are fitted very closely by those determined by crystal-field theory under the assumption of the spin-orbit coupling, Heisenberg exchange interaction, and tetragonal crystalline field (see Figs. 4 through 7). Points with error bars are determined by diagonalizing the 4×4 interaction matrix to fit Mössbauer spectra, and represent the estimated confidence in this fitting. The solid curves are determined from crystal-field theory. In this fitting, we adjusted various parameters, which turned out to be in reasonable agreement with those reported by others: $\langle r^{-3}\rangle=4.4$ a.u. and $Q=0.21$ b are essentially the same as those reported by others.[23,26] $H_c=-488$ kG is also nearly the same as -500 kG reported by Okiji and Kanamori.[26] The covalency factor α^2 for many ferrous compounds[23] is reported to be between 0.6 and 0.8, and our adjusted covalency factor of 0.69 is also in this region. This implies a spin-orbit coupling constant $\lambda=\alpha^2\lambda_0=102.3°$K. The spin direction of $[\bar{1}\bar{1}3]$ (that is, 25° from the c axis) is nearly the same as the 27.3° value reported by van Laar,[3] even though a comparison with these results is of limited value, because most samples of cobaltous oxides used by people in the past were probably CoO(I, II) instead of pure CoO(I).

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Upper Bound on the Magnetoelectric Susceptibility

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The change in the free energy that occurs when electric and magnetic fields are simultaneously applied to a magnetoelectric medium is calculated. It is shown that a quadratic form related to this change in the free energy is positive definite, from which it follows that all elements of the magnetoelectric-susceptibility tensor must be smaller than the geometric mean of appropriate elements of the magnetic- and electric-susceptibility tensors. It is pointed out that the diamagnetic contribution to the magnetic-susceptibility tensor is negligible in materials in which the magnetoelectric effect is allowed. It is concluded that the magnetoelectric susceptibility should be small compared with unity, except possibly in ferroelectric or ferromagnetic materials.

INTRODUCTION

A MAGNETOELECTRIC medium is one in which there exists a linear relationship between an electric field and the medium's magnetic polarization and between a magnetic field and the medium's electric polarization. The possibility of such an effect was first pointed out by Landau and Lifshitz.[1] Subsequently, Dzyaloshinskii[2] predicted that the magnetoelectric effect should occur in Cr_2O_3. Experimentally, the effect was first seen by Astrov[3] in Cr_2O_3, and additional observations have been made on this and other materials by several investigators.[4–9]

The purpose of this paper is to show that the ordinary electric and magnetic susceptibilities provide an upper bound on the magnitude of the magnetoelectric effect. This is done by calculating the change in the free energy that occurs when electric and magnetic fields are simultaneously applied to a magnetoelectric medium. An expression for this energy change is obtained by using the method of "thermodynamic perturbation theory."[10] It is shown that a quadratic form related to this change in the free energy is positive definite, from which it follows that all elements of the magnetoelectric-susceptibility tensor must be smaller than the geometric mean of appropriate elements of the magnetic- and electric-susceptibility tensors.

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CALCULATION OF THE UPPER BOUND

Let us apply uniform electric and magnetic fields to a magnetoelectric material. The material will be considered to have the form of a flat oblate ellipsoid, and to be positioned in the field region in such a manner that the fields are perpendicular to the ellipsoid's axis of revolution. Then the applicable electric and magnetic demagnetizing factors can be made arbitrarily close to zero, and we shall not have to introduce any demagnetizing corrections to our calculated susceptibilities.

In fact, this is possible only when there are no off-diagonal elements of the various susceptibility tensors connecting fields in the plane of the disk with polarizations perpendicular to the disk. In the case of the 58 magnetic classes in which the magnetoelectric effect is allowed, this requirement can be met in 56 by using materials cut suitably with respect to the crystalline reference axes.[11,12] Only in the triclinic classes, 1 and $\bar{1}'$, wherein the magnetoelectric-susceptibility tensor has no crystalline symmetry, do the above considerations not apply.

