Magnetoelectric effect in the spin-flop phase of Cr_2O_3 and the problem of determining the magnetic structure

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The magnetoelectric effect has been studied in the spin-flop phase of Cr_2O_3 in pulsed magnetic fields up to 200 kOe over the temperature range 4.2–300 K. It is shown theoretically that the coefficient α_{33} in this phase is described as a function of the components of the antiferromagnetism vector by $\alpha_{33}=\chi_\perp \lambda_6 L_y(L_y^2-3L_x^2)$. In other words, this coefficient is relativistically small in comparison with other components of the magnetoelectric tensor. An experiment involving a careful orientation of the magnetic field with respect to the c axis of the crystal revealed $\alpha_{33}\simeq 0$, within the experimental error. Possible reasons for a nonzero observed value of α_{33} are discussed.

The compound Cr_2O_3 is a classic material, for which a linear magnetoelectric effect was first predicted theoretically[1] and observed experimentally.[2] Many subsequent studies have been aimed at determining the behavior of the magnetoelectric effect in Cr_2O_3 and learning about the mechanisms which give rise to this effect.[3,4] There has been considerably less study of the linear magnetoelectric effect in strong magnetic fields.[5,6] In the study of this effect many problems remain unresolved.

In the absence of a magnetic field, the spins of the Cr^{3+} ions are antiferromagnetically ordered along the c axis of the rhombohedral crystal, and the magnetic symmetry of Cr_2O_3 is such that the tensor of the linear magnetoelectric effect has exclusively diagonal components.[1,2] In a strong magnetic field $H\|c$ the spins of the Cr^{3+} ions tilt into the basal plane; i.e., a spin-flop transition occurs. There is the question of whether it is possible to study the magnetic symmetry in the spin-flop phase by measuring the linear magnetoelectric effect. The idea here is to determine how the magnetoelectric tensor depends on the direction of the spins. Recent papers published on this question disagree wildly. An attempt to determine the magnetic symmetry of Cr_2O_3 in the spin-flop phase was undertaken in Ref. 6. Working from the results of Ref. 7, Ohtani and Kohn[6] suggested that the magneotelectric tensor was of the form

$$\hat{\alpha}_{sf}=\begin{vmatrix} 0 & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & 0 & 0 \\ \alpha_{31} & 0 & 0 \end{vmatrix}$$

in the case in which the spins are directed along the $a(x)$ axis (the binary axis) of the crystal (magnetic symmetry $2'/m$), while it was of the form

$$\hat{\alpha}_{sf}=\begin{vmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & \alpha_{23} \\ 0 & \alpha_{32} & \alpha_{33} \end{vmatrix}$$

in the case in which the spins were directed along the $b(y)$ axis, which runs normal to the binary axis (magnetic symmetry $2/m'$). For an arbitrary orientation of the Cr^{3+} spins in the basal plane [magnetic point symmetry ($1'$)], all nine components of the magnetoelectric susceptibility tensor are nonzero.

Ohtani and Kohn[6] experimentally observed a polarization along the c axis in the spin-flop phase in the orientation $H \parallel c$. They interpreted this result as meaning that the crystal had a nonvanishing coefficient α_{33}. It was thus concluded that the magnetic point symmetry in the spin-flop phase is either $2/m'$ (the Cr^{3+}spins lie along the normal to the binary axis) or $1'$ (the spins lie in the basal plane at some angle with the binary axis).

According to the expression given for the magnetoelectric effect in Refs. 8 and 9, on the other hand, the magnetoelectric tensor should not have an axial anisotropy in the spin-flop phase. In other words, the coefficient α_{33} must be zero in both the $2'/m$ ($L00$) phase and the $2/m'$ ($0L0$) phase.

In this letter we are reporting an experimental and theoretical study of this problem. A further reason why we regard this problem as interesting and important is that Ohtani and Kohn[6] suggest using the vanishing or nonvanishing of the coefficient α_{33} of the magnetoelectric tensor as a test for determining the magnetic symmetry of Cr_2O_3 in the spin-flop phase.

Let us examine the electric polarization induced by a magnetic field. We start from the following expression for the magnetoelectric interaction:

$$\Phi_{\mathrm{ME}}=-\lambda_1[m_x(L_xE_y+L_yE_x)+m_y(L_xE_x+L_yE_y)]-\lambda_2(L_xm_x+L_ym_y)E_z$$
$$-\lambda_3(m_xE_x+m_yE_y)L_z-\lambda_4m_z(L_xE_x+L_yE_y)-\lambda_5\, m_zL_zE_z, \qquad (1)$$

where L_i and m_i are components of the antiferromagnetic and weak ferromagnetic vectors, E_i are the components of the electric field, and λ_i are magnetoelectric coefficients. This expression agrees with expressions given for the magnetoelectric effect in a book by Turov.[8] Defining the electric polarization by $P_i=-\partial\Phi/\partial E_i$, and substituting the expression[10]

