Magnetoelectric Effect and Metamagnetic Transitions in $DyAlO_3$

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The magnetoelectric (ME) effect has been studied as a function of applied magnetic field ($\vec{H}$) in a crystal of metamagnetic $DyAlO_3$. The ME signal at a frequency of 150 Hz was measured along the [001] direction of the orthorhombic unit cell at temperature $T = (1.45 \pm 0.05)$ °K. Two types of metamagnetic transitions were studied. The first involved a reversal on a single magnetic sublattice in $\vec{H} \parallel [110]$, while the second involved the simultaneous reversal of two of the four magnetic sublattices in $\vec{H} \parallel [010]$. The ME signal decreased abruptly at the critical fields (≈ 6 kOe) for metamagnetic transitions, as determined from magnetization measurements on the same sample. In agreement with simple physical arguments, the ME susceptibility was found approximately to scale with the number of antiferromagnetic spins in the material. The experimental data were compared to theoretical curves and the results were discussed in terms of magnetic point symmetries.

I. INTRODUCTION

Magnetic fields may induce transitions involving changes of symmetry in magnetic materials, which can have profound effects on the magnetoelectric (ME) susceptibility. This was first observed experimentally in an investigation[1] of "spin flop" in antiferromagnetic Cr_2O_3. More recently, the influence on the ME susceptibility of metamagnetic transitions in Ising-like (i.e., high-anisotropy) systems has been studied by Rado[2] in $DyPO_4$ and by Mercier and Bauer[3] in $TbAlO_3$. The latter investigation was confined to temperatures (T) close to the Néel point T_N.

In the present work, we have studied the effects of metamagnetic transitions[4,5] on the ME susceptibility in antiferromagnetic $DyAlO_3$. The metamagnetic behavior in this compound is unusual, in that the four magnetic sublattices may be reversed singly or in pairs, depending on the direction of the applied magnetic field. The existence of an ME effect in $DyAlO_3$ was demonstrated experimentally by Mercier and Bauer[3] in polycrystalline material. In this laboratory, the ME susceptibility was measured[6] previously as a function of temperature in a single crystal of $DyAlO_3$, with careful attention given to the critical region close to T_N.

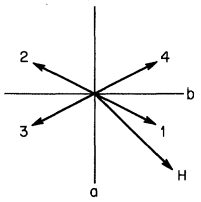
II. CRYSTAL STRUCTURE AND MAGNETIC BEHAVIOR

The crystal structure[7–9] of $DyAlO_3$ is orthorhombic and belongs to the space group D_{2h}^{16}-$Pbnm$. The lattice parameters[8] are given by $a = 5.21_5$ Å, $b = 5.31_1$ Å, and $c = 7.40_7$ Å. The unit cell contains four Dy^{3+} ions, which are located on mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The point symmetry at the rare-earth sites is monoclinic C_{1h} and the Dy^{3+} ground state $^6H_{15/2}$ is therefore split by the crystal field in a series of eight Kramers doublets. Only the lowest doublet is thermally populated at $T < 4$ °K, and that doublet is magnetically very anisotropic.[4]

At low temperatures, the magnetic moments at the Dy^{3+} sites are confined to particular directions in the mirror planes.[4,5,9] The material behaves as an Ising-like antiferromagnet, with a Néel temperature $T_N = (3.52 \pm 0.01)$ °K according to a measurement[10] of the specific heat. At $T < T_N$, the magnetic space group[9] is $Pb'n'm'$, and the antiferromagnetic structure[9] is of the type G_xA_y, which may be pictured in terms of a four-sublattice model (Fig. 1). The angle[4,9] between the sublattice magnetization and the b axis of the crystal is fixed by the crystal field at $33° \pm 2°$ for each of the four sublattices (Fig. 1). Consistent with the Ising approximation, this angle is independent of temperature[9] at $T < T_N$ and of magnetic fields[4,5] in $H \leq 60$ kOe.

Metamagnetic behavior[4,5] may occur in $DyAlO_3$ for magnetic fields applied in the mirror planes (i.e., $\vec{H} \perp [001]$). In a metamagnetic transition,[11] the material transforms in high magnetic fields to a state which minimizes the Zeeman energy at the expense of magnetic dipolar and exchange interactions. The transition involves an abrupt reversal of the magnetization on one or more of the magnetic sublattices, so as to produce an increase in the magnetization parallel to $\vec{H}$. This behavior has been observed in measurements[5] of the bulk magnetization at 1.45 °K in $DyAlO_3$. Prior to the magnetization measurements, anomalies due to the metamagnetic transitions were observed[4] in the optical Zeeman pattern at 1.2 °K. In both of these studies, it was observed that the metamagnetic behavior differed (see below) for different directions of $\vec{H}$ relative to the crystallographic axes. No transitions were seen in magnetic fields along the c axis ($\vec{H} \parallel [001]$).

