moment $(4\mu_B)$, an unfrozen part of the orbital moment $\Delta M_L \approx 1\mu_B$ (since in the octahedral sites it is found in the triplet orbital state $l=1$), i.e., this cation has a moment of $\approx 5\mu_B$. When $T_t$ is reached (an also for $T < T_t$) the magnetization decreases by $1\mu_B$, i.e., by 20%, on account of the negative s–d exchange. As follows from curve 1 in Fig. 6, this reduces $\sigma_s$ by $\sim 22\%$.

According to the data of many investigators (see Ref. 4) the measured values of $\sigma_s$ for magnetite lie in the range $(4.08\text{–}4.2)\mu_B$, i.e., the value $\sigma_0 \approx 4\mu_B$ estimated above is close to the experimental values.

It is important to note that the magnetization of the electron subsystem $(\sigma_s)_e$, like that of the rare-earth sublattice in iron garnets, is induced by the moderately strong exchange field of the iron cations of sublattice B. According to estimates by molecular field theory, it is several times smaller than the A–B exchange field that determines the Curie temperature of magnetite. Experiments show that an external field $H \sim 10^4$ Oe gives rise to an intense paraprocess in the electron sublattice, which is of the an-

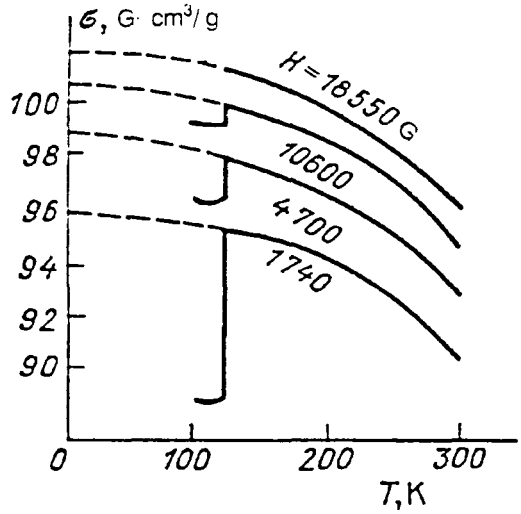


FIG. 9. $\sigma(T)$ curves for magnetite taken in different magnetic fields, according to the data of Weiss and Forrer.

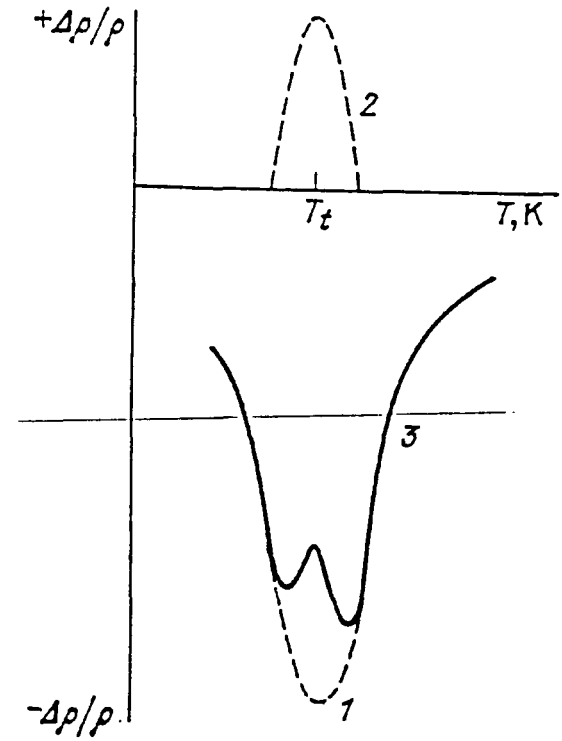


FIG. 10. Schematic illustration of the anomalies in the temperature dependence of the isotropic magnetoresistance near $T_t$. *1*) The maximum of the negative magnetoresistance due to delocalization of the hopping electrons by the field $H$; *2*) the maximum of the positive magnetoresistance due to the antiferromagnetic paraprocess; *3*) the resultant curve of the isotropic magnetoresistance.

tiferromagnetic type, since $(\vec{\sigma}_s)_e$ and $H$ are oppositely directed (Fig. 8a).