$$\mathbf{m}=\chi_\perp\,[\mathbf{H}-(\mathbf{H}\cdot\mathbf{L})\mathbf{L}]+\chi_\parallel(\mathbf{H}\cdot\mathbf{L})\mathbf{L}$$

into (1), we find an expression for the electric polarization:

$$\mathbf{P}=\chi_\perp\,[\mathbf{H}-(\mathbf{H}\cdot\mathbf{L})\mathbf{L}]\begin{vmatrix} \lambda_1L_y+\lambda_3L_z & \lambda_1L_x & \lambda_2L_x \\ \lambda_1L_x & -\lambda_1L_y+\lambda_3L_z & \lambda_2L_y \\ \lambda_4L_x & \lambda_4L_y & \lambda_5L_z \end{vmatrix}$$

$$+\chi_{\parallel}(\mathbf{H}\cdot\mathbf{L})\begin{vmatrix} 2\lambda_1 L_x L_y & + & (\lambda_3+\lambda_4)L_x L_y \\ \lambda_1(L_x^2-L_y^2) & + & (\lambda_3+\lambda_4)L_y L_z \\ \lambda_2(L_x^2+L_y^2) & + & \lambda_5 L_z^2 \end{vmatrix}. \quad (2)$$

From this expression we can easily determine the coefficients of the magnetoelectric tensor α_{ij}. They evidently depend on the direction of **L** and also the magnetic susceptibilities $\chi_\perp$ and $\chi_\parallel$ (the latter dependence is important for interpreting the temperature dependence of the magnetoelectric effect).

We wish to stress that the coefficient α_{33} found from (2) (for $H\|c$ and $H\perp c$) is zero, although from the standpoint of the magnetic symmetry it may be nonzero.[7] The explanation is that expression (2) was derived from an expression for the magnetoelectric interaction which incorporates only the terms linear in L. Nonzero values of the coefficient α_{33} can be found by incorporating terms of third or higher order in L in the magnetoelectric energy. There are 16 invariant combinations of the type $E_r m_s L_i L_j L_k$, where the subscripts take on the values x, y, z. We are actually interested in invariants of the type $E_z m_z L_i L_j L_k$ with $L_z=0$, since we are concerned with only the spin-flop phase. There is only a single invariant of this type:

$$V_3=-\lambda_6 E_z m_z L_y(L_y^2-3L_x^2)m_z. \quad (3)$$

A direct check quickly shows that this combination is indeed an invariant of the $R3\bar{c}$ group. It is sufficient to test the "action" of only the generating elements of the group: 1^-, 3_z^+, and 2_x^-, where the superscripts $(-, +)$ specify the parity of the corresponding element under an interchange of sublattices.[8] For example, we have $1^-\mathbf{L}=\mathbf{L}$, $1^-E_z=-E_z$, $2_x^-L_x=-L_x$, $2_x^-L_y=L_y$, $2_x^-m_x=-m_x$, $3_z^+E_z=E_z$, and $3_z^+m_z=m_z$. It is easy to verify that interaction (3) gives rise to the following term in the coefficient α_{33} of the magnetoelectric tensor:

$$\alpha_{33}=\chi_\perp\lambda_6 L_y(L_y^2-3L_x^2)=4\chi_\perp\lambda_6 L^3\sin\varphi\sin(\varphi-\pi/3)\sin(\varphi+\pi/3)$$

$$=-\chi_\perp\lambda_6 L^3\sin 3\varphi, \quad (4)$$

where $L=(\cos\varphi, \sin\varphi, 0)$. The last equation in (4) stresses the axial symmetry of this coefficient. Since the ratio of the relativistic interactions (primarily the spin–orbit interaction) to the electrostatic interactions (primarily the exchange interaction) serves as a small parameter in the expansion of the anisotropic thermodynamic potential in the powers of the antiferromagnetism vector, the constant α_{33} is relativistically small in comparison with the other components of the magnetoelectric tensor, which are nonzero even in first order in **L**. Because of all these considerations, the constant α_{33} could hardly be a reliable test of the magnetic structure in the spin-flop phase. The additional terms which arise in the other components of the magnetoelectric tensor in third order in L_i will not be discussed here, since (as mentioned above) they are small in comparison with the nonzero values of these components in the approximation linear in L_i.

The axial anisotropy of the magnetoelectric tensor, i.e., the anisotropy with respect to rotation around the threefold axis, arises only in third order in L_i and is relativistically small.

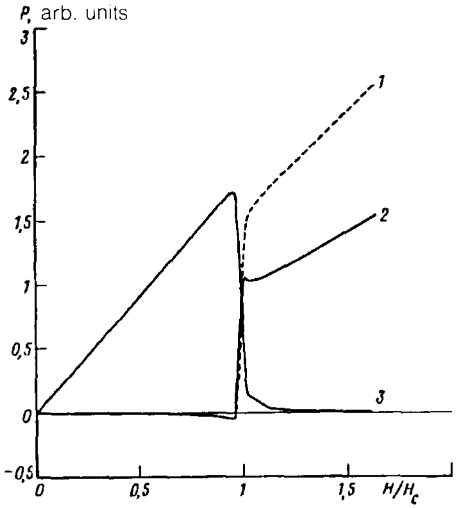

FIG. 1. Experimental results on the polarization P as a function of the magnetic field H at 4.2 K. 1) P_y-H_z; 2) P_x-H_z; 3) P_z-H_z.

