

Table I. Values of α , A , α' , and A' for the expressions $C_\nu = A\epsilon^{-\alpha} + B$ and $C_\nu = (A'/\alpha')(\epsilon^{-\alpha} - 1) + B'$.

$T > T_c$	Eq. (1)	$T < T_c$
$\alpha = 0.13 \pm 0.01$	$\alpha = 0.125$	$\alpha' = -0.01 \pm 0.01$
$A = (1.09 \pm 0.09)R$	$A = 1.103R$	$A' = (0.53 \pm 0.04)R$

the values of A and A' depend on the normalization of C_p to Moser's data, but the error involved in this normalization is much less than the standard deviation of the least-squares fit). A comparison of the α 's and of the A 's shows that the experimental data for $T > T_c$ agree extremely well with the predictions of Eq. (1). That is, not only α but also A serves as a basis of comparison between theory and experiment. Since our data display a positive α , renormalization with its characteristic nonpositive α ¹¹ cannot apply for $T > T_c$ and $\epsilon \geq 10^{-5}$. Column 3 of Table I indicates that $\alpha' \approx 0$, so that $C_\nu \approx -A' \ln \epsilon + B'$ provides a good representation of our data for $T < T_c$. The good agreement between theory and the experimental results above T_c suggests that the experimental data below T_c are also Ising-like. Thus, when firmly established, the Ising model results below T_c should be close to logarithmic in ϵ , at least over the range $2 \times 10^{-5} \leq \epsilon \leq 2 \times 10^{-2}$.

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MAGNETOELECTRIC EVIDENCE FOR THE ATTAINABILITY OF TIME-REVERSED ANTIFERROMAGNETIC CONFIGURATIONS BY METAMAGNETIC TRANSITIONS IN DyPO₄

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The experimental observation and an atomic mechanism of the linear magnetoelectric effect in DyPO₄ are reported and shown to provide evidence for the feasibility of isothermal forced switching between time-reversed (i.e., moment-reversed) antiferromagnetic configurations by means of metamagnetic transitions.

This Letter reports the observation of the linear magnetoelectric (ME) effect in DyPO₄, an antiferromagnet in which the application of a static magnetic field H along the antiferromagnetic axis causes a metamagnetic (i.e., relative-

ly abrupt) transition of the ionic magnetic moments from an initially antiparallel configuration A_i to a parallel configuration. It should be noted that this is the first study of the influence of metamagnetic transitions on the magnetoelectric

effect. Also reported in this Letter is a new quantum mechanical mechanism of the ME effect and its application to DyPO₄. These results make it possible to answer an important and previously overlooked question: "What is the relation between A_f and that antiparallel configuration A_f which finally prevails after the removal of H?" Our ME evidence leads not only to the answer which could have been anticipated (at least if the crystal contains only a single antiferromagnetic domain), that A_f is identical either with A_i or with its time-reversed, i.e., moment-reversed modification A_i', but also to the more interesting answer (which applies irrespective of the existence of domain structure) that the choice between A_f=A_i and A_f=A_i' is governed solely by the sign of H. The feasibility of forced switching between the two energetically degenerate configurations of the ionic moments, which we demonstrate experimentally by simply reversing the H used in the metamagnetic transition, may offer new approaches for studies of spontaneous sublattice reversals and other basic aspects of antiferromagnetism. We wish to point out, moreover, that the switching method reported in this Letter is potentially applicable to an isothermal storage and retrieval of information in materials (such as DyPO₄, but having a higher Néel temperature T_N) which are both metamagnetic and magnetoelectric.

