Spin-reorientation transition in magnetite as an example of spinodal decomposition in a magnetic system

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The nature of the spin-reorientational transition $\Phi\langle 100\rangle \rightleftarrows \Phi\langle 111\rangle$ in magnetite at low temperatures is studied. It is assumed that this magnetic phase transition occurs through spinodal decomposition.

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In magnetite, there are three phase transitions in a narrow temperature range: a) in the vicinity of 115–119 K, there is a structural phase transition, in which the symmetry of the crystal lattice changes from rhombic to cubic[1]; b) in the interval 122–128 K, there is a spin reorientation transition[2] $\Phi\langle 100\rangle \rightleftarrows \Phi\langle 111\rangle$[2]; c) in the interval 135–140 K, there is a phase transition due to the direct overlapping of the t_{2g} orbitals of the cations Fe^{3+} located at the octahedral sites, i.e., direct exchange $Fe_B^{3+} - Fe_B^{3+}$.[3]

The presence of three-phase transitions in magnetite causes an anomalous behavior of its electrical and magnetic properties. In spite of the large number of experimental and theoretical papers concerning the low-temperature properties of magnetite, their interpretation gives rise to great difficulties. In particular, the nature of the anomalous behavior of the magnetocaloric effect (MCE), the ΔT effect, has still not been clarified. According to the measurements made by Krasovskiĭ and Fakidov,[4] at low temperatures the MCE in magnetite has a minimum and the ΔT effect of the first measurement is observed. The essence of this phenomenon consists of the fact that the initial application of a magnetic field changes the temperature of the specimen irreversibly, while with subsequent switching on of the field, a reversible MCE is observed.

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The presence of a negative MCE in magnetite contradicts the results predicted in Ref. 5, according to which at low temperatures the magnetoresistance (MR) has a minimum. For this reason, it was interesting to clarify the reason for the anomalous behavior of MCE in magnetite at low temperature.

The ΔT effect, magnetization I, magnetic permeability μ, and magnetoresistance $\Delta R/R$ were measured for a synthetic polycrystalline specimen of magnetite with stoichiometric composition Fe_3O_4. The specimen was synthesized using ceramic technology. The first annealing was carried out at a temperature of 1100 °C for two hours in a $CO_2 + H_2$ medium, while the final sintering was performed at a temperature of 1300 °C in the same medium. X-ray structural and phase analyses showed that the specimen is a single-phase spinel with a lattice parameter $a = 8.392$ Å.

In Fig. 1, the continuous lines show the results of our measurements, while the dashed lines indicate the temperature dependences of the first magnetic-anisotropy constant K_1 and the heat capacity C_p (synthetic magnetite specimen), taken from Refs. 2 and 6. It is evident that the minimum in the MCE is observed where the permeability

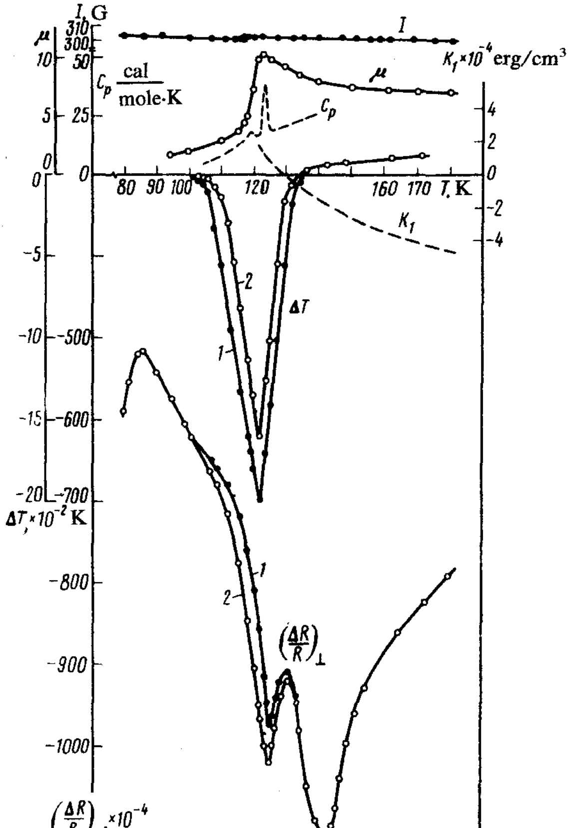

FIG. 1. Temperature of the ΔT effect, transverse magneto resistance $(\Delta R/R)_\perp$, measured in a 10-kOe field, magnetization I, magnetic permeability μ, first magnetic anisotropy constant K_1, and the heat capacity of magnetite C_p (1 is the first measurement; 2 is the second measurement).

