

# Self-Reversal of Magnetization in Titanomagnetite: Effective Field Theory

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Received March 10, 2017

**Abstract**—In this paper, we analyze the self-reversal of magnetization in titanomagnetites as a function of the Ti content and the distribution of Fe<sup>3+</sup> to Fe<sup>2+</sup> ion transitions in sublattices (which is associated with the law of charge conservation). The dependence of the Curie point on the Ti concentration and the temperature dependence of the mean magnetic moment per iron atom at different Ti concentrations and different cation distributions in sublattices are calculated.

DOI: 10.1134/S1069351318010044

## INTRODUCTION

The question concerning the self-reversal of magnetization has long been a subject of scientific discussion (Krasa et al., 2005; Trukhin and Bezaeva, 2006 and references to the works of the other authors). Particular attention is paid to natural ferromagnetics such as titanomagnetite and hemoilmenite. Different authors suggest different mechanisms capable of leading to a total or partial self-reversal. For instance, in (Krasa et al., 2005) it has been fairly convincingly shown that this effect can be accounted for by the magnetostatic interaction of two magnetic phases—the parent magnetic phase and the partially oxidized daughter phase, which have different blocking temperatures. In turn, in (Trukhin and Bezaeva, 2006), as a probable cause of the self-reversal of the magnetization in titanomagnetites, the authors consider the competition between the magnetic moments of sublattices in two-sublattice magnetics (Néel N-type self-reversal mechanism). However, in our opinion, when using the mechanism suggested by Néel's theory, we should take into account the peculiarities of the crystal lattice of titanomagnetite.

Magnetite has a crystal structure of inverted spinel (Fe<sup>3+</sup>) [Fe<sup>2+</sup>Fe<sup>3+</sup>]O<sub>4</sub>. At the octahedral sites —(Fe<sup>3+</sup>), there are only cations with valence +3, and at the tetrahedral sites [Fe<sup>2+</sup> Fe<sup>3+</sup>], the number of cations doubles and they have valences 2+ and 3+. In each unit cell of magnetite there are 16 Fe<sup>3+</sup> and eight Fe<sup>2+</sup> cat-

ions. Ti substitutes for Fe<sup>3+</sup> in the *B*-sublattice and simultaneously causes the transition of Fe<sup>3+</sup> into Fe<sup>2+</sup> in both the *A*- and *B*-sublattices (Butler, 1991). Therefore, in our opinion, a simple carryover of Néel's approach to titanomagnetite is not entirely correct. As in this case, four groups of ions contributed to the competition of the magnetic moments: Fe<sup>2+</sup> and Fe<sup>3+</sup> from sublattice *A* and Fe<sup>2+</sup> and Fe<sup>3+</sup> from sublattice *B*. Even if we only consider the interaction of ions pertaining to different sublattices, we should take into account three types of negative exchange interaction Fe<sub>*A*</sub><sup>2+</sup>Fe<sub>*B*</sub><sup>2+</sup>, Fe<sub>*A*</sub><sup>2+</sup>Fe<sub>*B*</sub><sup>3+</sup> = Fe<sub>*B*</sub><sup>2+</sup>Fe<sub>*A*</sub><sup>3+</sup>, Fe<sub>*A*</sub><sup>3+</sup>Fe<sub>*B*</sub><sup>3+</sup>.

In the general case, as noted above, Ti substitution for Fe<sub>*B*</sub><sup>3+</sup> ions by Ti causes the Fe<sup>3+</sup> to Fe<sup>2+</sup> transition in the remaining trivalent ions in both the *A*- and *B*-sublattices. This transition is in principle possible in a certain proportion and should be controlled by the condition of the minimum free energy of the system of ions which interact with the crystal lattice and with each other. Clearly, the presence of impurities, vacant sites, and distortions of the crystal lattice can change the relative number of Fe<sup>3+</sup> to Fe<sup>2+</sup> transitions in each sublattice, and this can significantly affect the result of the competition between the magnetic moments of sublattices (Butler, 1992).