Three types of metamagnetic transitions which have been investigated in $DyAlO_3$ are listed in Fig. 1, together with the critical fields H_c at which the



ALIGNMENT	TRANSITION	CRITICAL FIELD
$H \parallel [100]$	$1234 \rightarrow 1\bar{2}3\bar{4}$ $\alpha \rightarrow 0$	11.3 ± 0.5 kOe
$H \parallel [010]$	$1234 \rightarrow 1\bar{2}\bar{3}4$ $\alpha \rightarrow 0$	6.0 ± 0.1
$H \parallel [110]$	$1234 \rightarrow 1\bar{2}34 \rightarrow 1\bar{2}\bar{3}4$ $\alpha \rightarrow \alpha/2(?) \rightarrow 0$	6.25 ± 0.10, ≈24

FIG. 1. Four-sublattice model of the magnetic structure (Ref. 9) in $DyAlO_3$ and description of the metamagnetic behavior (Refs. 4 and 5) for magnetic fields $\vec{H}$ applied in the (001) plane. The four vectors describing the magnetization on the sublattices make a constant angle of 33° ± 2° with the b axis of the crystal (Ref. 9).

transitions were observed[5] to occur (at $T = 1.45\,^{\circ}$K). In an obvious notation, we denote the antiferromagnetic arrangement of the four sublattices by the symbol 1234 and put a bar over the label of the sublattice which reverses at H_c. For $\vec{H} \parallel [100]$ or $\vec{H} \parallel [010]$, two sublattices reverse at H_c (Fig. 1) to give a net magnetization parallel to $\vec{H}$. For $\vec{H} \parallel [110]$, however, the transition proceeds in two steps. The low-field step produces a reversal on sublattice 2 only at $H_c = (6.25 \pm 0.10)$ kOe.[5] This leaves sublattices 3 and 4 in an antiferromagnetic arrangement ($1\bar{2}34$) which persists in magnetic fields up to ≈ 24 kOe. The high-field step causes sublattice 3 to reverse in $H \gtrsim 24$ kOe, which gives rise to the state $1\bar{2}\bar{3}4$ with a net magnetization parallel to the b axis.[5] This state has the maximum possible component of magnetization along [110] in this structure, and, therefore, it is the state which minimizes the Zeeman energy for $\vec{H} \parallel [110]$.

The metamagnetic behavior in $DyAlO_3$ may be understood in terms of two interpenetrating collinear antiferromagnets A and B, comprising magnetic sublattices 1, 2 and 3, 4, respectively. Sublattices 2 and 3 may be reversed in separate steps when $\vec{H}$ is applied along the [110] direction, because $\vec{H}$ is then more closely aligned (Fig. 1) with A (sublattices 1 and 2) than with B (sublattices 3 and 4). The exchange and magnetic dipolar interactions[4,5] within A (or within B) are much stronger than the interactions between A and B. The total effective field on an ion in the antiferromagnetic state at $T \ll T_N$ is ~ 10 kOe, of which only 1–2 kOe come from the A-B interactions.[4,5] The A and B sublattices behave independently, therefore, in a zeroth-order approximation, and this is why it is possible to reverse one of the A sublattices in $\vec{H} \parallel [110]$, while leaving the B sublattices relatively undisturbed.

III. MAGNETOELECTRIC CONSIDERATIONS

In a material which exhibits the linear ME effect,[12] an applied electric field E induces a magnetization M which is proportional to E, and an applied magnetic field H induces an electric polarization P which is proportional to H. Because the ME effect depends sensitively on symmetry, its measurement provides a powerful tool for investigating magnetic phase transitions. We have studied the [001] component P of the magnetically induced electric polarization in $DyAlO_3$ as it varies through the metamagnetic transitions in the material.

In terms of the quantities P, H, M, and E, which are defined in the previous paragraph, the ME susceptibility may be written $(\alpha/4\pi) = P/H$ or, equivalently, $(\alpha/4\pi) = M/E$. If $(\alpha/4\pi) \sim 10^{-3}$ Gaussian units, as in $DyAlO_3$,[3] then one may show that an electric field $E = 10^4$ V/cm induces a magnetization $4\pi M \sim 0.4$ G, or that a magnetic field $H = 10^4$ Oe induces an electric polarization $4\pi P \sim 4 \times 10^{-8}$ C/cm^2. Thus, the ME effect is small, but measurable.

