MECHANISM OF THE MAGNETOELECTRIC EFFECT IN AN ANTIFERROMAGNET

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A crystal placed in an applied electric field may experience a magnetization which is proportional to the electric field. This magnetoelectric effect was first observed experimentally by Astrov[1] in a monocrystal of antiferromagnetic Cr_2O_3. Even earlier, Landau and Lifshitz[2] had pointed out the possibility that this effect (and its inverse) may exist in some spin-ordered materials, and Dzyaloshinskii[3] had predicted specifically that it could exist in Cr_2O_3. Both of these theories are based on symmetry arguments and thermodynamics only.

In the present Letter we propose a simple phenomenological theory of the temperature dependence of the magnetoelectric effect. This theory correctly predicts the experimental observations presented in the accompanying Letter[4] for both the parallel ($\parallel$) and perpendicular ($\perp$) orientations of the electric field with respect to the axis of spontaneous antiferromagnetism (z axis). In addition, we tentatively suggest a possible atomic mechanism which conforms to the restrictions imposed by our phenomenological theory. Rough numerical estimates based on this mechanism explain the observed values of the magnetoelectric effect to within an order of magnitude.

We begin by introducing a fictitious magnetic field $\vec{h}$ which we define by the requirement that the magnetization $\vec{M}$ induced by $\vec{h}$ be identical with that induced by the applied electric field $\vec{E}^a$. Since the quantity $\alpha_{\parallel}/4\pi$, which may be called the "parallel magnetoelectric susceptibility," is defined[3] by $\alpha_{\parallel} = B_z/E_z{}^a$, our definition of $\vec{h}$ leads to

$$\alpha_{\parallel} = 4\pi M_z/E_z{}^a = 4\pi \chi_{\parallel} h_z/E_z{}^a, \qquad (1)$$

where the applied magnetic field $\vec{H}^a$ is assumed to be zero (so that $B_z = 4\pi M_z$) and the parallel antiferromagnetic volume susceptibility is denoted by $\chi_{\parallel}$. If we recall that experimentally M_z is proportional to $E_z{}^a$, and that the magnetoelectric effect vanishes unless the material under consideration possesses an ordered spin arrangement, it seems reasonable to assume that h_z has the form

$$h_z = a_{\parallel} E_z{}^a \langle S_z \rangle_{av}, \qquad (2)$$

where $\langle S_z \rangle_{av}$, which is proportional to the zero-field sublattice magnetization M_0, represents the thermal average of the expectation value of the z component of the ionic spin, and $a_{\parallel}$ is an essentially temperature-independent constant of the material. By combining Eqs. (1) and (2) we obtain

$$\alpha_{\parallel} = 4\pi a_{\parallel} \chi_{\parallel} \langle S_z \rangle_{av}, \qquad (3)$$

and on the basis of analogous arguments we obtain

$$\alpha_{\perp} = 4\pi a_{\perp} \chi_{\perp} \langle S_z \rangle_{av}. \qquad (4)$$

The temperature dependence of $\alpha_{\parallel}$ and $\alpha_{\perp}$ is seen to be determined by $\chi_{\parallel} M_0$ and $\chi_{\perp} M_0$, respectively. If we express these quantities in terms of the equations resulting from the Néel-Van Vleck molecular field theory[5] of a two-sublattice antiferromagnet, we can make the following predictions: As the temperature T increases from $0°K$ to the Néel temperature, T_N, the quantity $\alpha_{\perp}$ should decrease monotonically from some finite value to zero in the manner of the sublattice magnetization; the quantity $\alpha_{\parallel}$, on the other hand, should increase from zero to some maximum value and then return to zero. Both of these qualitative predictions have been verified experimentally.[4] As shown in Fig. 1, even the quantitative agreement between the calculated and measured α's is satisfactory. The existing discrepancies between theory and experiment are no worse in the case of the α measurements (Fig. 1) than in the case of the χ measurements[6] (Fig. 2 of reference 6). In both cases these discrepancies may at least in part be attributed to the fact that a two-sublattice model is not strictly applicable to Cr_2O_3.

According to the above considerations, electric fields should have "tuning" (and other) effects on antiferromagnetic resonance, and these effects should be calculable by simply using our fictitious $\vec{h}$ in place of (or in addition to) the actual $\vec{H}^a$ throughout the usual resonance equations. We also suggest that by applying a strong magnetic field parallel to the antiferromagnetic axis and making use of the Néel "spin-flop" effect,[5] it should be possible to "switch" from a
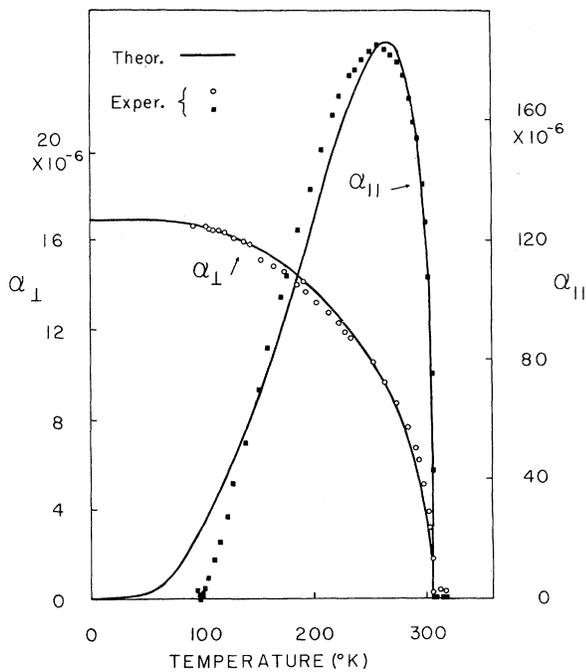
FIG. 1. Comparison of calculated and measured magnetoelectric susceptibilities. The theoretical curves are based on Eqs. (3) and (4) and the following numerical values: $T_N = 360°$K, $\theta (= $ Curie-Weiss constant$) = -0.38 T_N$, $a_{\parallel} = 38.7 \times 10^{-3}$, and $a_{\perp} = 1.32 \times 10^{-3}$. The experimental points are taken from Folen, Rado, and Stalder, reference 4.

