Magnetic phase transitions in orthoferrite with a Morin point

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The magnetic phase diagram of the $YFe_{0.7}Mn_{0.3}O_3$ orthoferrite crystal is studied by measuring the differential magnetic susceptibility in a broad temperature range between 4 and 450°K in strong magnetic fields up to 300 kOe. The compound exhibits a transition from weak ferromagnetism to pure antiferromagnetism at $T_M = 280$°K, which is similar to the Morin transition in hematite. The states of the magnetic system below and above the Morin transition are determined on the basis of Mössbauer absorption spectra measured for a single-crystal sample. The sign of the biquadratic anisotropy constant is determined and it is concluded that the Morin transition in the crystal under consideration is a first-order phase transition.

INTRODUCTION

It is known that in certain antiferromagnets $\alpha - Fe_2O_3$[1], $DyFeO_3$[2], $La_{0.9}Bi_{0.1}CrO_3$[3]) a transition from a state with weak ferromagnetism to the usual antiferromagnetic state is observed with changing temperature. In[4] they reported observation of a similar transition in the system $YFe_{1-x}Mn_xO_3$ at $0.1 < x < 0.4$. We shall call this transition, in analogy with hematite, the Morin transition (MT). In orthoferrites, to which the system $YFe_{1-x}Mn_xO_3$ belongs, only the spin-flip transitions with conservation of the weak ferromagnetism have been investigated in detail. This spin flip occurs usually in the form of two second-order phase transitions separated by a temperature interval 10–100°K[5]. The MT was investigated in detail only in hematite, but no detailed study of transitions of this type was made in orthoferrites.

To determine the singularities of magnetic phase transitions in rhombic crystals, we investigated the temperature dependences of the field-transition field in $YFe_{0.7}Mn_{0.3}O_3$ having a Néel temperature $T_N = 440$°K and a TM temperature $T_M = 280$°K. The temperature vs. composition phase diagram of the magnetic states of this system was investigated in[6]. At $x < 0.6$, the crystals of this system are rhombic with a space group $D_{2h}^{16} - P_{bnm}$[7]. The axes of the unit rhombic cell are designates by a, b, and c ($a < b < c$).

EXPERIMENTAL PROCEDURE

The single crystal with composition $YFe_{0.7}Mn_{0.3}O_3$, from which the samples were cut for the magnetic and Mössbauer measurements, was grown by zone melting without a crucible and with radiation heating[8] by A. M. Balbashin and A. Ya. Chervonenkis at the Moscow Power Institute. The samples for the magnetic measurements measured $2 \times 2 \times 5$ mm. The crystal axes were oriented along the magnetic field accurate to about 3°.

The magnetic phase transitions were investigated by us by measuring the differential magnetic susceptibility. To obtain a pulsed magnetic field ($H_{max} = 300$ kOe, duration from zero to zero $\tau_{00} \sim 10$ msec) we discharged a capacitor bank into a many-turn solenoid. A signal proportional to the time derivative of the projection of the magnetic moment of the sample on the external field was fed to one of the channels of a two-beam long-persistence S1-42 oscilloscope. This signal was taken from two series-connected compensated coils, in one of which the investigated sample was placed. An integrated signal proportional to the field was fed from a Rogowski loop, to the other channel of the oscilloscope.

The magnetic moment was measured with a magnetometer with vibrating sample, analogous to that described by Foner[9]. We used one of the samples on which the differential susceptibility was investigated. The magnetization curves of the $YFe_{0.7}Mn_{0.3}O_3$ samples were plotted in a magnetic field up to 7 kOe parallel to the c axis. The spontaneous magnetization was determined by extrapolation to $H = 0$. The temperature dependence of the spontaneous magnetization is shown in Fig. 1a, which shows for comparison also the temperature dependence of the hyperfine field at the Fe^{57}, obtained from Mossbauer-effect (ME) measurements. The scale was chosen such that the curves coincided in the temperature region close to T_N.

