Distinguishing features of the magnetization of single-crystal $PbMn_2O_4$

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The magnetization of single-crystal antiferromagnetic $PbMn_2O_4$ is investigated in three mutually perpendicular directions. It is shown that when the magnetic field is oriented in the basal plane of the crystal, magnetic field acquires also perpendicular components along the trigonal axis as well as in the basal plane. With increasing magnetic field strength the total magnetization deviates from its original direction. Possible explanations of this effect are proposed.

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A magnetization component perpendicular to the applied magnetic field was observed in a number of antiferromagnets through the use of the recently developed vibration magnetometer with three pairs of coils,[1] which permits simultaneous investigations of the components of the magnetic moment of a sample in three mutually perpendicular directions. This phenomenon, weak ferromagnetism of higher order,[2] was investigated in the crystals $NiCO_3$ and $CoCo_3$ (Ref. 3, space group D_{3d}^6), $FeCl_2$ (Ref. 4, D_{3d}^5), and $CsMnF_3$ (Ref. 5, D_{6h}^4), in which a magnetization component perpendicular to the basal plane was produced at definite directions of the magnetic field in this plane. In $FeCl_2$ crystals, in addition, a magnetization component perpendicular to the magnetic field appeared also in the basal plane.[5] In investigations of the magnetization processes it was always presumed that in magnetically ordered crystals the total moment of the sample rotates towards the applied-field direction when the magnetic field is increased. This presumption is based on the fact that in the expansion of the thermodynamic potential in powers of the ferromagnetism and antiferromagnetism vectors **m** and **l** the magnetic field **H** enters explicitly only in the Zeeman term $-\mathbf{m}\cdot\mathbf{H}$ that increases in absolute value with increasing **H** and has a minimum at $\mathbf{m}\|\mathbf{H}$, while the terms that depend on **m** and determine the magnetic anisotropy of the crystal are insignificantly changed, since $\mathbf{m}\approx$ const in fields that are not too weak, while in antiferromagnets $\mathbf{m}\ll\mathbf{l}$. The value of **l** is usually practically independent of **H**. Nonetheless, reversal of the magnetization component parallel to the magnetic field was observed in the weakly ferromagnetic crystal $Ni_3B_7O_{13}I$ (symmetry group C_{2v}^5) in a magnetic field directed along the [111] axis; this reversal is possibly due to the deflection of the magnetization away from the magnetic-field direction. Unfortunately, the other components were not investigated in Ref. 6. Furthermore, although the behavior of the total magnetization with changing magnetic field was not analyzed in Refs. 3–5, it can be seen from the data of Refs. 4 and 5 that the magnetization deviates monotonically albeit negligibly (by up to 3 degrees) away from the field direction in an $FeCl_2$ crystal.[1]

The vibration-magnetometer method was used in the present study to investigate, in three mutually perpendicular directions, the behavior of the magnetization components of the $PbMn_2O_4$ crystal in magnetic fields up to 20 kOe applied in the basal plane. The measurements were made at room temperature.

Hardly any studies were made of the hexagonal antiferromagnet lead manganate $PbMn_2O_4$. Only one published experimental paper[7] reports the growth of $PbMn_2O_4$ crystals and investigation of their magnetic properties below 63 K and of their dielectric properties below 300 K. A thermodynamic treatment of the results of Ref. 7 is given in Ref. 8. An x-ray structure analysis of the crystal has shown that at room temperature the compound is hexagonal, with cell parameters $a = 10.01$ Å and $c = 13.58$ Å, and with probable space groups D_{3h}^2, D_{6h}^2, or D_{6h}^3, of which D_{3h}^2 is noncentrosymmetric. The results of the magnetic measurements[7] have shown that below 63 K lead manganate has a weak ferromagnetic moment. The dielectric measurements have revealed a broad maximum of the dielectric constant at 250 K and the presence of dielectric hysteresis loops in the interval 20–70 K. Above 70 K, owing to the increased electric conductivity of the crystals, no dielectric loops were plotted. Al'shin *et al.*[8] have proposed that a ferroelectric transition takes place above the magnetic-ordering point, and that the paramagnetic phase of the crystal belongs to the C_{3v} group. Above 63 K, a rather high spontaneous magnetization is still observed and amounts at 120 K to more than 30% of the magnetization at 20 K (in Ref. 7 the magnetization is given in relative units). Consequently, 63 K is not the temperature at which the magnetic order is completely destroyed.