2) The onset of an antiferromagnetic paraprocess at $T_t$ can account for the anomalous sign of the magnetocaloric effect at $T_t$ (see Fig. 7). The cause of this effect is that when the field $H$ is applied in the presence of an antiferromagnetic paraprocess, the magnetic entropy of the magnetite sample increases, whereas for a paraprocess of the ferromagnetic type the magnetic entropy decreases; this latter is what occurs in the region of the Curie point, where $\Delta T$ has the normal (positive) sign.

In connection with the sharp decrease in the spontaneous magnetization around $T_t$ that was observed in Ref. 39, one should recall that sharp changes in the temperature dependence of the saturation magnetization of magnetite have also been observed[2,40] around $T_t$. These changes were attributed to the influence of the magnetic anisotropy. However, an analysis of Refs. 2 and 40 shows that this conclusion is incorrect, since the magnetic fields used in these studies were manifestly higher than the saturation fields.

Figure 9 shows curves of $\sigma(T)$ measured in different fields $H$ for a natural magnetite crystal, according to the data of Weiss and Forrer.[2] It is seen that the sharp negative jump in the magnetization at $T_t = 120$ K diminishes as the field $H$ increases. This is a consequence of the onset of the antiferromagnetic paraprocess, which increases in intensity as $H$ increases.

3) The new model of the transition at $T_t$ also makes it possible to interpret the complex behavior of the magnetoresistance at temperatures near and just above $T_t$ (Fig. 7).

The peak of the negative magnetoresistance at $T_t$ is formed by two contributions of isotropic magnetoresistances:

a) a very large contribution due to the delocalization of the conduction electrons by the magnetic field (shown schematically by curve *1* in Fig. 10);

b) an isotropic, but smaller, positive contribution (curve *2*) that arises directly at $T_t$ owing to the "destruction" of the magnetization $(\sigma_s)_e$ by the magnetic field and the antiferromagnetic paraprocess that arises here. The latter creates magnetic disorder (the magnetic entropy in the electron sublattice increases), and the scattering of the conduction electrons increases as a result. Curve *3* shows the resultant curve of the magnetoresistance, obtained by subtracting the corresponding ordinates. It is very similar to the experimental curve (see Fig. 7).

4) The sharp decrease in the electrical conductivity at temperatures $T < T_t$ (see Fig. 2), which in the Verwey model is attributed to the influence of cation ordering, is explained in the new model as being due to the enhancement of the localization of the conduction electrons owing to the increase in the exchange field created by the magnetic cations.

It follows from all we have said that the low-temperature transformation in magnetite is not a "structural–electronic" phase transition, as is postulated in the Verwey model, but a "magnetic–electronic" transition. (However, this does not rule out the possibility[19,20] of ordering of the $Fe^{2+}$ and $Fe^{3+}$ cations according to Verwey[15] in the region $T > T_t$.)

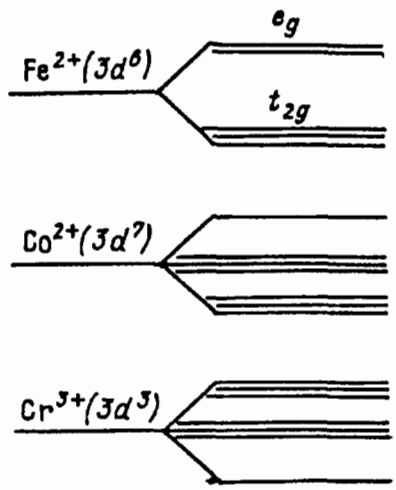


FIG. 11. Splitting of the orbital levels of the cations $Fe^{2+}$, $Co^{2+}$, and $Cr^{3+}$ in an octahedral crystalline field (schematic).

## 5. ANOMALIES ARISING IN THE SINGLE-ION MAGNETIC ANISOTROPY AND MAGNETOSTRICTION AS A RESULT OF THE HOPPING ELECTRONS

As in other ferrites, the magnetic anisotropy and magnetostriction in magnetite are of a single-ion nature, i.e., they are due to the interaction of the unfrozen part of the orbital moment of the transition-element atom with the crystalline field.