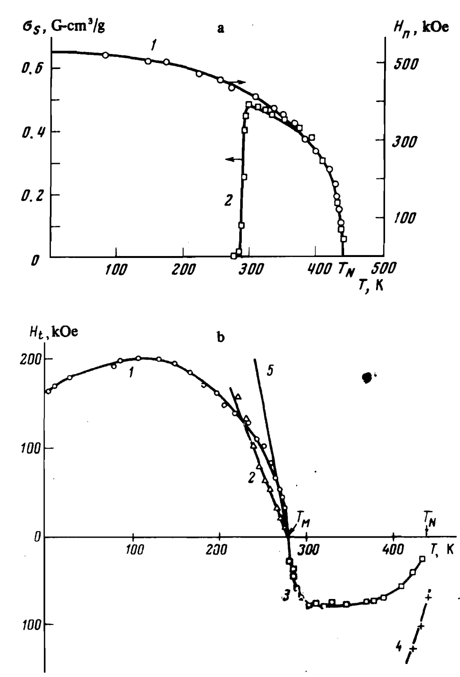

FIG. 1. a) Temperature dependences obtained for $YFe_{0.7}Mn_{0.3}O_3$. Curve 1—effective field H_n at the Fe^{57} nucleus. Curve 2—spontaneous magnetic moment σ_S parallel to the c axis. b) Magnetic phase-transition fields. Curves: 1—H‖b, 2—H‖c, 3 and 4—H‖a. Curve 5—plot of H_t^c obtained by a theory that takes into account only the bilinear anisotropy.

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The sample for the Mössbauer-effect measurements was a single-crystal plate approximately 100 μ thick with diameter 6 mm. The plane of the plate coincided with the bc plane of the crystal. For the temperature measurements, the sample was placed in a cryostat or in an oven with automatic control of the temperature, which was monitored with a chromel-copel thermocouple and maintained constant with accuracy not worse than $\pm 0.1^\circ$K. The Mössbauer-effect measurements were performed with a single-channel γ spectrometer operating with constant velocity of the source (CO^{57} in Cr). The γ-ray beam was parallel to the a axis. The spectra were plotted in a zero magnetic field.

EXPERIMENTAL RESULTS

Figure 2 shows the results of the Mössbauer experiments, and illustrates directly the spin-flip process in the MT. The second and fifth lines of the Mössbauer spectrum of Fe^{57}, which correspond to transitions without changes of the magnetic quantum number, have an intensity proportional to $\sin^2\theta$, where θ is the angle between the direction of the magnetizations of the sublattices and the γ-ray propagation direction[10]. We see that these lines appear when the temperature drops from 290 to 280°K. Consequently, in this temperature interval the magnetizations of the sublattices become reoriented from the a axis to a plane perpendicular to this axis. But inasmuch as the spontaneous magnetization vanishes in the same temperature interval (Fig. 1a), it can be stated that the sublattices become reoriented during the MT process from the a axis to the b axis. Thus, this experiment confirms a conclusion obtained earlier on the basis of neutron-diffraction investigations[11]. In[11] they investigated also the Mössbauer effect on polycrystalline $YFe_{0.8}Mn_{0.2}O_3$, but it was impossible to obtain uniquely the angle of rotation of the magnetic moments on the basis of the obtained data.

At low temperatures, in a magnetic field parallel to the b axis, a very narrow peak of the differential magnetic susceptibility was observed (curve 1 of Fig. 3). The amplitude of the peak decreases and its width decreases when the MT is approached. In the interval from 220 to 280°K, the temperature dependence of the

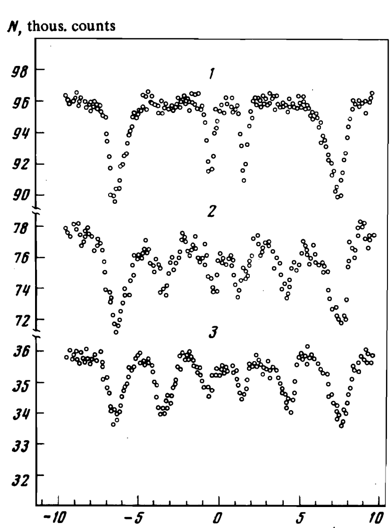
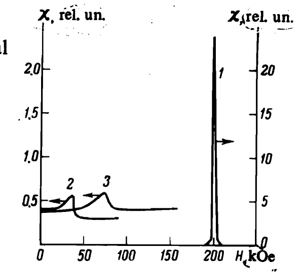


FIG. 2. Mössbauer absorption spectra of single crystal $YFe_{0.7}Mn_{0.3}O_3$. γ-ray beam parallel to the a axis. Curves 1, 2, and 3 correspond to 293, 288, 281°K, respectively.

FIG. 3. Dependence of the differential magnetic susceptibility on the external field. Curves: 1) H||b, T = 95°K; 2) H||c, T = 264°K; 3) H||a, T = 310°K. The relative units is the same for the right and left-hand scales.



field corresponding to this susceptibility peak is well described by the parabola

$$(H_t^b)^2 = -(370\pm25)(T - T_M) \text{ kOe}^2/\text{K}.$$

Below T_M, in a field parallel to the c axis, a peak (and a jump) of the magnetic susceptibility is observed (curve 2 of Fig. 3). When the temperature is lowered, the field in which the singularity of the magnetic susceptibility takes place increases linearly, and the singularity itself decreases and becomes practically indiscernible below 200°K. The temperature dependence of the transition field in the investigated temperature interval is described by a straight line with a slope −2.6 ± 0.2 kOe/°K and is shown in Fig. 1b (curve 2).