## EFFECTIVE FIELD AND EXCHANGE INTEGRALS

Neel's explanation of the different types of spontaneous magnetization dependences on temperature in two-sublattice ferrimagnetics was based on the theory of the molecular (effective) field. Due to its simplicity, this theory continues to be successfully used despite the fact that it insufficiently accurately describes the temperature dependence of the magnetization close to the Curie point and at the temperatures close to absolute zero. An example of the successful application of the effective field theory in multiple-sublattice magnetics can be found in (Fabian et al., 2015) where the authors study the magnetic properties of the hematite–ilmenite system.

In the effective field approximation, energy  $E_{ik}$  of the exchange interaction of magnetic moments  $m_i$  and  $m_k$  can be written out in the following form:

$$E_{ik} = -J_{ik} \langle m_i \rangle \langle m_k \rangle = -\langle m_i \rangle H_i, \quad (1)$$

where the effective field  $H_i = J_{ik} \langle m_k \rangle$ , the magnetic moment  $\text{Fe}^{3+}$  is  $5\mu_B$ , the magnetic moment of  $\text{Fe}^{2+}$  is  $4\mu_B$  (where  $\mu_B$  is the Bohr magneton), and  $\langle m_k \rangle$  is the thermodynamic mean of the magnetic moment  $\langle m_k \rangle$ . Since the exchange interaction between sublattices is negative, the exchange integral should be set to be negative ( $J_{ik} < 0$ ).

The distribution of iron ions by groups ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  from sublattice  $A$  and  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  from sublattice  $B$ ) will be determined by the concentration  $x$  of the Ti ions and the relative distribution of the number of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  transitions in the sublattices  $\alpha$  ( $0 < \alpha < 1$ ). This means that the fraction  $x$  of  $\text{Fe}^{3+}$  substituted by Ti in sublattice  $B$  causes  $\alpha x$  transitions of  $\text{Fe}^{3+}$  into  $\text{Fe}^{2+}$  in sublattice  $A$  and  $(1 - \alpha)x$  causes

such transitions in sublattice  $B$ . Thus, there will be  $\alpha x n$   $\text{Fe}^{2+}$  ions in sublattice  $A$  and there will be  $(1 - \alpha)x n$   $\text{Fe}^{3+}$  ions in sublattice  $A$ , where  $n = 8$  is the number of tetrahedral sites in the unit cell of magnetite that are occupied by cations.

Correspondingly, the number of  $\text{Fe}^{2+}$  ions in sublattice  $B$  will be  $n + (1 - \alpha)x n = (1 + (1 - \alpha)x)n$ , and the number of  $\text{Fe}^{3+}$  ions will be  $(1 - x)n - (1 - \alpha)x n = (1 - 2x + \alpha x)n$ .

The relative thermodynamically mean magnetic moment per iron ion  $M = \langle m \rangle / m$ , placed in the external magnetic field  $H$ , is determined by the relationship  $M = B_S(mH/(k_B T))$ , where  $k_B$  is the Boltzmann constant,  $T$  is temperature,  $B_S$  is the Brillouin function, and  $S = 5/2$  for the  $\text{Fe}^{3+}$  ion and  $S = 4/2$  for the  $\text{Fe}^{2+}$  ion. The analysis of the temperature dependence of the effective magnetic moment will be noticeably easier if we use the Ising model where the Brillouin function  $B_S(x)$  is replaced by the hyperbolic tangent which corresponds to  $S = 1/2$ . We considered it possible to use this model in the discussed case because the method of the molecular field itself is rather crude, whereas the Ising model allows the use of the theory of random interaction fields which has a considerable advantage over the simple molecular field theory and within which the Curie point of titanomagnetite calculated by us as a function of the Ti content at  $\alpha = 1$  corresponds to the empirical data (Belokon and Nefedev, 2001; Belokon et al., 2015; O'Reilly, 1984).