We describe the experimental results in the following coordinate system: the z axis is directed along the threefold axis, x and y lie in the basal plane of the crystal, with x directed along the symmetry plane and y perpendicular to it. When transforming to a spherical frame, we shall designate by ϑ and φ the polar and azimuthal angles of the ferromagnetism vector **m**, by ϑ_1 and φ_1 the angles of the antiferromagnetism vector **l**, and by ϑ_2 and φ_2 the same for the electric-polarization vector **p**. The polar angles are reckoned from the threefold axis, and the azimuthal from the vertical symmetry plane.

Figure 1 shows the three components of the $PbMn_2O_4$ magnetization as functions of the magnetic field H applied in the basal plane of the crystal. The figure shows that all three magnetization components are observed and increase with increasing field. Also observed are a hysteresis loop and a

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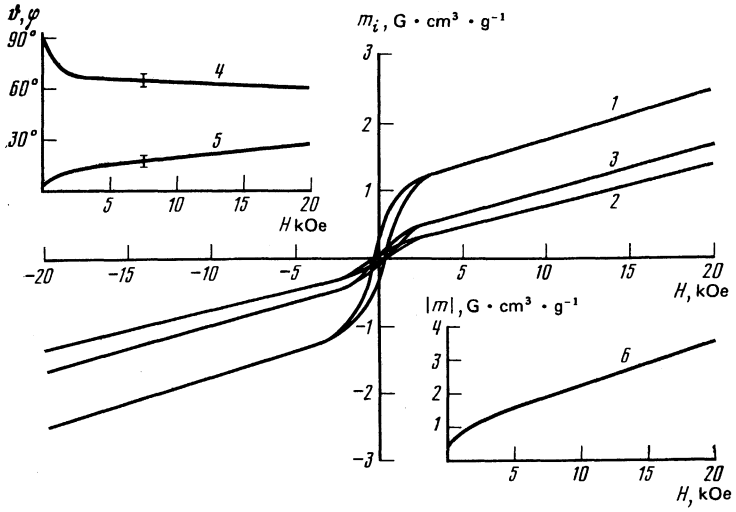

FIG. 1. Experimental dependences of the magnetization components m_i on the magnetic field H. Curves: 1) $i=x$, 2) $i=y$, 3) $i=z$. In the upper inset: 4) $\vartheta(H)$, 5) $\varphi(H)$; in the lower inset: 6) $|m(H)|$.

spontaneous magnetic moment. The magnetization component perpendicular to the magnetic field depend on the direction of **H** in the basal plane. Figure 1 shows the results for those field directions in the basal plane, for which the largest values of these components have been observed. Owing to the poor reproducibility of the experimental results, we were unable to investigate the magnetic anisotropy quantitatively. The poor reproducibility of the experiment consisted in the fact that when the magnetic field was rotated in the basal plane through a large angle ($\sim 90°$) the easy-magnetization direction changed by $\sim 30°$. At a smaller field rotation the curves were reproducible. The experimental errors for the latter case are indicated in Fig. 1.

To explain the observed phenomenon, we consider the expansion of the thermodynamic potential Φ in powers of the vectors **m**, **l**, and **p**. An expression for Φ, accurate to terms of sixth order in **l** for the C_{3v} class to which $MbMn_2O_4$ apparently belongs[8] is given in Ref. 8. Retaining only terms we need to describe the experiment, we express Φ in the form

$$\Phi = \frac{B}{2}\mathbf{m}^2 + \frac{a}{2}l_z^2 + \frac{b}{4}l_z^4 + d(l_x m_y - l_y m_x) + \frac{c}{12}(l_+^6 + l_-^6) - \mathbf{mH} + \frac{f}{6}(l_+^3 + l_-^3)l_z + \frac{f_1}{6i}(l_+^3 - l_-^3)m_z + \frac{f_2}{2i}(m_+ l_+^2 - m_- l_-^2)l_z + \frac{e}{2}(p_+ l_+ m_+ - p_- l_- m_-) - \frac{\alpha}{2}p_z^2 + \frac{\beta}{2}p_\perp^2 + \frac{\gamma}{6}(p_+^3 + p_-^3)p_z + \frac{\sigma}{4}p_z^4, \tag{1}$$

where $q_\pm = q_x \pm iq_y$, $q = m, l, p$. The term with the coefficient f_2 (Ref. 2) is not given in Ref. 8.

