we have

$$\mathbf{M}^L(\mathbf{r}) = \frac{1}{4\pi c} \nabla \times \int \frac{\mathbf{j}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

$$- \frac{1}{8\pi c} \nabla\nabla \cdot \int \frac{\mathbf{r}' \times \mathbf{j}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \quad (A7)$$

which, together with (A2), defines the magnetization-density operator. This expression together with the transformation of $\mathbf{j}(\mathbf{r})$ introduced by Trammell[3] gives an expression which is useful for calculations of magnetization densities in ions, where angular momentum is conserved. (A7) can be used directly to calculate orbital-magnetization densities in metals, where the electrons are described by Bloch waves. On introducing these transformations in (A1), that equation becomes

$$\frac{d^2\sigma}{d\Omega d\epsilon} = \left(\frac{\gamma e}{\hbar c}\right)^2 \frac{k'}{k} \sum_{qq'} p_q |\langle q'| \hat{K} \times [\mathbf{M}(\mathbf{K}) \times \hat{K}] | q\rangle|^2$$

$$\times \delta\left(\frac{\hbar^2}{2m_0}(k'^2 - k^2) + E_{q'} - E_q\right).$$

Note that only the transverse-magnetization density $\hat{K} \times [\mathbf{M}(\mathbf{K}) \times \hat{K}] = \mathbf{M}(\mathbf{K}) - K[K \cdot \mathbf{M}(\mathbf{K})]$ contributes to the neutron scattering.

Statistical Mechanics and Origin of the Magnetoelectric Effect in Cr2O3*

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Expressions for the temperature dependence of the magnetoelectric susceptibility parallel and perpendicular to the trigonal axis in Cr2O3 are presented. A two-sublattice model is used. The relation between the sublattice magnetization and the temperature is derived from experimental results for the parallel magnetic susceptibility. All statistical averages appearing in the expressions for the magnetoelectric susceptibilities are then evaluated using this susceptibility-derived result. Using this technique, quantitative agreement with the experimental results is obtained. For the parallel case, three mechanisms that have been previously proposed as contributing to the parallel magnetoelectric susceptibility are considered. It is concluded that the parallel effect is dominated at low temperatures by the electric-field-induced g shift and at higher temperatures by the electric-field-induced shift in the intrasublattice exchange energy. For the perpendicular case, three mechanisms are also considered; two of them, an electric-field-induced antisymmetric exchange term and an electric-field-induced g shift, have not previously been discussed. It is concluded that the perpendicular effect is dominated by the electric-field-induced shift in the single-ion anisotropy energy. Crystal-field aspects of the perpendicular effect are presented, and it is argued that the electric-field-induced g shift is actually 1–2 orders of magnitude smaller than the crystal-field estimate.

INTRODUCTION

THE possibility of a linear magnetoelectric (ME) effect, wherein a material exhibits an induced magnetization which is proportional to an applied electric field and an induced electric moment which is proportional to an applied magnetic field, was first pointed out by Landau and Lifshitz.[1] Such an effect can exist only in materials having an ordered magnetic structure. Dzyaloshinski[2] subsequently pointed out that the ME effect should exist in Cr2O3, and the electrically induced effect was first observed in this material by Astrov.[3] This was followed by the observation of the magnetically induced ME effect in Cr2O3 by Rado and Folen.[4] Further work[5–7] showed that the ME effect in Cr2O3 is strongly anisotropic and temperature-dependent.

The first proposal of an atomic mechanism that could provide an explanation of the ME effect was made by Rado.[8] He indicated that the dependence of the single-ion anisotropy energy on an externally applied field would cause an ME effect both parallel and

[1] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1960), p. 119.

[2] I. E. Dzyaloshinski, Zh. Eksperim. i Teor. Fiz. **37**, 881 (1959) [English transl.: Soviet Phys.—JETP **10**, 628 (1960)].

[3] D. N. Astrov, Zh. Eksperim. i Teor. Fiz. **38**, 984 (1960) [English transl.: Soviet Phys.—JETP **11**, 708 (1960)].

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[5] D. N. Astrov, Zh. Eksperim. i Teor. Fiz. **40**, 1035 (1961) [English transl.: Soviet Phys.—JETP **13**, 729 (1961)].