The main contribution to the anisotropy and magnetostriction of magnetite is from the $Fe^{2+}(3d^6)$ cation. Figure 11 shows a schematic diagram of the splitting of the orbital level of the $Fe_B^{2+}$ cation in an octahedral field. It is seen that the fivefold degenerate level of this cation is split into an upper twofold degenerate level (doublet $e_g$) and a lower threefold degenerate level (triplet $t_{2g}$), i.e., the $Fe_B^{2+}$ cation has an orbital magnetic moment that is incompletely frozen by the crystalline field and, hence, it should give appreciable values of the magnetic anisotropy constant $K_1$ and anisotropic magnetostriction constants $\lambda_{100}$ and $\lambda_{111}$.

Also shown in Fig. 11 is the splitting diagram of the orbital level of the cation $Co^{2+}$ in an octahedral field. It is seen that this cation is also found in a triplet orbital state, so that the cobalt ferrite $CoFe_2O_4$ should have large values of $K_1$, $\lambda_{100}$, and $\lambda_{111}$.

This conclusion is borne out by experiment for cobalt ferrite, but it is not for magnetite, and in this respect it behaves anomalously. For example, for a single crystal of the ferrite $Co_{0.8}Fe_{2.2}O_4$ at 300 K the data of Ref. 46 gives $K_1=2.7\cdot 10^6$ erg/cm$^3$, $\lambda_{100}=-590\cdot 10^{-6}$, $\lambda_{111}=120\cdot 10^{-6}$. For magnetite at this same temperature, values an order of magnitude smaller were obtained:[47] $K_1=-1.1\cdot 10^{-6}$ erg/cm$^3$, $\lambda_{100}=-20\cdot 10^{-6}$, $\lambda_{111}=78\cdot 10^{-6}$. For polycrystalline samples of $CoFe_2O_4$ and $Fe_3O_4$ the saturation magnetostriction $\lambda_s$ was found to be $110\cdot 10^{-6}$ and $40\cdot 10^{-6}$, respectively.

Slonczewski[48] conjectured that the discrepancy in the values of the magnetostriction for spinel ferrites from the predictions of his single-ion theory of magnetostriction may be due to a partial compensation of the magnetostrictive stresses as a result of the exchange of valences between the $Fe^{3+}$ and $Fe^{2+}$ cations, if the latter are present in the ferrite.

In Ref. 49 it was hypothesized that the unexpectedly low values of the magnetostriction in magnetite are due to a decrease in the unfrozen part of the orbital moment of the $Fe^{2+}$ cation owing to the presence of electron transitions between the heterovalent cations $Fe^{3+}$ and $Fe^{2+}$ in octahedral positions, resulting in decreased values of $\lambda_s$ and $K_1$.

To check this hypothesis, measurements were made of the magnetostriction, coercive force, and electrical resistance of magnetite and the spinel $Fe_2CrO_4$. In magnetite, $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$, the cations $Fe^{2+}$ and $Fe^{3+}$ are present in equal numbers in the B positions, while in the spinel $Fe^{3+}Fe^{2+}Cr^{3+}O_4$ the chromium cation $Cr^{3+}(3d^3)$ is present in the B sites in place of $Fe^{3+}$.

Figure 11 shows the splitting diagram of the orbital level of the cation $Cr^{3+}(3d^3)$ in an octahedral field. It is seen that this cation in the B positions is found in a singlet orbital state and therefore has a completely frozen orbital moment.

Whereas in magnetite an intense hopping of electrons between the $Fe^{2+}$ and $Fe^{3+}$ cations in the $B$ positions occurs, in the compound $Fe_2CrO_4$ no such hopping occurs between $Fe^{2+}$ and $Cr^{3+}$ in the B positions. This is borne out by measurements of the electrical resistivity. It was found that at 120 K the resistivity $\rho$ of the chromium compound is $\sim 3.39\cdot 10^4$ $\Omega\cdot$cm, while for magnetite $\rho\sim 1.45\cdot 10$ $\Omega\cdot$cm.

