On the nature of a low-temperature transition in magnetite

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The analysis of anomalies in spontaneous magnetization, susceptibility of the paraprocess, and the magnetocaloric effect in magnetite (Fe_3O_4) in the region of the low-temperature transition T_t= 100–120 K has motivated a suggestion that the "weak" sublattice in this transition is the subsystem of hopping electrons with ordered spins (the "electron magnetic" sublattice). The resulting low-temperature transition at T_t is nothing but a phase transition in the weak sublattice at the point T_B. *© 1996 American Institute of Physics.* [S1063-7761(96)01212-7]

1. INTRODUCTION

Magnetite (Fe_3O_4), which is a natural ferrimagnet,[1] is contained in large quantities in the Earth crust. It has a structure of inverse spinel, $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$, and is usually classified with ferrite spinels. Its magnetic and electric properties, however, are strikingly different from those of the latter. In particular, a transition occurs in a temperature range T_t= 100–120 K,[1)] in which its magnetic and electric parameters have notable anomalies.

The cause of the anomalous properties of magnetite is the large concentration of conductance electrons supplied by Fe^{2+} cations in octahedrons. According to some estimates,[2] their concentration in magnetite is $n \sim 10^{22}$, i.e., close to the concentration typical of metals. At the room temperature and above, when the degree of electron localization at the cations is not so high, the electrons can be treated as occupying a continuous band.[3] At temperatures below the room temperature their degree of localization is higher. In this case they are treated as hopping electrons ($Fe^{2+} \rightleftharpoons Fe^{3+}$).[4] This localization not only leads to notable changes in electric parameters of magnetite, but (as will be demonstrated below) also changes its magnetic parameters at temperatures $T<T_t$.

2. TWO VIEWPOINTS ON THE NATURE OF THE LOW-TEMPERATURE TRANSITION IN MAGNETITE

Properties of magnetite have been studied for more than one hundred years, and researchers have focused attention on the transition at T_t. At present there are two viewpoints on its nature.

1. Vervey's hypothesis (1939–41)[5] about an order–disorder structural transition. In the low-temperature phase for $T<T_t$ the Fe^{2+} and Fe^{3+} cations are located alternately in octahedrons. This ordering of cations is established owing to electron hopping, since the diffusion of ions is impossible at low temperatures. Therefore the transition at T_t is sometimes called structural-electronic in literature. Evidence in favor of this hypothesis is provided by the singularities in its resistivity[5] and specific heat[6] at T_t, small changes in parameters and symmetry of its lattice, etc. In recent years Vervey's hypothesis has been criticized in the literature.

2. According to the second viewpoint,[2] a magnetic order–disorder transition occurs at T_t, but this transition is peculiar and unlike the transition at the Curie point T_C. This hypothesis is supported by the following experimental facts: a negative maximum of the magnetocaloric effect[7,8] near T_t (Fig. 1) (near T_C it is positive), an anomaly (drop) in the spontaneous magnetization[9] (Fig. 2) (as well as a drop in the saturation magnetization reported in Refs. 10 and 11), and an increase in the susceptibility of the paraprocess[9] near T_t (Fig. 2).

The question arises whether similar changes in physical parameters have been detected in other ferrimagnets. The answer is that similar effects are observed in ferrimagnets with a "weak" sublattice.

3. FERRIMAGNETS WITH A WEAK SUBLATTICE

According to the concept of a weak sublattice proposed in 1961,[12] all ferrimagnets are divided, according to the temperature dependence of their spontaneous magnetization $I_s(T)$, into two groups. Those of the first group have no weak sublattice, so the $I_s(T)$ curve has a normal (Weiss) shape (Q-curve, according to Néel's classification[1].) The second group includes ferrimagnets with a "weakly or-

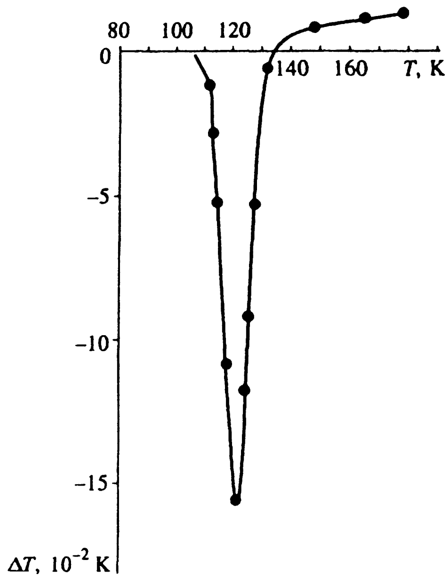

FIG. 1. Maximum of the negative ΔT-effect near T_t at H= 10 kOe plotted from the data of Ref. 8.