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

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perpendicular to the trigonal axis of Cr_2O_3. An alternative proposal, put forward by Date et al.,[9] was that the influence of an external electric field on the intrasublattice exchange interaction (i.e., a two-ion effect) underlies the parallel ME effect (this mechanism does not give any contribution to the perpendicular effect). The statistical mechanics of the above mechanisms was examined by Rado,[10] using a two-sublattice model together with the usual molecular-field-theory result for the temperature dependence of the sublattice magnetization. He found, in the case of Cr_2O_3, that both the single-ion[8] and two-ion[9] mechanisms yielded expressions for the ME susceptibility as a function of temperature that were in qualitative agreement with the experimental results. However, good quantitative agreement was lacking. In particular, both mechanisms failed to explain the sign reversal of the parallel ME susceptibility at 80–100°K and the finite value of this susceptibility at 0°K.[5,6,11] Rado suggested that the lack of quantitative agreement between theory and experiment was partly due to the fact that a two-sublattice model is not strictly applicable to Cr_2O_3.

The purpose of this paper is to show that good quantitative agreement between theory and experiment is obtainable using a two-sublattice model when the restrictions imposed by the molecular-field theory are eased. Instead of using the molecular-field theory to obtain the relation between the sublattice magnetization and the temperature, we derive this relationship from the experimental parallel magnetic susceptibility measured by Foner.[12] In doing this, we have made use of the suggestion of Callen and Shtrikman[13] that the functional dependence between the statistical moments of the spin operator which follow from the molecular-field theory has a greater range of validity than the molecular-field theory itself. Thus we calculate the expressions for the magnetic and ME susceptibilities using the molecular-field theory, but we evaluate the statistical averages appearing in these expressions from our experimentally derived reduced magnetization.

Application of this procedure to MnF_2, $CuCl_2 \cdot 2H_2O$, and FeF_2 has yielded results for the sublattice magnetization that are in excellent agreement with those obtained by direct measurements.[14]

For the parallel case, we use a spin Hamiltonian containing both the single-ion term of Rado[8] and the two-ion term of Date et al.[9] We write this two-ion term in an effective-field formalism. We also include a single-ion term leading to a Van Vleck temperature-independent term in the magnetic susceptibility. This term is necessary to explain the nonvanishing of the parallel

susceptibility at 0°K.[12,15] Lastly, we add a term reflecting the effect of an externally applied electric field on the g factor. The existance of such an effect was pointed out by Royce and Bloembergen,[16] and its importance in connection with the nonvanishing of the parallel ME effect at 0°K was pointed out by Alexander and Shtrikman.[17] We find that good quantitative agreement with the available data over the entire temperature range is obtainable using the two-ion electric-field-induced intralattice exchange mechanism and the single-ion electric-field-induced g-shift mechanism. This is in agreement with studies of the electric-field splitting of paramagnetic resonance lines in ruby (Al_2O_3: Cr^{3+}),[16,18] according to which the single-ion mechanism is too small by one to two orders of magnitude to account for the parallel ME effect.[10]

For the perpendicular case, we again use a spin Hamiltonian containing both single-ion and two-ion terms. A possible two-ion or exchange origin of the perpendicular ME effect has not been discussed previously for Cr_2O_3; we here show that such a mechanism can arise from an electric-field-induced Dzyaloshinski–Moriya[19,20] antisymmetric-exchange effect. This effect is normally forbidden in Cr_2O_3 because of its point-group symmetry,[19] but, because of the reduction in symmetry when an external perpendicular electric field is applied, a nonzero antisymmetric exchange effect becomes possible. As in the parallel case, we write this two-ion term in an effective-field formalism. In addition, we consider terms reflecting the effect of the externally applied electric field on the g factor.[16] A crystal-field analysis indicates that these terms should dominate the observed perpendicular ME susceptibility; however, we find that good quantitative agreement with experiment is provided by the single-ion electric-field-induced anisotropy shift alone. Reasons for the failure of the crystal-field analysis are given, and it is argued that the electric-field-induced g shift is actually 1–2 orders of magnitude smaller than the crystal-field estimate.

PARALLEL CASE

We shall use essentially the method and notation of Rado.[10] We consider Cr_2O_3, below its Néel temperature T_N, to be made up of two interlocking sublattices, each containing $\frac{1}{2}N$ Cr^{3+} ion with $S=\frac{3}{2}$. For each sublattice we introduce a separate Cartesian coordinate system x, y, z and we also define an external Cartesian coordinate system ξ, η, ζ such that ζ is parallel to the positive direction of one sublattice (denoted "+") and

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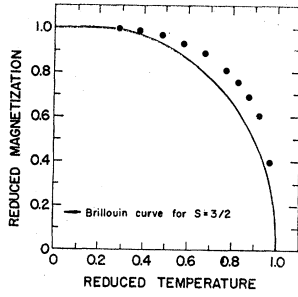[20] T. Moriya, Phys. Rev. 120, 91 (1960).