We show in the Appendix that the perturbation in the Hamiltonian in the presence of the external fields may be taken as

$$V=\sum[(e/mc)\mathbf{p}\cdot\mathbf{A}+(e^2/2mc^2)A^2-e\phi-\boldsymbol{\mu}_s\cdot\nabla\times\mathbf{A}]. \tag{1}$$

Here e, m, $\mathbf{p}$, and $\boldsymbol{\mu}_s$ are, respectively, the (magnitude of the) electron charge, the electron mass, the electron momentum, and the electron-spin magnetic-moment operator and c is the speed of light. The summation is over all electrons in the system, which we take to be of unit volume. The scalar and vector potentials ϕ and $\mathbf{A}$ are related to the uniform fields $\mathbf{E}$ and $\mathbf{H}$ that would be present in the absence of the magnetoelectric material by

$$\phi=-\mathbf{E}\cdot\mathbf{r}, \tag{2a}$$

$$\mathbf{A}=\tfrac{1}{2}(\mathbf{H}\times\mathbf{r}). \tag{2b}$$

Note that Coulomb gauge is being used throughout; thus $\nabla\cdot\mathbf{A}=0$. By use of Eq. (2), Eq. (1) becomes

$$V=\sum[-(\boldsymbol{\mu}_L+\boldsymbol{\mu}_s)\cdot\mathbf{H}+e\mathbf{r}\cdot\mathbf{E}+(e^2/8mc^2)r_\perp{}^2H^2], \tag{3}$$

where

$$\boldsymbol{\mu}_L=-(e/2mc)\mathbf{r}\times\mathbf{p} \tag{4}$$

is the electron-orbital magnetic-moment operator, and $\mathbf{r}_\perp=\mathbf{r}-\mathbf{r}\cdot\mathbf{H}\mathbf{H}/H^2$ is the component of $\mathbf{r}$ perpendicular to $\mathbf{H}$. Note that $\boldsymbol{\mu}_L$ is not gauge-independent.

Now, for the 56 magnetic classes of interest, it is possible to obtain individual upper bounds on all the elements of the magnetoelectric-susceptibility tensor by considering only cases in which the external electric and magnetic fields are perpendicular or parallel to each other. The fields must, of course, be suitably positioned with respect to the crystalline axes of any particular material. Thus we will have, in any particular case, only one component of $\mathbf{E}$, namely, E_ξ ($\xi=1$, 2, or 3), and only one component of $\mathbf{H}$, namely, H_η ($\eta=1$, 2, or 3), with either $\xi=\eta(\mathbf{E}\,||\,\mathbf{H})$ or $\xi\neq\eta(\mathbf{E}\perp\mathbf{H})$.

We can now write Eq. (3) as

$$V=a^\eta H_\eta+b^\xi E_\xi+\tfrac{1}{2}d^\eta H_\eta{}^2, \tag{5}$$

where the superscripts on the operators a^η, b^ξ, and d^η indicate that they depend on the directions in which the electric and magnetic fields are applied. (Superscripts are used for convenience only, and no summation is implied.)

We now calculate the free energy of the magnetoelectric medium, using the method of "thermodynamic perturbation theory."[10] This method gives

$$F=F_0+\langle V\rangle_{\text{Av}}-\tfrac{1}{2}\sum_{n,m\neq n}\frac{|V_{nm}|^2(\omega_m-\omega_n)}{E_n{}^{(0)}-E_m{}^{(0)}}-(2kT)^{-1}\langle(V_{nn}-\langle V\rangle_{\text{Av}})^2\rangle_{\text{Av}}. \tag{6}$$

Here F_0 is the unperturbed free energy, $E_n{}^{(0)}$ and $E_m{}^{(0)}$ are eigenvalues of the unperturbed Hamiltonian, k is Boltzmann's constant, and T is the temperature. The symbol $\langle\ \rangle_{\text{Av}}$ denotes

$$\langle W\rangle_{\text{Av}}=\sum_n\omega_n W_{nn}, \tag{7a}$$

where

$$\omega_n=\exp[(F_0-E_n{}^{(0)})/kT]. \tag{7b}$$

Let us denote by F_2 that portion of F which consists of terms second-order in the field components. Then, upon subsituting Eq. (5) into Eq. (6), we obtain

$$F_2=-\tfrac{1}{2}\sum_{n,m\neq n}\frac{|a_{nm}{}^\eta H_\eta+b_{nm}{}^\xi E_\xi|^2}{E_n{}^{(0)}-E_m{}^{(0)}}(\omega_m-\omega_n)-(2kT)^{-1}\langle[(a_{nn}{}^\eta-\langle a^\eta\rangle_{\text{Av}})H_\eta+(b_{nn}{}^\xi-\langle b^\xi\rangle_{\text{Av}})E_\xi]^2\rangle_{\text{Av}}+\tfrac{1}{2}\langle d^\eta\rangle_{\text{Av}}H_\eta{}^2. \tag{8}$$

