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AUTHOR(S):

MATSUBARA, Kakuei; SHIGEKI, Susumu; OTANI, Yasuyuki

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Physical Properties of Magnetic Domain Switching in a Single Crystal of an Anti-Ferro Magnetic Medium Cr_2O_3

By

Kakuei MATSUBARA,* Susumu SHIGEKI**, and Yasuyuki OTANI*

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The physical properties of a domain switching under an application of electric and magnetic fields are described, with respect to a single crystal of Cr_2O_3 which belongs in a magnetic point group $\bar{3}m$. Major results obtained in this study are as follows: (1) experimental results on anisotropic tensor components of a magnetic susceptibility $\chi_{em}^{a\beta}$ in the Cr_2O_3 single crystal are found to be in reasonable agreement with the theoretical result in the case of $\bar{3}m$, in which the non-diagonal elements χ_{ij} are zero and $\chi_{11}=\chi_{22}$ is required. (2) A temperature dependence of a domain switching time τ_s of the used Cr_2O_3 single crystal follows to approximately $\tau_s^{-1} \approx 1.6 \times 10^{17} \exp(-9550/T)$.

From the numerical value in the parenthesis, it appears that the used crystal has an average energy of domain walls corresponding to 0.86 eV. Further, it is concluded that an inversion probability in the domain switching in general depends on the Boltzmann factor.

1. Introduction

The magneto-electric effect, called the ME effect, is a linear phenomena which implies an induction of a magnetization due to an applied electric field and an electrical polarization due to an applied magnetic field. The first proposal of the ME effect was offered by P. Curie,¹⁾ and later it was certified theoretically by A. Perrier²⁾ that the effect might arise from the crystal symmetry. On the other hand, the reversible effect can be attributed to the known physical principle that a momentum equation is invariable with a $(t) \rightarrow (-t)$ transformation.

In practice, I. E. Dzyaloshinskii³⁾ presented evidence that the anti-ferro magnet Cr_2O_3 has a magnetic symmetry which allows the ME effect. Subsequently, D. N. Astrov⁴⁾ made the first successful observation of the magnetization under an applied field with a single crystal of Cr_2O_3 . Also, the opposite effect, i.e. the production of an electric polarization due to an applied magnetic field, was observed by G. T. Rado.⁵⁾

* Department of Electrical Engineering.

** Department of Electrical Engineering. Present address: Mitsubishi Electric Co. Ltd.

Detailed arguments for a phenomenological relationship of the ME effect with a crystal anisotropy were made by Rado and M. Dato.⁶⁾ Later, a temperature dependence of this effect was discussed by Hornreich and S. Shtrikman.⁷⁾ According to T. H., O, Dell,⁸⁾ the ME effect can generally be expected with such media whose crystal symmetry changes under the application of both magnetic and electric fields.

It is possible to inverse the polarity of the electric susceptibility of the Cr_2O_3 single crystal by means of the application of both external electric and magnetic fields. The effect is ascribed to an inversion of magnetic domains in the Cr_2O_3 crystal, and this is generally known in terms of domain switching. Evidence of the subject was dealt with by T. J. Martin⁹⁾ and W. F. Brown,¹⁰⁾ yet the study is still in an early stage. In this study, therefore, we have made more refined measurements to make clear the physical mechanism of the domain switching.

2. The synopsis of the magneto-electric effect

The ME effect for an isotropic magneto-electric medium is generally represented by

$$\mathbf{P} = \chi_e \mathbf{E} + \chi_{em} \mathbf{B}, \quad (1a)$$

and

$$\mathbf{M} = \chi_{me} \mathbf{E} + \chi_m \mathbf{B}, \quad (1b)$$

where P and M are the electric polarization and the magnetization, χ_e and χ_m are each the electric and magnetic susceptibilities, while χ_{em} and χ_{me} give the respective magneto-electric susceptibilities. As a matter of convenience, hereafter such effects corresponding to Eqs. (1a) and (1b) are denoted as $(ME)_B$ and $(ME)_E$.