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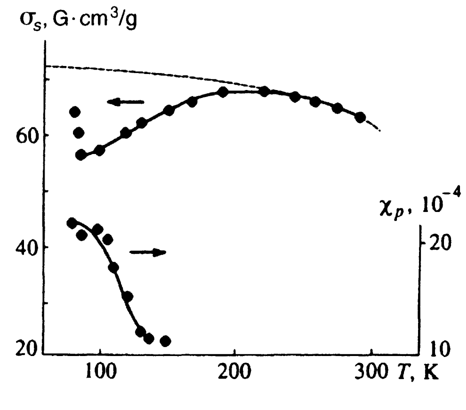

FIG. 2. Anomalies of the spontaneous magnetization σ_s and susceptibility of the paraprocess χ_p near T_t plotted from the data of Ref. 9.

dered'' sublattice (hereafter termed as a weak sublattice), so the peak on its $I_s(T)$ curve is broadened (curves *1* in Fig. 3). The existence of the weak sublattice in a ferrimagnet is the cause of anomalous shapes of the $I_s(T)$ curve (N-, M-, and P-curves, according to Néel's classification). The weak-sublattice model[12] suggests that the magnetic ordering is due to a negative exchange field H_{ex} generated by a ''strong'' sublattice (usually the sublattice of iron or cobalt ions). At a certain temperature T_B termed as a low-temperature point in Ref. 12,[2)] thermal motion leads to a partial disorder in the weak lattice; as a result, a maximum in the paraprocess susceptibility χ_p is detected at T_B along with maxima in the related effects, namely the magnetocaloric effect (ΔT), magnetostriction due to the paraprocess ($d\lambda_p/dH$), and isotropic magnetoresistance ($\Delta\rho/\rho$). Note that in these ferrimagnets a noncollinear magnetic structure is impossible because in these materials there is no competition between exchange interactions in sublattices (one sublattice is strong, the other is weak), so a paraprocess due to destruction of a noncollinear structure by external field H is impossible.

The effects due to the paraprocess at the point T_B were predicted theoretically,[13] taking as an example $Gd_3Fe_5O_{12}$ ferrite and using the molecular-field method without the exchange interaction of the Gd^{3+} cations, i.e., the exchange within the weak sublattice. In other ferrimagnets, such as R–Fe intermetallic compounds, the situation may be more complicated since the exchange interaction within the weak sublattice should be taken into account (this is probably why M- and P-curves of $I_s(T)$ are different).

Table I lists ferrimagnets in which the transition at the

TABLE I. Ferrimagnets with a low-temperature transition at the point T_B.

	Ferrimagnets	T_B, K	Θ_{com}, K	T_C, K	References
1	$Gd_3Fe_5O_{12}$	70–100	295	556	[14–17]
2	$Tb_3Fe_5O_{12}$	58	250	553	[16]
3	$Dy_3Fe_5O_{12}$	42	220	552	[16]
4	$Ho_3Fe_5O_{12}$	32	130	548	[16]
5	$Er_3Fe_5O_{12}$	20	85	547	[16]
6	$Li_{0.5}Fe_{1.25}Cr_{1.25}O_4$	102	320	500	[18]
7	$HoFe_3$	170	395	570	[19]
8	Mn_5Ge_2	113	400	670	[20]
9	Tm_6Fe_{23}	200	–	450	[21]
10	$Li_{0.975}Ti_{0.95}Fe_{1.075}O_4$	$\ll$80	–	380	[22]
11	$Li_{0.5}Fe_{1.7}Al_{0.8}O_4$	500	–	650	[23]