FIG. 1. Reduced sublattice magnetization versus reduced temperature for Cr_2O_3. [Points show results calculated from $\chi_\perp$ of Ref. 12, curve is molecular-field results for $S=\frac{3}{2}$].

antiparallel to the positive z direction of the second sublattice (denioted "—"). The magnetization of each sublattice lies en the positive z direction of its own coordinate syst.m, and this will be taken to be the axis of quantization In this section we shall consider the case of electric and magnetic fields E_ζ and H_ζ that are applied in the positive ζ direction.

We assign, to each Cr^{3+} ion, the following spin Hamiltonian:

$$\mathcal{3C}^\pm = -g_{||}\beta S_z H_z{}^{\text{eff}\pm} \pm g_{||}\beta a_{||} S_z{}^2 E_\zeta \pm g_{||}\beta b_{||} S_z \text{ME}_\zeta$$
$$+ g_{||}\beta c_{||} S_z H_\zeta E_\zeta - \beta^2 \delta H_\zeta{}^2 + \mathcal{3C}_a. \quad (1)$$

Here we have, from left to right, a Zeeman term due to the effective magnetic field $H_z{}^{\text{eff}\pm}$, a single-ion ME term,[8] a two-ion ME term,[9] an electric-field-induced g-shift term,[16,17] a Van Vleck term,[15] and a nonfield-dependent anisotropy term $\mathcal{3C}_a$. The symbols $g_{||}$, β, M, and S_z represent, respectively, the spectroscopic splitting factor in the z direction (essentially equal to 2 in the case of Cr_2O_3), the Bohr magneton, the spontaneous sublattice magnetization, and the z component of the electron-spin operator. The constants $a_{||}$, $b_{||}$, $c_{||}$, and δ fix the magnitudes of the various terms. [In the notation of Royce and Bloembergen,[16] $g_{||}\beta a_{||} = \frac{3}{2}R_{333}$ and $g_{||}\beta c_{||} = T_{333}$].

Rado[10] has discussed in detail the statistical behavior of the first three terms in Eq. (1). We thus concentrate our attention on the remaining terms. We shall assume that $\mathcal{3C}_a$ is diagonal in m; we therefore may combine it with Rado's $\mathcal{3C}_0$, leaving only the contributions to the susceptibilities of the remaining two terms to be determined.

We first consider the ordinary magnetic susceptibility. Here the Van Vleck term will give an additive contribution

$$\chi_\nu = 2N\beta^2 \delta \quad (2)$$

to the usual molecular-field result.[10,21] Equation (2) is essentially the result found by Silverstein and Jacobs[15] in their explanation of the nonvanishing of the parallel susceptibility[12] in the zero-temperature limit. Thus the

total parallel susceptibility is given by[10,21,22]

$$\chi_{||} = \frac{(Ng_{||}{}^2\beta^2 S^2/kT)B_s{}'(x)}{1+(A+\Gamma)(Ng_{||}{}^2\beta^2 S^2/2kT)B_s{}'(x)} + 2N\beta^2\delta. \quad (3)$$

Here A and Γ are the molecular-field coefficients representing the inter- and intrasublattice exchange interactions, k is Boltzmann's constant, T is the temperature, $B_s(x)$ is the Brillouin function, and $B_s{}'(x) = \partial B_s(x)/\partial x$.

We now proceed to fit the $\chi_{||}$ of Eq. (3) to the experimental results of Foner,[12] first introducing a suitable diamagnetic correction.[15] We take $N = 4.13 \times 10^{22}$ cm^{-3} and

$$T_N = Ng_{||}{}^2 S(S+1)(A-\Gamma)/6k = 310°\text{K}. \quad (4)$$

Using Eq. (3), we find that $2N\beta^2\delta = 11.6 \times 10^{-6}$ emu/cm^3 and that the quantity

$$\Delta = Ng_{||}{}^2\beta^2 S(S+1)(A+\Gamma)/6k \quad (5)$$

is 660°K. With these quantities now determined, the temperature dependence of $B_s{}'(x)$ is found, and from this we determine the relation between the temperature T and the argument of the Brillouin function x. Knowing $T = T(x)$, we use

$$\langle m \rangle = SB_s(x) \quad (6)$$

to determine $\langle m \rangle/S$, the reduced magnetization, as a function of T.[14] [The brackets $\langle \ \rangle$ denote a statistical average over a canonical distribution]. The result of this calculation is shown in Fig. 1. For comparison we also show in Fig. 1 the usual molecular-field result, which follows from Eq. (6) when the relation[10,22]

$$T = 3S(S+1)^{-1}T_N B_s(x)/x \quad (7)$$

is used for $T = T(x)$. Figure 1 indicates that the molecular-field theory gives a poor approximation to the reduced magnetization in Cr_2O_3. Similar results have been found for many other materials, including $\alpha - Fe_2O_3$,[23] MnF_2,[14,24] $CuCl_2 \cdot 2H_2O$,[14,25] and FeF_2.[14,26,27]

We shall not here go into the possible reasons for the deviation of the magnetization in Cr_2O_3 from the molecular-field prediction. Instead, we shall simply take the magnetization curve of Fig. 1 as given and proceed with our examination of the contributions to the ME susceptibility. (*Note added in proof.* Neutron-diffraction measurements of the sublattice magnetization[27a] are in agreement with the susceptibility-derived results of Fig. 1.)