The expected changes in the ME signal in $DyAlO_3$ due to the metamagnetic transitions may be derived from heuristic arguments based on the symmetry of the material. In the magnetic space group $Pb'n'm'$ of the antiferromagnetic crystal, an anti-inversion transformation $\bar{1}'$ interchanges antiparallel spins on sublattices 1 and 2 in Fig. 1. (An anti-inversion transformation is spatial inversion followed by time reversal—i.e., reversal of all spin directions.) A similar transformation interchanges spins on sublattices 3 and 4. The ME tensor[13] reverses sign under spatial inversion and it also reverses sign under time reversal. Hence, the $\bar{1}'$ operation is consistent with a nonvanishing ME effect. On the other hand, when the spins on sublattices 1 and 2 are aligned in the same direction (in high magnetic fields), then the spins on the two sublattices are connected by spatial inversion $\bar{1}$, in which case the ME tensor must vanish for the two sublattices. It may be seen, therefore, that reversing the spins on one of the sublattices in $DyAlO_3$ has the effect of reducing the number of spins that contribute to the ME effect by 50%. (These arguments are not exact, however, because magnetostrictive strains will tend to destroy the inversion and anti-inversion symmetries in the intermediate state ($1\bar{2}34$). This should be a higher-order effect, as far as the ME susceptibilities are concerned, and it will not be considered further.) Reversing the spins on two of the sublattices (i.e., on sublattices 2 and 3 or on 2 and 4 in Fig. 1) results in a 100% reduction in the number of spins that contribute, and the ME effect must therefore

vanish.

More formally, it may be shown that the orthorhombic point group $m'm'm'$ in antiferromagnetic $DyAlO_3$ is reduced to the monoclinic subgroup m' by reversing the spins on sublattice 2. If the spins on sublattice 3 (or on sublattice 4) are also reversed, then the magnetic point group becomes $mm'm'$, for which the ME effect is forbidden by symmetry. The ME tensor[13] is diagonal in the orthorhombic point group $m'm'm'$ and it contains three diagonal terms as well as two off-diagonal terms in the monoclinic point group m'. The off-diagonal terms connect only those directions perpendicular to the c axis, and so a magnetic field perpendicular to c does not induce an ME polarization parallel to c.

As described in Ref. 6, the ME susceptibility along the c axis in $DyAlO_3$ may arise from single-ion effects[2,14] and from two-ion effects.[2,6] It is likely by analogy with[2,14] $DyPO_4$ that the single-ion terms dominate. In the single-ion case, the ME susceptibility α would be expected to scale with the number of antiferromagnetic spins. Thus, a 50% reduction in the ME signal along the c axis would be expected on reversing sublattice 2 in Fig. 1. Concerning the two-ion effects, it may be recalled from Sec. II that the A-B interactions in $DyAlO_3$ may be as little as 10% of the A-A interactions. Under these conditions, a reversal on sublattice 2 leads to relatively minor changes in the interaction fields for ions on sublattices 3 and 4. These are the sublattices that contribute to the ME susceptibility in the intermediate state ($1\bar{2}34$). Thus, a reduction of ~50% in α on reversing sublattice 2 might be anticipated on the basis of the two-ion model, as well. The qualitative arguments in this section have been summarized in Fig. 1, where we list the changes in α, as hypothesized above, due to the metamagnetic transitions in $DyAlO_3$.

IV. EXPERIMENT

Crystals of $DyAlO_3$ were grown from a PbO-PbF_2-B_2O_3 flux, and a c platelet which was free of flux inclusions was selected for use in this experiment. The platelet was ground to a thickness of 0.6 mm, and cut to a rectangular shape 0.39 cm $\times$0.16 cm. The long side of the rectangle was parallel to [110]. The same sample was used in the magnetization measurements[5] on $DyAlO_3$.

The ME signal was derived from a sensitive charge amplifier operating at a frequency of 150 Hz. The input to the charge amplifier was connected to silver-paste electrodes on the (001) faces of the sample (Fig. 2). The signal was therefore proportional to the [001] component of the electric polarization in the material.

The sample was mounted in a static magnetic field H_{dc} of up to 11 kOe for the ME measurements.