The relative thermodynamically mean magnetic moment  $M$  per ion in each subgroup in the Ising model will satisfy the following relationships in the effective field theory:

$$\begin{cases} M_1 = \text{Th} \left[ \frac{4(5M_4 J_1 (1 - 2x + \alpha x) + 4M_3 J_2 (1 + (1 - \alpha)x)) \mu_B^2}{k_B T} \right], \\ M_2 = \text{Th} \left[ \frac{5(4M_3 J_1 ((1 + (1 - \alpha)x)) + 5M_4 J_3 (1 - 2x + \alpha x)) \mu_B^2}{k_B T} \right], \\ M_3 = \text{Th} \left[ \frac{4(4M_1 J_2 \alpha x + 5M_2 J_1 (1 - \alpha x)) \mu_B^2}{k_B T} \right], \\ M_4 = \text{Th} \left[ \frac{5(4M_1 J_1 \alpha x + 5M_2 J_3 (1 - \alpha x)) \mu_B^2}{k_B T} \right]. \end{cases} \quad (2)$$

Here  $J_k$  includes the number  $n$  as a factor,  $J_1 = J_{14}n = J_{23}n$ ,  $J_2 = J_{13}n$ ,  $J_3 = J_{24}n$ , where indices 1 and 2 correspond to the groups of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in sublattice  $A$ , whereas indices 3 and 4 correspond to the groups of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in sublattice  $B$ .

Close to the phase transition  $T_c$ , we can replace the hyperbolic tangents in Eqs. (2) by their arguments and write out the system of homogeneous equations with respect to  $M_k$ . Setting the determinant of this system to zero, we obtain the equation for finding  $T_c$ .

We introduce the following denotations:  $\frac{\mu_B^2}{k_B T} = \frac{1}{t}$ , where  $\mu_B = 927 \times 10^{-23}$  erg/Gs, and  $k_B = 1.38 \times 10^{-16}$  erg K<sup>-1</sup>.

The determinant has the following form:

$$\begin{vmatrix} 1 & 0 & \frac{16J_2(1+(1-\alpha)x)}{t} & \frac{20J_1(1-2x+\alpha x)}{t} \\ 0 & 1 & \frac{20J_1(1+(1-\alpha)x)}{t} & \frac{25J_3(1-2x+\alpha x)}{t} \\ \frac{16J_2\alpha x}{t} & \frac{20J_1(1-\alpha x)}{t} & 1 & 0 \\ \frac{20J_1\alpha x}{t} & \frac{25J_3(1-\alpha x)}{t} & 0 & 1 \end{vmatrix}. \tag{3}$$

The exchange integrals  $J_k$  can be calculated from the benchmark points of the dependence of  $t_c$  on  $x$ . For instance, at  $x = 1$  and  $\alpha = 1$ , the dependence reflects the phase transition  $T_c = 123$  K of the ulvospinel for which only the Fe<sup>2+</sup> ions remain in the *A*- and *B*-sublattices. Then the determinant of system (3) has the following form:

$$\frac{-256J_2^2 + t_c^2}{t_c^2} = 0. \tag{4}$$

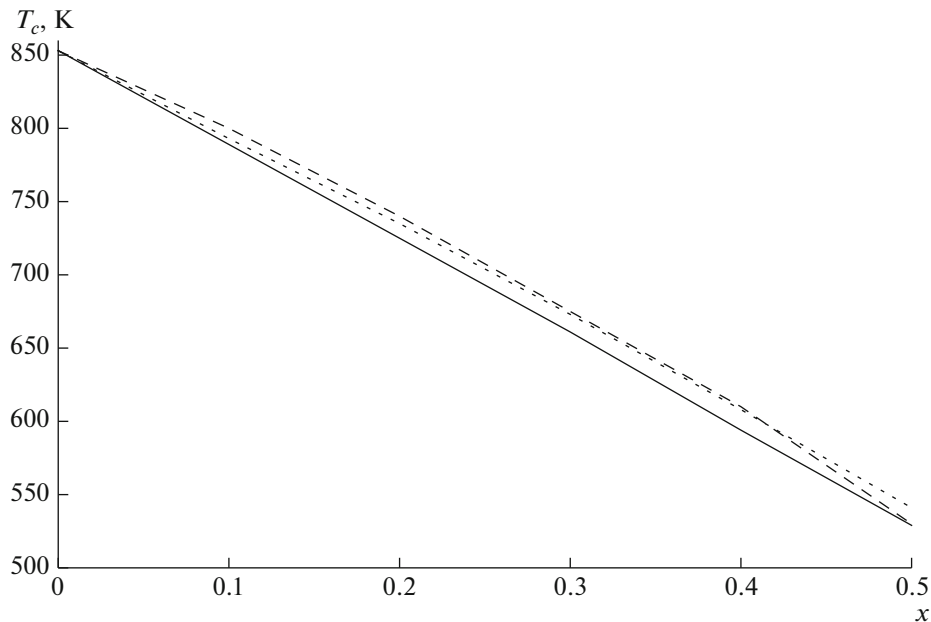
Based on this, we can find the value of the exchange integral  $J_2 = 1.23 \times 10^{25} \frac{\text{Gs}^2}{\text{erg}}$ .

