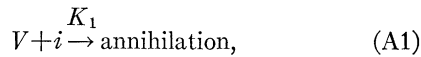


ACKNOWLEDGMENT

Appreciation is expressed to Miss E. Wolfson for obtaining the computer solutions.

APPENDIX I

If di-interstitial formation is also to be taken into account, one has the kinetic scheme



The corresponding differential equations are

$$dV/dt = -K_1Vi, \quad (\text{A4})$$

$$di/dt = -K_1Vi - K_2i - K_3i^2 + K_4i_2, \quad (\text{A5})$$

$$di_2/dt = (1/2)K_3i^2 - (1/2)K_4i_2. \quad (\text{A6})$$

These equations reduce to Eqs. (3) and (4) of the text if the last two terms of Eq. (A5) cancel. This, in turn, implies that the di-interstitials are present either in steady state or are maintained in equilibrium with the free interstitials. In either case $di_2/dt = 0$ and Eqs. (3) and (4) of the text result. This approximation is known to be valid, from a previous study,¹ when the temperature is high and/or the binding energy of a di-interstitial is small.

Statistical Theory of Magnetoelectric Effects in Antiferromagnetics*

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It is shown on the basis of a statistical mechanical calculation involving the molecular field approximation and the free energy that the spin-orbit mechanism previously proposed by the author leads not only to the electrically induced but also to the magnetically induced magnetoelectric effect. In addition, this mechanism is found to lead to a magnetoelectric contribution to the electric susceptibility. For a two-sublattice antiferromagnet, the temperature dependence of the magnetoelectric susceptibilities is shown to be quantitatively different from but qualitatively similar to that predicted in the previous work on a phenomenological basis. Although even purely magnetic data indicate that a two-sublattice model is not strictly applicable to Cr_2O_3 , a comparison of the present theory with experiments suggests (with the help of data on the electric field splitting of certain paramagnetic resonance lines in ruby) that the spin-orbit mechanism accounts for a significant part of the magnetoelectric effects observed in Cr_2O_3 . The Appendix contains a revised derivation of some known thermodynamic relations relevant to magnetoelectric effects. It also contains a proposal, based on thermodynamic and symmetry considerations, that "piezomagnetoelectric" and "gyroelectric" effects may exist.

I. INTRODUCTION

SPIN-ORDERED materials may exhibit an induced magnetic polarization which is proportional to an applied electric field and an induced electric polarization which is proportional to an applied magnetic field. These effects will be referred to, throughout the present paper, as the electrically induced magnetoelectric effect $[(\text{ME})_E]$ and the magnetically induced magnetoelectric effect $[(\text{ME})_H]$, respectively. The $(\text{ME})_E$ effect was first observed experimentally by Astrov¹ and the $(\text{ME})_H$ effect by Rado and Folen.² Additional experiments, carried out independently at this Laboratory and in the U.S.S.R., revealed an anisotropy in the temperature de-

pendence of the magnetoelectric susceptibilities,^{3,4} established new evidence for the existence of antiferromagnetic domains,^{2,4} and resulted in the observation of magnetic annealing effects in an antiferromagnetic material.^{2,4} Single crystals of antiferromagnetic Cr_2O_3 were used in all the experiments cited.

Even before these experiments were performed, it had been pointed out by Landau and Lifshitz⁵ on the basis of thermodynamic and symmetry considerations that magnetoelectric $[\text{ME}]$ effects may, in principle, exist in spin-ordered materials. Subsequently, Dzyaloshinskii⁶

³ V. J. Folen, G. T. Rado, and E. W. Stalder, *Phys. Rev. Letters* **6**, 607 (1961).

⁴ D. N. Astrov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **40**, 1035 (1961) [translation: *Soviet Phys.—JETP* **13**, 729 (1961)].

⁵ 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.)

⁶ I. E. Dzyaloshinskii, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **37**, 881 (1959) [translation: *Soviet Phys.—JETP* **10**, 628 (1960)].

* The main results of this paper were presented as part of an invited talk at the Baltimore Meeting of the American Physical Society, March 26, 1962.

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

² G. T. Rado and V. J. Folen, *Phys. Rev. Letters* **7**, 310 (1961).

showed on the basis of similar but more detailed considerations that in the specific case of Cr_2O_3 the existence of ME effects would be compatible with the magnetic symmetry of the material. Recent reviews include a discussion of relevant thermodynamic and symmetry considerations⁷ as well as of experimental and theoretical studies^{7,8} on ME effects.

In a first attempt⁹ to provide an atomic theory of ME effects, we started with a phenomenological treatment of the temperature dependence of the parallel and perpendicular magnetoelectric susceptibilities, $\alpha_{11}/4\pi$ and $\alpha_1/4\pi$, which agrees qualitatively with the experimental results. Then we proposed a quantum mechanical mechanism which appears to be a possible explanation of the physical origin of the $(\text{ME})_E$ effect in the perpendicular as well as in the parallel case. This mechanism involves a combined action of the externally applied electric potential, the odd part of the crystalline electric potential, and the spin-orbit coupling, and its mathematical representation is a fourth-order energy perturbation in which the spin-orbit coupling appears quadratically. We shall, henceforth, refer to this mechanism as the spin-orbit mechanism. Rough numerical estimates indicated that it accounts for at least a significant part of the measured α 's. More recently, Date, Kanamori, and Tachiki¹⁰ proposed an alternative mechanism and pointed out that it applies to the parallel case only. Their mechanism differs from ours in that the spin-orbit coupling is replaced by an intra-sublattice exchange interaction which is taken to first order. The third-order process obtained in this way leads to the same temperature dependence as the phenomenological expression⁹ suggested earlier.

One purpose of the present paper is to demonstrate that the spin-orbit mechanism affords a possible explanation of the $(\text{ME})_H$ effect as well as of the $(\text{ME})_E$ effect. This is accomplished by means of a statistical mechanical calculation. Starting with the spin Hamiltonian which describes the spin-orbit mechanism,⁹ we use perturbation theory to calculate, in the molecular field approximation, the Helmholtz free energy of a two-sublattice antiferromagnet subject to applied electric and magnetic fields. The α 's for both ME effects are then obtained with the help of thermodynamic relations. According to these calculations, the statistically and phenomenologically derived temperature dependences of the α 's are slightly different. The fact that such a difference exists was recognized for the $(\text{ME})_E$ effect by Kanamori and Tachiki.¹¹ In addition to predicting the α 's, our equations for the free energy yield the well-known formulas for χ_{11} and χ_1 , the parallel and perpendicular magnetic susceptibilities, and also expressions

for $\Delta\kappa_{11}$ and $\Delta\kappa_1$, the previously overlooked magnetoelectric contributions to the electric susceptibilities. In Sec. II we present the theoretical method and calculate these three susceptibilities for the parallel case, and in Sec. III we extend the calculations to the perpendicular case.

Another purpose of this paper is to determine to what extent the spin-orbit mechanism accounts for the ME effects in Cr_2O_3 . In Sec. IV we compare the magnitudes as well as the temperature dependences of the theoretical α 's with the corresponding experimental quantities. The magnitudes of the theoretical α 's are estimated on the basis of spin Hamiltonian parameters determined by recent experiments^{12,13} on the electric field splitting of certain paramagnetic resonance lines in ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{+++}$), and the temperature dependences of the theoretical α 's are calculated both with and without the use of experimental data^{14,15} on the magnetic susceptibilities of Cr_2O_3 . It is found, however, that all comparisons between theory and experiment are hampered by the fact that a two-sublattice model is not strictly applicable to Cr_2O_3 . For this and other reasons, our conclusion in Sec. IV that the spin-orbit mechanism accounts for a significant part of the ME effects in Cr_2O_3 is necessarily qualitative.

In the Appendix we derive some known thermodynamic relations relevant to magnetoelectric effects in a form which is directly applicable to the statistical treatment. Also presented in the Appendix is an account of the thermodynamics of the "piezomagnetoelectric" effects¹⁶ and of the hitherto overlooked "gyroelectric" effects.