Note here that the terms in F_2 proportional to $H_\eta{}^2$ are not individually gauge invariant. That is, such quantities as paramagnetic and diamagnetic susceptibility are not individually gauge invariant; only their sum, the total magnetic susceptibility, has this property.[13]

Inspection of Eq. (8) shows that the first two terms on the right side (i.e., those coming from the second-order correction) are negative for all values of H_η and E_ξ. (For the first term, this follows from the fact that $\omega_m-\omega_n$ and $E_n{}^{(0)}-E_m{}^{(0)}$ have the same algebraic sign.)

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Consider now the last term on the right side in Eq. (8), which involves the quantity d^η. Comparing Eqs. (3) and (8), we see that

$$\langle d^\eta\rangle_{Av}=\sum(e^2/4mc^2)\langle r_\perp{}^2\rangle_{Av}. \tag{9}$$

The negative of the expression on the right side of Eq. (9) is the diamagnetic contribution $\chi_{\eta\eta}{}^d$ to the magnetic susceptibility. Combining the above observations, we have

$$F_2+\tfrac{1}{2}\chi_{\eta\eta}{}^dH_\eta{}^2\leq 0. \tag{10}$$

The equality holds only for $H_\eta=E_\xi=0$.

Now the free energy F_2, which corresponds to a choice of **E**, **H**, and T as independent variables, may be written, for the disk-shaped specimens discussed earlier, as

$$F_2=-\tfrac{1}{2}\chi_{\eta\eta}H_\eta{}^2-(\alpha_{\eta\xi}/4\pi)H_\eta E_\xi-\tfrac{1}{2}\kappa_{\xi\xi}E_\xi{}^2, \tag{11}$$

where $\chi_{\eta\eta}$, $(\alpha_{\eta\xi}/4\pi)$, and $\kappa_{\xi\xi}$ are appropriate elements of the magnetic-, magnetoelectric-, and electric-susceptibility tensors, respectively. This has been discussed for the magnetoelectric case by Dzyaloshinskii[2] and by Rado.[14] Substituting Eq. (11) into (10) gives

$$\tfrac{1}{2}\chi_{\eta\eta}{}^pH_\eta{}^2+(\alpha_{\eta\xi}/4\pi)H_\eta E_\xi+\tfrac{1}{2}\kappa_{\xi\xi}E_\xi{}^2\geq 0, \tag{12}$$

where $\chi_{\eta\eta}{}^p$, the paramagnetic contribution to the magnetic susceptibility, is equal to $\chi_{\eta\eta}-\chi_{\eta\eta}{}^d$.

From the positive definiteness of the quadratic form appearing in (12), we may conclude that[15]

$$\kappa_{\xi\xi}>0, \tag{13a}$$

$$\chi_{\eta\eta}{}^p>0, \tag{13b}$$

$$\alpha_{\eta\xi}/4\pi<(\chi_{\eta\eta}{}^p\kappa_{\xi\xi})^{1/2}. \tag{13c}$$

The inequality (13a) expresses a well-known limitation on the diagonal components of the electric-susceptibility tensor.[10] The inequality (13b) expresses an analogous limitation on the paramagnetic-susceptibility tensor. The inequality (13c), however, places an upper bound on every element of the magnetoelectric-susceptibility tensor. We thus have the result that each element of the magnetoelectric-susceptibility tensor must be smaller than the geometric mean of appropriate elements of the paramagnetic- and electric-susceptibility tensors. We remark that the inequalities (13b) and (13c) might be capable of improvement by a judicious choice of gauge; that is unnecessary, however, in view of the approximation to be made.