point T_B has been detected. The table indicates that this transition in ferrimagnets is not a rare effect but is typical of all ferrimagnets with a weak sublattice, including both ferrimagnets with the $I_s(T)$ curve of type N (i.e., with a magnetic compensation point Θ_{com}) and ferrimagnets characterized by M- and P-curves (specifically numbers 9, 10, and 11 in Table I). The difference between them is that in the first case a paraprocess of ferromagnetic type takes place at the point T_B, and there is a maximum of the positive ΔT-effect at this point, whereas in the second case the paraprocess is of antiferromagnetic type, and there is a maximum of a negative ΔT-effect at this point, i.e., similar to that at the point T_t in magnetite[7,8] (Fig. 1).

From this we conclude that there is a weak sublattice in magnetite, and its low-temperature transition point T_B is nothing but T_t.

4. THE WEAK SUBLATTICE IN MAGNETITE IS THE ELECTRON MAGNETIC SUBLATTICE

The role of the weak sublattice in magnetite is played by the magnetically ordered subsystem of hopping electrons, i.e., the electron magnetic sublattice[24] introduced[2] in a temperature range below T_t in order to interpret the anomalous drop in spontaneous magnetization, negative ΔT-effect, and anomalous behavior of magnetoresistance around the point of the low-temperature transition T_t, this sublattice is formed because hopping electrons are localized for $T<T_t$ at iron cations in octahedrons, and the negative exchange field H_{ex} generated by iron ions aligns spins of these electrons (the effect of the Vonsovskii negative s–d-exchange[25]). As a result a structure with three sublattices is formed (Fig. 4). The

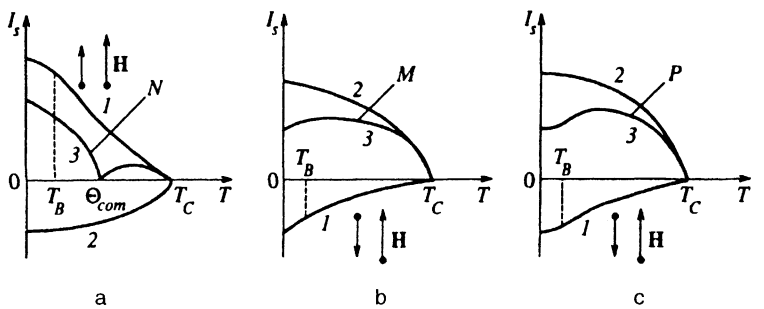

FIG. 3. Spontaneous magnetization of (*1*) weak and (*2*) strong sublattices as functions of temperature, and (*3*) Néel's (a) N-, (b) M-, and (c) P-curves of $I_s(T)$. The arrows near the curves *1* show the alignment of the weak sublattice magnetic moment with respect to external magnetic field.

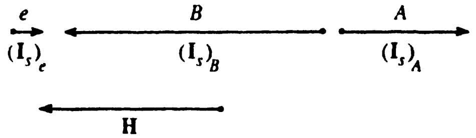

FIG. 4. Magnetic structure of magnetite at temperatures below T_t; $(\mathbf{I}_s)_e$, $(\mathbf{I}_s)_B$, and $(\mathbf{I}_s)_A$ are the spontaneous magnetizations of the weak, octahedral, and tetrahedral sublattices, respectively.

magnetic moment of the electron magnetic sublattice (e-sublattice), which makes about 20% of the total moment of the combined BA sublattice, reduces the spontaneous magnetization of the magnetite below T_t; as a result, the curve of $I_s(T)$ looks like Néel's M- or P-curve (in the sense that I_s drops in the interval below T_t). The alignment of the magnetization vector $(\mathbf{I}_s)_e$ with respect to the external field $\mathbf{H}$ indicates that around T_t an intense paraprocess of the antiferromagnetic type should take place, i.e., the process taking place in the weak sublattice of a ferrimagnetic characterized by an M- or P-curve of $I_s(T)$.

Figure 5 shows the approximate curves in the temperature range where the effect of the weak (electron magnetic) sublattice is essential. Curve *1* shows the magnetic moment $M_s(T)$ of the weak sublattice, curve *2* is the magnetic moment of the iron cations versus temperature, and curve *3* is an anomalous curve $M_s(T)$ of magnetite similar to Neél's M- or P-curves.