II. THEORY FOR THE PARALLEL CASE

We consider a two-sublattice antiferromagnet of unit volume containing $N/2$ identical magnetic ions in its "+ sublattice" and also in its "- sublattice." Next we choose some rectangular coordinate system ξ, η, ζ , whose positive ζ direction is parallel to the magnetization of one of the sublattices. This sublattice will be referred to as the + sublattice. In addition, we find it convenient to introduce a separate rectangular coordinate system x, y, z for each of the sublattices. By definition, the positive x, y, z directions of the + sublattice coordinate system are *parallel* to the positive ξ, η, ζ directions, whereas the positive x, y, z directions of the - sublattice coordinate system are *antiparallel* to the positive ξ, η, ζ directions.

¹² J. O. Artman and J. C. Murphy, Bull. Am. Phys. Soc. **7**, 14 (1962).

¹³ E. B. Royce and N. Bloembergen, Bull. Am. Phys. Soc. **7**, 200 (1962), and private communication.

¹⁴ S. Foner (private communication). More recent data by Foner show that the absolute value of χ_1 at 4.2°K is 1.17×10^{-4} , and that χ_{11} at 4.2°K varies (depending on the sample) from 4 to 6% of its value at T_N . Note that the χ 's of the present paper refer to unit volume.

¹⁵ T. R. McGuire, E. J. Scott, and F. H. Grannis, Phys. Rev. **102**, 1000 (1956).

¹⁶ G. T. Rado, paper presented at the Seventh Conference on Magnetism and Magnetic Materials, Phoenix, Arizona, Nov. 13-16, 1961; see also reference 7.

⁷ G. T. Rado and V. J. Folen, J. Appl. Phys. Suppl. **33**, 1126 (1962).

⁸ G. T. Rado and V. J. Folen, J. Phys. Soc. Japan **17**, Suppl. B-1, 244 (1962).

⁹ G. T. Rado, Phys. Rev. Letters **6**, 609 (1961).

¹⁰ M. Date, J. Kanamori and M. Tachiki, J. Phys. Soc. Japan **16**, 2589 (1961).

¹¹ J. Kanamori and M. Tachiki (private communication).

We take the direction of quantization for each sublattice to be the positive z direction of its own coordinate system. Throughout Sec. II, we assume that the external electric and magnetic fields, \mathbf{E} and \mathbf{H} , are applied parallel to the positive ζ direction. This configuration will be referred to as the "parallel case."

A. Spin Hamiltonian

To each magnetic ion in a sublattice (specified by the superscript $+$ or $-$) we assign the spin Hamiltonian

$$\mathcal{H}^\pm = -g\mu_B S_z H_z^{\text{eff}\pm} \pm g\mu_B a_{11} S_z^2 E_\zeta, \quad (1)$$

which contains a Zeeman term arising from the effective magnetic field $H_z^{\text{eff}\pm}$ and a magnetoelectric term proposed by the author.⁹ The symbols g , μ_B , and S_z denote, respectively, the spectroscopic splitting factor, the Bohr magneton, and the operator describing the z component of the spin. Since the molecular field $H_z^{\text{mol}\pm}$, which will be seen to contribute to $H_z^{\text{eff}\pm}$, acts on the spin moments but not on the orbital moments, we ought to use the value $g=2$ only in that portion of $H_z^{\text{eff}\pm}$ which involves $H_z^{\text{mol}\pm}$. For the sake of simplicity, however, we shall avoid this fine distinction and assume as an approximation that g has the value 2 throughout this paper.

The magnetoelectric term of Eq. (1) embodies the spin-orbit mechanism. On the basis of fourth-order perturbation theory, the order of magnitude of the coefficient a_{11} pertaining to either sublattice was shown⁹ to be given by the typical term

$$a_{11} \approx \frac{E_z e^2 \lambda^2 \langle i|z|j\rangle \langle j|z|k\rangle \langle k|L_z|l\rangle \langle l|L_z|i\rangle}{g\mu_B \Delta_1 \Delta_2 \Delta_3}, \quad (2)$$

where e , λ , and L_z denote, respectively, the electronic charge, the spin-orbit parameter, and the operator describing the z component of the orbital angular momentum. Here $-E_z e z$ is the linear portion of the crystalline electric potential, $\langle i|z|j\rangle$ and $\langle k|L_z|l\rangle$ are appropriate matrix elements, and Δ_1 , Δ_2 , and Δ_3 are differences between appropriate eigenvalues of the unperturbed ($E_\zeta = H_\zeta = 0$) part of \mathcal{H}^\pm . Since $\langle i|z|j\rangle$ vanishes except between states of different parity, one of these Δ 's will usually represent an optical splitting. A very rough estimate applicable to Cr^{+++} in Cr_2O_3 yielded the value⁹ $a_{11} \approx 0.6 \times 10^{-3}$. For the purposes of the present paper, however, the quantity a_{11} (which is dimensionless in the Gaussian system) is treated as a parameter whose value is to be determined by means of suitable experiments.

The Zeeman term of Eq. (1) will now be expressed in terms of the applied fields. We define $H_z^{\text{eff}\pm}$ by

$$H_z^{\text{eff}\pm} = H_z^{\text{mol}\pm} \pm H_\zeta, \quad (3)$$

and use the molecular field¹⁷ relation

$$\mathbf{H}^{\text{mol}\pm} = -A\mathbf{M}^\mp - \Gamma\mathbf{M}^\pm \quad (4)$$

to write Eq. (3) in the form

$$H_z^{\text{eff}\pm} = A M_z^\mp - \Gamma M_z^\pm \pm H_\zeta, \quad (5)$$

where A and Γ are molecular field coefficients describing the inter- and intra-sublattice exchange interactions, respectively, and \mathbf{M}^\pm is the sublattice magnetization. Since the applied fields are small, it is appropriate to make the usual assumption that half of the induced magnetization

$$M_\zeta = M_z^+ - M_z^- \quad (6)$$

is associated with each sublattice. Denoting the spontaneous magnetization of either sublattice by M_{0z} , we may thus put

$$M_z^\pm = M_{0z} \pm \frac{1}{2} M_\zeta, \quad (7)$$

which may be combined with Eq. (5) to give

$$H_z^{\text{eff}\pm} = (A - \Gamma) M_{0z} \mp \frac{1}{2} (A + \Gamma) M_\zeta \pm H_\zeta. \quad (8)$$

If we now use the constitutive equation

$$M_\zeta = \chi_{11} H_\zeta + (\alpha_{11}/4\pi) E_\zeta, \quad (9)$$

which is derived in the Appendix as Eq. (A14b), then Eq. (8) becomes

$$H_z^{\text{eff}\pm} = (A - \Gamma) M_{0z} \pm \left[1 - \frac{1}{2} (A + \Gamma) \chi_{11} \right] H_\zeta \mp (A + \Gamma) (\alpha_{11}/8\pi) E_\zeta, \quad (10)$$

which shows that the ME effects cause $H_z^{\text{eff}\pm}$ to depend on E_ζ as well as on H_ζ .