measurement of $\alpha_{\parallel}$ to a measurement of $\alpha_{\perp}$.

In attempting to explain the physical origin of the magnetoelectric effect, we think of the electron cloud of each magnetic ion as being distorted by $\vec{E}^a$. As a result of spin-orbit coupling, the spins are "aware" of this distortion and hence they may give rise to an induced magnetization. To construct a specific model, we assume that the unperturbed Hamiltonian consists of a part describing the free ion (say, Cr^{+++}), a part describing that portion of the crystalline electric potential which is an even function of the coordinates, and a part describing the Zeeman energy arising from the exchange field. In a material like Cr_2O_3 the ground state is then non-degenerate. We further assume that the perturbing Hamiltonian is linear in the potential arising from $\vec{E}^a$, linear in the potential arising from the constant part $\vec{E}^C$ of the crystalline field, and quadratic in the spin-orbit energy $\lambda \vec{L} \cdot \vec{S}$. Thus the order of magnitude of the fourth-order energy correction is given by

$$W \approx (e\vec{E}^a \cdot \vec{r})(e\vec{E}^C \cdot \vec{r})(\lambda \vec{L} \cdot \vec{S})^2/(\Delta_1 \Delta_2 \Delta_3), \qquad (5)$$

where Δ_1, Δ_2, Δ_3, are appropriate splittings calculable from the eigenvalues of the unperturbed Hamiltonian. Alternatively, the quantity

$$W = 2 \mu_B \vec{S} \cdot \vec{h} \qquad (6)$$

may be regarded as the Zeeman shift produced by $\vec{h}$. From Eqs. (5) and (6), it follows that $\vec{h}$ is consistent with Eq. (2) provided we take

$$a \approx e^2 E_z{}^c r^2 \lambda^2 L^2 /(2 \mu_B \Delta_1 \Delta_2 \Delta_3) \qquad (7)$$

as an approximate measure of either of the (unequal) quantities $a_{\parallel}$ and $a_{\perp}$. The quantity r^2 denotes z^2 and xz in the parallel and perpendicular cases, respectively, and L^2 denotes $L_z{}^2$ and $L_x L_z$ in these two cases. It should be noted that the α's resulting from the substitution of Eq. (7) into Eqs. (3) and (4) do fulfill the requirement of being invariant with respect to the product of the space inversion and time reversal transformations, while being noninvariant with respect to either of these transformations separately. For a very rough numerical estimate applicable to Cr_2O_3, we use $\Delta_1 \approx \Delta_2 \approx 2 \times 10^4$ cm^{-1}, $\Delta_3 \approx 1.6 \times 10^5$ cm^{-1} (parity considerations), $r \approx 10^{-8}$ cm, $\lambda \approx 10^2$ cm^{-1}, and $eE_z{}^C z \approx 1.7 \times 10^3$ cm^{-1} (point charge calculations based on the structure of αFe_2O_3). The value[7] $a \approx 0.6 \times 10^{-3}$ resulting from Eq. (7) may be consistent with the values $a_{\parallel} = 38.7 \times 10^{-3}$ and $a_{\perp} = 1.32 \times 10^{-3}$ required to fit the experimental curves of $\alpha_{\parallel}$ and $\alpha_{\perp}$ by means of Eqs. (3) and (4). More accurate estimates based on actual calculations of the relevant matrix elements are under way.

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[1]D. N. Astrov, J. Exptl. Theoret. Phys. (U.S.S.R.) 38, 984 (1960) [translation: Soviet Phys.-JETP 11, 708 (1960)].

[2]L. D. Landau and E. M. Lifshitz, Electrodynamics of Continuous Media (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1960), p. 119. (English translation of a 1958 Russian Edition.)

[3]I. E. Dzyaloshinskii, J. Exptl. Theoret. Phys. (U.S.S.R.) 37, 881 (1959) [translation: Soviet Phys.-JETP 10, 628 (1960)].

[4]V. J. Folen, G. T. Rado, and E. W. Stalder, preceding Letter [Phys. Rev. Letters 6, 607 (1961)].

[5]See, for example, T. Nagamiya, K. Yosida, and R. Kubo, Advances in Phys. 4, 1 (1955), paragraph 4.

[6]T. R. McGuire, E. J. Scott, and F. H. Grannis, Phys. Rev. 102, 1000 (1956).

[7]Both a and α are dimensionless in the Gaussian units used in the present paper.