Magnetic properties and magnetoelectric effect in $Co_{1.75}Mn_{1.25}O_4$ crystals

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The magnetic and magnetoelectric properties of $Co_{1.75}Mn_{1.25}O_4$ crystals are investigated experimentally. Coexistence of ferrimagnetism and ferroelectricity and a magnetoelectric effect were found. Rotational hysteresis in the torque curves is explained by magnetoelectric coupling. An anisotropy of the magnitude of the magnetization is found experimentally. This anisotropy is explained by the presence of magnetoelectric terms in the thermodynamic potential.

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In ordinary ferro- and ferrimagnets, the coupling of the spin system with the electric field is weak, and therefore it may be supposed that the electric polarization is independent of the magnetic field. But there are crystals in which the coupling of magnetic and electric properties is important. One such is the ferrimagnetic crystal $Co_{1.75}Mn_{1.25}O_4$, which has not hitherto been obtained in monocrystalline form. Its crystallographic and magnetic properties can be judged on the basis of a paper of Wickham and Croft,[1] which gives the dependence upon composition of the magnetic saturation moment at 4.2 K, the lattice parameters, and the Curie temperature of polycrystalline specimens of $Co_{3-x}Mn_xO_4$. From this paper it follows that for compositions with $x < 1.25$ the crystals have a cubic structure of the spinel type, while for compositions with $x > 1.25$ there appears a tetragonal distortion that increases with increase of x. A neutron diffraction investigation has been made only for the composition [2]$CoMn_2O_4$ (polycrystals); it showed that the direction of the spin moments of the sublattices lies along axes of the type [110]. The space symmetry group of $CoMn_3O_4$ above the Curie temperature is D_{4h}^{19}; below it, the magnetic space symmetry has been determined as C_{2v}^{19}. Analysis of the symmetry of a $CoMn_2O_4$ crystal has shown[3] that in it a linear magnetoelectric effect can occur. In the magnetoelectric susceptibility tensor there should be two nonvanishing coefficients: α_{23} and α_{32}.

Crystals of $Co_{1.75}Mn_{1.25}O_4$ were grown by Yu. N. Yarmukhamedov in a two-zone furnace, in quartz ampules, by the method of chemical transport reaction (the transport agent was Cl_2), at source temperature 750–800 °C and crystallization-zone temperature 700–750 °C. The initial material had been previously synthesized from the oxides CoO and Mn_3O_3. Investigation by x-rays established that the crystals are cubic, with lattice parameter 8.3 Å; this enables us, in accordance with Wickham and Croft,[1] to make its composition more precise: $Cp_{1.75}Mn_{1.25}O_4$. This composition is critical in the sense that a slight increase of the cobalt in it stabilizes the cubic structure, and a slight decrease of the cobalt distorts it to tetragonal.

We investigated the magnetic anisotropy by the torque method in magnetic fields up to 20 kOe, over the temperature range 78–170 K (170 K is the Curie temperature of the crystal investigated). Magnetization curves were taken with a PAR vibration magnetometer (USA), with the specimen vibrating perpendicularly to the magnetic field of a superconducting solenoid, in magnetic fields up to 63 kOe and over the temperature range 4.2–78 K. In addition, magnetization curves were taken by the vibrationmagnetometer method in the field of an electromagnet (up to 20 kOe). In this magnetometer, as distinguished from the usual methods of investigation, it was possible to carry out a measurement of the magnetization not only parallel to the magnetic field, but also in two other directions perpendicular to the field.

The electrical resistivity of the specimens, measured by an electrometer method, is 10^{13} Ω·cm at 78 K and 10^4 Ω·cm at 293 K. The electric polarization was measured with a VK2-16 electrometer. Here the specimen was placed between the poles of the electromagnet. The electric polarization of the crystal in direction [110] was measured without a magnetic field and in a magnetic field up to 20 KOe, applied in various crystallographic directions.