Next we decompose \mathcal{H}^\pm into a field-independent part \mathcal{H}_0 and a field-dependent part V^\pm , and regard \mathcal{H}_0 as the unperturbed Hamiltonian and V^\pm as the perturbation. (It will be seen in Sec. III that in the perpendicular case V^\pm is *not* diagonal.) After substitution of Eq. (10) into Eq. (1) we have

$$\mathcal{H}^\pm = \mathcal{H}_0 + V^\pm; \quad (11)$$

$$\mathcal{H}_0 = -g\mu_B (A - \Gamma) M_{0z} S_z; \quad (12)$$

$$V^\pm = \pm g\mu_B \{ [(A + \Gamma) (\alpha_{11}/8\pi) S_z + a_{11} S_z^2] E_\zeta - [1 - (A + \Gamma) (\chi_{11}/2)] S_z H_\zeta \}. \quad (13)$$

The matrix elements of V^\pm follow directly from an inspection of Eq. (13) because we work throughout this paper in a representation in which S_z is diagonal. Denoting the spin magnetic quantum number by m , and simplifying the notation, we obtain

$$V_{nm}^\pm \equiv \langle n | V^\pm | m \rangle = \pm V_{nm} \delta_{nm}, \quad (14a)$$

$$V_{mm} = g\mu_B m \{ [(A + \Gamma) (\alpha_{11}/8\pi) + a_{11} m] E_\zeta - [1 - (A + \Gamma) (\chi_{11}/2)] H_\zeta \}, \quad (14b)$$

¹⁷ For a review of antiferromagnetism, see T. Nagamiya, K. Yosida, and R. Kubo, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1955), Vol. 4, p. 1.

where δ_{nm} is the Kronecker symbol. We also note, for future reference, that on the basis of Eq. (12) the m th eigenvalue of \mathcal{H}_0 is given by

$$E_m^{(0)} = -g\mu_B m(A - \Gamma)M_{0z}. \quad (15)$$

B. Free Energy

According to statistical mechanics, the Helmholtz free energy per ion, f^\pm , may be obtained from

$$\exp(-f^\pm/kT) = \sum_m \exp(-E_m^\pm/kT), \quad (16)$$

where k is Boltzmann's constant, T is the absolute temperature, and E_m^\pm is the m th eigenvalue of \mathcal{H}^\pm . Correspondingly, we have in the absence of applied fields

$$\exp(-f_0/kT) = \sum_m \exp(-E_m^{(0)}/kT), \quad (17)$$

where f_0 is the unperturbed value of f^\pm . In calculating E_m^\pm we use, on the basis of second-order perturbation theory,

$$E_m^\pm = E_m^{(0)} + V_{mm}^\pm + \sum'_n \frac{|V_{nm}^\pm|^2}{E_m^{(0)} - E_n^{(0)}}, \quad (18)$$

where the prime indicates $n \neq m$. This approximation is adequate for the present problem because we are interested only in those terms of the free energy which are proportional to \mathbf{E}^2 , \mathbf{H}^2 , or $\mathbf{E} \cdot \mathbf{H}$. Such terms will be referred to as "second-order terms" throughout this paper. After substituting Eq. (18) into Eq. (16) and expanding the resulting expression for f^\pm to second order, we use Eq. (17) to obtain

$$\begin{aligned} f^\pm = f_0 + \sum_m V_{mm}^\pm w_m + \sum_m \sum'_n \frac{|V_{nm}^\pm|^2}{E_m^{(0)} - E_n^{(0)}} w_m \\ - (1/2kT) \sum_m (V_{mm}^\pm)^2 w_m \\ + (1/2kT) \sum_m (V_{mm}^\pm w_m)^2, \end{aligned} \quad (19)$$

where the quantity

$$w_m = \exp[(f_0 - E_m^{(0)})/kT] \quad (20)$$

denotes the unperturbed canonical distribution. Equation (19), which is known from "thermodynamic perturbation theory,"¹⁸ is based on the assumptions that the matrix elements of the perturbation are small compared to kT and small compared to the appropriate differences between the unperturbed energy levels. It is easily verified that under the usual experimental conditions both of these assumptions are valid in the present problem.

¹⁸ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), paragraph 32. The complication discussed in the footnote on p. 94 of this reference does not occur in the present paper because the expansion underlying our Eq. (19) involves the perturbation *per ion*.

Since the perturbation is diagonal [see Eq. (14a)] in the *parallel* case, Eq. (19) becomes

$$\begin{aligned} f^\pm = f_0 + \langle V_{mm}^\pm \rangle_{av} - (1/2kT) \\ \times [\langle (V_{mm}^\pm)^2 \rangle_{av} - \langle V_{mm}^\pm \rangle_{av}^2], \end{aligned} \quad (21)$$

where the symbol $\langle \rangle_{av}$ indicates an average over the unperturbed canonical distribution. Using Eqs. (14) and noting that V_{mm} is linear in E_ζ and H_ζ , we replace Eq. (21) by

$$F_2^\pm = - (N/4kT) (\langle V_{mm}^2 \rangle_{av} - \langle V_{mm} \rangle_{av}^2), \quad (22)$$

where $F^\pm = (N/2)f^\pm$ is not the free energy of a sublattice but just an abbreviation, and the subscript 2 expresses the fact that only second-order terms have been retained.

To calculate the free energy, F , of the whole two-sublattice antiferromagnet, we use the equation

$$F_2 = F_2^+ + F_2^- - F_2^{\text{int}}, \quad (23)$$

where F^{int} is the free energy corresponding to all the exchange interactions, and where we again retained second-order terms only. If we had omitted the F_2^{int} term of Eq. (23), then the inter- and intra-sublattice exchange interactions (which we have represented by means of molecular fields) would each have been counted twice. Since the M_ζ term of Eq. (8) leads to

$$F_2^{\text{int}} = - (M_\zeta/2) [- (A + \Gamma) M_\zeta/2] = (A + \Gamma) M_\zeta^2/4, \quad (24)$$

we may combine Eqs. (23) and (22) to obtain

$$\begin{aligned} F_2 = - (N/2kT) (\langle V_{mm}^2 \rangle_{av} - \langle V_{mm} \rangle_{av}^2) \\ - (A + \Gamma) M_\zeta^2/4. \end{aligned} \quad (25)$$

Substitution of Eqs. (9) and (14b) into Eq. (25) then yields

$$F_2 = c_{HH} H_\zeta^2 + c_{EH} E_\zeta H_\zeta + c_{EE} E_\zeta^2, \quad (26)$$

where the coefficients are given by

$$\begin{aligned} c_{HH} = - (Ng^2\mu_B^2/2kT) [1 - (A + \Gamma)(\chi_{11}/2)]^2 \\ \times [\langle m^2 \rangle_{av} - \langle m \rangle_{av}^2 - (A + \Gamma)\chi_{11}^2/4]; \end{aligned} \quad (27a)$$

$$\begin{aligned} c_{EH} = (Ng^2\mu_B^2/kT) [1 - (A + \Gamma)(\chi_{11}/2)] \\ \times [(A + \Gamma)(\alpha_{11}/8\pi) (\langle m^2 \rangle_{av} - \langle m \rangle_{av}^2) \\ + a_{11} (\langle m^3 \rangle_{av} - \langle m^2 \rangle_{av} \langle m \rangle_{av})] \\ - (A + \Gamma)\chi_{11}\alpha_{11}/8\pi; \end{aligned} \quad (27b)$$

$$\begin{aligned} c_{EE} = - (Ng^2\mu_B^2/2kT) [(A + \Gamma)^2(\alpha_{11}/8\pi)^2 (\langle m^2 \rangle_{av} - \langle m \rangle_{av}^2) \\ + a_{11}(A + \Gamma)(\alpha_{11}/4\pi) (\langle m^3 \rangle_{av} - \langle m^2 \rangle_{av} \langle m \rangle_{av}) \\ + a_{11}^2 (\langle m^4 \rangle_{av} - \langle m^2 \rangle_{av}^2)] - (A + \Gamma)(\alpha_{11}/8\pi)^2. \end{aligned} \quad (27c)$$

Equation (26), which is seen to contain the $E_\zeta H_\zeta$ term characteristic of parallel ME effects, will now be used to calculate the parallel susceptibilities.

C. Susceptibilities

Before calculating α_{11} , we test our statistical method by deriving the well-known molecular field equation for

χ_{11} . This equation will, in addition, enable us to write our result for α_{11} in a relatively simple and useful form.