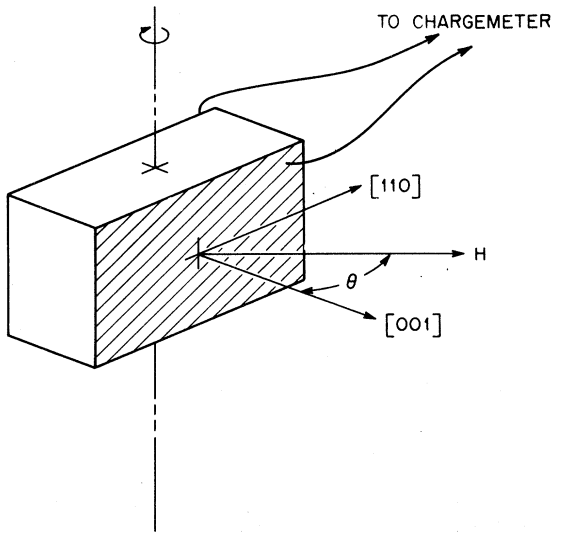


FIG. 2. Experimental arrangement for studying the effect of metamagnetic transitions on the ME signal in $DyAlO_3$. The orientation of the crystal is appropriate to the experiment described in Fig. 4 below.

Modulation coils were driven with an ac signal to produce an alternating magnetic field H_{ac} which was parallel to H_{dc}, and which induced the alternating electric polarization in the material. The amplitude of H_{ac} at 150 Hz was about 10 Oe peak to peak.

The data were obtained by a simple nulling technique. A small pickup coil provided a reference signal proportional to H_{ac}. The reference signal was attenuated and added to or subtracted from the ME signal to produce a null. The attenuation was recorded with a plus or minus sign, depending on whether addition or subtraction produced the null. The phase shifted somewhat through the transition regions, but this phase information was not recorded, and, therefore, the present experiments do not give information on possible dissipative behavior.

The measurements were carried out with the sample mounted directly in pumped liquid helium at a temperature of (1.45 ± 0.05) °K. The sample was cooled through T_N in biasing fields (H_{dc} = 200 Oe and E_{dc} = 10 statvolts/cm) parallel to [001] to ensure the formation of a single ME domain. The electric field was maintained throughout the experiment. The maximum signal at 1.4 °K corresponded to an ME susceptibility along [001] of $P/H \approx 1.5\times10^{-3}$ Gaussian units.

The sample could be rotated relative to the total magnetic field, $H = H_{dc} + H_{ac}$, as shown in Fig. 2. The axis of rotation was estimated to be within 5° of normal to H. The data were recorded as a function of the angle θ between H and the c axis of the crystal. The results have been plotted in Sec. V

in the form of normalized curves $\alpha(\theta)/\alpha(0)$ vs θ, in which $\alpha(\theta)$ is the ME signal at angle θ, and $\alpha(0)$ is the ME signal at $\theta = 0$, at the start of the experiments at $T = 1.45\,^{\circ}\mathrm{K}$. Metamagnetic behavior could be studied by applying a large H_{dc} and rotating the crystal until the magnetic field in the (001) plane, $H\sin\theta$, reached the critical value, as listed in Fig. 1. With a maximum available H_{dc} of 11 kOe, it was apparent from the data in Fig. 1 that the two transitions with $H_c \approx 6$ kOe could be investigated.

To study the transition $1234 \rightarrow 1\bar{2}\bar{3}4$, the sample was mounted with the [100] direction along the axis of rotation. The [010] direction could then be rotated into the direction of H to induce the metamagnetic transition. In the absence of metamagnetic behavior, it was expected that the ME signal would be proportional to the component $H_{ac}\cos\theta$ of the ac drive field along [001]. Thus, an angular dependence of the form $\alpha(\theta)/\alpha(0) = \cos\theta$, could be anticipated under these conditions. For large values of H_{dc}, $\alpha(\theta)$ was expected to decrease to zero at angles greater than θ_c^{I}, as given by

$$H_{dc}\sin\theta_c^{\mathrm{I}} = (6.0 \pm 0.1)\ \text{kOe}\ ,$$

where (6.0 ± 0.1) kOe is the critical field (Fig. 1) for $H \parallel [010]$.

To study the transition $1234 \rightarrow 1\bar{2}34$ the sample was mounted as shown in Fig. 2, so that the [110] direction could be rotated into H. In this case, $\alpha(\theta)/\alpha(0)$ may be expected to decrease by ~50% (cf. Sec. III) at angles greater than θ_c^{II}, as given by

$$H_{dc}\sin\theta_c^{\mathrm{II}} = (6.25 \pm 0.10)\ \text{kOe}\ .$$

The signal may be expected to vary, therefore, from $\alpha(\theta)/\alpha(0) = \cos\theta$, at low angles, to $\alpha(\theta)/\alpha(0) = k\cos\theta$, with $k \approx 0.5$, at higher angles.