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[27a] L. M. Corliss and J. M. Hastings, J. Phys. Radium **25**, 557 (1964); H. Shaked and S. Shtrikman (to be published).

Using the formalism of Rado,[10] we find that the electric-field-induced g-shift term in Eq. (1) gives a second-order contribution to the free energy of

$$F_2' = Ng\beta c_{||}\langle m\rangle. \tag{8}$$

Combining Eq. (8) with Rado's results,[10] we find the total parallel ME susceptibility to be

$$\frac{\alpha_{||}}{4\pi} = (\chi_{||}-\chi_\nu)\left[(b_{||}'+a_{||}G_{||})\langle m\rangle - \frac{c_{||}(u_{||})^{-1}kT\langle m\rangle}{g_{||}\beta(\langle m^2\rangle - \langle m\rangle^2)}\right], \tag{9}$$

where $G_{||}$ is a temperature-dependent factor[10] which is given by

$$G_{||} = -\frac{\langle m^3\rangle - \langle m^2\rangle\langle m\rangle}{\langle m\rangle(\langle m^2\rangle - \langle m\rangle^2)}, \tag{10}$$

and

$$b_{||}' = \tfrac{1}{2}Ng_{||}\beta b_{||}, \tag{11a}$$

$$u_{||} = 1 - \tfrac{1}{2}(A+\Gamma)(\chi_{||}-\chi_\nu). \tag{11b}$$

At $T=0°$K, the ME susceptibility is given by

$$\alpha_{||}/4\pi(T=0°K) = -Ng_{||}\beta c_{||}S. \tag{12}$$

Thus we see that, from among the ME mechanisms expressed in our Hamiltonian, the electric-field-induced g shift alone is responsible for the nonzero parallel ME susceptibility at absolute zero. This is in accordance with the suggestion of Alexander and Shtrikman.[17]

We now consider two possible cases: In the first, the parallel ME susceptibility is attributed exclusively to the electric-field-induced g shift together with the electric-field-induced shift in the intrasublattice ex-
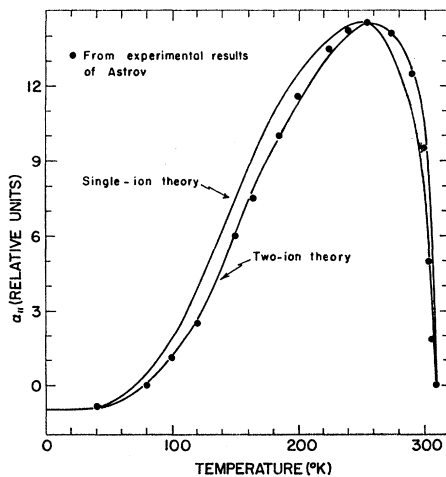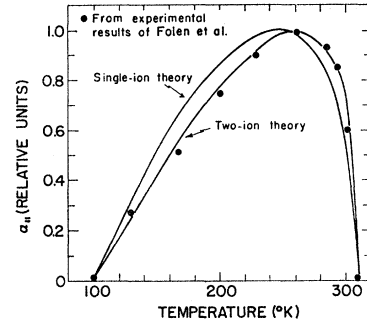

FIG. 3. Parallel magnetoelectric susceptibility versus temperature for Cr₂O₃ computed using single-ion and two-ion theories. [Points are experimental results of Ref. 6.]

change interaction.[9] For this case Eq. (9) becomes

$$\frac{\alpha_{||}}{4\pi} = (\chi_{||}-\chi_\nu)\left[b_{||}'\langle m\rangle - \frac{c_{||}(u_{||})^{-1}kT\langle m\rangle}{g_{||}\beta(\langle m^2\rangle - \langle m\rangle^2)}\right]. \tag{13}$$

In the second case, the parallel ME susceptibility is attributed exclusively to the electric-field-induced g shift together with the electric-field-induced shift in the anisotropy energy.[8,10] For this case, Eq. (9) becomes

$$\frac{\alpha_{||}}{4\pi} = (\chi_{||}-\chi_\nu)\left[a_{||}G_{||}\langle m\rangle - \frac{c_{||}(u_{||})^{-1}kT\langle m\rangle}{g_{||}\beta(\langle m^2\rangle - \langle m\rangle^2)}\right]. \tag{14}$$

In Fig. 2 we show the ME susceptibilities as given by Eqs. (13) and (14) together with the experimental results of Astrov.[5] For both Eqs. (13) and (14) we computed all statistical averages using the $\langle m\rangle$-versus-T relation of Fig. 1 (as derived from $\chi_{||}$) and *not* by means of the $\langle m\rangle$-versus-T relation derived from the molecular-field theory. Also, for both Eqs. (13) and (14), we fixed the values of the parameters $c_{||}$ and $b_{||}'$ or $a_{||}$ by setting $\alpha_{||}$ equal to the experimental values at $T=0°$K and $T=255°$K.