1. Magnetic Susceptibility

From Eq. (A16) we obtain the thermodynamic relation

$$\chi_{11} = -\partial^2 F_2 / \partial H_z^2, \quad (28)$$

where F has been replaced by F_2 because we are concerned throughout this paper with field-independent susceptibilities only. Using Eqs. (26) and (28), we thus have

$$\chi_{11} = -2c_{HH}, \quad (29)$$

which may be solved with the help of Eq. (27a) to yield

$$\chi_{11} = \frac{(Ng^2\mu_B^2/k)(\langle m^2 \rangle_{av} - \langle m \rangle_{av}^2)}{T + (A + \Gamma)(Ng^2\mu_B^2/2k)(\langle m^2 \rangle_{av} - \langle m \rangle_{av}^2)}. \quad (30)$$

The various averages appearing in this and subsequent equations may be expressed in a form appropriate for numerical calculations. To do this, we begin by recalling that the Brillouin function

$$B_S(u) = \frac{2S+1}{2S} \coth\left(\frac{2Su+u}{2S}\right) - \frac{1}{2S} \coth\left(\frac{u}{2S}\right) \quad (31)$$

is obtained from

$$B_S(u) = \sum_{m=-S}^S (m/S) \exp(um/S) / \sum_{m=-S}^S \exp(um/S). \quad (32)$$

Identifying, henceforth, the variable u with

$$u = -SE_m^{(0)}/mkT, \quad (33)$$

we see on the basis of Eq. (20) and our definition of $\langle \rangle_{av}$ that Eq. (32) leads to

$$\langle m \rangle_{av} = SB_S(u). \quad (34)$$

Similarly, differentiation of Eq. (32) gives

$$\langle m^2 \rangle_{av} - \langle m \rangle_{av}^2 = S^2 B_S'(u), \quad (35)$$

where $B_S'(u)$ denotes $dB_S(u)/du$. By substituting Eq. (35) into Eq. (30), we thus obtain

$$\chi_{11} = \frac{3S(S+1)^{-1}CB_S'(u)}{T + 3S(S+1)^{-1}\Theta B_S'(u)}, \quad (36)$$

where

$$C = Ng^2\mu_B^2 S(S+1)/3k \quad (37)$$

is the Curie constant, and

$$\Theta = C(A + \Gamma)/2 \quad (38)$$

will be called the Curie-Weiss constant. As discussed in Sec. IV, the value of Θ may be deduced from appropriate experimental results. Equation (36) agrees exactly with the result derived in the literature¹⁷ by means of a method not involving the free energy.

In calculations of the temperature dependence of χ_{11} and the other susceptibilities (including the perpendicular ones), we require an explicit relation between u and T . Although such a relation is well known, we now derive it in order to introduce two quantities which will be used later on: the Néel point, T_N , and a combined quantum mechanical and statistical average, $\langle \rangle_{av}$. It should be noted that $\langle \rangle_{av}$ differs from the purely statistical average $\langle \rangle$ introduced earlier.

By definition, we have

$$M_{0z} = (N/2)g\mu_B \langle S_z \rangle_{av} = (N/2)g\mu_B \text{Tr}(S_z \rho), \quad (39)$$

where ρ is the statistical operator, and Tr denotes the trace. For ρ we may use the canonical expression

$$\rho = \exp(-\mathcal{H}_0^e/kT) / \text{Tr} \exp(-\mathcal{H}_0^e/kT), \quad (40)$$

where \mathcal{H}_0^e denotes the exact Hamiltonian corresponding to vanishing applied fields. If we adopt the molecular field approximation, then \mathcal{H}_0^e becomes \mathcal{H}_0 and (in the representation introduced earlier) the elements of the statistical matrix become $\rho_{nm} = w_m \delta_{nm}$. In the molecular field approximation we thus have

$$\langle S_z \rangle_{av} = \langle m \rangle_{av}, \quad (41)$$

which may be combined with Eqs. (34) and (39) to give

$$M_{0z} = (N/2)g\mu_B SB_S(u). \quad (42)$$

Substitution of Eq. (15) into Eq. (33) yields

$$u = g\mu_B S(A - \Gamma)M_{0z}/kT, \quad (43)$$

so that with the help of Eqs. (42) and (37) we obtain

$$T = 3S(S+1)^{-1}(C/2)(A - \Gamma)B_S(u)/u. \quad (44)$$

Since u as well as M_{0z} approaches zero in the limit in which T approaches T_N , expansion of Eq. (44) gives

$$T_N = C(A - \Gamma)/2, \quad (45)$$

so that Eq. (44) yields the required relation

$$T = 3S(S+1)^{-1}T_N B_S(u)/u. \quad (46)$$

2. Magnetoelectric Susceptibility

From Eq. (A17) we obtain

$$\alpha_{11}/4\pi = -\partial^2 F_2 / \partial E_z \partial H_z, \quad (47)$$

where the commutability of $\partial/\partial E_z$ and $\partial/\partial H_z$ insures that our result for α_{11} will apply to the $(\text{ME})_H$ as well as to the $(\text{ME})_E$ effect. Using Eqs. (26) and (47), we thus have

$$\alpha_{11}/4\pi = -c_{EH}, \quad (48)$$

which may be solved with the help of Eq. (27b) to yield

$$\frac{\alpha_{11}}{4\pi} = -\frac{a_{11}(Ng^2\mu_B^2/k)(\langle m^3 \rangle_{av} - \langle m^2 \rangle_{av} \langle m \rangle_{av})}{T + (A + \Gamma)(Ng^2\mu_B^2/2k)(\langle m^2 \rangle_{av} - \langle m \rangle_{av}^2)}. \quad (49)$$

To express Eq. (49) in terms of Brillouin functions, we note that

$$\langle m^2 \rangle_{av} = \sum_{m=-S}^S m^2 \exp(um/S) / \sum_{m=-S}^S \exp(um/S) \quad (50)$$

follows by analogy from Eqs. (34) and (32). After combining the expressions obtained by differentiating Eqs. (50) and (35), we have

$$\langle m^3 \rangle_{av} - \langle m^2 \rangle_{av} \langle m \rangle_{av} = S^3 B_{S''}(u) + 2S^3 B_{S'}(u) B_S(u), \quad (51)$$

where $B_{S''}(u)$ denotes $d^2 B_S(u)/du^2$. Substitution of Eqs. (35), (38), and (51) into Eq. (49) then results in

$$\frac{\alpha_{II}}{4\pi} = - \frac{3S^2(S+1)^{-1} a_{II} C [B_{S''}(u) + 2B_{S'}(u) B_S(u)]}{T + 3S(S+1)^{-1} \Theta B_{S'}(u)}. \quad (52)$$

3. Relation between Magnetoelectric and Magnetic Susceptibilities

We shall find it useful to express our results for α_{II} in the form

$$\alpha_{II}/4\pi = a_{II} \chi_{II} \langle m \rangle_{av} G_{II}, \quad (53)$$

where G_{II} is a temperature-dependent factor. With the help of Eqs. (49) and (30) we obtain

$$G_{II} = \frac{\langle m^2 \rangle_{av} \langle m \rangle_{av} - \langle m^3 \rangle_{av}}{\langle m^2 \rangle_{av} \langle m \rangle_{av} - \langle m \rangle_{av}^3}, \quad (54)$$

and from Eqs. (52), (36) and (34) we get

$$G_{II} = - \frac{B_{S''}(u) + 2B_{S'}(u) B_S(u)}{B_{S'}(u) B_S(u)}, \quad (55)$$

which provides less insight than Eq. (54) but proves more useful for numerical calculations.

In order to compare Eq. (53) with our phenomenological result⁹

$$\alpha_{II}/4\pi = a_{II} \chi_{II} \langle \langle S_z \rangle \rangle_{av}, \quad (56)$$

we use Eq. (41) to write Eq. (56) in the form

$$\alpha_{II}/4\pi = a_{II} \chi_{II} \langle m \rangle_{av}, \quad (57)$$

which is valid in the molecular field approximation. By comparing Eqs. (53) and (57) we see that in this approximation the statistical and phenomenological expressions for α_{II} differ solely by the factor G_{II} . Representative numerical values of this factor were computed on the basis of Eq. (55) for the case $S=3/2$, which applies to Cr^{+++} . It was found that as u increases from zero to infinity, which corresponds [according to Eq. (46)] to T decreasing from T_N to 0°K , the factor $-G_{II}$ increases monotonically from 0.640 to 1.333. Thus, the effect of applying the G_{II} correction to the phenomenological α_{II} is to change its temperature dependence quantitatively but not qualitatively, and to change its magnitude by a factor of the order of unity.