In the case of maghemite ( $T_c = 948$  K),  $n$  Fe<sup>3+</sup> ions will remain in sublattice *A* and  $(1 + \frac{2}{3})n$  Fe<sup>3+</sup> ions will remain in sublattice *B*:

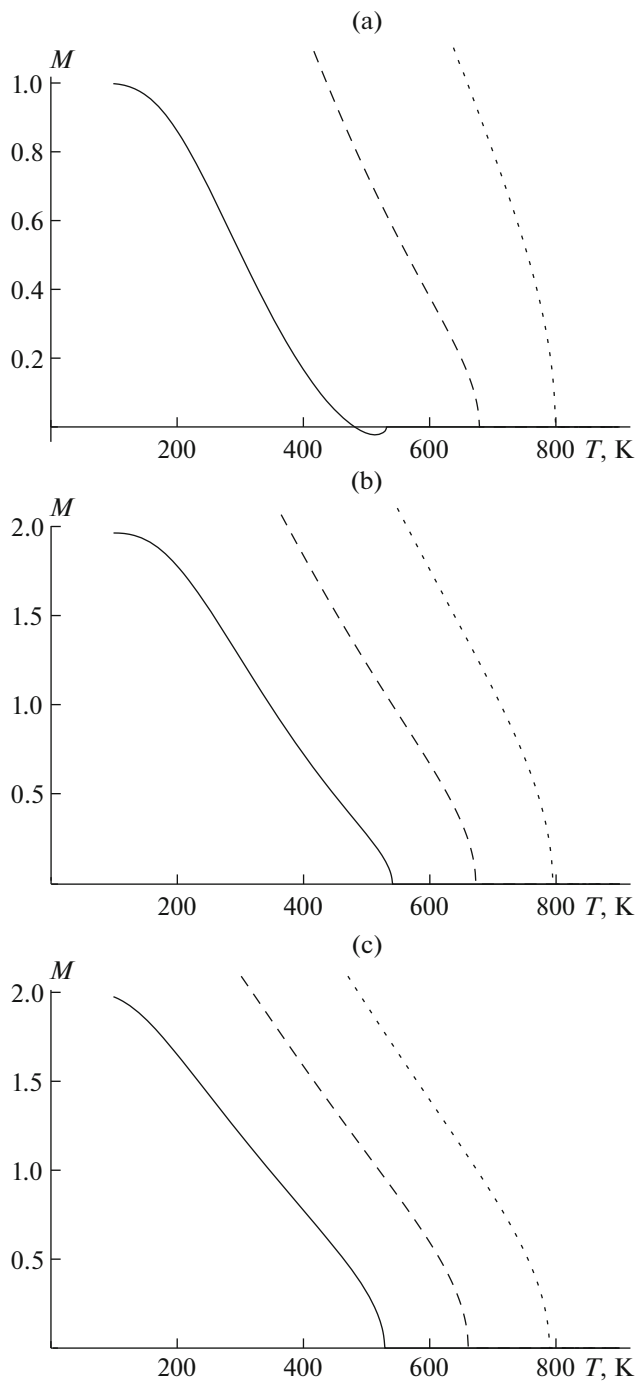
$$\begin{cases} M_2 = 5 \times \frac{5M_3J_3}{3t_c}, \\ M_3 = 5 \times 1 \times \frac{5M_2J_3}{t_c}. \end{cases} \tag{5}$$

Hence,  $J_3 = 4.72 \times 10^{25} \frac{\text{Gs}^2}{\text{erg}}$ .