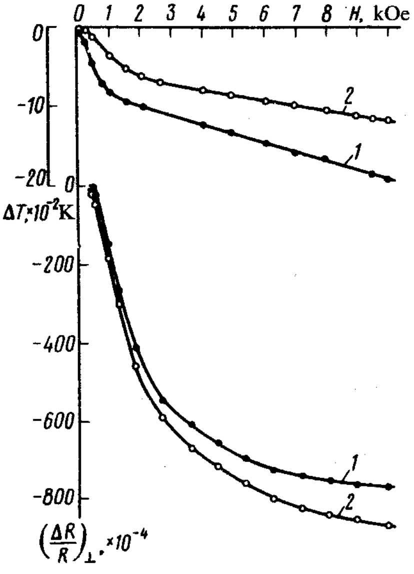

FIG. 2. The isotherms of the ΔT effect and the magnetic resistance, measured at 120 K.

μ has a maximum, i.e., where the quantity K_1 changes sign. This means that the anomalous behavior of MCE occurs in the region of the spin-reorientation transition. It was also established that the effects of the first measurement occur not only for MCE but also for MR. In addition, the temperature regions for the existence of the first measurement effects, determined from the curves $\Delta T(T)$ and $\Delta R/R(T)$, coincide. It has been observed for the first time that in the region of the spin-reorientational transition there is a splitting of the maximum on the curve $\Delta R/R(T)$. This behavior of MR is typical, since previously in the region of the spin-reorientation transition in hexaferrites,[7] gadolinium,[8] and copper ferrite[9] it was found that both effects $(\Delta R/R)_{\parallel}$ and $(\Delta R/R)_{\perp}$ acquire a positive sign due to technological magnetization processes.

It was shown theoretically in Ref. 10 that in magnetites with a cubic crystal structure, the spin system in the region of the spin-reorientational transition $\Phi\langle 100\rangle \rightleftarrows \Phi\langle 111\rangle$ must be in a metastable state. At the same time, from the isotherms $\Delta T(H)$ and $\Delta R/R(H)$ (Fig. 2), measured at 120 K, it is evident that the effects of the first measurement of MR and MCE already exist in weak magnetic fields. Therefore, the spin system of magnetite in the region of the spin-reorientational transition is already unstable to weak, external perturbations. The state of the system, which is unstable to both strong and weak, external perturbations, is called the labile state, while the curve bounding the region of labile states is a spinodal. The spinodal separates the region of positive and negative values of the derivative $\partial S/\partial T$ (S is the entropy), while on the spinodal itself, this derivative vanishes.[11] For this reason, the heat capacity $C = T(\partial S/\partial T)$ also will change sign from positive to negative. Such a phase transition, when the system can be first transformed into the labile state, is called a spinodal decomposition (SD). At present, SD has been discovered in different molecular systems. In addition, Skripov *et al.*[11] propose that SD can also occur in magnetic systems. Analysis of behavior of MCE and MR leads to the conclusion that the spin-reorientational transition in magnetite is an example of SD in a magnetic system.

The function characterizing the response of a magnetic system to an external perturbation is the heat capacity $C_H = T(\partial S/\partial T)_H$, which must change sign from positive to negative as a result of transition through the spinodal. Since the heat capacity C_H enters into the equation for the MCE,

$$dT = -(T/C_H)(\partial I/\partial T)_H dH,$$

in magnetically ordered substances in the labile state, the sign of the MCE must coincide with the sign of the derivative $(\partial I/\partial T)_H$. It is evident from Fig. 1 that in the region of the anomalous behavior of MCE, the derivative $(\partial I/\partial T)_H$ is everywhere negative. For this reason, MCE must be negative in magnetite in the region of the spin-reorientational transition, which occurs through the SD, consistent with experimental results.

The measured heat capacity C_p of magnetically ordered substances consists primarily of the lattice heat capacity C_{lat} and the magnetic heat capacity C_{mag}, which characterizes the state of the spin system. The trough observed on the curve $C_p(T)$ (Fig. 1) indicates that C_{mag} strives to become negative in the given temperature range. Thus, it can be assumed that the results of Ref. 6 confirm the appearance of a labile state of the magnetic system in magnetite in the region of the spin-reorientational transition $\Phi\langle 100\rangle \rightleftarrows \Phi\langle 111\rangle$.

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