4. Magnetoelectric Contribution to the Electric Susceptibility

From Eq. (A15) we obtain

$$\kappa_{II} = -\partial^2 F_2 / \partial E_z^2, \quad (58)$$

so that with the help of Eq. (26) we have

$$\Delta \kappa_{II} = -2c_{EE}, \quad (59)$$

where c_{EE} is given by Eq. (27c). The reason for writing $\Delta \kappa_{II}$ rather than κ_{II} in Eq. (59) is that on the basis of the incomplete Hamiltonian of Eq. (11) we cannot calculate the entire electric susceptibility, which contains an ionic as well as an electronic part, but merely that contribution ($\Delta \kappa_{II}$) to its electronic part which arises from ME effects. Since the numerical value of $\Delta \kappa_{II}$ turns out to be very small (roughly of the order of 10^{-6} in the case of Cr_2O_3) even at high temperatures, we shall omit the step of expressing c_{EE} and hence $\Delta \kappa_{II}$ in terms of Brillouin functions. It is interesting, however, to consider the physical origin of $\Delta \kappa_{II}$. We recall, for this purpose, that the spin-orbit mechanism of the $(\text{ME})_E$ effect may be described pictorially by imagining the electron cloud of each magnetic ion to be distorted by the applied electric field, so that as a result of spin-orbit coupling the spins may respond to this distortion in such a way as to give rise to an induced magnetization.⁹ Similarly, the spin-orbit mechanism of the $(\text{ME})_H$ effect may be described by imagining the spins to be aligned by the applied magnetic field, so that as a result of spin-orbit coupling the ionic electron cloud may respond to this alignment in such a way as to give rise to an induced polarization. Since Eqs. (59) and (27c) show that $\Delta \kappa_{II}$ vanishes if a_{II} is zero, we may combine these pictorial descriptions by attributing the $\Delta \kappa_{II}$ effect to a polarization caused by a "back reaction" of the spins on the ionic electron cloud. This interpretation agrees with our result that $\Delta \kappa_{II}$ depends on a_{II} quadratically.

III. THEORY FOR THE PERPENDICULAR CASE

Using the same coordinate systems as in Sec. II, we now assume that \mathbf{E} and \mathbf{H} are applied parallel to the positive ξ direction. This configuration will be referred to as the "perpendicular case." Since much of the analysis and discussion pertaining to this case is entirely analogous to that given in Sec. II, we proceed to derive the final results without explaining many of the intermediate steps.

A. Spin Hamiltonian

Instead of Eq. (1), we now use the spin Hamiltonian

$$\mathcal{H} \pm = -g\mu_B (S_x H_x^{\text{eff} \pm} + S_z H_z^{\text{eff} \pm}) \pm g\mu_B (a_L/2) (S_x S_z + S_z S_x) E_z, \quad (60)$$

where the magnetoelectric term⁹ is written in symmetrical form. To obtain the order of magnitude of the coefficient a_L , we may use Eq. (2) with one of the z 's

replaced by x and one of the L_z 's replaced by L_x . Although this shows that our very rough estimate of a_{11} applies to a_1 also, there can be little doubt that the magnitudes of a_{11} and a_1 actually differ.

By combining molecular field equations analogous to Eqs. (3)–(8) with the relation

$$M_\xi = \chi_1 H_\xi + (\alpha_1/4\pi) E_\xi, \quad (61)$$

which follows from Eq. (A14a), we obtain

$$H_x^{\text{eff}\pm} = \pm [1 - (A + \Gamma)\chi_1/2] H_\xi \mp (A + \Gamma)(\alpha_1/8\pi) E_\xi; \quad (62)$$

$$H_z^{\text{eff}\pm} = (A - \Gamma) M_{0z}. \quad (63)$$

Thus it is seen that \mathcal{H}^\pm may again be written in the form of Eq. (11) provided Eq. (12) for \mathcal{H}_0 is retained but Eq. (13) for V^\pm is replaced by

$$V^\pm = \pm g\mu_B \{ [(A + \Gamma)(\alpha_1/8\pi) S_x + (a_1/2)(S_x S_z + S_z S_x)] E_\xi - [1 - (A + \Gamma)(\chi_1/2)] S_x H_\xi \}. \quad (64)$$

Inspection of Eq. (64) shows that the matrix elements of V^\pm have the form

$$V_{nm}^\pm = \pm V_{nm} (1 - \delta_{nm}), \quad (65)$$

where V_{nm} (which we do not give explicitly) vanishes unless n is either $m+1$ or $m-1$.

B. Free Energy

Upon inserting Eq. (65) into Eq. (19) and avoiding the previously mentioned “double counting” of all the exchange interactions, we obtain

$$F_2 = N \langle \sum_n' [|V_{nm}|^2 / (E_m^{(0)} - E_n^{(0)})] \rangle_{\text{av}} - (A + \Gamma) M_\xi^2 / 4, \quad (66)$$

as the replacement of Eq. (25). After using the equation

$$E_m^{(0)} - E_n^{(0)} = -(N/2) g^2 \mu_B^2 (m - n) (A - \Gamma) \langle m \rangle_{\text{av}}, \quad (67)$$

which follows from Eqs. (15), (42), and (34), we find that with the help of Eq. (61) and the easily calculable sums

$$\sum_n' [\langle n | S_x | m \rangle^2 / (m - n)] = m/2, \quad (68a)$$

$$\sum_n' [\langle n | S_x | m \rangle^2 (m + n) / (m - n)] = (3/2) [m^2 - S(S + 1)/3], \quad (68b)$$

$$\sum_n' [\langle n | S_x | m \rangle^2 (m + n)^2 / (m - n)] = (m/2) [8m^2 - 4S(S + 1) + 1], \quad (68c)$$

we may write Eq. (66) in the form

$$F_2 = d_{HH} H_\xi^2 + d_{EH} E_\xi H_\xi + d_{EE} E_\xi^2, \quad (69)$$

where the coefficients are given by

$$d_{HH} = -(A - \Gamma)^{-1} [1 - (A + \Gamma)(\chi_1/2)]^2 - (A + \Gamma)\chi_1^2/4; \quad (70a)$$

$$d_{EH} = [(A - \Gamma)\langle m \rangle_{\text{av}}]^{-1} [1 - (A + \Gamma)(\chi_1/2)] \times \{ (A + \Gamma)(\alpha_1/4\pi)\langle m \rangle_{\text{av}} + 3a_1[\langle m^2 \rangle_{\text{av}} - S(S + 1)/3] \} - (A + \Gamma)\chi_1\alpha_1/8\pi; \quad (70b)$$

$$d_{EE} = -[(A - \Gamma)\langle m \rangle_{\text{av}}]^{-1} \{ (A + \Gamma)^2 (\alpha_1/8\pi)^2 \langle m \rangle_{\text{av}} + 3a_1(A + \Gamma)(\alpha_1/8\pi)[\langle m^2 \rangle_{\text{av}} - S(S + 1)/3] + (a_1^2/4)[8\langle m^3 \rangle_{\text{av}} - (4S^2 + 4S - 1)\langle m \rangle_{\text{av}}] \} - (A + \Gamma)(\alpha_1/8\pi)^2. \quad (70c)$$

Equation (69), which is seen to contain the $E_\xi H_\xi$ term characteristic of perpendicular ME effects, will now be used to calculate the perpendicular susceptibilities.

C. Susceptibilities

By analogy with Eqs. (29), (48), and (59), we have

$$\chi_1 = -2d_{HH}, \quad (71)$$

$$\alpha_1/4\pi = -d_{EH}, \quad (72)$$

$$\Delta\kappa_1 = -2d_{EE}, \quad (73)$$

where the commutability of $\partial/\partial E_\xi$ and $\partial/\partial H_\xi$ insures that our result for α_1 will apply to the $(\text{ME})_H$ as well as to the $(\text{ME})_E$ effect.