For materials having localized permanent magnetic moments, the diamagnetic contribution of Eq. (9) will be far outweighted by the paramagnetic contribution of the unpaired electrons. Since all magnetoelectric materials must, of necessity, be of this type in order for the effect to be allowed, we may neglect the small diamagnetic susceptibility. Thus, for all practical purposes, inequality (13c) becomes

$$\alpha_{\eta\xi}/4\pi<(\chi_{\eta\eta}\kappa_{\xi\xi})^{1/2}. \tag{14}$$

COMPARISON WITH EXPERIMENT

The most studied magnetoelectric material to date is Cr_2O_3.[3–5,16,17] The highest value of $\alpha_{||}$, the magnetoelectric coefficient parallel to the trigonal axis, that has been reported is[16] $\alpha_{||}=8\times10^{-4}$, at a temperature of approximately 285°K. This would correspond[3–5] to an $\alpha_{||}$ of about 8.6×10^{-4} at $T\simeq255$°K, the temperature at which $\alpha_{||}$ is maximum in Cr_2O_3. It has been estimated[14] that $\alpha_{||}$ $(T=255$°K) may be as large as 14×10^{-4}.

Using values of $\kappa_{||}=0.85$ [18] and $\chi_{||}=9.2\times10^{-5}$,[19] at 255°K ($\chi_{||}{}^d$ is negligible at this temperature[20]), we find that $4\pi(\kappa_{||}\chi_{||})^{1/2}=0.1$. Thus we see that $\alpha_{||}$ $(T=255$°K) is approximately 1% of the upper bound given by Eq. (14). All quantities are given in gaussian units.

It is easily shown[21] that, according to conventional theory, the inequality

$$\alpha_{\eta\xi}<(\mu_{\eta\eta}\epsilon_{\xi\xi})^{1/2} \tag{15}$$

must be satisfied in order to insure that the system be thermodynamically stable. Here $\mu_{\eta\eta}$ and $\epsilon_{\xi\xi}$ are elements of the permeability and permittivity tensors, respectively. For the case of $\alpha_{||}$ in Cr_2O_3, Eq. (15) gives as an upper bound, $(\mu_{||}\epsilon_{||})^{1/2}=3.4$. We thus obtain an improvement of more than an order of magnitude by using Eq. (14) rather than Eq. (15) to place an upper bound on the magnetoelectric susceptibility.

DISCUSSION

By considering the change in the free energy of a magnetoelectric medium in the presence of applied magnetic and electric fields, we have calculated an upper bound on the magnetoelectric susceptibility. This upper bound is given by the geometric mean of appropriate magnetic and electric susceptibilities. It thus appears that the chances of finding substances with large magnetoelectric susceptibilities will be better in ferromagnetic as opposed to antiferromagnetic materials. We note that the magnetoelectric susceptibility in $Ga_{2-x}Fe_xO_3$ $(x\simeq1)$,[7] which is ferromagnetic,[22] is an order of magnitude greater than that of Cr_2O_3, which is antiferromagnetic. It may also be concluded that materials which are both ferromagnetic and ferro-

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electric may have relatively large magnetoelectric susceptibilities.

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APPENDIX

It is clear that the derivation of the upper bound presented here did not depend on the particular character of the operators a^η and b^ξ appearing in Eq. (5). An important point, however, was that no term of the form $c^{\eta\xi}H_\eta E_\xi$ appeared in Eq. (5). If such a term had been present, it would have contributed to the $(\alpha_{\mu\xi}/4\pi)H_\eta E_\xi$ magnetoelectric-susceptibility term in Eq. (12) through the $\langle V\rangle_{\text{Av}}$ term in Eq. (6). Since such a term may be positive or negative, we could no longer show that the quadratic form of Eq. (12) was positive definite, and our derivation would fail.