Figure 1 shows torque curves taken in the (110) plane of a $Co_{1.75}Mn_{1.25}O_4$ crystal, at 78 K, in magnetic fields $H = 2$ kOe (a), $H = 5$ kOe (b), and $H = 20$ kOe (c). The curves were taken for rotation of the specimen in the magnetic field clockwise (the dotted line 1) and counter-

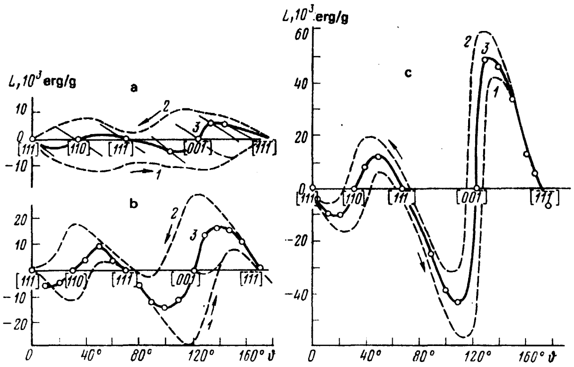

FIG. 1. Torque curves of a $CO_{1,75}Mn_{1,25}O_4$ crystal at 78 K, in the (110) plane. Curves 1, cockwise rotation of the crystal; Curves 2, counterclockwise rotation; Curves 3, each measurement made on demagnetized specimen. a, $H = 2$ KOe; b, $H = 5$ kOe; c, $H = 20$ kOe.

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clockwise (the dotted curve 2). In order not to crowd the figure, the experimental points have not been plotted on the curves. The figure shows that there is rotational hysteresis, which decreases with increase of the magnetic field. The first application of the magnetic field was made when this field was parallel to the $[00\bar{1}]$ axis of the crystal and after the crystal had been heated above the Curie point and then cooled to 78 °K. The initial section is the torque curve from direction $[00\bar{1}]$ to the junction with Curve 1. If after each torque measurement the field is shut off and the crystal is heated above the Curie point and then cooled to the prescribed temperature, and the magnetic field is then applied, the solid curves 3 obtained are midway between Curves 1 and 2.

Curves 3 are the usual torque curves of a cubic crystal with an axis of easy magnetization (EM) coinciding with axes of the type [111]. The value of the maximum torque increases approximately linearly with increase of the magnetic field. The direction of first application of the magnetic field (in this case the axis $[00\bar{1}]$) becomes the axis of EM and remains so until the crystal is turned in a magnetic field farther than 20–30°. Figure 1a shows also sections of the torque curves for cases in which the direction of first application of the field to the crystal is one of various crystallographic directions, and the crystal is rotated through not too large angles. (These directions are marked in Fig. 1a by circles.) The curves show that principal axes of the crystal become axes of easy magnetization in this plane if the magnetic field is applied along them. But if the field is applied in a direction not parallel to a principal axis of the crystal, the direction that becomes an easy axis is one that differs by 20–30° from the direction of the magnetic field. The larger the value of the magnetic field applied to the crystal, the more rapidly (that is, upon rotation through a smaller angle) does the magnetic-field-induced direction of EM disappear. This is illustrated by the torque curves of Figs. 1b and 1c, taken in magnetic fields of 5 and 20 kOe. The first direction of application of the magnetic field is again the axis $[00\bar{1}]$. If the magnetic field is applied to the demagnetized crystal along one of the axes of the type [111], this axis remains a direction of EM longer (that is, upon rotation of the crystal through a larger angle) than does an axis of the type [001].

Figure 2 shows magnetization curves at 78 and at 4.2 K. The curves were taken along two crystallographic axes: $[11\bar{1}]$, an axis of EM, and $[00\bar{1}]$, an axis of hard magnetization (see Fig. 1). The curves were taken on a crystal that had been demagnetized (by heating above 170 K). The arrows on the curves indicate the direction of change of the magnetic field. The magnetization curves constitute a linear variation of the magnetization with the field ($\sigma = \sigma_0 + \chi H$) over the whole range of fields from $H = 0$ to $H = 63$ kOe (if we disregard the initial section, where displacement of domain boundaries occurs). Repeated magnetization of the crystal follows this same linear curve. Because antiferromagnets with a weak ferromagnetic moment have this form of magnetization curve, we measured the component of the magnetization perpendicular to the field in fields up to 20 kOe, for various orientations of the magnetic field. It was found that in fields above 2 kOe, the perpendicular component was small. Therefore $Co_{1.75}Mn_{1.25}O_4$ crystals are ferrimagnetic.