Solution of Eqs. (71) and (70a) yields

$$\chi_1 = 1/A, \quad (74)$$

which agrees exactly with the result derived in the literature¹⁷ by means of a method based on the vanishing of the net torque acting on each sublattice. With the help of Eqs. (38) and (45), we may write Eq. (74) in the more useful form

$$\chi_1 = C/(T_N + \Theta). \quad (75)$$

From Eqs. (72) and (70b) we derive

$$\alpha_1/4\pi = -(3a_1/2A)[\langle m^2 \rangle_{\text{av}} - S(S + 1)/3]/\langle m \rangle_{\text{av}}, \quad (76)$$

which may be combined with Eqs. (34), (35), (38), and (45) to yield the equivalent expression

$$\frac{\alpha_1}{4\pi} = -\frac{3a_1 SC[B_s'(u) + B_s^2(u) - (S + 1)/3S]}{2(T_N + \Theta)B_s(u)}. \quad (77)$$

These results for α_1 may be written in the form

$$\alpha_1/4\pi = a_1 \chi_1 \langle m \rangle_{\text{av}} G_1, \quad (78)$$

where G_1 is a temperature-dependent factor which is seen to be given by

$$G_1 = -(3/2)[\langle m^2 \rangle_{\text{av}} - S(S + 1)/3]/\langle m \rangle_{\text{av}}^2, \quad (79)$$

or by

$$G_1 = -(3/2)[B_s'(u) + B_s^2(u) - (S + 1)/3S]/B_s^2(u). \quad (80)$$

Comparison of Eq. (78) with our phenomenological result⁹

$$\alpha_1/4\pi = a_1\chi_1\langle\langle S_z \rangle\rangle_{av} \quad (81)$$

shows that in the molecular field approximation [in which Eq. (41) applies] the statistical and phenomenological expressions for α_1 differ solely by the factor G_1 . Numerical computations based on Eq. (80) and the value $S=3/2$ show that as u increases from zero to infinity, which corresponds [according to Eq. (46)] to T decreasing from T_N to 0°K, the factor $-G_1$ increases monotonically from 0.480 to 0.667. Thus the effect of applying the G_1 correction to the phenomenological α_1 is to change its temperature dependence quantitatively but not qualitatively, and to change its magnitude by a factor of the order of unity.

In regard to $\Delta\kappa_1$, which is given by Eqs. (73) and (70c), our comments are analogous to those made in connection with $\Delta\kappa_{11}$.

IV. COMPARISON WITH EXPERIMENTS

Theoretical predictions based on the spin-orbit (or any other) mechanism cannot, at present, be compared with experiments in an entirely valid manner. The reason is that the two-sublattice model, which was used in Secs. II and III, is not strictly applicable to Cr_2O_3 . According to Eq. (36), χ_{11} should approach zero as the temperature is decreased toward 0°K. The experimental data of Foner¹⁴ show, however, that in the liquid-helium region χ_{11} is essentially temperature-independent and equal to about 6.5% of its value at T_N . This discrepancy is, of course, a purely magnetic rather than magnetoelectric problem. Theoretical estimates indicate that it is perhaps due to Van Vleck-type temperature-independent paramagnetism. Another possible explanation is that the magnetizations of the sublattices are not antiparallel but slightly canted.¹⁹ Existing neutron diffraction evidence²⁰ neither supports nor eliminates this possibility.²¹ Thus the cause of the discrepancy is not known at present, and no improvement over the two-sublattice model is in sight.

A semiquantitative comparison between the theory of Secs. II and III and the experimental results on Cr_2O_3 will now be carried out by using either calculated χ 's ("method A") or measured χ 's ("method B"). Because of the discrepancy discussed above, neither method turns out to be completely satisfactory. In both methods we begin by choosing a convenient set of u values and then computing the corresponding T values with the help of Eq. (46), the value $S=3/2$, and the experimentally determined $T_N=306^\circ\text{K}$. Next we calculate α_{11} and α_1 by using Eqs. (53) and (78), respectively. This is accomplished by determining $\langle m \rangle_{av}$, G_{11} , and G_1 with the

use of Eqs. (34), (55), and (80), respectively, obtaining χ_{11} and χ_1 on the basis of either method A or B, and choosing such numbers for a_{11} and a_1 that the largest values of the calculated $|\alpha_{11}|$ vs T and $|\alpha_1|$ vs T curves agree with the largest values of the corresponding experimental curves.

In method A we calculate χ_{11} and χ_1 from Eqs. (36) and (75), respectively. This requires a knowledge of C and Θ . We obtain $C=0.1288$ from Eq. (37) by using $N=4.13\times 10^{22} \text{ cm}^{-3}$, the value deduced from x-ray data²² on the volume of the unit cell of Cr_2O_3 . Because of the absence of adequate data on the χ of Cr_2O_3 for $T>T_N$, we cannot follow the usual procedure of obtaining Θ from the well-known formula $\chi=C/(T+\Theta)$ which applies in the paramagnetic region. Instead, we determine Θ by requiring that the maximum of the calculated $|\alpha_{11}|$ vs T curve occur at about the same temperature as the maximum of the corresponding experimental curve. This procedure yields $\Theta=-0.38T_N=-116^\circ\text{K}$ for the case where the G_{11} correction is neglected ($G_{11}=1$), and a slightly more negative value for the case where the G_{11} correction is taken into account. The inclusion of the latter value would be a refinement of doubtful validity because a negative Θ value is clearly incompatible with antiferromagnetism. Some justification for the procedure used in determining Θ is provided by the fact that the two-sublattice model is in any case inadequate for Cr_2O_3 , as pointed out at the beginning of this section, so that it is perhaps not unreasonable to treat Θ as an adjustable parameter. An additional justification for this step is supplied by the χ data of McGuire *et al.*¹⁵ which suggest that the agreement between theory and experiment is only fair and may require different Θ values for $T<T_N$ than for $T\geq T_N$. In view of the fact that method A suffers from the disadvantage of an "artificial" Θ , it should be noted that this method has the advantage of consistency resulting from the use of the same theoretical model for the χ 's as for the α 's.

In method B we take χ_{11} and χ_1 from the experimental results of Foner.¹⁴ Since his data are in relative units, we multiply them by a temperature-independent factor which makes them agree at very low temperatures with the nearly temperature-independent value $\chi_1\approx 1.3\times 10^{-4}$ obtained from the measurements of McGuire *et al.*¹⁵ by using the value 5.21 for the density of Cr_2O_3 . This method has the disadvantage of inconsistency resulting from the use of χ 's which are not obtained from the theory underlying the calculation of the α 's. The advantage of this method is, of course, that the experimental χ 's are surely more reliable than the calculated ones.

Figure 1 compares the temperature dependence of the measured⁸ α 's (circles and squares) with that calculated on the basis of method A using the theoretically de-

¹⁹ R. Orbach, Phys. Rev. **115**, 1189 (1959).

²⁰ B. N. Brockhouse, J. Chem. Phys. **21**, 961 (1953); R. Nathans, T. Riste, G. Shirane, and C. G. Shull, Bull. Am. Phys. Soc. **2**, 21 (1957).

²¹ R. Nathans and L. M. Corliss (private communication).

²² R. W. G. Wyckoff, *Crystal Structure* (Interscience Publishers, Inc., New York, 1948), Vol. I.

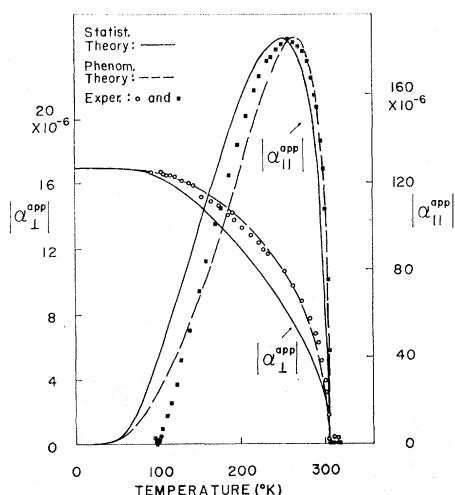


FIG. 1. Temperature dependence of measured and calculated magnetoelectric susceptibilities. The experimental points (after reference 3) were obtained by means of the $(ME)_E$ effect. The theoretical curves, which involve *calculated* magnetic susceptibilities, are based on the statistical (solid lines) and phenomenological (dashed lines) theories presented in this paper.

terminated G 's (solid lines). Corresponding curves for $G_{11}=G_1=1$ (dashed lines) are also shown. The experimental data do not represent actual α 's but rather α_{11}^{app} and α_1^{app} , the superscript "app" indicating that these are apparent values because the demagnetization corrections (which will be discussed below) have not yet been applied. Since the value of Θ was determined for the case $G_{11}=G_1=1$ only, the agreement between the $G \neq 1$ curves and experiment could still be improved somewhat. However, we intentionally selected the curves shown in Fig. 1 in order to illustrate the effect of the G correction alone. It is seen that the $G \neq 1$ curves and the $G=1$ curves agree with experiment only qualitatively, and that the extent of the agreement with experiment is about the same for both sets of curves.