High-resolution optical spectroscopy observations have shown¹ that DyPO₄ [space group D_{4h}¹⁹ (I4/amd)] is an Ising-like two-sublattice antiferromagnet, with T_N = 3.50 ± 0.08°K, in which the moments of the Dy³⁺ ions are coaxial with the tetragonal c axis. The moments located at the sites in the center and corners of the unit cell are oppositely oriented to the moments located at the inversion-related sites on the faces of the unit cell.¹ These facts lead us to conclude that the magnetic point group of a DyPO₄ crystal at temperatures below T_N is 4'/m'mm', where the prime denotes the time-reversal transformation. Symmetry considerations show that this group allows a linear ME effect and that

$$F = -\alpha(E_x H_x - E_y H_y) \tag{1}$$

is the ME contribution to the free-energy density. The Cartesian axes x, y, z are parallel, respectively, to the tetragonal axes a, a', c of the crystal, and

$$\begin{pmatrix} \alpha & 0 & 0 \\ 0 & -\alpha & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{2}$$

is the matrix of the ME susceptibility tensor $\vec{\alpha}$ in the x, y, z coordinate system.

Using primarily the magnetically induced² ME effect ($\alpha = P_x/H_x$), we measured α at 1 kHz as a function of the temperature T on an x-ray-oriented single crystal of DyPO₄. The dimensions of the crystal along x, y, z are 0.80, 1.0, and 2.8 mm, respectively. It was found that the value of $|\alpha|$ (which is dimensionless in Gaussian units) decreases monotonically with increasing T from roughly 2×10^{-4} at T = 1.5°K to zero at T = T_N ≈ 3.38°K. More revealing, however, is the influence on α of a static magnetic field H_c applied along the c axis, i.e., along the axis of antiferromagnetism. The experimental results, presented in Fig. 1, show that repeated variation of H_c according to the sequence 0 → +14 kOe → 0 → -14 kOe → 0 causes α to traverse the path a → b → c → d → a. Thus α changes its sign after passing through zero at b and d. However, α does not change its sign if H_c is varied according to the sequence 0 → -14 kOe → 0, causing α to follow the path a → d → a, or if H_c is varied according to the sequence 0 → +14 kOe → 0, causing α to follow the path c → b

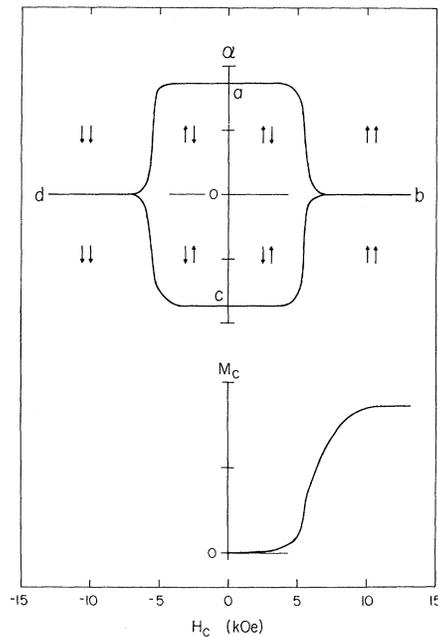


FIG. 1. Upper curve: Measured dependence of the magnetoelectric susceptibility α (in arbitrary units) on the static magnetic field H_c (uncorrected for demagnetization) applied along the c axis of a DyPO₄ crystal. At the temperatures used ($1.5^\circ\text{K} \leq T \leq 1.6^\circ\text{K}$), α is essentially independent of T. The meaning of a, b, c, d and of the arrows is explained in the text. Lower curve: Measured dependence of the static magnetization M_c (in arbitrary units) on H_c in the same crystal in the same temperature range.

- *c*. Hence we have the remarkable result that the relative sign of α is determined solely by the sign of that H_c which caused the most recent metamagnetic transition prior to the measurement of α .

According to the atomic mechanism proposed below, the observed changes in the sign of α are due to reversals of all the sublattice moments. These reversals, shown in Fig. 1 by the arrows depicting the sublattices of the inferred magnetic structures, have been deduced from the present experiment and theory. Perhaps these reversals may be made plausible by supposing, on the basis of symmetry, that the antiparallel configuration nucleated after the removal of $+H_c$ should be just the time-reversed modification of that nucleated after the removal of $-H_c$.