Figure 3 gives (Curve 1) values of the spontaneous magnetization at 78 K, obtained from magnetization curves, and also rotation diagrams (dependences of the magnetization on the direction of the magnetic field during rotation of the crystal in the [110] plane) at 78 and at 4.2 K in magnetic fields of various values. Curves 2–6 were taken for clockwise and counterclockwise rotation of the crystal (the direction of rotation is indicated by arrows). As in the case of the torque curves, rotational hysteresis is observed, decreasing with increase of the value of the magnetic field. At 78 K, it disappears at field 20 kOe; at 4.2 K, it exists even in field 63 kOe. The curves of Fig. 3 indicate the existence in $Co_{1.75}Mn_{1.25}O_4$ of anisotropy of the magnitization. This anisotropy cannot be explained by lagging of the magnetization behind the field. As was mentioned above, the experiment to determine the component of

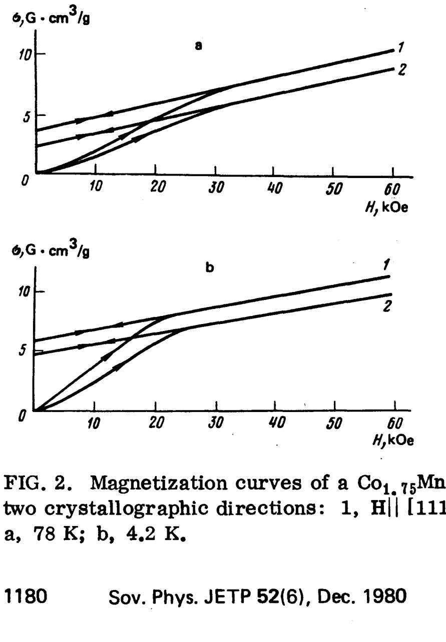

FIG. 2. Magnetization curves of a $Co_{1.75}Mn_{1.25}O_4$ crystal in two crystallographic directions: 1, $H \parallel [111]$; 2, $H \parallel [100]$. a, 78 K; b, 4.2 K.

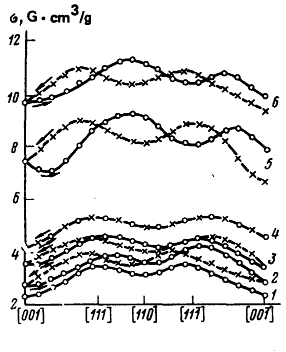

FIG. 3. Dependence of magnetization on direction of magnetic field in the (110) plane: 1, spontaneous magnetization at 78 K; 2, magnetization in field 5 kOe at 78 K; 3, magnetization in field 10 kOe at 78 K; 4, magnetization in field 20 kOe at 78 K; 5, magnetization in field 40 kOe at 4.2 K; 6, magnetization in field 63 kOe at 4.2 K.

the magnetization perpendicular to the field indicates that it is small. At field 20 kOe and temperature 78 K, the lag of the magnetization behind the field amounts to no more than two degrees.

The existence of anomalous magnetic properties (anisotropy of the magnetization, rotational hysteresis) and the high electrical resistivity (above $10^{13}\ \Omega\cdot$cm in the temperature range investigated) suggested the existence of a magnetoelectric effect in $Co_{1.75}Mn_{1.25}O_4$ crystals. With this motivation, electrical measurements were made on the same specimens as the magnetic; they consisted of qualitative investigations of the electric polarization P. A measurement was made of the spontaneous electric polarization in direction [110]. If a spontaneous polarization exists in some crystallographic direction, then there necessarily exists a component of it in direction [110], $P_{[110]}$. It was found that the crystal has a spontaneous electric polarization of not less than 10^{-5} $\mu C/cm^2$ at 95 K. These same measurements were carried out for the component $P_{[110]}$ of the electric polarization in a magnetic field, when the magnetic field is rotated in the (001) plane from direction $[1\bar{1}0]$ (Fig. 4a), passing through directions [100] (Fig. 4b) to [110] (Fig. 4c), and again rotating into direction $[1\bar{1}0]$ (Fig. 4d). The direction of change of the magnetic field is shown in the figures by arrows.

Figure 4 shows that there is a magnetoelectric effect in a $Co_{1.75}Mn_{1.25}O_4$ crystal (the change of electric polarization $\Delta P_{[110]}$ in magnetic field 20 kOe has the order of magnitude 10^{-5} $\mu C/cm^2$); the magnetoelectric hysteresis loops have a butterfly shape if the magnetic field is applied at angle 90° to the direction of measurement of the electric polarization, and a more complicated shape in other directions. It is interesting that rotation of the magnetic field through 90° and back led to a change of sign of the magnetoelectric effect (see Figs. 4a and 4d).