Figure 2 compares the temperature dependence of the measured³ α 's (circles and squares) with that calculated on the basis of method B using the theoretically determined G 's (solid lines). Corresponding curves for $G_{11}=G_1=1$ (dashed lines) are also shown. As in Fig. 1, the experimental data represent α_{11}^{app} and α_1^{app} . The

TABLE I. Comparison of a values deduced from measurements of the ME susceptibilities in Cr_2O_3 and of the electric field splitting of EPR lines in $Al_2O_3:Cr^{+++}$.

	From ME data by using				From EPR data by using
	Method A		Method B		ME spin Hamiltonian
$ a_1 \times 10^3$	3.9 ^a	9.4 ^b	21 ^a	49 ^b	9.7 ± 2^c
$ a_{11} \times 10^3$	108 ^a	169 ^b	420 ^a	654 ^b	28.7 ± 0.5^d

^a Based on the data of reference 3.

^b Based on the data of reference 4.

^c Based on the data of reference 13.

^d Based on the data of references 12 and 13.

agreement between theory and experiment is again only qualitative for both sets of curves.

In order to determine whether the a values which we deduced by using experimental α 's in conjunction with Eqs. (53) and (78) are reasonable, we show in Table I a comparison of these a values with the a values deduced from the measured electric field splitting of certain electron paramagnetic resonance (EPR) lines in ruby. Such measurements were first carried out successfully by Artman and Murphy¹² and then by Royce and Bloembergen.¹³ The latter authors interpreted their results in terms of a spin Hamiltonian which is a generalized version of that proposed by the author⁹ and used as the last terms of Eqs. (1) and (60). The coefficients of their spin Hamiltonian which correspond to a_{11} and a_1 are $\frac{2}{3}R_{333}$ and R_{113} , respectively. When expressed in the Gaussian units used in the present paper, the R coefficients are dimensionless (Oe cm/statV) and have the values listed in the last column of Table I. (It should be noted that calculations similar to those of Secs. II and III show that the remaining R 's do not contribute to $\Delta\kappa_{11}$, α_{11} , and α_1 .)

Also relevant to Table I is the role of demagnetizing effects² in the determination of the a values. Whenever the a 's were deduced from measurements carried out at this Laboratory,³ we corrected the underlying α 's for demagnetizing effects. For the particular samples used, these corrections are expressed by the relations $\alpha_{11} \approx 2\alpha_{11}^{app}$ and $\alpha_1 \approx 2\alpha_1^{app}$. The α 's measured by Astrov,⁴ on the other hand, already include what amounts to a demagnetization correction. Another point requiring comment is the validity of the experimental α 's. Because of the existence^{2,4} of domain structure in Cr_2O_3 , it is doubtful that any of the experimental α 's are really

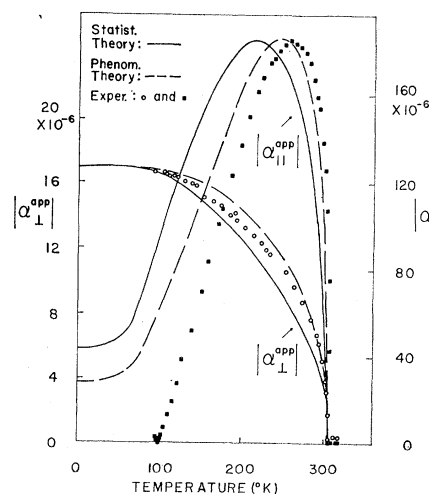


FIG. 2. Temperature dependence of measured and calculated magnetoelectric susceptibilities. The experimental points (after reference 3) were obtained by means of the $(ME)_E$ effect. The theoretical curves, which involve *measured* magnetic susceptibilities (after reference 14), are based on the statistical (solid lines) and phenomenological (dashed lines) theories presented in this paper.

maximum values characteristic of a single-domain sample. Furthermore, all the experiments involve various geometrical difficulties, and the preliminary α values³ obtained at this Laboratory by means of the $(ME)_E$ effect may have to be increased by a factor as large as 4. As a result of all these complications and the limited applicability of the two-sublattice model (as well as of the α 's measured in ruby) to Cr_2O_3 , it appears that only a qualitative conclusion can be obtained from Table I and Figs. 1 and 2 in regard to the importance of the spin-orbit mechanism in Cr_2O_3 . This conclusion is that in Cr_2O_3 the contribution of the spin-orbit mechanism to the observed ME effects is significant.

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APPENDIX. THERMODYNAMICS OF MAGNETOELECTRIC, PIEZOMAGNETOELECTRIC AND GYROELECTRIC EFFECTS

A. Some Thermodynamic Relations

We now derive the thermodynamic relations which make it possible to obtain the electric polarization, \mathbf{P} , and the magnetization, \mathbf{M} , from the quantity F calculated in Secs. II and III. It should be recalled that this F is the Helmholtz free energy as deduced by statistical mechanics from certain specific Hamiltonians. The form of these Hamiltonians shows that F is based on a thermodynamic system whose internal energy *does* include the interactions $-\mathbf{P} \cdot \mathbf{E}$ and $-\mathbf{M} \cdot \mathbf{H}$ between the polarizations and the applied fields, but does *not* include the electric and magnetic energies existing in the absence of a polarizable sample. Because of the latter fact, the thermodynamic potential Φ , which occurs in earlier treatments^{5,6} and in a recent review,⁷ cannot lead directly to the desired thermodynamic relations.

According to the thermodynamic definition of F , we have

$$F = U - TS, \quad (A1)$$

where U , T , and S denote, respectively, the internal energy, absolute temperature, and entropy. From the first and second laws of thermodynamics we obtain

$$dU = TdS + dW, \quad (A2)$$

where dW is an infinitesimal amount of work done on a sample. For the kind of system associated with our statistical F , the appropriate expression for dW (verified below) turns out to be

$$dW = \sum_i x_i dX_i - \mathbf{P} \cdot d\mathbf{E} - \mathbf{M} \cdot d\mathbf{H}, \quad (A3)$$

where the X_i represent intensive variables (e.g., stresses)

other than components of \mathbf{E} and \mathbf{H} , and the x_i represent extensive variables (e.g., strains) other than components of \mathbf{P} and \mathbf{M} . Equations (A1), (A2), and (A3) may be combined to give

$$dF = -SdT + \sum_i x_i dX_i - \mathbf{P} \cdot d\mathbf{E} - \mathbf{M} \cdot d\mathbf{H}. \quad (A4)$$

The condition that dF be an exact differential then leads to the desired thermodynamic relations

$$x_i = \left. \frac{\partial F}{\partial X_i} \right|_{T, \mathbf{E}, \mathbf{H}}; \quad (A5)$$

$$\mathbf{P} = - \left. \frac{\partial F}{\partial \mathbf{E}} \right|_{T, X_i, \mathbf{H}}; \quad (A6)$$

$$\mathbf{M} = - \left. \frac{\partial F}{\partial \mathbf{H}} \right|_{T, X_i, \mathbf{E}}. \quad (A7)$$

It remains to verify Eq. (A3). By definition, U is given by

$$U = \tilde{U} + \sum_i x_i X_i - \mathbf{P} \cdot \mathbf{E} - \mathbf{M} \cdot \mathbf{H}, \quad (A8)$$

for the kind of system associated with our statistical F . In Eq. (A8) and in what follows, a quantity marked with a tilde is understood to be based on a system in which the internal energy does *not* include the interaction energies $\sum_i x_i X_i$, $-\mathbf{P} \cdot \mathbf{E}$, and $-\mathbf{M} \cdot \mathbf{H}$. By combining Eqs. (A2), (A3), and (A8), we obtain

$$d\tilde{U} = TdS - \sum_i X_i dx_i + \mathbf{E} \cdot d\mathbf{P} + \mathbf{H} \cdot d\mathbf{M}, \quad (A9)$$

which may be written in the form

$$d\tilde{U} = TdS + d\tilde{W}. \quad (A10)$$

The verification of Eq. (A3) consists in the fact that Eqs. (A9) and (A10) yield just the expected expression for $d\tilde{W}$.