Figures 12a and b show isotherms of the magnetostriction for the two samples. It is seen that the magnetostriction of the $Fe_2CrO_4$ sample is almost an order of magnitude larger than that of magnetite. It should be noted that the anisotropic magnetostrictions $(\lambda)_\parallel$ and $(\lambda)_\perp$ in magnetite reach saturation in comparatively low fields ($\sim 3$ kOe), whereas for $Fe_2CrO_4$ the curves have not reached saturation even in fields of $10^4$ Oe. This indicates that the $Fe_2CrO_4$ sample has a large magnetic anisotropy.

Thus the results confirm the hypothesis as to the influence of the hopping mechanism $Fe^{2+}\rightleftarrows Fe^{3+}$ on the contribution to the magnetostriction from the octahedral $Fe^{2+}$ ions in magnetite.

There is another fact that also supports what we have said. In Ref. 50 it was found that when a certain amount of the iron in magnetite is replaced by tetravalent titanium cations $Ti^{4+}(3d^0)$, the magnetostriction increased sharply even though the magnetization decreased, since the $Ti^{4+}$ cation does not have a magnetic moment. For a crystal of the spinel ferrite $Ti_{0.56}Fe_{2.44}O_4$ at 80 K the magnetostriction reaches giant values: $\lambda_{100}=990\cdot 10^{-6}$, $\lambda_{111}=330\cdot 10^{-6}$. As the number of the $Ti^{4+}$ cations in the octahedral sites is increased, the number of $Fe^{3+}$ cations decreases, and, hence, so does the number of electron hops between $Fe^{2+}$ and $Fe^{3+}$ cations, i.e., here the $Fe^{2+}$ cations in the octahedral sites function in terms of the magnetostriction (and anisotropy) like cations having a partially unfrozen orbital moment. It was suggested in Ref. 50 that

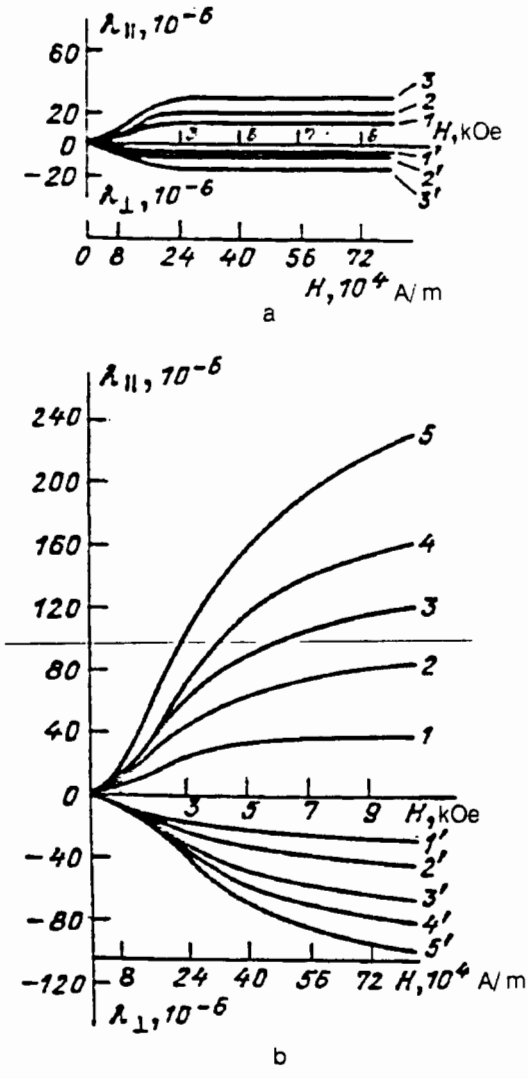


FIG. 12. a: Isotherms of the longitudinal $(\lambda)_{\parallel}$ and transverse $(\lambda)_{\perp}$ magnetostriction of a polycrystalline sample of magnetite: 1,1′) 125 K; 2,2′) 185 K; 3,3′) 292 K. b: Isotherms of the magnetostriction of a polycrystalline sample of $Fe_2CrO_4$: 1,1′) 295 K; 2,2′) 250 K; 3,3′) 220 K; 4,4′) 180 K; 5,5′) 80 K.

when the $Ti^{4+}$ content in magnetite exceeds 0.5, then a portion of the $Fe^{3+}$ cations in the tetrahedral sites are converted to $Fe^{2+}$, which would also increase the values of $\lambda_{100}$ and $\lambda_{111}$.