In Fig. 3 we show the ME susceptibilities as given by Eqs. (13) and (14) together with the experimental results of Folen et al.[6] As in Fig. 2, all the statistical averages appearing in these equations were computed using the $\chi_{||}$ derived $\langle m\rangle$-versus-T relation of Fig. 1 rather than the molecular-field result. Here the parameters appearing in Eqs. (13) and (14) were fixed by setting $\alpha_{||}$ equal to the experimental values at $T=100°$K and $T=255°$K.

If, in Fig. 3, we had extended our theoretical results to $T=0°$K, we would find that the ratio $\alpha_{||}(T=255°K)/\alpha_{||}(T=0°K)$ is 13.55 as compared to 14.50 in Fig. 2. This difference of about 6.5% is responsible for the shift of the zero crossing of $\alpha_{||}$ from the 80°K value measured by Astrov[5] to the 100°K value of Folen et al.[6] An intermediate zero-crossing temperature of 95°K has been observed by Foner and Hanabusa.[11]

Inspection of Figs. 2 and 3 clearly shows that the expression for the ME susceptibility given by Eq. (13)
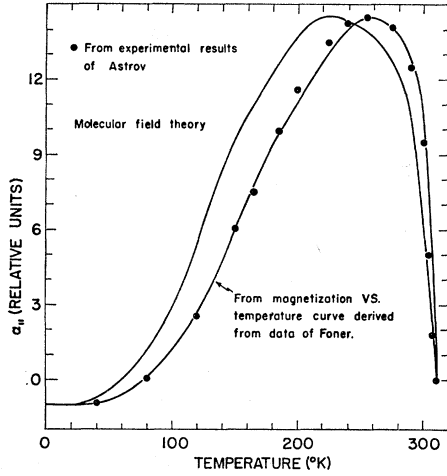

FIG. 2. Parallel magnetoelectric susceptibility versus temperature for Cr₂O₃ computed using single-ion and two-ion theories. [Points are experimental results of Ref. 5.]

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FIG. 4. Parallel magnetoelectric susceptibility versus tempera-
ture for Cr_2O_3 as computed using molecular-field and suscepti-
bility-derived expressions for the sublattice magnetization. [Points
are experimental results of Ref. 5.]

is in excellent quantitative agreement with the experi-
mental results, while that given by Eq. (14) is not
nearly as satisfactory. Thus, from a study of the temper-
ature dependence of the parallel ME susceptibility, it is
possible to conclude that, in Cr_2O_3, it is the two-ion
mechanism of electric-field-dependent intrasublattice
exchange rather than the single-ion mechanism of
electric-field-dependent anisotropy energy which domi-
nates the parallel ME effect in the range 100–300°K.

To emphasize the importance of using the experi-
mentally derived $\langle m \rangle$-versus-T relation in computing
the statistical averages appearing in Eqs. (13) and
(14), we compare, in Fig. 4, the ME susceptibility
calculated from Eq. (13) using both the $\chi_{||}$ derived and
the molecular-field results for $\langle m \rangle$ versus T. The experi-
mental results of Astrov[5] are also given in Fig. 4. We
note that only qualitative agreement between theory
and experiment is obtained when the molecular-field-
theory $\langle m \rangle$-versus-T relation is used. Thus only when
the $\chi_{||}$ derived $\langle m \rangle$-versus-T relation is used in com-
puting the statistical average is it possible to decide
between the two-ion and single-ion ME mechanisms.
It is, of course, not surprising that the molecular-field-
theory does not give an adequate description of the ME
effect in Cr_2O_3 in view of its failure to explain the tem-
perature dependence of the ordinary parallel magnetic
susceptibility.[12,28]

We show in Table I the values of the various param-
eters used to obtain the curves of Figs. 2–4. We also
include in Table I the value of $a_{||}$ obtained by studies
of the electric-field splitting of paramagnetic resonance
lines in ruby $(Al_2O_3:Cr^{3+})$.[16,18]

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

Since the crystal-field analysis of the parallel ME
effect has been discussed previously,[17] we shall not
consider this aspect of the problem here.