On cooling of the crystal in a magnetic field below the Curie point, there arises in it a magnetization, and consequently also an electric polarization. During this process, an electric charge appears on the surface of the crystal. A change of the direction of the magnetic field promotes a change of the direction of the magnetization and the appearance of a new ferroelectric domain. But because of the low conductivity (low temperatures), these electric charges impede the creation of a new electric domain, and consequently the rotation of the magnetization vector. The lower the temperature, the more difficult is remagnetization of the crystal. Therefore at 78 K in field 20 kOe, there is no longer rotational hysteresis (Fig. 3, Curve 4), while at 4.2 K the hysteresis is large even at magnetic field 63 kOe (Fig. 3, Curve 6).

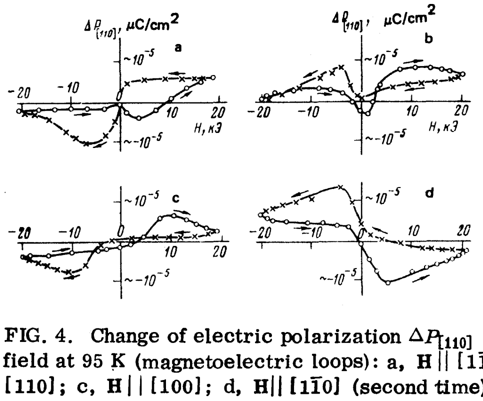

FIG. 4. Change of electric polarization $\Delta P_{[110]}$ in a magnetic field at 95 K (magnetoelectric loops): a, H || $[1\bar{1}0]$; b, H || [110]; c, H || [100]; d, H || $[1\bar{1}0]$ (second time).

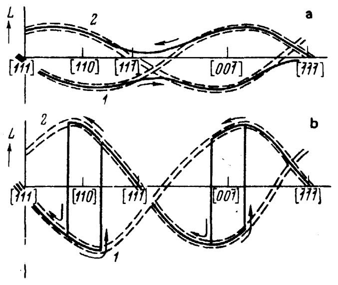

FIG. 5. Schematic drawing explaining the shape of the torque curves of Fig. 1.

Figure 5 explains the shape of the torque curves in weak magnetic fields (a) and in strong magnetic fields (b). The magnetic field distorts the cubic crystal and induces a uniaxial magnetic anisotropy. The electric polarization stabilizes it, by the mechanism indicated above. The form of the curves of the torque L of a uniaxial crystal is described by the formula $L = K \sin 2\theta$, where θ is the angle between the direction of EM and the magnetization, and where K is the constant of uniaxial magnetic anisotropy. On rotation of the crystal in weak magnetic fields, the transition from one torque curve, on which the axis of EM is the axis [111] (dotted curve 1), to another with axis of EM $[11\bar{1}]$ (dotted curve 2) occurs near the direction $[11\bar{1}]$; in strong fields, it occurs considerably earlier. The solid curve, which is the torque curve for rotation of the crystal through 180° clockwise and counterclockwise, explains the experimental curves of Fig. 1.

The presence of a magnetoelectric effect permits us to to write the thermodynamic potential in the following form:

$$\Phi = {}^1/_2 \varkappa_{ij} P_i P_j + {}^1/_2 \nu_{ij} M_i M_j - P_i E_i - M_i H_i + \alpha_{ij} M_i P_j.$$

Minimization of Φ with respect to the magnetization M and the electric polarization P leads to the following equilibrium conditions:

$$\nu_{ij} M_j - H_i + \alpha_{ij} P_j = 0, \quad \varkappa_{ij} P_j - E_i + \alpha_{ij} M_j = 0,$$

whence follows a linear relation between the magnetization and the value of the applied magnetic field (see Fig. 2). The experimentally observed anisotropy of the magnetization (Fig. 3) follows from these same conditions. In fact, the magnetization

$$M_i = a_{ij} H_j + b_{ij} E_j$$

is different for different directions of the magnetic field. Here a_{ij} and b_{ij} are material tensors that can be expressed in terms of $\varkappa_{ij}$, ν_{ij}, and α_{ij}. It is different also in different crystallographic directions in the absence of a field (anisotropy of the spontaneous magnetization, Fig. 3, Curve 1).