One can see in Fig. 5 that the temperature range in which the effect of the weak sublattice is substantial is quite narrow. Although many publications have been devoted to magnetite, no detailed and reliable data on the spontaneous magnetization I_s in this range are available, although they are very important for justifying the concept of the magnetic nature of the low-temperature transition at $T_t = 100-120$ K discussed in the paper.

Let us consider additional evidence in favor of the above statement that an intense paraprocess of antiferromagnetic type should take place around T_t. Figure 6 shows isothermal curves of the magnetite magnetization plotted using the data

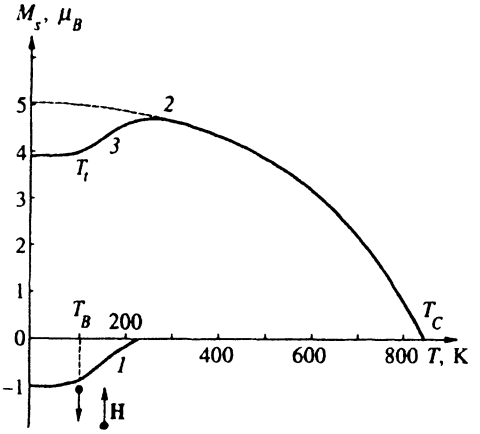

FIG. 5. Curves of magnetite magnetization versus temperature in the low-temperature range: (*1*) magnetization of the weak sublattice; (*2*) sum magnetization of the combined BA-sublattice; (*3*) total magnetization.

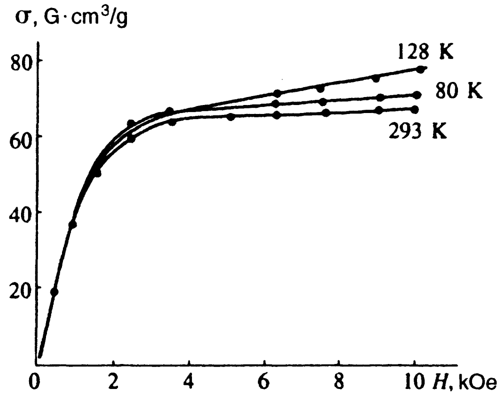

FIG. 6. Isothermal curves of magnetite magnetization taken at temperatures of 293 K, 80 K, and around T_t at 128 K in magnetic fields of up to 10 kOe.

from Ref. 9 taken at room temperature (293 K), at a temperature below T_t (80 K), and around T_t (128 K) in a magnetic field of up to 10 kOe. One can see that the magnetization curve is affected by magnetic anisotropy in a field $H_{an} \approx 2-3$ kOe. A close estimate is derived using the formula

$$H_{an} = 2K_1/I_s \approx 1 \text{ kOe},$$

given the values $K_1 = -2\times10^5$ erg/cm^3 around T_t (Ref. 26) and $I_s = \rho\sigma_s = 5\times80 \approx 400$ G (ρ is a density). In a field higher than 2–3 kOe we observe a paraprocess whose intensity is maximum around T_t.

In conclusion, note that the magnetic order–disorder transition occurs at $T = T_B$ (hence at T_t) in the exchange field H_{ex} generated by the strong sublattice. As a result, the magnetic fluctuations (''critical states'' due to competition between the exchange interaction and thermal motion) so common around the Curie temperature in ferro- and ferrimagnets are nearly absent. The transition at T_B is a magnetic order–disorder phase transition delayed, as it were, by the exchange field (analogous to the way the Curie transition is retarded by an external magnetic field H). Hence it follows that the transition at T_B should be spread over a certain temperature range, as is the case in the magnetite transition at T_t.

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1) This transition was studied in natural magnetite crystals (with impurities), in synthetic samples, and in ceramics (often with considerable deviations from stoichiometry). The spread in T_t was within the range of 100–120 K.

2) In earilier publications by the author this point was denoted T_N. In order to avoid confusion with the Néel temperature, the subscript has been replaced with B.

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