V. RESULTS

A. Rotation into [010]

The experimental results obtained with [100] along the axis of rotation are given in Fig. 3. The x-shaped points were taken in $H_{dc} = 200$ Oe, well below the critical fields for metamagnetic transitions in $DyAlO_3$. These data display the expected $\cos\theta$ dependence on angle, as given by the dot-dashed curve. The points shown as circles were taken in $H_{dc} = 10$ kOe, corresponding to a critical angle $\theta_c^{\mathrm{I}} = 37^{\circ}$. The data follow $\cos\theta$ at low angles and decrease rapidly at θ_c^{I}, as expected. For comparison with the ME data, the solid curve No. 1 gives the magnetization in $DyAlO_3$, as calculated from the data in Ref. 5, for a magnetic field $H_{dc}\sin\theta$ along [010]. The magnetization is shown normalized to the measured magnetization along [010] in an applied field of 14.5 kOe, which was close to saturation.[5] The magnetization increases rapidly at angles between θ_c^{I} and ~50°, and it may be seen that the apparent ME susceptibility reverses sign in this transition region. (A reversal in sign of the ME signal had also been observed in Ref. 1, for values of H_{dc} close to the critical field for "spin flop" in antiferromagnetic Cr_2O_3.) At higher angles, $\theta \gtrsim 60^{\circ}$, the ME signal drops to zero, as required by symmetry (cf. Sec. III). The sign reversal in the

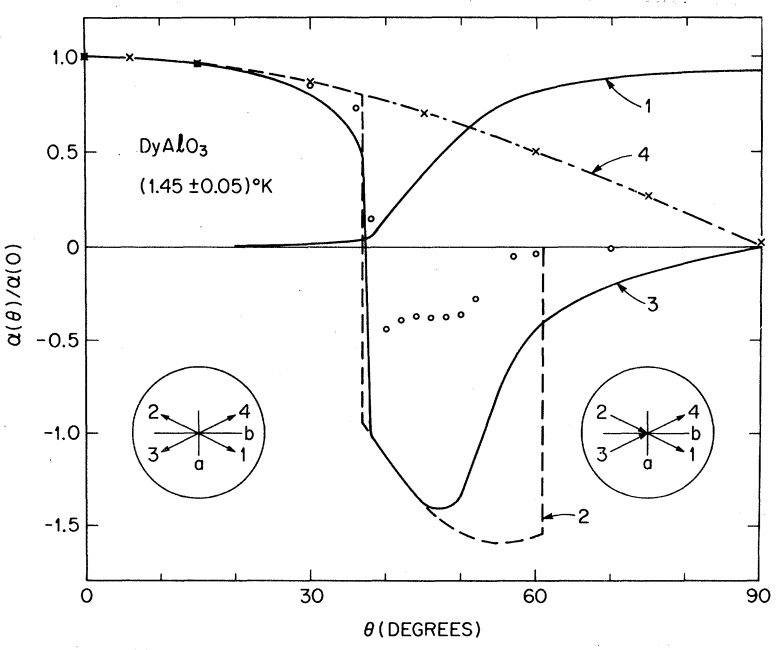


FIG. 3. ME data for rotation into the [010] direction in $DyAlO_3$. The x-shaped points are for $H_{dc} = 200$ Oe. The circular points are for $H_{dc} = 10$ kOe. The insets show the arrangement of the four magnetic sublattices at low θ and at high θ in $H_{dc} = 10$ kOe. The solid curve No. 1 is the normalized magnetization calculated from the data in Ref. 5. The dot-dashed curve No. 4 is $\cos\theta$. A description of theoretical curves Nos. 2 and 3 is given in the text.

transition region is attributable to the experimental configuration, which puts a component of the ac magnetic field in the (001) plane, as well as along the c axis. This will be described in detail in Sec. VI, where the theoretical curves Nos. 2 and 3 are derived.