We note, however, that the observed electric polarization can acquire an axial dependence experimentally even when only the terms linear L_i are taken into account in the α_{ij} tensor, because of the magnetic anisotropy in the basal plane. Let us assume that the vector $L=(L_x,L_y,0)$ is rotated around the c axis by a relatively weak auxiliary magnetic field $H_\perp=(\Delta H_x,\Delta H_y,0)$, which rotates in the basal plane. We then find from (2)

$$P_z=\chi_\perp \lambda_4 L\Delta H\cos(\varphi-\varphi_H),$$

where φ_H is the azimuthal angle of the field ΔH. Since the dependence of $\Delta\varphi=\varphi-\varphi_H$ on φ_H is governed by the real magnetic anisotropy in the basal plane, the observed polarization could in principle reveal this anisotropy.

In the experiments we measured the components P_x, P_y, and P_z as a function of a pulsed magnetic field H (up to 200 kOe) oriented along the c axis of the crystal. The test samples were high-quality crystals free of blocks. Curve 3 in Fig. 1 shows the experimental results on the electric polarization P_z as a function of the external magnetic field $H\|c$. As expected, $P_z(H_z)$ is linear in weak fields, while in a sufficiently strong field H_c, which induces the spin-flop transition, the electric polarization abruptly vanishes. This result is evidence that the component α_{33} vanishes, in contrast with the results of Refs. 5, 6, and 11. We wish to stress that the polarization P_z (along the z axis) observed experimentally is extremely sensitive to the precision with which the magnetic field is oriented with respect to the c axis. If the field deviates from the c axis by an appreciable angle θ_H, the Cr^{3+} spins do not lie strictly in the basal plane in the spin-flop phase. In this case the antiferromagnetism vector has a small projection onto the c axis. This projection accounts for the nonzero value of the coefficient α_{33}, and hence for the polarization along the c axis. Blocks in the crystal oriented at some small angle with respect to the c axis might also result in the observation of a nonzero α_{33}.

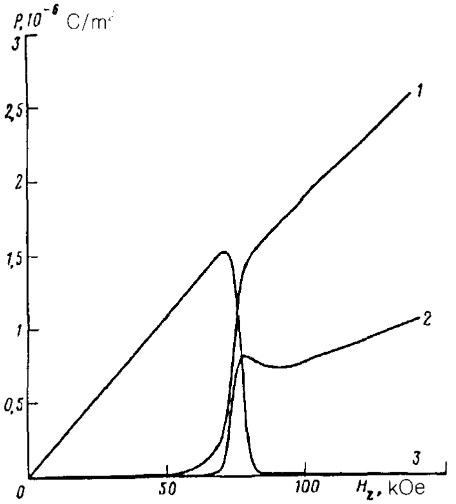

FIG. 2. Theoretical behavior of the polarization P as a function of the magnetic field H/H_c ($\theta_H=30'$, $\varphi_H=265°$) at 4.2 K. 1) P_y-H/H_c; 2) P_x-H/H_c; 3) P_z-H/H_c.

When $P_z(H_z)$ disappears in the course of the spin-flop transition, the polarization vector acquires nonzero components $P_x(H_z)$ and $P_y(H_z)$ because of the change in magnetic symmetry (curves 2 and 1 in Fig. 1). These curves have some interesting characteristic anomalies in the vicinity of the spin-flop transition. To see the origin of these anomalies, we take a closer look at the kinematics of the antiferromagnetism vector **L** as a function of the field. Here we make use of the thermodynamic potential, whose magnetic component is

$$\Phi_m=\Delta\chi(\mathbf{HL})^2/2-KL_z^2+K_6\sin^6\theta\sin(6\varphi), \qquad (5)$$

where $L\equiv(\sin\theta\cos\varphi,\ \sin\theta\sin\varphi,\ \cos\theta)$. The competition between the energy $\Delta\chi(\mathbf{LH})^2/2$ and the anisotropy energies $-KL_z^2$ and $K_6\sin^6(\theta)\sin(6\varphi)$, combined with the small value of the anisotropy constant K_6 in the *ab* plane, has the consequence that the vector **L** initially moves away from the field as the field is increased, while remaining in the plane passing through the field H and the c axis (H is not strictly parallel to the c axis). It then rotates toward the plane passing through the c axis and the easy axis in the *ab* plane closest to $H_\perp$. The projection of **L** onto one of the axes in the *ab* plane (curve 1 in Fig. 1) increases continuously, and the corresponding polarization component P_y varies monotonically. For the projection of **L** onto the other axis, the growth gives way to a decrease, and P_x correspondingly has a "peak-shaped" anomaly (curve 2 in Fig. 1). Theoretical curves of $P_{x,y,z}(H)$ in arbitrary units are drawn in Fig. 2.

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