A possible explanation for the onset of a crystal magnetization along the z axis when a magnetic field is applied in the basal plane was considered by Bazhan for both an easy-axis[3] and an easy-plane[4] antiferromagnet. The explanation is based on a thermodynamic invariant of the thermodynamic potential with coefficient f_1, which leads to the appearance of m_z when a definitely directed component of **l** appears in the basal plane. In our experiment, besides the appearance of m_z, we have observed also a deflection of the vector **m** in the basal plane away from the magnetic field direction (Fig. 1, curve 5), and we confine ourselves hereafter to an explanation of only this effect.

Since the direction of the vector **l** cannot be uniquely determined from the available experimental data, we consider two cases: (1) the vector **l** makes an angle with the basal plane, and (2) the crystal is easy-plane. We direct the magnetic field in the basal plane along the x axis and express the potential (1) in spherical coordinates under the condition that $(\mathbf{l}\cdot\mathbf{m}) = 0$ ($\varphi_1 = \varphi + \pi/2$), $\mathbf{l}^2 = \text{const}$, and $m_z = 0$

$$\Phi = \frac{B}{2}m^2 + \frac{a}{2}l^2\cos^2\vartheta_1 + \frac{b}{4}l^4\cos^4\vartheta_1 - dlm\sin\vartheta_1 + \frac{c}{6}l^6\sin^6\vartheta_1\cos 6\varphi - mH\cos\varphi + \frac{f}{3}l^4\cos\vartheta_1\sin^3\vartheta_1\sin 3\varphi - \frac{f_1}{3}l^3 m\sin^3\vartheta_1\cos 3\varphi - \frac{f_2}{3}l^3 m\sin^2\vartheta_1\cos\vartheta_1\sin 3\varphi + epml\sin\vartheta_1\sin\vartheta_2\cos(\varphi_2 + 2\varphi) - \frac{\alpha}{2}p^2\cos^2\vartheta_2 + \frac{\beta}{2}p^2\sin^2\vartheta_2 + \frac{\gamma}{3}p^4\cos\vartheta_2\sin^3\vartheta_2\cos 3\varphi + \frac{\sigma}{4}p^4\cos^4\vartheta_2. \tag{2}$$

In the first case the deflection of the magnetization away from the magnetic field can be indirectly explained as follows: the presence of weak ferromagnetism (invariant with coefficient d) leads to rotation of the vector **l** from the C_3 axis towards the basal plane in the magnetic field applied in the basal plane; this deflection is larger the stronger the field. At the appropriate signs of the coefficients c and f_2, the corresponding invariants, which increase like $\sin^6\vartheta_1$ and $\sin^3\vartheta_1$, can explain the observed effect. Retaining in Φ the first six terms and minimizing with respect to φ, ϑ, and m we obtain, if the anisotropy in the plane is less than the anisotropy along the principal axis ($cl^6 \times \sin^2\vartheta_1 \ll al^2 + bl^4$), a system of equations for the equilibrium values of φ, ϑ_1, and m:

$$Bm-dl\sin\vartheta_1-Il\cos\varphi=0,$$
$$-al^2\sin\vartheta_1-bl^4\cos^2\vartheta_1\sin\vartheta_1-dlm=0,$$
$$mH\sin\varphi-cl^6\sin^6\vartheta_1\sin 6\varphi=0. \quad (3)$$

From (3) we easily find that at $H=0$ the angle ϑ is determined from the condition

$$\sin^2\vartheta_1^0=\frac{aB+bBl^2+d^2}{bBl^2} \quad \text{at} \quad 0\leqslant\frac{aB+bBl^2+d^2}{bBl^2}\leqslant 1$$

and $\sin\vartheta_1^0=0$ at $aB+bBl^2+d^2<0$ (here $b>0$). If we put for simplicity $b=0$ and $\vartheta_1^0=0$, we can obtain an exact solution of the system (3) for ϑ_1 and m:

$$\sin\vartheta_1=-\frac{dH\cos\varphi}{(aB+d^2)l}, \qquad m=\frac{Ha\cos\varphi}{(aB+d^2)},$$