Another interpretation of the experimental data is that, owing to the hopping of electrons from $Fe^{2+}$ to $Fe^{3+}$ and back, the iron cations take on a valence intermediate between 2 and 3, and such cations will not be found in a singlet orbital state (in the case of $Fe^{3+}$) or in the triplet orbital state (in the case of $Fe^{2+}$). Since the number of $Fe^{3+}$ and $Fe^{2+}$ cations in the octahedral sites in magnetite are equal, the iron cations will have a valence of 2.5, and such a cation will obviously have a lower unfrozen orbital moment in the crystalline field (its properties will be closer to those of the "singlet" cation $Fe^{3+}$).

Ordinarily the phenomenon of intermediate valency of cations is investigated in rare-earth compounds containing

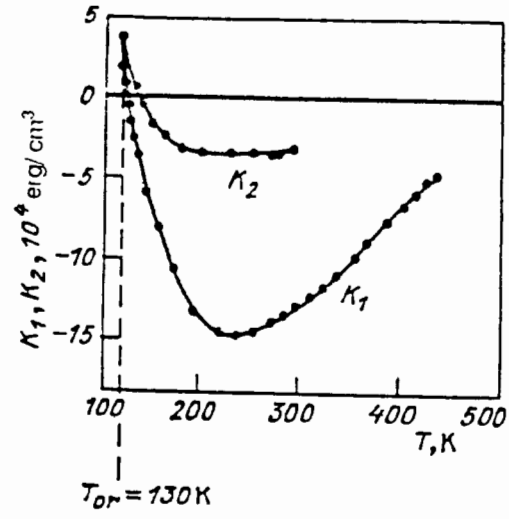


FIG. 13. Temperature dependence of the magnetic anisotropy constants $K_1$ and $K_2$ of magnetite (Ref. 47).

Ce, Sm, and Yb, in which the $4f$ electron shell loses stability, since the states $4f^n$ and $4f^{n-1}$ become close in energy.[51] An analogous situation evidently exists in magnetite for the $Fe^{3+}$ and $Fe^{2+}$ cations in the octahedral sites.

Interestingly, the majority of good catalysts are materials containing cations of intermediate valence, and magnetite is in fact a good catalyst.[6]

At low temperatures, anomalies are observed in the temperature dependence of the magnetic anisotropy constants $K_1$ and $K_2$ of magnetite.[47,52,53] Figure 13 shows $K_1(T)$ and $K_2(T)$ according to the data of Ref. 47. It is seen that at temperatures 130–135 K the constants $K_1$ and $K_2$ change sign. According to Ref. 55, the temperature $T_{or}$ at which $K_1$ changes sign is the temperature of a magnetic phase transition of the magnetoorientation type. In magnetite, according to the theory of magnetoorientation transitions,[55] this transition is second order, since the constants $K_1$ and $K_2$ are of the same sign.

At $T_{or}$ the magnetic susceptibility $\chi$ measured in a weak field has a maximum.[52] All the other characteristics related to technical magnetization processes at $T_{or}$ also have extrema.

Some authors[52,60] attribute the change in sign of $K_1$ to the influence of the transformation $T_t$, but this is unjustified and incorrect. Although the transitions $T_t$ and $T_{or}$ are close in temperature, analysis of the experimental results of many investigators shows that they are different phase transitions.