On rotating the crystal back to $\theta = 0°$, it was observed that $\alpha(0)$ did not return to its original value. The data obtained for decreasing θ did exhibit an angular dependence (not shown) which was qualitatively similar to that of the circular points in Fig. 3. It was also observed that the algebraic sign of $\alpha(0)$ could be reversed by reversing H_{dc} at $\theta = 90°$ prior to rotating the crystal back to $\theta = 0°$. These results would appear to reflect changes in the ME domain structure at $\theta = 0°$, depending on the past history of the sample (cf. Sec. VII). It is reasonable also to suppose that the ME domain structure varies through the transition region, so that a detailed comparison with theory is not meaningful in that region.

B. Rotation into [110]

The data in Fig. 4 were obtained with the sample oriented as in Fig. 2, so as to rotate the [110] direction into $\vec{H}$. A dc magnetic field was applied, of magnitude $H_{dc} = 10$ kOe, corresponding to a critical angle $\theta_c^{II} = 39°$. Curve No. 1 gives the derived magnetization,[5] normalized to the value at 14.5 kOe, for a magnetic field $H_{dc}\sin\theta$ along [110]. The experimental ME points vary as $\cos\theta$ at low angles, and decrease rapidly near θ_c^{II}, as expected. The transition region, in which the ME signal reverses sign, is more narrow here than in Fig. 3, the demagnetizing fields being smaller along the long dimension of the specimen. The points cross the abscissa again at the upper end of the transition region, near $\theta = 50°$, and come close to $\frac{1}{2}\cos\theta$ (the dashed curve) at higher angles.

The ME data were reproducible in Fig. 4, the same curve being obtained for increasing θ (circular points) and for decreasing θ (x-shaped points). This would indicate that the assumed single ME domain structure at $\theta = 0°$ was "remembered" during the circle from $\theta = 0°$ to 90° to 0°. This is perhaps not too surprising, in view of the fact that the spins on sublattices 3 and 4 are still antiferromagnetically aligned in $H_{dc} = 10$ kOe along [110]. It does indicate that the data at each θ setting are representative of an unique state of the crystal. Under these conditions, a detailed comparison with theory becomes more meaningful.

VI. INTERPRETATION

In this section we will present a simple interpretation of the data, which gives rise to the calculated curves, Nos. 2 and 3, in Figs. 3 and 4. These curves relate the observed signal to the ME susceptibility along [001] in $DyAlO_3$, and to the magnetization curves No. 1 in Figs. 3 and 4. The theory correctly describes the sign reversals in the measured signal. With the exception of the transition region in Fig. 3, where the data were observed not to be reproducible, the shape and magnitude of the calculated curves are in reasonable agreement with experiment.

In a metamagnetic transition in $DyAlO_3$, the ME susceptibility changes from some value, say a_0, at

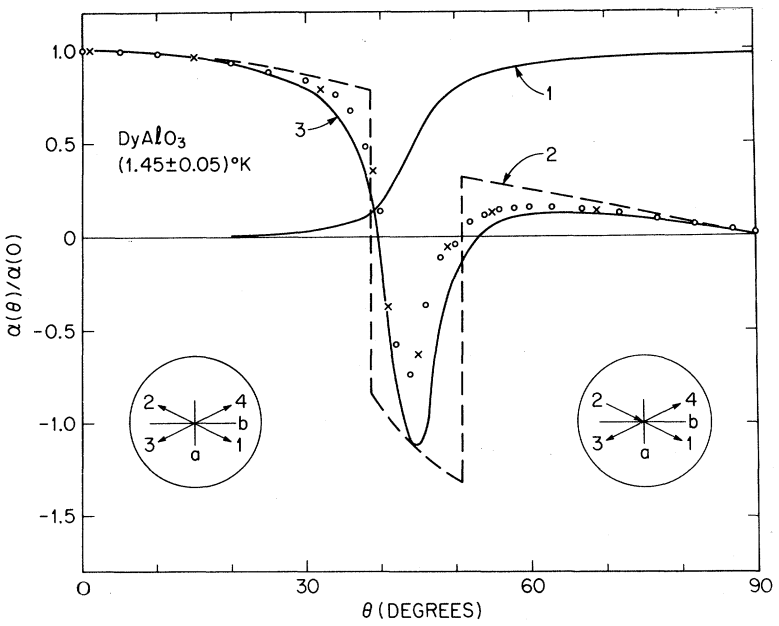


FIG. 4. ME data for rotation into the [110] direction in $DyAlO_3$, with $H_{dc} = 10$ kOe. The circular points are for increasing θ and the x-shaped points are for decreasing θ. The insets show the arrangement of the four sublattices at low θ and at high θ in $H_{dc} = 10$ kOe. The solid curve No. 1 is the normalized magnetization calculated from the data in Ref. 5. The theoretical curves Nos. 2 and 3 are described in the text.

