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$_3$O$_4$) in the region of the low-temperature
transition $T_c = 100–120$ 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 $T_c$ is nothing but a phase transition in the
weak sublattice at the point $T_B$.

1. INTRODUCTION

Magnetite (Fe$_3$O$_4$), which is a natural ferrimagnet, is contained in large quantities in the Earth crust. It has a struc-
ture of inverse spinel, Fe$^{3+}$[Fe$^{3+}$Fe$^{2+}$]O$_4$, and is usually classified with ferrite spinels. Its magnetic and electric prop-
eties, however, are strikingly different from those of the latter. In particular, a transition occurs in a temperature range
$T_c = 100–120$ K, 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, their concentration in magnetite is $n \approx 10^{23}$, 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. At temperatures below the room tempera-
ture their degree of localization is higher. In this case they are treated as hopping electrons (Fe$^{2+} \leftrightarrow$Fe$^{3+}$). This local-
ization not only leads to notable changes in electric parameters of magnetite, but (as will be demonstrated below) also
changes its magnetic parameters at temperatures $T<T_c$.

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 $T_c$. At present there are two viewpoints on its nature.

1. Vervey’s hypothesis (1939-41) about an order–disorder structural transition. In the low-temperature phase
for $T<T_c$, the Fe$^{3+}$ and Fe$^{2+}$ 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 $T_c$ is some-
times called structural-electronic in literature. Evidence in favor of this hypothesis is provided by the singularities in its
resistivity and specific heat at $T_c$, small changes in param-
eters and symmetry of its lattice, etc. In recent years Vervey’s hypothesis has been criticized in the literature.

2. According to the second viewpoint, a magnetic order–disorder transition occurs at $T_c$, but this transition is pecu-
lar 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 near $T_c$
- an anomaly (drop) in the spontaneous magnetization near $T_c$
- an increase in the susceptibility of the paraprocess near $T_c$

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, all ferrimagnets are divided, according to the tem-
perature 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). The
second group includes ferrimagnets with a "weak" sublattice.

FIG. 1. Maximum of the negative $\Delta T$-effect near $T_c$ at $H = 10$ kOe plotted from the data of Ref. 8.
TABLE I. Ferrimagnets with a low-temperature transition at the point $T_B$.

<table>
<thead>
<tr>
<th>Ferrimagnets</th>
<th>$T_B$, K</th>
<th>$\Theta_{comp}$, K</th>
<th>$T_C$, K</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gd$_2$Fe$_2$O$_4$</td>
<td>70–100</td>
<td>295</td>
<td>556</td>
</tr>
<tr>
<td>2</td>
<td>Tb$_2$Fe$_2$O$_4$</td>
<td>58</td>
<td>250</td>
<td>553</td>
</tr>
<tr>
<td>3</td>
<td>Dy$_2$Fe$_2$O$_4$</td>
<td>42</td>
<td>220</td>
<td>552</td>
</tr>
<tr>
<td>4</td>
<td>Ho$_2$Fe$_2$O$_4$</td>
<td>52</td>
<td>130</td>
<td>548</td>
</tr>
<tr>
<td>5</td>
<td>Er$_2$Fe$_2$O$_4$</td>
<td>20</td>
<td>85</td>
<td>547</td>
</tr>
<tr>
<td>6</td>
<td>Lu$_2$Fe$_2$O$_4$</td>
<td>102</td>
<td>320</td>
<td>500</td>
</tr>
<tr>
<td>7</td>
<td>HoFe$_2$</td>
<td>170</td>
<td>395</td>
<td>570</td>
</tr>
<tr>
<td>8</td>
<td>MnFe$_2$</td>
<td>113</td>
<td>400</td>
<td>670</td>
</tr>
<tr>
<td>9</td>
<td>TbMn$_2$</td>
<td>200</td>
<td>–</td>
<td>450</td>
</tr>
<tr>
<td>10</td>
<td>Lu$_2$Fe$_2$O$_4$</td>
<td>$\leq 80$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>Lu$_2$Fe$_2$O$_4$</td>
<td>500</td>
<td>–</td>
<td>650</td>
</tr>
</tbody>
</table>

The effects due to the paraprocess at the point $T_B$ were predicted theoretically, taking as an example Gd$_2$Fe$_2$O$_4$ 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 $I_x(T)$ are different).