PERPENDICULAR CASE

The coordinate system used for the parallel case is
taken over without change for the perpendicular case.
In this section, however, we consider the case of E and
H fields applied in the positive ξ direction.

For the perpendicular case we assign, to each Cr^{3+} ion,
the spin Hamiltonian

$$\mathcal{3C}^{\pm} = -g_{||}\beta S_z H_z^{\text{eff}\pm} - g_{\perp}\beta S_x H_x^{\text{eff}\pm} \pm g_{\perp}\beta(a_{\perp}/2)$$

$$\times (S_x S_z + S_z S_x)E_\xi \pm g_{\perp}\beta b_{\perp}(S_x H_z^{\text{eff}\mp} - S_z H_x^{\text{eff}\mp})E_\xi$$

$$\pm g_{\perp}\beta c_{\perp}S_z H_\xi E_\xi + \mathcal{3C}_a. \quad (15)$$

Here we have, from left to right, two Zeeman terms
due to the two effective fields $H_x^{\text{eff}\pm}$ and $H_z^{\text{eff}\pm}$, a
single-ion ME term[8] written symmetrically with respect
to the spin operator, a two-ion ME term, a term due to
the electric-field-induced g shift, and a non-field-de-
pendent anisotropy term $\mathcal{3C}_a$.

The physical basis for the two-ion ME term is the
following: When a perpendicular electric field E_ξ is
applied to Cr_2O_3, each spin inclines slightly so as to
have a component in the ξ direction. This can be
thought of as an electric-field-induced Dzyaloshinski
vector D_η[19,20] which causes a net magnetic moment
to appear in the ξ direction. More formally, the following
symmetry considerations apply: The antiferromagnet
Cr_2O_3 has the point symmetry $\bar{3}'m'$.[19,29] When a canting
of the spins from the antiferromagnetic axis occurs,
this symmetry is reduced to $2/m'$ or $\bar{1}'$ depending on
whether the plane of the canted spins includes or does
not include one of the twofold axis of $\bar{3}'m'$.

Consider an electric field applied along the anti-
ferromagnetic axis of Cr_2O_3. Then the symmetry of the
material plus the field is $\bar{3}'$. In this case, a canting of
the spins would require a further reduction in symmetry.
Suppose instead that the electric field is in the plane

TABLE I. Comparison of coefficients obtained from ME meas-
urements in Cr_2O_3 and those obtained from EPR studies in ruby
$(Al_2O_3:Cr^{3+})$.

	From the ME data of Ref. 5	Ref. 6	From EPR of Refs. 16 and 18
$\lvert Ng_{||}\beta c_{||}\rvert \times 10^{+6}$	2.12	1.43	
$\lvert b_{||}'\rvert \times 10^{+3}$	448	284	
$\lvert a_{||}\rvert \times 10^{+3}$	448	284	28.7
$\lvert b_{\perp}'\rvert \times 10^{+3}$	16.9	6.65	
$\lvert a_{\perp}\rvert \times 10^{+3}$	50.6	19.9	9.7

[29] R. R. Birss, Rept. Progr. Phys. 26, 307 (1963).

perpendicular to the antiferromagnetic axis of Cr_2O_3. Then the symmetry of the material plus the field is $2/m'$ or $\bar{1}'$, depending on whether the field is applied along one of the twofold axes of $\bar{3}'m'$ or not. For this case, a canting of the spins in the plane containing the antiferromagnetic axis and the applied field will not require any further reduction in symmetry. In this case, a Dzyaloshinski-Moriya term in the Hamiltonian is not excluded by symmetry considerations and should therefore be included. Thus, we introduce a Dzyaloshinski-Moriya antisymmetric-exchange term[19,20] into our Hamiltonian which, when D_η is written to first order in E_ξ, is expressed in the effective-field formalism by the two-ion term in Eq. (15). As in Eq. (1), the constants $a_\perp$, $b_\perp$, and $c_\perp$ fix the magnitudes of the various effects and $g_\perp$ (taken equal to 2) is the spectroscopic-splitting factor perpendicular to the z direction. [In the notation of Royce and Bloembergen,[16] $g_\perp\beta a_\perp = R_{113}$ and $g_\perp\beta c_\perp = T_{131}$. The matrix elements T_{111} and T_{113} do not contribute to the ME effect.]