$H = 0$ to a different value, say a_1, at $H > H_c$. At the same time, the magnetization M increases from zero at $H = 0$ to a saturation value M', at $H > H_c$. We make the simple assumption (cf. Sec. VII) that the variation in the ME susceptibility from a_0 to a_1 is proportional to the increase in the normalized magnetization $\nu = M/M'$ from 0 to 1.

Based on this assumption, the total electric polarization along the c axis in the experiments described above is given by

$$P = [(1-\nu)a_0 + \nu a_1] H \cos\theta \ ,$$

where H is the total magnetic field

$$H = H_{dc} + H_{ac} \ ,$$

and θ is the angle between H and the c axis of the crystal (Fig. 2). The normalized magnetization ν is a function of the component of H in the (001) plane, which is given by

$$H' = H \sin\theta \ .$$

As was described in Sec. IV, it was expected that $a_1 = 0$ for the measurements in Fig. 3, and that $a_1 \approx 0.5\, a_0$ for the measurements in Fig. 4.

The ME signal $\alpha(\theta)$ was proportional to the ac component of the total electric polarization. Carrying out a Taylor-series expansion of P about $H = H_{dc}$, and retaining the terms linear in H_{ac}, we obtain

$$\frac{\alpha(\theta)}{\alpha(0)} = (\cos\theta)\left\{1 - \left(1 - \frac{a_1}{a_0}\right) \times \left[\nu(H') + H' \frac{d\nu}{dH'}\right]\right\}_{H' = H'_{dc}} \ ,$$

where $H'_{dc} = H_{dc} \sin\theta$. Since $\nu(H')$ varies from 0 to 1 in the transition region, $\alpha(\theta)/\alpha(0)$ varies from $\cos\theta$ at low angles to $(a_1/a_0)\cos\theta$ at higher angles. This was the anticipated dependence on angle, as described in Sec. IV. However, a term involving the quantity $H'(d\nu/dH')$ also appears in the expression for $\alpha(\theta)/\alpha(0)$, and this term drives the signal negative in the transition regions. The quantity $H'(d\nu/dH')$ is present because H_{ac} has a nonvanishing component in the (001) plane which causes $\nu(H')$ to oscillate at 150 Hz about its average value $\nu(H'_{dc})$.

The curves No. 2 in Figs. 3 and 4 were calculated from the expression for $\alpha(\theta)/\alpha(0)$, by substituting for $\nu(H')$ an idealized magnetization $\nu_i(H')$ at $T = 0\,^\circ$K. It was assumed that the transition at $T = 0\,^\circ$K would be broadened only by demagnetizing fields (ΔH), so that the transition region extends from H_c to $H_c + \Delta H$. The idealized magnetization $\nu_i(H')$ is zero in low fields $H' \leq H_c$, and unity in high fields $H' \geq H_c + \Delta H$. In the transition region, $\nu_i(H')$ increases linearly from 0 to 1 with a constant slope, as given by $d\nu_i/dH' = (\Delta H)^{-1}$. The demagnetizing fields ΔH were evaluated by fitting $\nu_i(H')$ to the experimental[5] $\nu(H')$ at $T = 1.45\,^\circ$K, which gave $\Delta H = 2.75$ kOe for $H' \parallel [010]$ in Fig. 3 and $\Delta H = 1.50$ kOe for $H' \parallel [110]$ in Fig. 4. The calculated curves No. 2 are in qualitative agreement with the data, assuming $a_1 = 0$ in Fig. 3 and $a_1 = 0.5\, a_0$ in Fig. 4. It is not surprising that the edges of the transition regions are somewhat smeared out in the data at $T = 1.45\,^\circ$K, as compared to the idealized behavior at $T = 0\,^\circ$K.

Curves No. 3 were calculated from the expression for $\alpha(\theta)/\alpha(0)$, by substituting for $\nu(H')$ and $d\nu/dH'$ on a point-by-point basis from the experimental[5] magnetization curves. As was the case for curves No. 2, it was assumed that $a_1 = 0$ in Fig. 3, and that $a_1 = 0.5\, a_0$ in Fig. 4. In Fig. 4, where the data were found to be reproducible throughout the transition region, the calculated curve No. 3 gives a reasonable description of all of the salient features of the observed behavior.