Above T_N all the way to the Néel point, in a magnetic field parallel to the a axis, a susceptibility peak is observed and is also connected with a magnetic phase transition (Fig. 1b, curve 3). Near T_N in stronger fields (~100 kOe), a jump is observed on the plot of the differential magnetic susceptibility against the field (Fig. 1b, curve 4). This anomaly will be discussed below. No anomalies of the differential magnetic susceptibility were observed at $T < T_M$ in fields up to 300 kOe parallel to the a axis.

DISCUSSION OF RESULTS

A theoretical analysis of the magnetization processes in orthorhombic antiferromagnets with Dzyaloshinskiĭ interaction was carried out on the basis of a phenomenological Hamiltonian by a number of workers[12-14]. Just as in[14], we use a two-sublattice model of the antiferromagnetic orthoferrite. We express the magnetic energy in the form $\mathscr{E} = 2M_0\mathscr{H}$,

$$\mathscr{H} = \tfrac{1}{2}Em^2 - D(m_z l_x - m_x l_z) - \mathbf{mH} + \tfrac{1}{2}A_1 l_x^2 + \tfrac{1}{2}C_1 l_z^2 + \tfrac{1}{4}A_2 l_x^4 + \tfrac{1}{4}C_2 l_z^4 + \tfrac{1}{4}F l_x^2 l_z^2,$$

where $\mathbf{m} \equiv (\mathbf{M}_1 + \mathbf{M}_2)/2M_0$ and $\mathbf{l} \equiv (\mathbf{M}_1 - \mathbf{M}_2)/2M_0$ are the ferro- and antiferromagnetic vectors, $\mathbf{M}_1$ and $\mathbf{M}_2$ are the magnetic moments of the sublattices, M_0 is their magnitude, the axes x, y, and z are directed along the axes a, b, and c of the crystal, and H is the external magnetic field.

As noted above, in the crystal investigated by us, in the absence of a magnetic field, the following two states are realized:

1) at $T < T_M$ $\mathbf{m} = 0$, $\mathbf{l} = (0, 1, 0)$,

2) at $T > T_M$ $\mathbf{m} = (0, 0, D/E)$, $\mathbf{l} = (1, 0, 0)$.

The results of our investigations of the magnetic phase diagram enable us to estimate the magnetic interactions in the investigated crystal. Let us consider the possible magnetization processes corresponding to the observed singularities of the differential magnetic susceptibility.

Below the MT, in a field parallel to the b axis, the sharp susceptibility peak corresponds to the flopping of the magnetic sublattices from the b axis to a plane perpendicular to this axis (spin flop). In a field parallel to the a axis, a rotation of the sublattices around the fields, analogous to that observed in CoF_2[15] and in hematite ($T < T_M$) is observed[16] 1). The difference between our case and hematite is that in $YFe_{0.7}Mn_{0.3}O_3$ in the ac plane there is strong anisotropy, such that in fields up to 150 kOe parallel to the a axis no phase transition corresponding to the completion of the rotation of the sublattices from the b axis to the c axis is observed all the way to temperatures close to T_N. Thus, it can be concluded that the c axis is the difficult axis for the antiferromagnetic vector. Consequently, the flopping of the sublattices apparently takes place in the ab plane.

It can be shown that the expressions for the fields of the phase transitions in terms of the parameters of the phenomenological Hamiltonian coincide, apart from the notation, with the analogous formulas derived for hematite with allowance for biquadratic anisotropy[19]. Since the data obtained by us in pulsed fields are insufficient for a quantitative treatment of the observed phase transition, we determined only the sign of the constant of the biquadratic anisotropy, which determines the type of reorientation transition (see, e.g.,[20]). We first estimate the magnitudes of the exchange interaction and of the Dzyaloshinskii interaction. We take as the initial value the exchange-interaction constant in $YFeO_3$ (T_N = 650 K) E = 12 800 kOe, determined from the value of the perpendicular susceptibility. Further, assuming (in accordance with the molecular-field theory) that E is proportional to T_N for $YFe_{0.7}Mn_{0.3}O_3$ which has $T_N = 400°K$, we obtain E = 8700 kOe. To extrapolate our magnetization data to 0°K in the molecular field approximation, we determined the Dzyaloshinskiĭ field $D = \sigma_0 E/2M_0$ = 60 kOe (σ_0 is the spontaneous magnetization at 0°K). We recognize here that the contribution to the spontaneous magnetization of the Mn^{3+} ions polarized by the exchange internal field is small (~10%) in comparison with the contribution of the iron sublattices at temperatures exceeding 300°K.