At  $x = 0$  and  $\alpha = 1$ , the phase transition point of magnetite takes place  $T_c = 853$  K and



**Fig. 1.** Dependence of temperature  $T_c$  on concentrations  $x$  of Ti ions calculated for cases  $\alpha = 1$  (solid line),  $\alpha = 0.5$  (dotted line),  $\alpha = 0$  (dashed line).



**Fig. 2.** (a) Dependence of mean magnetic moment  $M$  per atom expressed in terms of Bohr magnetons in temperature  $T$  for cases  $\alpha = 0$  at  $x = 0.1$  (dotted line),  $x = 0.3$  (dashed line),  $x = 0.5$  (solid line); (b) same for cases  $\alpha = 0.5$  at  $x = 0.1$  (dotted line),  $x = 0.3$  (dashed line),  $x = 0.5$  (solid line); (c) same for cases  $\alpha = 1$  at  $x = 0.1$  (dotted line),  $x = 0.3$  (dashed line),  $x = 0.5$  (solid line).

$$\frac{-400J_1^2t_c^2 - 625J_3^2t_c^2 + t_c^4}{t_c^4} = 0, \quad (6)$$

$$\text{then } J_1 = 3.48 \times 10^{25} \frac{\text{Gs}^2}{\text{erg}}.$$

With allowance for the direction of the magnetic moments of the ions in the sublattices, the mean magnetic moment per atom expressed in Bohr magnetons can be determined as

$$M = -(4M_1\alpha x + 5M_2(1 - \alpha x) - 4M_3(1 + (1 - \alpha)x) - 5M_4(1 - 2x + \alpha x)). \quad (7)$$

Using the Wolfram Mathematica software, we can solve the system of equations (2) with the known  $J_1, J_2, J_3, \alpha$ , and  $x$  for the particular temperature values  $T$ , and, thus, find  $M_1, M_2, M_3, M_4$ , and  $M$ . The dependence of temperature  $T_c$  on the concentrations  $x$  of the Ti ions calculated for the cases  $\alpha = 1$  (solid line),  $\alpha = 0.5$  (dotted line), and  $\alpha = 0$  (dashed line) is shown in Fig. 1. We note that in the case  $\alpha = 0$ , when the transitions of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  are implemented in sublattice  $B$ , the remaining  $\text{Fe}^{3+}$  ions at  $x = 0.5$  pass into  $\text{Fe}^{2+}$  so that the variant  $\alpha = 0$  only makes sense at  $x \leq 0.5$ .

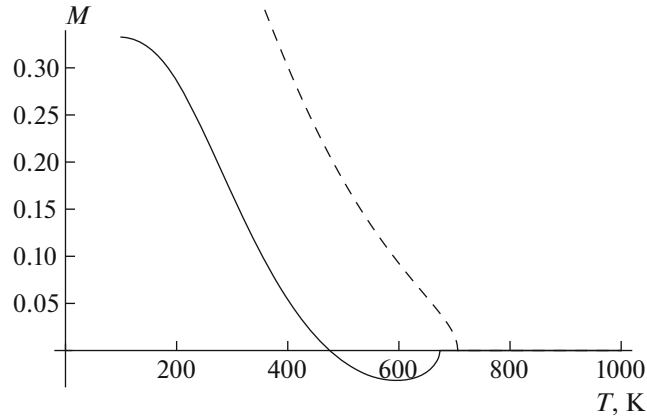
From graph 1 it can be seen that the temperature of the phase transition as a function of the Ti concentration barely depends on parameter  $\alpha$  and corresponds to the empirical curve obtained by O'Reilly (O'Reilly, 1984). However, the dependence of  $M$  on temperature  $T$ , which we can derive by solving system (2) noticeably differs for the different parameters  $\alpha$  (Fig. 2).

From Fig. 2 it can be seen that even in the extreme case  $\alpha = 0$ ; the effect of self-reversal is only possible when the Ti concentration  $x$  is close to the highest possible Ti content for this  $\alpha$  value, i.e.,  $x = 0.5$ . For the cases  $\alpha = 0.5$  and  $\alpha = 1$ , the magnetic moment monotonically increases with the decrease of temperature.