from which we obtain from (3) a condition for φ:

$$\sin\varphi=\frac{cd^2H^4\cos^5\varphi}{a(aB+d^2)^5}\sin 6\varphi. \quad (4)$$

It can be seen from (4) that at $H^4<a(aB+d^2)^5/6cd^6$ the equilibrium value is $\varphi=0$, and at

$$\frac{a(aB+d^2)^5}{6cd^6}<H^4<\frac{(aB+d^2)^4l^4}{d^4}$$

φ increases monotonically with the field until the vector l lands in the basal plane. In this case the maximum value of φ is larger the larger the ratio $cd^2l^4/a(aB+d^2)$, but cannot exceed $\pi/6$. A similar analysis leads apparently to just the same $\varphi(H)$ dependence also when the invariant with the coefficient f_2 is taken into account.

Even though the obtained dependences of m and ϑ_1 on H are in qualitative agreement with experiment if the constants are suitably chosen ($H_E=Bl/2\sim 10^6$ Oe, $H_D=dl\sim 10^5$ Oe, $H_a=al^3\sim 10^4$ Oe, $H_c=cl^5\sim 10^4$ Oe), so appreciable an anisotropy of the vector l in the basal plane (H_c) seems to us to be quite unlikely.

Another more probable explanation is based, in our opinion, on the existence of the magnetoelectric effect in $PbMn_2O_4$ (Ref. 8). We assume now that the crystal has magnetic anisotropy of the easy plane (case 2) and a spontaneous electric polarization along the C_3 axis. We neglect in Eq. (2) the terms with coefficients b, c, f, f_1, f_2 and put $a>0$, $d>0$, $\alpha\sim\beta\sim\gamma/p^2\sim\sigma/p^2>0$. We minimize Φ under the condition that the influence of the magnetoelectric interaction on the electric system ($|eml|\ll|\beta p|$) and the departure of l from the plane ($f\sim 0$) are small, i.e., $\sin\vartheta_1\approx 1$ and $\cos\vartheta_2\approx 1$. It follows then from $\partial\Gamma/\partial p=0$ that $p^2=\alpha/\sigma$ and therefore we obtain from $\partial\Phi/\partial\xi\vartheta_z=0$

$$\sin\vartheta_2=-\frac{eml\cos(\varphi_2+2\varphi)}{\beta p} \quad (5)$$

and from $\partial\Phi/\partial m$, if $\beta\gg epl\sin\vartheta_2$, it follows that $m=(dl+H\cos\varphi)/B$.

Substituting the expressions obtained for ϑ_2 and m in the equations $\partial\Phi/\partial\varphi=\partial\Phi/\partial\varphi_z=0$ we obtain

$$H\sin\varphi-elp\sin(\varphi_2+2\varphi)\sin\vartheta_2=0, \quad (6)$$
$$eml\sin(\varphi_2+2\varphi)+\gamma p^3\sin^2\vartheta_2\sin 3\varphi_2=0. \quad (7)$$

It follows from (7) that in weak fields, when $eml\gg\gamma p^3\sin^2\vartheta_2$, we have $\sin(\varphi_2+2\varphi)\sim 0$, and from (6) we obtain $\sin\varphi\sim 0$. With increasing field, the second term of (7) increases more rapidly than the first ($|\sin\varphi|$ increases). It can be easily seen from (6) and (7) that at a sufficiently large magnetoelectric interaction ($2epl/H>1$) the angle φ can reach $\pi/6$.

Comparison of the electric and magnetic energies shows that to explain the observed effect the electric polarization must be of the order of 10^{-3} $\mu C/cm^2$ (the known ferroelectrics have polarizations from 10^{-5} to 200 $\mu C/cm^2$). It is possible that the poor reproducibility of the magnetic measurements is due to the fact than when the direction of the magnetic field is reversed not the entire volume of the sample is electrically repolarized. A final assessment of the origin of the magnetization components perpendicular to the field will possible obtained after the magnetoelectric effect is investigated by a dynamic method.

[1)] A correction, pointed out by A. N. Bazhan, was introduced in the data of Ref. 4, viz., the magnetization parallel to the field in the basal plane is found in experiment to exceed by an order of magnitude the value cited in Ref. 4.

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