B. Thermodynamics of Magnetoelectric Effects in Cr_2O_3

The constitutive equations required in Secs. II and III will now be obtained by a method which differs from that of Dzyaloshinskii⁶ only in that we use F instead of Φ . If we restrict F to second-order terms in the field components, then the magnetic symmetry of chromic oxide^{6,7} requires that F be of the form

$$F = F_0 - \frac{1}{2} [\kappa_1 (E_\xi^2 + E_\eta^2) + \kappa_{11} E_\xi^2 + \chi_1 (H_\xi^2 + H_\eta^2) + \chi_{11} H_\xi^2] + F_{ME}, \quad (A11)$$

$$F_{ME} = -(\alpha_1/4\pi) (E_\xi H_\xi + E_\eta H_\eta) - (\alpha_{11}/4\pi) E_\xi H_\xi, \quad (A12)$$

where the ξ axis is chosen to be along the principal axis (c axis) of the Cr_2O_3 crystal, F_0 is the value of F for $\mathbf{E} = \mathbf{H} = 0$, and F_{ME} is the magnetoelectric term. By applying the relations (A6) and (A7) to Eq. (A11), we

obtain the constitutive equations

$$P_{\xi,\eta} = \kappa_{11} E_{\xi,\eta} + (\alpha_{11}/4\pi) H_{\xi,\eta}, \quad (\text{A13a})$$

$$P_{\zeta} = \kappa_{11} E_{\zeta} + (\alpha_{11}/4\pi) H_{\zeta}, \quad (\text{A13b})$$

$$M_{\xi,\eta} = \chi_{11} H_{\xi,\eta} + (\alpha_{11}/4\pi) E_{\xi,\eta}, \quad (\text{A14a})$$

$$M_{\zeta} = \chi_{11} H_{\zeta} + (\alpha_{11}/4\pi) E_{\zeta}, \quad (\text{A14b})$$

where the subscript ξ, η signifies that either ξ or η applies throughout the equation in question. On the basis of Eqs. (A6), (A7), (A13), and (A14) we have

$$\kappa_{11} = -\partial^2 F / \partial E_{\xi}^2, \quad (\text{A15})$$

$$\chi_{11} = -\partial^2 F / \partial H_{\xi}^2, \quad (\text{A16})$$

$$\alpha_{11}/4\pi = -\partial^2 F / \partial E_{\xi} \partial H_{\xi}, \quad (\text{A17})$$

and analogous relations for the perpendicular susceptibilities.

C. Thermodynamics of Piezomagnetoelectric Effects in Cr_2O_3

It was pointed out by the author¹⁶ on the basis of symmetry considerations that the thermodynamic potential Φ may contain terms which are linear in the stress tensor components σ_{ij} , in the electric field components E_k , and in the magnetic field components H_l . Such terms lead to the possible existence of "piezomagnetoelectric" (PME) effects.¹⁶ We now discuss these effects in terms of the free energy, F , and give some specific theoretical results for a material whose magnetic symmetry is that of Cr_2O_3 .

In general, the piezomagnetoelectric contribution to F must have the form

$$F_{\text{PME}} = \sum_{ijkl} \pi_{ijkl} \sigma_{ij} E_k H_l, \quad (\text{A18})$$

where each of the indices i, j, k , and l is understood to be summed over the coordinates ξ, η , and ζ . The coefficients π_{ijkl} are subject to the restriction that they be compatible with the magnetic symmetry of the crystal under consideration. Thus, the number of independent coefficients will usually be smaller than 54, the largest possible number which we may expect on the basis of the fact that the stress tensor is symmetrical.

In the particular case of Cr_2O_3 the magnetic point group [which contains, in agreement with Eq. (A18), the product of the space inversion and time reversal transformations] requires that F_{PME} be invariant with respect to two additional operations: One is a 120° rotation about the ζ axis, which is the threefold rotation axis, and the other is a 180° rotation about the ξ axis, which we choose to be one of the twofold rotation axes. A lengthy but straightforward calculation leads to the result that only 25 of the coefficients π_{ijkl} do not vanish, and that only 10 of these are independent. Denoting ξ, η , and ζ by 1, 2, and 3, respectively, we find that the nonvanishing coefficients are:

$$\begin{aligned} \pi_{1111} &= \pi_{2222}; \pi_{1122} = \pi_{2211}; \pi_{1133} = -\pi_{2233} = \pi_{1231}; \\ \pi_{1133} &= \pi_{2233}; \\ \pi_{3311} &= \pi_{3322}; \pi_{3333}; \pi_{1212} = \pi_{1221} = (\frac{1}{2})(\pi_{1111} - \pi_{1122}); \\ \pi_{1123} &= -\pi_{2223} = \pi_{1213}; \pi_{2311} = -\pi_{2322} = \pi_{3112} = \pi_{3121}; \\ \pi_{2323} &= \pi_{3113}; \pi_{2332} = \pi_{3131}. \end{aligned} \quad (\text{A19})$$

The generalized constitutive equations and stress-strain relations may then be obtained by using Eqs. (A5), (A6), (A7), (A18), and (A19), and letting the X_i and x_i be the stress and strain tensor components, respectively.

Attempts to observe a PME effect in Cr_2O_3 with our (ME)_H apparatus² have not been successful, and rough theoretical estimates based on the values of the α 's and the elastic constants indicate, in fact, that the PME effects are very small in this material. It is worth noting, however, that PME effects may be regarded alternatively as producing a piezoelectric effect in the presence of a magnetic field, a piezomagnetic effect in the presence of an electric field, as well as a stress-dependent contribution to the magnetoelectric effects.

D. Thermodynamics of Gyroelectric Effects

We suppose that the sample under consideration (and the coordinate system ξ, η, ζ which is rigidly attached to it) rotates with an angular velocity Ω relative to some inertial coordinate system. From the theory of the gyromagnetic effects it is known that such a rotation produces the same magnetization in the sample as the "gyromagnetic field"

$$\mathbf{H}_{\text{gyro}} = (2m_e c / g' e) \Omega, \quad (\text{A20})$$

where m_e , c , and g' are the electronic mass, the velocity of light, and the magnetomechanical factor, respectively. Since an angular velocity is similar to a magnetic field in that both of these quantities are axial vectors and both change their sign under the time reversal transformation, it seems reasonable to extend the thermodynamic and symmetry considerations underlying the ME (and PME) effects by replacing \mathbf{H} by \mathbf{H}_{gyro} throughout this Appendix. Thus, we expect the existence of two additional new effects: electric polarization by rotation, which is analogous to the Barnett effect, and rotation by electric polarization, which is analogous to the Einstein-de Haas effect. Since the numerical value of $2\pi(2m_e c / g' e)$ is only about 0.36×10^{-6} Oe sec (we use $g' \approx 2$ although, strictly speaking, g' is a tensor), it is seen that for practical values of Ω these "gyroelectric" effects will be very small unless the material under consideration has very large α 's. However, it is interesting that gyroelectric effects may exist, at least in principle, even though the electric polarization (unlike the magnetization) is not intrinsically gyroscopic. The physical origin of these gyroelectric effects is the possibility of an interplay between gyromagnetic and magnetoelectric effects.