Since the anisotropy energy $\mathcal{K}_a$ of Cr_2O_3 is small,[12] we shall neglect this term; Eq. (15) then leads to the usual result for the perpendicular magnetic susceptibility[10,21,22]

$$\chi_\perp = 1/A. \qquad (16)$$

Using Eqs. (4) and (5) to determine A, we find, from Eq. (16), that $\chi_\perp = 25.4$ emu/g. This is in agreement with the experimentally measured perpendicular susceptibility[12] at $T = T_N$; however, the experimental $\chi_\perp$ in fact decreases by approximately 10% as the temperature is reduced from T_N to 0°K. This decrease is not reflected in Eq. (16) because of our neglecting the $\mathcal{K}_a$ term in Eq. (15). For consistency, we shall use $\chi_\perp$ as given by Eq. (16) rather than the experimental results of Foner[12] in calculating $\alpha_\perp$.

Again using the formalism of Rado,[10] we find that both the two-ion and g-shift terms of Eq. (15) behave according to his "phenomenological theory." Thus we find the total perpendicular ME susceptibility to be

$$\alpha_\perp/4\pi = \chi_\perp\langle m\rangle(a_\perp G_\perp - b_\perp'), \qquad (17)$$

where $G_\perp$ is a temperature-dependent factor[10] which is given by

$$G_\perp = -\tfrac{3}{2}[\langle m^2\rangle - \tfrac{1}{3}S(S+1)]\langle m\rangle^2, \qquad (18)$$

and

$$b_\perp' = [2b_\perp + c_\perp(u_\perp)^{-1}(A-\Gamma)(N/2)g_\perp\beta, \qquad (19)$$

where

$$u_\perp = 1 - \tfrac{1}{2}(A+\Gamma)\chi_\perp. \qquad (20)$$

Again we study two possible cases: In the first, the perpendicular ME susceptibility is attributed exclusively to the electric-field-induced Dzyaloshinski-type term and/or the electric-field-induced g shift.[16] For this
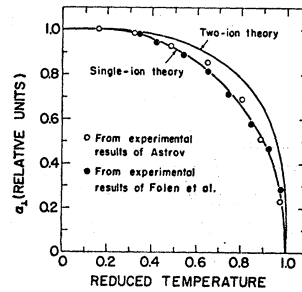
FIG. 5. Perpendicular magnetoelectric susceptibility versus temperature for Cr_2O_3 computed using single-ion and two-ion theories [Empty and filled circles are experimental results of Refs. 5 and 6, respectively.]

case, Eq. (18) becomes

$$\alpha_\perp/4\pi = -b_\perp'\chi_\perp\langle m\rangle. \qquad (21)$$

In the second case, the perpendicular ME susceptibility is attributed exclusively to the electric-field-induced shift in the anisotropy energy.[8] For this case, Eq. (18) becomes

$$\alpha_\perp/4\pi = a_\perp G_\perp\chi_\perp\langle m\rangle. \qquad (22)$$

In Fig. 5 we show the ME susceptibilities as given by Eqs. (21) and (22) together with the experimental results of Astrov[5] and Folen et al.[6] As previously, we have computed all statistical averages using the susceptibility derived $\langle m\rangle$-versus-T relation of Fig. 1. All results, both theoretical and experimental, are normalized to $\alpha_\perp = 1$ at $T = 0°K$.

An inspection of Fig. 5 clearly shows that the expression for the ME susceptibility given by Eq. (22) is in excellent quantitative agreement with the experimental results, while that given by Eq. (21) is not nearly as satisfactory. Thus, from a study of the temperature dependence of the perpendicular ME susceptibility, we conclude that in Cr_2O_3 it is the single-ion mechanism of electric-field-dependent anisotropy energy that underlies the perpendicular ME effect.

The importance of using the experimentally derived $\langle m\rangle$-versus-T relation in computing the statistical averages in Eqs. (21) and (22) may be seen by comparing our Fig. 5 with Rado's Fig. 1,[10] where the molecular-field results for $\langle m\rangle$-versus-T are used. It is seen that the difference between the perpendicular ME susceptibilities given by Eqs. (21) and (22) is of the same order of magnitude as the difference between the susceptibility-derived and molecular-field results for the temperature dependence of the sublattice magnetization. This, then, emphasizes the importance of using a more realistic expression for the temperature dependence of the magnetization than the usual molecular-field result.

We show in Table I the values of the various parameters used to obtain the theoretical curves of Fig. 5. We also include in Table I the value of $a_\perp$ obtained by studies of the electric-field splitting of paramagnetic resonance lines in ruby ($Al_2O_3:Cr^{3+}$).[16]

Let us now briefly consider the crystal-field aspects of the perpendicular case. In the crystal-field formalism

the spin Hamiltonian, in the absence of an external electric field, is[30]

$$\mathcal{3C}^{\pm} = -2\beta(\delta_{ij} - \lambda\Lambda_{ij})S_i H_j{}^{\text{eff}\pm} - \lambda^2\Lambda_{ij}S_i S_j. \quad (23)$$

Here δ_{ij} is the Kronecker delta, λ is the spin-orbit coupling constant, Λ_{ij} is a tensor (diagonal in the case of Cr_2O_3) that gives the orbital contribution to the spin Hamiltonian, S_i and S_j are components of the spin operator, and summation over repeated indices i, j is understood.