The part of the magnetization due to the Mn^{3+} ions can be estimated by calculating the magnetization of these ions in the internal exchange field. According to estimates made by Bystrov[21], the exchange integrals inside the ion pairs $Fe^{3+} - Fe^{3+}$ and $Fe^{3+} - Mn^{3+}$ are equal respectively to −10 and −2°K. We use for the calculations the usual molecular-field formula [(3.6) of[22]]. Summing the appropriately weighted contributions from different surroundings of the Mn^{3+} ion, we find that the molecular field at this ion in $YFe_{0.7}Mn_{0.3}O_3$ is equal to 1400 kOe. We then use the tables of the Brillouin functions[22] to obtain the estimate given above for the magnetization of the Mn^{3+} ions.

Without allowance for the biquadratic anisotropy, the fields of the transitions at H ∥ b and H ∥ c are given, in analogy with hematite, by

$$H_t^b=(A_1E-D^2)^{1/2},\quad H_t^c=(A_1E-D^2)/(A_1^2+D^2)^{1/2}.$$

If we now determine A_1 from our experimental values of H_t^b and calculate H_t^c (curve 5 of Fig. 1b), then the obtained transition fields exceed the experimental values of H_t^c. This is evidence that an important role should be played here by biquadratic anisotropy, with $A_2 < 0$. The MT takes place when A_1 decreases with increasing temperature, when $A_1 + \frac{1}{2}A_2 - D^2/E = 0$.

This is a first-order phase transition when $A_2 < 0$, and proceeds like two second-order phase transitions if $A_2 > 0$. Thus, the fact that the biquadratic-anisotropy constant is negative, indicates that the investigated MT is a first-order transition.

Our estimate of the sign of the biquadratic-anisotropy constant contradicts the calculation of this constant on the basis of the one-ion model and the experimentally known parameters of the spin Hamiltonian[21]. The apparent reason is that one cannot neglect in the calculation the constant a of the spin Hamiltonian, as was done in[21]. That this constant is large is indicated also by data on EPR on Mn^{3+} ions in rutile[23].

The sharp decrease of the bilinear anisotropy constant, which leads to a reorientation of the spins in crystals of the system $YFe_{1-x}Mn_xO_3$, can be attributed to the different temperature dependences of the contributions of opposite signs to the bilinear anisotropy from the Fe^{3+} and Mn^{3+} ions[24]. The biquadratic-anisotropy constant, which determines the type of transition, depends little on the temperature in the transition region.

Above the MT, the susceptibility peak observed by us in a field parallel to the a axis can be connected with the rotation of the antiferromagnetic vector from the a axis approximately to the b axis (since the c axis is the difficult one), which terminates at

$$H_{t1}^a\approx(|A_1|E-D^2)^{1/2}.$$

Further, at $H > H_{t1}^a$, a rotation of the sublattices will take place from the b axis to the difficult c axis. This rotation is analogous to the above-discussed sublattice rotation at $T < T_M$ in a field parallel to the c axis, and is due to the Dzyaloshinskiĭ interaction. It is completed in a field

$$H_{t2}^a=(EC_1-D^2)/(C_1^2+D^2)^{1/2},$$

in which case the susceptibility decreases jumpwise if this transition is of second order.

The possibility of such a magnetization process in a rhombic antiferromagnet was noted by Turov[12]. It can be assumed that it is to this transition that the anomalies of the differential susceptibility observed above 400°K in fields of about 100 kOe correspond (Fig. 1b, curve 4). Observation of a transition near H_{c2}^a is possible when T_N is approached, since the exchange, Dzyaloshinskiĭ-interaction, and anisotropy fields become small, and consequently also H_{t2}^a.

CONCLUSION

Our data offer evidence that the biquadratic-anisotropy constant in the region of the Morin transition in $YFe_{0.7}Mn_{0.3}O_3$ is negative and that it is intermediate for first order. Above the MT, the magnetic anisotropy of the crystal is such that the Dzyaloshinskiĭ vector is parallel to the anisotropy axis that is intermediate for the sublattice spins (b). In a magnetic field parallel to the easy axis (a), two magnetic phase transitions are observed on the magnetization curve. First is the flopping of the sublattices to a direction coinciding with the intermediate axis, followed by rotation of the sublattices around the field towards the difficult axis (c). This situation is typical of rhombic weak antiferromagnets with a Dzyaloshinskiĭ vector parallel to the intermediate anisotropy axis, but was observed here for the first time.

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