Figure 1 also shows that the decrease of $|\alpha|$ to zero occurs for values of H_c corresponding to the steepest portion of the magnetization curve. The fact that this decrease is much more abrupt than the rise of M_c undoubtedly reflects the discontinuous nature of the change in magnetic symmetry (from $4'/m'mm'$ to $4/mm'm'$) upon parallel alignment of the moments by H_c . Although the optical studies¹ did detect such an alignment, detailed evidence for its metamagnetic³ nature is supplied by the present M_c measurements which were performed by means of a ballistic method. We find, moreover, that full alignment of the moments (i.e., the use of a sufficiently large $|H_c|$) is a necessary condition for reversals of the sign of α . In the case of Fig. 1, for example, $|H_c| = 10.3$ kOe does suffice for reversals whereas $|H_c| = 9.8$ kOe does not, even though in the latter field the value of M_c is at most 2% below saturation. Repeated cycling of H_c between +14 and -14 kOe causes the hysteresis in α as well as in M_c to become negligibly small, and the ME data suggest that this sample is probably a single antiferromagnetic domain after this treatment. Heating the sample to 300°K (rather than merely to 4.2°K) causes its memory of the sign of α to be completely erased.

In constructing an atomic mechanism of the ME effect in DyPO_4 , we find it convenient to use a Cartesian coordinate system ξ, η, ζ which is related to the x, y, z system by a $\frac{1}{4}\pi$ rotation about the $\zeta \equiv z$ axis. Thus we replace Eq. (1) by

$$F = -\alpha(E_\xi H_\eta + E_\eta H_\xi) \quad (3)$$

and the matrix (2) by

$$\begin{pmatrix} 0 & \alpha & 0 \\ \alpha & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (4)$$

We assume that the unperturbed Hamiltonian \mathcal{H}_0 contains contributions describing the free Dy^{3+} ion (including spin-orbit coupling), the even part of the crystalline potential energy, and the (axial) exchange and dipolar interactions. Because of the three latter contributions, the $J = \frac{15}{2}$ manifold of the ${}^6H_{15/2}$ ground state of the free Dy^{3+} ion is decomposed into eight exchange- and dipole-split Kramers doublets which are not pure m_J states. The ground doublet, for example, is expected to contain not only $m_J = \pm \frac{15}{2}$ but also admixtures of $m_J = \pm \frac{7}{2}$, $\mp \frac{1}{2}$, and $\mp \frac{9}{2}$ due to the tetragonal potential as well as admixtures due to that part of the exchange interaction which is nondiagonal in the low-lying crystal field states. Now we calculate the value of F at 0°K by considering the combined action of three perturbations, namely the odd part $eV^{(u)}$ of the crystalline potential energy, the interaction $-e\vec{E} \cdot \vec{r}$ with the applied electric field, and the Zeeman energy $\mu_B(\vec{L} + 2\vec{S}) \cdot \vec{H}$ due to the applied magnetic field. Comparison of the resulting expression with Eq. (3) yields

$$\alpha = \frac{4e^2\mu_B}{v} \times \sum_{k,l} \frac{\langle 0|V^{(u)}|l\rangle\langle l|\xi|k\rangle\langle k|L_\eta + 2S_\eta|0\rangle}{(W_k - W_0)(W_l - W_0)}, \quad (5)$$

where the W 's are appropriate eigenvalues of \mathcal{H}_0 and the factor 4 denotes the number of Dy^{3+} ions in the unit cell of volume $v = a^2c$. In a detailed calculation we would replace the \vec{H} in the Zeeman energy by an effective magnetic field⁴ (which contains contributions due to the exchange and dipolar fields produced by the induced magnetization) and subtract from F a self-energy term⁴ to avoid double counting of the interactions between ions. The two sublattices are related to each other by the product of space inversion and time reversal and thus contribute equally to Eqs. (3) and (5). Upon parallel alignment of the sublattices (e.g., in a metamagnetic transition) the magnetic point group of the crystal becomes $4/mm'm'$ so that Eqs. (3) and (5) become invalid. In fact, the $4/mm'm'$ symmetry requires the vanishing of all components of $\vec{\alpha}$ irrespective of microscopic considerations. It should also be noted that the pres-