The only way in which an applied electric field in the ξ direction can influence the Hamiltonian of Eq. (23) is by acting on Λ_{ij}. Let us write

$$\Lambda'_{ij} = \Lambda_{ij} + g_\perp \beta \tau_{ij} E_\xi, \quad (24)$$

where $g_\perp \tau_{ij} = (\partial\Lambda_{ij}/\partial E_\xi)$, the derivative being evaluated at $E_\xi = 0$. Substituting Eq. (24) into Eq. (23), keeping only terms to first order in E_ξ, and comparing the result with Eq. (15), we immediately find that

$$a_\perp = -\lambda^2(\tau_{13} + \tau_{31}), \quad (25a)$$

$$c_\perp = 2\beta\lambda\tau_{31}, \quad (25b)$$

and, since Λ_{ij} is a symmetrical tensor, $\tau_{13} = \tau_{31}$. Thus,

$$a_\perp = -c_\perp\lambda/\beta. \quad (26)$$

Using Eqs. (19) and (26) and taking[17] $\lambda = 87$ cm^{-1}, we find that the electric-field-induced g-shift contribution to $b_\perp'$ is approximately nine times the $b_\perp'$ values given in Table I. Thus, from a crystal-field analysis, we should expect that the electric-field-induced g shift should be the dominant factor in the perpendicular ME effect, at least insofar as to the two-ion contribution is negligible. Since the results shown in Fig. 5 indicate that in fact the $a_\perp$ term dominates the perpendicular ME effect, it seems that the crystal-field analysis greatly overestimates the electric-field-induced g-shift terms. [It is unlikely that the sum of the electric-field-induced g-shift and two-ion terms comprising $b_\perp'$ vanishes because there is no fundamental connection between the two mechanisms.]

The conclusion that we have overestimated the electric-field-induced g-shift terms is supported by the results of Lohr and Lipscomb.[31] They find that the anisotropy term of Cr^{3+} is dominated by matrix elements connecting the $t_2{}^3$ ($^4A_2$) ground state to $t_2{}^3$ ($^2T_2$), while only matrix elements connecting $t_2{}^3$ ($^4A_2$) to $t_2{}^2e(^4T_2)$ contribute to the g shift and that the g shift is therefore reduced by almost an order of magnitude

below the crystal-field estimate. With this in mind, it does not appear unreasonable that the electric-field-induced g shift could be 1–2 orders of magnitude smaller than the crystal-field estimate given above.

Additional support for a reduction of 1–2 orders of magnitude may be obtained from the results of the parallel case. If we accept the results of Artman and Murphy[32] that the magnitudes of $a_\perp$ in ruby and Cr_2O_3 are of the same order, then it follows that the electric-field-induced g shift for the parallel case is in fact almost two orders of magnitude less than the value obtained from a crystal-field analysis.[17] We should note, however, that while the electric-field-induced g shift in the perpendicular case can be due only to the dependence of Λ_{ij} on E_ξ, this is not true in the parallel case. Here the E_ξ dependence of both λ and Λ_{ij} can contribute to the electric-field-induced g shift. Thus a direct comparison of the magnitudes of the two effects is difficult.

CONCLUSIONS

To summarize, we have examined the parallel and perpendicular ME effect in Cr_2O_3. Our basic approach is the same as that of Rado[10]; however, we have used susceptibility-derived results[14] for the sublattice magnetization rather than those of the molecular-field theory in computing the various statistical averages that appear in the theory. In other respects we have used the molecular-field approximation; in particular, we have written those ME terms in our Hamiltonian that have a two-ion origin in an effective-field formalism.

For the parallel case, we considered three mechanisms that can contribute to the ME effect and concluded, from the temperature dependence of $\alpha_{||}$,[5,6] that the effect is dominated at low temperatures by the electric-field-induced g shift[17] and at higher temperatures by the electric-field-induced shift in the intrasublattice exchange energy.[9] The importance of using the susceptibility-derived expression for the sublattice magnetization instead of the molecular-field result is shown.

For the perpendicular case, we again considered three mechanisms that can contribute to the ME effect and concluded, from the temperature dependence of $\alpha_\perp$[5,6] that the effect is dominated by the electric-field-induced shift in the single-ion anisotropy energy.[8,10] Crystal-field aspects of the perpendicular case were presented and discussed in the light of the above conclusion.

ACKNOWLEDGMENT

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