Table I lists ferrimagnets in which the transition at the 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 $I_x(T)$ curve of type $N$ (i.e., with a magnetic compensation point $\Theta_{comp}$) 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 $\Delta T$-effect at this point, whereas in the second case the paraprocess is of antiferromagnetic type, and there is a maximum of a negative $\Delta T$-effect at this point, i.e., similar to that at the point $T_N$ in magnetic ferrimagnets (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 $T_N$.

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 introduced in a temperature range below $T_B$ in order to interpret the anomalous drop in spontaneous magnetization, negative $\Delta T$-effect, and anomalous behavior of magnetoresistance around the point of the low-temperature transition $T_B$. This sublattice is formed because hopping electrons are localized for $T<T_B$ 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 Vonsovski and d-exchange). As a result a structure with three sublattices is formed (Fig. 4). The
FIG. 4. Magnetic structure of magnetite at temperatures below \( T \); magnetic moment of the electron magnetic sublattice \((I_e)\), of the combined BA sublattice, reduces the spontaneous curve of magnetization of the magnetite below that \((I)\), which makes about 20% of the total moment \( M \), with respect to the external field.

Magnetic moment of the electron magnetic sublattice \((e\text{-sublattice})\), which makes about 20% of the total moment of the combined BA sublattice, reduces the spontaneous magnetization of the magnetite below \( T \), as a result, the curve of \( I(T) \) looks like Niel’s \( M \)- or \( P \)-curve (in the sense that \( I_p \) drops in the interval below \( T \)). The alignment of the magnetization vector \((I_e)\) with respect to the external field \( H \) indicates that around \( T \), 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 \( I_e(T) \).

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 \( M_e(T) \) 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 Niel’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 \( M_e \) of the weak sublattice is available, although they are very important for justifying the concept of the magnetic curve discussed in the paper.

Let us consider additional evidence in favor of the above statement that an intense paraproces of antiferromagnetic type should take place around \( T \). Figure 6 shows isothermal curves of the magnetite magnetization plotted using the data from Ref. 9 taken at room temperature (293 K), at a temperature below \( T \) (80 K), and around \( T \) (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 \( H_m = 2 \text{–} 3 \text{kOe} \). A close estimate is derived using the formula \( H_m = 2K/\rho \), one kOe, given the values \( K = -2 \times 10^4 \text{erg/cm}^3 \) around \( T \) (Ref. 26) and \( \rho = \rho_{Ho} = 5 \times 10^3 \text{g/cm}^3 \). In a field higher than 2-3 kOe we observe a paraprocess whose intensity is maximum around \( T \).

In conclusion, note that the magnetic order–disorder transition occurs at \( T = T_\alpha \) (hence at \( T \)) 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 \( T \) 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 \( T \) should be spread over a certain temperature range, as is the case in the magnetite transition at \( T \).

I acknowledge helpful discussions with I. K. Kamilov, R. Z. Levitin, and S. A. Nikitin.

\[ \text{FIG. 5. Curves of magnetic magnetization versus temperature in the low-} \]

\[ \text{temperature range: (1) magnetization of the weak sublattice; (2) sum mag-} \]

\[ \text{netization of the combined BA-sublattice; (3) total magnetization.} \]

This transition was studied in natural magnetite crystals (with inclusions), in synthetic samples, and in ceramics (often with considerable deviations from stoichiometry). The spread in \( T \) was within the range of 100-120 K.

In earlier publications by the author this point was denoted \( T_\alpha \). In order to avoid confusion with the Niel temperature, the subscript has been replaced with \( B \).

\[ \text{FIG. 6. Isothermal curves of magnetic magnetization taken at temperatures} \]

\[ \text{of 293 K, 80 K, and around} \ T \text{at 128 K in magnetic fields of up to 10 kOe.} \]


34 S. V. Yonovskii, Magnetism [in Russian], Nauka, Moscow (1971).


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