## OXIDIZED TITANOMAGNETITE

We can fairly easily consider the extreme idealized case of the substitution of  $\text{Ti}^{4+}$  ions for  $\text{Fe}^{3+}$  ions in sublattice  $B$  of maghemite. In the ideal case of fully oxidized magnetite,  $n$   $\text{Fe}^{2+}$  ions are changed into the sum of  $\frac{2}{3}n$   $\text{Fe}^{3+}$  ions and  $\frac{1}{3}n$  vacant lattice sites. Then, with the entry of  $\text{Ti}^{4+}$  ions, sublattice  $A$  will contain  $\alpha xn$   $\text{Fe}^{2+}$  ions and  $(1 - \alpha x)n$   $\text{Fe}^{3+}$  ions, whereas sublattice  $B$  will contain  $(1 - \alpha)xn$   $\text{Fe}^{2+}$  ions and  $\left[\left(1 + \frac{2}{3}\right) - (2 - \alpha)x\right]n$   $\text{Fe}^{3+}$  ions.

The system of equations for determining the dependence of the magnetic moment on temperature is



**Fig. 3.** Dependence of mean magnetic moment  $M$  per atom expressed in terms of Bohr magneton on temperature  $T$  in case of fully oxidized titanomagnetite when  $\alpha = 0$  at  $x = 0.45$  (dashed line) and  $x = 0.5$  (solid line).

$$\left\{ \begin{array}{l} M_1 = \text{Th} \left[ \frac{4 \left( 5M_4 J_1 \left( \frac{5}{3} - (2 - \alpha)x \right) + 4M_3 J_2 (1 - \alpha)x \right) \mu_B^2}{k_B T} \right], \\ M_2 = \text{Th} \left[ \frac{5 \left( 4M_3 J_1 (1 - \alpha)x + 5M_4 J_3 \left( \frac{5}{3} - (2 - \alpha)x \right) \right) \mu_B^2}{k_B T} \right], \\ M_3 = \text{Th} \left[ \frac{4(4M_1 J_2 \alpha x + 5M_2 J_1 (1 - \alpha x)) \mu_B^2}{k_B T} \right], \\ M_4 = \text{Th} \left[ \frac{5(4M_1 J_1 \alpha x + 5M_2 J_3 (1 - \alpha x)) \mu_B^2}{k_B T} \right]. \end{array} \right. \quad (8)$$

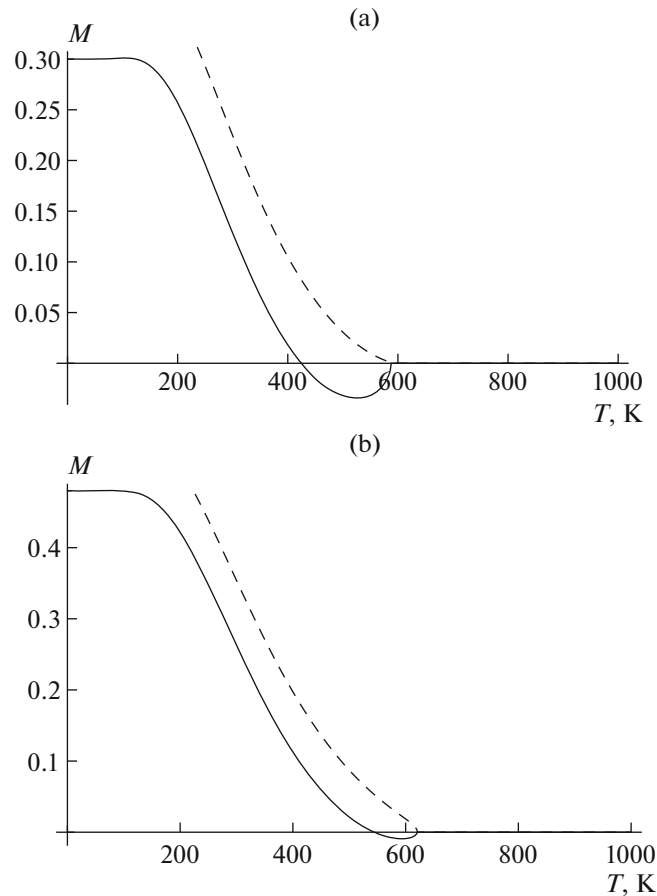
$$M = -(4M_1 \alpha x + 5M_2 (1 - \alpha x) - 4M_3 (1 - \alpha)x - 5M_4 \left( \frac{5}{3} - (2 - \alpha)x \right)). \quad (9)$$

Bohr magnetons in the case of fully oxidized titanomagnetite.