VII. DISCUSSION

The question of the "order"[11,15] of the metamagnetic transitions in $DyAlO_3$ is of interest from the point of view of understanding the magnetic behavior in the material, and it also has relevance to the theoretical analysis of Sec. VI (see below). It follows from symmetry and from physical arguments that a second-order transition between two magnetic states is possible when the point group in one state is a subgroup of the point group in the other state.[15] For the transition $1234 \rightarrow 1\bar{2}34$, which was studied in Fig. 4, the point group of the high-field state is m', which is a subgroup of $m'm'm'$ at $H = 0$. A second-order transition is therefore not ruled out by symmetry. For the transition, $1234 \rightarrow 1\bar{2}\bar{3}4$, which was studied in Fig. 3, the point group of the high-field state is $mm'm'$, which is not a subgroup of $m'm'm'$. Here, a second-order transition would be possible only if the point group in the transition region were a subgroup or a supergroup of both $m'm'm'$ and $mm'm'$. Hence, the two transitions differ fundamentally, and, in view of the experimental evidence (Sec. V A) concerning hysteresis in the ME data, it seems likely that the transition in Fig. 3 ($1234 \rightarrow 1\bar{2}\bar{3}4$) is of first order, and that the transition in Fig. 4 ($1234 \rightarrow 1\bar{2}34$) is of second order.

It may be shown that the expression for $\alpha(\theta)/\alpha(0)$ in Sec. VI should be valid in a first-order transition at $T = 0\,^\circ$K. In that case, the sample in the transition region should be in a mixed state, containing a fraction ν of material in the high-field configuration (with ME susceptibility a_1) and a fraction $1-\nu$ in the low-field configuration (with ME susceptibility a_0). A linear dependence on ν follows for the ME susceptibility $(1-\nu)a_0 + \nu a_1$. (This assumes that the ME domain structure of the material could be

held constant through the transition, which was not the case for the data in Fig. 3.) It is not clear, however, that the same expression should be valid in a second-order transition. It might be possible, of course, to express the ME susceptibility as a power series in ν for a second-order transition. The linear expression $(1-\nu)a_0+\nu a_1$ would then be the leading term in such a series. In view of these considerations, it is interesting that the calculated curve No. 3 gives as good agreement as it does with the data in Fig. 4. This would seem to provide experimental evidence that the change in ME susceptibility is (at least approximately) proportional to $\nu(H')$ in a second-order transition.

In earlier work[2] on $DyPO_4$, Rado showed that the ME susceptibility could be reversed in sign by cycling that material through a metamagnetic transition in high values of H_{dc}. A similar result was described above for the transition in $DyAlO_3$ involving a simultaneous reversal of the spins on two sublattices (Sec. V A). However, the two materials differ in symmetry (and, therefore, in the form of the ME tensor), and the experimental arrangements were not identical in the two cases. The hysteretic behavior which we observed in $DyAlO_3$ may be understood qualitatively as related to the phenomenon of "magnetoelectric annealing".[16] In ME annealing the sample is cooled through T_N in applied E_{dc} and H_{dc}. The sample may contain ME domains (i.e., regions of time-reversed symmetry), but ME annealing tends to establish a predominance of one type of domain, for this minimizes the ME contributions to the free energy. The ME susceptibility may be reversed in sign by reversing either E_{dc} or H_{dc} before cooling the sample through T_N. In the experiments described in Sec. V A, the sample of $DyAlO_3$ was cycled through θ_c^I at 1.45 °K, and it was found that $\alpha(0)$ could be reversed in sign by reversing H_{dc}. At $\theta=90°$ and $H_{dc}=10$ kOe, the magnetic point symmetry ($mm'm'$) was the same as for paramagnetic $DyAlO_3$ ($T>T_N$) with $H_{dc}\parallel[010]$. In effect, the sample was transformed from a paramagnetic state at $\theta>\theta_c^I$ to an antiferromagnetic state at $\theta<\theta_c^I$. The nucleation of ME domains and the sign of $\alpha(0)$ could be influenced, therefore, by the applied H_{dc} and E_{dc}, as in ME annealing.

VIII. CONCLUSIONS

The ME susceptibility was found to be dependent on applied magnetic fields at $T=1.45$ °K in $DyAlO_3$. The signal measured along the c axis decreased abruptly at the critical fields for metamagnetic transitions in the (001) plane. In agreement with simple physical arguments, the ME susceptibility was found approximately to scale with the number of antiferromagnetic spins. A theoretical analysis, in which it was assumed that the change in ME susceptibility was proportional to the increase in bulk magnetization in the transition region, was found to reproduce the salient features of the experimental data. The behavior was discussed in terms of the magnetic point symmetries in the material.

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