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[1]D. G. Wickham and W. J. Croft, J. Phys. Chem. Solids 7, 351 (1958).
[2]B. Boucher, R. Buhl, and M. Perrin, J. Appl. Phys. 39, 632 (1968).
[3]D. E. Cox, Int. J. Magn. 6, 67 (1974); reprinted in Magnetoelectric Interaction Phenomena in Crystals (ed. A. J. Freeman and H. Schmid), Gordon and Breach, 1975, p. 111.

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Experimental investigation of the phase transition to the superfluid state in helium located in narrow pores

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The phase transition to the superfluid state of helium contained in narrow pores with dimensions of 100–600 Å has been investigated by the calorimetric method. Singularities typical of a first-order phase transition are observed for helium in narrow pores (100–200 Å). The parameter M in the ψ theory of superfluidity and the coefficients A_0, B_0 and C_0 in the three-term expansion of the thermodynamic potential are estimated. The latent heat of the transition and its dependence on the pore size are determined.

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1. In the phenomenological theory of superfluidity (the ψ theory),[1-3] the expansion of the thermodynamic potential in a power series in the order parameter has the form

$$\Phi_{II}=\Phi_I+A|\psi|^2+\frac{1}{2}B|\psi|^4+\frac{1}{3}C|\psi|^6 \;\ldots, \tag{1}$$

where Φ_I and Φ_{II} are the thermodynamic potentials of homogeneous, stationary He-I and He-II near the λ point, and A, B, C are expansion coefficients, which are temperature dependent. In a modified variant of the ψ theory,

$$A=-A_0(T_\lambda-T)|T_\lambda-T|^{1/3};\quad B=B_0|T_\lambda-T|^{2/3};\quad C=C_0. \tag{2}$$

Under conditions in which coefficients of type (2) are used, all the terms in (1) that are proportional to $|\psi|^2$, $|\psi|^4$, $|\psi|^6$, depend in the same manner on $T_\lambda - T$ at equilibrium, and there is no basis for discarding terms of higher order in $|\psi|^2$ as $T \to T_\lambda$. However, in narrow pores, where the equilibrium value of the density of the superfluid component ρ is less than the corresponding equilibrium value of for the bulk immobile He-II, the discarding of terms with $|\psi|^8$ and higher is already valid.

In the three-term expansion (1), two restrictions can be placed on the coefficients A_0, B_0, C_0 (2) by requiring that they furnish the correct experimental value of the jump in the specific heat in the free (bulk) liquid $\Delta c_M = 5.2 \times 10^7$ erg/g-deg, and the value of the coefficient in the temperature dependence of ρ_{se}:

$$\rho_{se}=1.43\rho_\lambda(T_\lambda-T)^{2/3}=\rho_{00}(T_\lambda-T)^{2/3}.$$

Introducing the dimensionless variable $\varphi=\psi/\psi_0$, where $\psi_0=(\rho_0/m)^{1/2}$, and the relative temperature $t = T_\lambda - T$, we obtain

$$\Phi_{II}-\Phi_I=\frac{3\Delta c_b}{(3+M)T_\lambda}\left(-t|t|^{1/3}|\varphi|^2+\frac{1}{2}(1-M)|t|^{2/3}|\varphi|^4+\frac{1}{3}M|\varphi|^6\right), \tag{3}$$

where $M = C_0\psi_0^4/A_0$ is a dimensionless parameter. Comparison of (3) with (1) gives

$$A_0=\frac{3\Delta c_b}{(3+M)T_\lambda\psi_{00}^2},\quad B_0=\frac{3(1-M)\Delta c_b}{(3+M)T_\lambda\psi_{00}^4},\quad C_0=\frac{3M\Delta c_b}{(3+M)T_\lambda\psi_{00}^4}. \tag{4}$$

The parameter M is not determined within the framework of the phenomenological theory and must be estimated from experiment. It is shown in the ψ theory[3] that the value of the parameter M determines the type of the phase transition to the superfluid state: for $M < 1$ this transition should be second order, while for $M > 1$, it should be first order.

The aim of the present work is the experimental investigation of the character of the phase transition to the superfluid state of helium contained in narrow pores, by the calorimeteric method, and the determination, on the basis of experimental data, of the parameter M and of the coefficients A_0, B_0, C_0 of the three-term expansion of the thermodynamic potential in a power series in the order parameter.

2. The method of measurement consists in the following: Heat is released at a given rate by a thermally isolated sample and the time dependence of the temperature in it is investigated.