The scatter in the values of $T_t$ and $T_{or}$ is due to the presence of impurities and nonstoichiometric composition of the magnetite samples (many of the investigations have been done on naturally occurring magnetite crystals). Experiments have shown that in the presence of defects in the crystal the transition $T_t$ is shifted to lower temperatures, whereas $T_{or}$ is shifted to higher temperatures. This has also been confirmed in experiments on the influence of nuclear irradiation of magnetite.[57] We note that a change in the

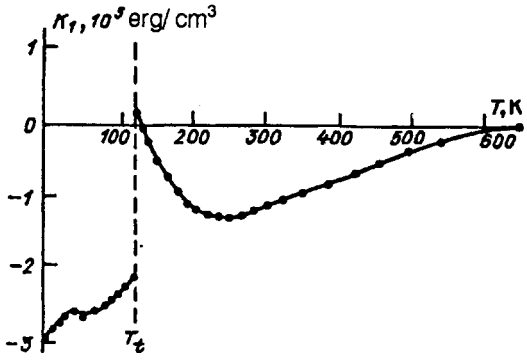


FIG. 14. Temperature dependence of the constant $K_1$ of magnetite in the region of the low-temperature transition, according to Chikazumi and co-workers (Refs. 60 and 61).

sign of $K_1$ is quite often observed in ferromagnets and ferrimagnets; it has two causes:

1) a magnetoelastic contribution to the magnetic anisotropy energy;[59]

2) a difference in the contributions of the sublattices of a ferrimagnet to the anisotropy energy.

In the papers of Chikazumi and co-workers[60,61] it is shown that the constant $K_1$ jumps upward, with a change in sign, as the transition $T_t$ is approached (Fig. 14).

This explains the sharp decrease in the magnetic susceptibility (measured in a weak field) and strong growth in the coercive force that were observed in Ref. 39 (Fig. 15) and also the increase in the hysteresis loss in rotating

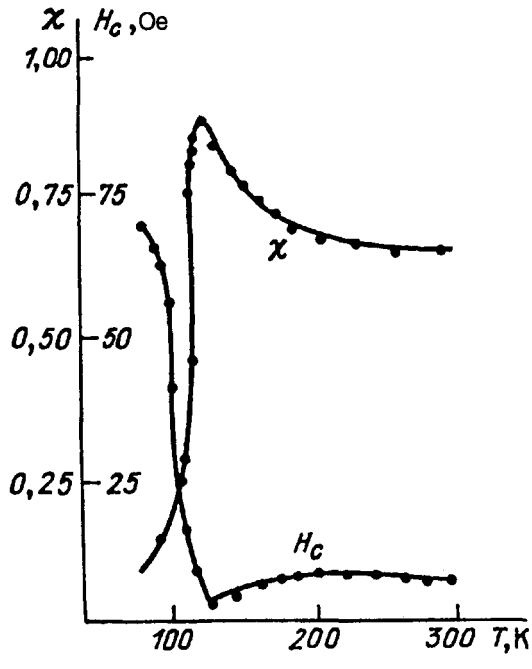


FIG. 15. Temperature dependence of the magnetic susceptibility $\chi$ (measured in a field of 20 Oe) and coercive force $H_c$ in the region of the low-temperature transformation of magnetite (Ref. 39).

fields[53,62] and the change of certain other characteristics of the technical magnetization.[65]

The nature of these effects is also due to the influence of electron processes (hopping of electrons) on the single-ion anisotropy of the $Fe^{2+}$ cation. As we have said, the microscopic mechanism of the single-ion anisotropy involves the interaction of the unfrozen part of the orbital moment of the transition-element cation with the anisotropic crystalline field and is determined by the spin–orbit coupling energy:[54]

$$E_{SL}=\lambda(LS)$$

where $\lambda$ is the spin–orbit interaction constant.

Proceeding from what we have said above concerning the influence of the hopping of electrons between the $Fe^{2+}$ and $Fe^{3+}$ cations, we can state that the jump-like growth of $K_1$ in the $T_t$ region is due to the onset of an abrupt localization of the hopping electrons under the influence of the negative exchange field created by the $Fe^{2+}$ and $Fe^{3+}$ cations, or, equivalently, to an abrupt slowing of the electron hops. The latter leads to an increase in the unfrozen part of the orbital moment of the $Fe^{2+}$ cation and, hence, to a strengthening of the spin–orbit interaction.