ent ME mechanism involves essentially the change due to \vec{E} of the spectroscopic splitting factor in a magnetically ordered material containing rare-earth ions. This change is given by a fourth-order process⁵ in the case of Cr_2O_3 but by a third-order process [Eqs. (3) and (5)] in the case of DyPO_4 .

Next we estimate the order of magnitude of $|\alpha|$. We use a point charge model and the site symmetry $\bar{4}2m$ to express $V^{(u)}$ by the third-order term

$$V^{(u)} = 15\xi\eta\zeta \sum_n (Q_n u_n v_n w_n / R_n^7), \quad (6)$$

where $\vec{r} = \vec{i}\xi + \vec{j}\eta + \vec{k}\zeta$ and $\vec{R}_n = \vec{i}u_n + \vec{j}v_n + \vec{k}w_n$ denote, respectively, the position of a $4f$ electron and of a neighboring ion (having charge Q_n) with respect to the nucleus of a central Dy^{3+} ion. The unit vectors $\vec{i}, \vec{j}, \vec{k}$ are parallel to the coordinate axes ξ, η, ζ , respectively. We approximate the $(\text{PO}_4)^{3-}$ complexes by charges $-3|e|$ located at the P^{5+} nuclei and neglect the (unknown) shielding of the $4f$ electrons of Dy^{3+} . Using $\xi \approx \eta \approx \zeta \approx 1 \text{ \AA}$ and the lattice parameters⁶ $a = 6.917 \text{ \AA}$ and $c = 6.053 \text{ \AA}$, we thus obtain $|eV^{(u)}| \approx 3.5 \times 10^4 \text{ cm}^{-1}$ after summing over four neighboring Dy^{3+} ions and four neighboring $(\text{PO}_4)^{3-}$ complexes. For $W_J - W_0$, which is the (unknown) separation between the ground level W_0 and a level W_J of opposite parity, we assume the value 10^5 cm^{-1} , while for $W_k - W_0$, which may be taken as the splitting of the lowest-lying Kramers doublet, we use the measured¹ value 3.60 cm^{-1} . The matrix element $\langle k | L_\eta + 2S_\eta | 0 \rangle$ equals $\frac{1}{2}s_\perp$, where s_\perp is the effective transverse spectroscopic splitting factor for a fictitious spin of $\frac{1}{2}$ and was measured¹ to be 0.51. Also required is the product ν of the admixture coefficients of certain states into the states $\langle 0 |$ and $|k \rangle$. Using $g_J = \frac{4}{3}$ and $J = \frac{15}{2}$ in $\nu = s_\perp g_J^{-1} (J + \frac{1}{2})^{-1}$, we obtain $\nu = 4.8 \times 10^{-2}$. The final result of our estimate is $|\alpha| \approx 4 \times 10^{-3}$, which may be compared with the measured $|\alpha| \approx 2 \times 10^{-4}$. While this theoretical estimate is necessarily

very approximate, it does indicate that the mechanism proposed here is probably significant in DyPO_4 .

We have also investigated the consequences of augmenting Eq. (5) by a perturbation involving that part of the axial exchange interaction which is nondiagonal in the crystal-field states. Although the value of $|\alpha|$ resulting from this fourth-order process does depend on spectroscopic data which are presently unavailable, it is probable that this value is about two orders of magnitude smaller than that resulting from our third-order process.

Additional work on DyPO_4 and on isostructural compounds⁶ is under way and will be reported at a later date.

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