We now wish to show that the leading contribution to a $c^{\eta\xi}H_\eta E_\xi$ term in Eq. (5) is negligible. To do this, it is useful to think of the many-electron Hamiltonian as an expansion of v/c, where the electron velocity v is small compared with the speed of light c. From this point of view, Eq. (1) gives the perturbation in the Hamiltonian to order zero in v/c. The many-electron Hamiltonian to order $(v/c)^2$ has been discussed in full by Slater,[23] and we shall not go into it in detail here. We simply note that, to order $(v/c)^2$, only the spin-orbit mechanism leads to a term of the type $c^{\eta\xi}H_\eta E_\xi$; all other mechanisms contribute only to the $a^\eta H_\eta$ and $b^\xi E_\xi$ terms in Eq. (5).

We now show that the term $c^{\eta\xi}H_\eta E_\xi$ arising from the spin-orbit mechanism is negligible in comparison with $H_\eta E_\xi$ terms in the free energy entering from the second-order contributions. For definiteness, we shall consider the case $\xi=\eta$. (The procedure for $\xi\neq\eta$ is completely analogous.) Then there will be first-order contributions to F_2 of the form

$$\sum\sum_{n,m}(e/4mc^2)\omega_n[\langle n\mid(\mathfrak{y}_s)_\perp\mid m\rangle\cdot\langle m\mid\mathbf{r}_\perp\mid n\rangle+\langle n\mid\mathbf{r}_\perp\mid m\rangle\cdot\langle m\mid(\mathfrak{y}_s)_\perp\mid n\rangle]H_\xi E_\xi, \quad \text{(A1)}$$

where $(\mathfrak{y}_s)_\perp=(\mathfrak{y}_s-\mathfrak{y}_s\cdot\mathbf{HH}/H^2)$ is the component of $\mathfrak{y}_s$ perpendicular to $\mathbf{H}$. The first summation is over all electrons in the system. From the Hamiltonian of Eq. (1), there will be a second-order contribution to F_2 of the form

$$\sum\Bigg\{\sum_{n,m\neq n}\frac{(\omega_m/\omega_n-1)e}{2[E_n^{(0)}-E_m^{(0)}]}\omega_n[\langle n\mid(\mu_s)_\xi\mid m\rangle\langle m\mid r_\xi\mid n\rangle+\langle n\mid r_\xi\mid m\rangle\langle m\mid(\mu_s)_\xi\mid n\rangle]+(e/2kT)\sum_n\omega_n\langle n\mid(\mu_s)_\xi\mid n\rangle\langle n\mid r_\xi\mid n\rangle\Bigg\}H_\xi E_\xi. \quad \text{(A2)}$$

Ignoring for the moment the matrix elements in (A1) and (A2), let us examine the ratios of the coefficients appearing in these two expressions. That is, we wish to find the maximum values of the ratios $R_1=kT/mc^2$ and $R_2=|\,(E_n^{(0)}-E_m^{(0)})/(\omega_m/\omega_n-1)\,|/2mc^2$.

As $k/mc^2\simeq10^{-10}$, and as we need be concerned only with temperatures of up to 1000°K, we find that the maximum value of the ratio R_1 is 10^{-7}.

To obtain a maximum for R_2, we make use of the fact that $g(x)=x/(1-e^{-\beta x})$ $(\beta=1/kT,\ x=E_m^{(0)}-E_n^{(0)})$ is a monotonically increasing function of x. Now, x will certainly be less than the ionization energy of a hydrogen atom, which is 13.5 eV. For this value of x, $kT\ll x$ at any reasonable temperature, and we have $R_2=|\,E_n^{(0)}-E_m^{(0)}\,|/2mc^2$. For $|\,E_n^{(0)}-E_m^{(0)}\,|=13.5$ eV, we find the maximum value of R_2 to be 10^{-5}.

Turning our attention to the matrix elements appearing in (A1) and (A2), we see that the first-order contribution in a given direction (say, z) is 10^{-5} times the sum of the second-order contributions in the x and y directions. But we already have shown that the second-order x and y contributions are bounded by $\chi_x\kappa_x$ and $\chi_y\kappa_y$, respectively. Thus we find that the upper bound on $\alpha_{zz}/4\pi$ is actually $\chi_z\kappa_z+10^{-5}(\chi_x\kappa_x+\chi_y\kappa_y)$. On physical grounds, we may drop this latter term just as we did with the diamagnetic contribution. This then justifies our use of Eq. (1) as the perturbation in the Hamiltonian caused by the external magnetic and electric fields.

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