Along with the growth in the single-ion anisotropy in the $T_t$ region there arises an anisotropic spontaneous magnetostriction of a single-ion nature (the influence of the magnetoelastic contribution to the magnetic anisotropy[59]).

The situation in regard to the onset of spontaneous magnetostriction at the transition $T_t$ is opposite to that which exists at the Curie point $T_c$ of cubic magnets. In the latter it is mainly an isotropic spontaneous magnetostriction that arises at their $T_c$ as a result of a change in the exchange energy, while the anisotropic spontaneous magnetostriction is negligible, since the constant $K_1$ here goes practically to zero, whereas at $T_t$ the isotropic (exchange) spontaneous magnetostriction is small and the anisotropic spontaneous magnetostriction is extraordinarily high, since $K_1$ increases abruptly. The anisotropic character of the latter is confirmed by the changes in the thermal expansion in the $T_t$ region.[64]

We assume that the anisotropic spontaneous magnetostriction is responsible for the distortion of the cubic symmetry of the magnetite crystal in the $T_t$ region. X-ray studies have shown[9,12–14] that these distortions are small, and there is ambiguity in the determination of their nature. Initially it was assumed that these distortions are of a tetragonal nature, while later it was stated that these distortions are orthorhombic, rhombic, monoclinic, etc. It is clear[63] that the cubic lattice of magnetite becomes unstable near $T_t$. This is possibly caused by magnetorelaxation effects, which, as studies have shown, are particularly intense near the transition $T_t$. These effects are reflected in the fact that magnetite exhibits magnetic after-effects and magnetic "annealing" in a magnetic field.[66] These effects in the $T_t$ region are governed by electron diffusion, i.e., it takes some time for the hopping of electrons between $Fe^{2+}$ and $Fe^{3+}$ in the octahedral i' s to take place (i.e., this hopping is a sluggish process).

Studies have shown that the measured values of the anisotropic magnetostriction,[66] anisotropic thermal expansion,[64] magnetoresistance,[43] and other magnetic characteristics of magnetite near the transition $T_t$ depend on whether or not a field $H$ has been applied to the sample prior to the measurements (the "first change" effect) and also on whether the sample has been cooled below $T_t$ in the presence of a field $H$ (magnetic annealing or thermomagnetic treatment).

## 6. CONCLUSION

The properties of magnetite, particularly in the region of the low-temperature transformation $T_t = 100$–$120$ K, have long remained unclear and even enigmatic in spite of the enormous number of studies that have been undertaken.

In this review article a new, "magnetic–electronic" model of the low-temperature transformation in magnetite is given, based on an analysis of the features of the temperature and field dependence of the spontaneous magnetization, magnetoresistance, and magnetocaloric effect and also of the anomalies due to electronic processes in the magnetic anisotropy and magnetostriction and the accompanying anomalies of the characteristics of the technical magnetization in the $T_t$ region. The most salient feature of this model is that it takes into account the influence of the negative $s$–$d$ exchange interaction on the hopping electrons. This model agrees with some experimental facts that do not fit into the familiar Verwey model of a "structural–electronic" transition. These experimental facts include:

1. The negative jump of the spontaneous magnetization and the maximum of the paraprocess susceptibility as $T_t$ is approached from the high-temperature side.

2. The anomalous (negative) sign of the magnetocaloric effect at $T_t$.

3. The smaller maximum of the negative isotropic magnetoresistance at $T_t$ as compared to that at temperatures $T > T_t$.

4. The jump in the anisotropy constant $K_1$ as $T_t$ is approached and the corresponding strong growth of the magnetic susceptibility, coercive force, and magnetic hysteresis loss.

5. The change in symmetry of the cubic lattice of magnetite in the $T_t$ region; it is conjectured that this is due to the onset of an anisotropic spontaneous magnetostriction.

A problem that needs further attention is to study the spontaneous magnetization and the physical effects at temperatures below the transformation $T_t$; in particular, the nature of the magnetoelectric effect discovered by Rado[68] must be elucidated in more detail.


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