In the case of partially oxidized magnetite, for instance, at the transition of only  $0.5 n \text{ Fe}^{2+}$  into  $\text{Fe}^{3+}$  in sublattice  $B$ , system (8) is transformed as given below:

Figure 3 illustrates the temperature dependence of the mean magnetic moment per atom in terms of the

$$\left\{ \begin{array}{l} M_1 = \text{Th} \left[ \frac{4 \left( 5M_4 J_1 \left( \frac{4}{3} - (2 - \alpha)x \right) + 4M_3 J_2 \left( \frac{1}{3} + (1 - \alpha)x \right) \right) \mu_B^2}{k_B T} \right], \\ M_2 = \text{Th} \left[ \frac{5 \left( 4M_3 J_1 \left( \frac{1}{3} + (1 - \alpha)x \right) + 5M_4 J_3 \left( \frac{4}{3} - (2 - \alpha)x \right) \right) \mu_B^2}{k_B T} \right], \\ M_3 = \text{Th} \left[ \frac{4(4M_1 J_2 \alpha x + 5M_2 J_1 (1 - \alpha x)) \mu_B^2}{k_B T} \right], \\ M_4 = \text{Th} \left[ \frac{5(4M_1 J_1 \alpha x + 5M_2 J_3 (1 - \alpha x)) \mu_B^2}{k_B T} \right]. \end{array} \right. \quad (10)$$



**Fig. 4.** Dependence of mean magnetic moment  $M$  per atom expressed in terms of Bohr magneton on temperature  $T$  in case of partially oxidized titanomagnetite when  $x = 0.5$  at  $\alpha = 0.3$  (solid line) and at  $\alpha = 0.4$  (dashed line); (b) same for  $x = 0.45$  at  $\alpha = 0.2$  (solid line) and  $\alpha = 0.3$  (dashed line).

$$M = -(4M_1\alpha x + 5M_2(1 - \alpha x) - 4M_3\left(\frac{1}{3} + (1 - \alpha)x\right) - 5M_4\left(\frac{4}{3} - (2 - \alpha)x\right)). \quad (11)$$

Figures 4a and 4b illustrate the temperature dependence of the mean magnetic moment per atom in terms of Bohr magnetons in the case of partially oxidized titanomagnetite.

We note that, in contrast to the fully oxidized titanomagnetites, where self-reversal takes place practically at  $\alpha = 0$ , in the case of partially oxidized titanomagnetite, the self-reversal is also possible at  $\alpha > 0$  (depending on the Ti concentration).

## DISCUSSION

Although relatively simple, the effective field method offers a fairly adequate description for the concentration dependence of the phase transition point of titanomagnetites and demonstrates the possibility of self-reversal of the magnetization as a result of the competition between the magnetic moments of ions pertaining to different sublattices. Our results are

consistent with the known results of the experiments on the influence of oxidation on the self-reversal ability of magnetization in titanomagnetites. Here, the critical role is played, besides the Ti concentration, by the parameter  $\alpha$ , which controls the ratio of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ion transitions between the sublattices. Another fact to be noted is that the Ti concentration  $x = 0.5$  at  $\alpha = 0$  leads to the emergence of the self-reversal effect with an arbitrary degree of oxidation. In fact, the physical interpretation of the results barely differs from that suggested by Néel and involves competition between the magnetic moments of two sublattices. In this case, the distribution of iron ions among the sublattices is specified depending on the Ti concentration  $x$ , the degree of oxidation, and the parameter  $\alpha$ .

## ACKNOWLEDGMENTS

We are grateful to V.P. Shcherbakov for his useful comments.

The work was supported by the Russian Ministry of Science and Education, state contract no. 3.7383.2017/BCh.

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*Translated by M. Nazarenko*