In view of Eqs. (1a) and (1b), it is evidently found that there is a linear relationship between P and B as well as between M and E . Precisely however, there is likewise the case that the higher order terms of χ_{em} and χ_{me} are responsible for a nonlinear ME effect; for example, (1) when the crystal symmetry changes with the spinfopping occurring in a high magnetic field, (2) when the magnetic domain is freely movable, (3) when a crystal which prohibits the ME effect from its symmetry causes the effect to rise for the sake of a second transformation of the crystal lattice.

From the temperature dependence of the ME susceptibility, it is possible to qualitatively account for a mechanism of the ME effect.^{11)~13)} A major cause of the $(ME)_E$ effect on Cr_2O_3 can be attributed to a corrective difference between two sublattices, one of which has upward spins and the other has downward spins. Now, we take an x - y - z space as a co-ordinate system corresponding to a sublattice such that the magnetization points in the direction of the z -axis. Further, we set the ξ , η , ζ axes as the basic co-ordinates with the ζ -axis directed toward the z -axis of the sublattices. Such a sublattice is denoted by a (+)-sign and thus another sublattice has the magnetization

of an opposite sign, i.e., a (−)-sign.

First, we shall consider the case wherein both E_ξ and H_ξ are applied to the direction of the ζ -axis, i.e., the c -axis of the crystal. A magnetic susceptibility of each sublattice has a temperature dependence as shown in Fig. 1(a). If we then propose that the (+) and (−) sublattices are separated as shown in Fig. 1(b) for some cause, e.g. by an external electric field, a net magnetization ought to have such a temperature dependence as shown in Fig. 1(c). It is previously known that the experimental data on the magnetization of Cr_2O_3 is in accord with a reasonable degree of the curve (c).

Next, we shall describe the cause whereby the difference between the two sublattices rises in actual manner. A spin Hamiltonian for the Cr^{3+} ions under a condition in which both E_ξ and H_ξ fields are parallel to the c -axis, is written as

$$\begin{aligned} \mathcal{H}^\pm = & -g_1\beta S_z H_z^{\text{eff}\pm} \pm g_1\beta a_1 S_z^2 E_\xi \pm g_1\beta b_1 S_z E_\xi \\ & + g_1\beta c_1 E_\xi - \beta^2 d H_\xi^3 + \mathcal{H}_a, \end{aligned} \quad (2)$$

where the first term gives the Zeeman splits, the second and the third terms are respective

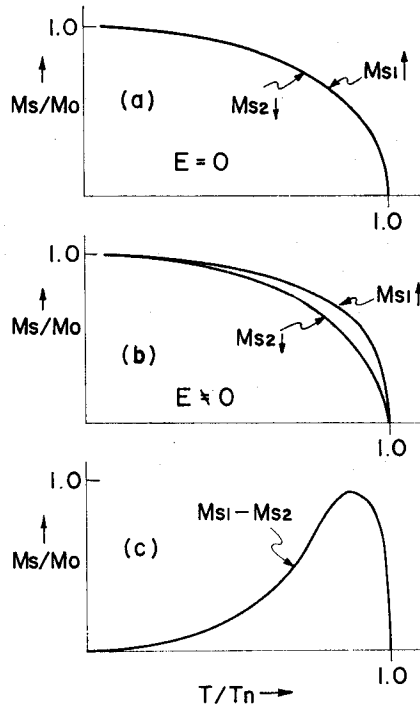


Fig. 1. View of variations of the magnetization in two sublattices of Cr_2O_3 with temperatures. (a) In the case of zero applied electric field, the net magnetization is zero at all temperatures. (b) When $E \neq 0$, the spin-up and the spin-down sublattices vary separately at slightly lower temperature than the Néel point T_N . (c) The difference between two-sublattices is responsible to the magneto-electric effect.

terms corresponding to single-ion and double-ion ME effects. The fourth indicates a g -shift term which is induced by an applied electric field, the fifth is the Van-Vleck term, and the sixth is an anisotropic term which is independent of these applied fields. In addition, g_{\parallel} is the parallel component of the known g -factor, β is the Bohr magneton, S_z is the z -component of electron spins, and M is the spontaneous magnetization in the sublattice, respectively.

Further, it should be added that the one-ion ME term indicates an energy variety which arises from a slight movement of Cr^{3+} ions by means of the electric field E_{ξ} . On the other hand, the double-ions ME term indicates a variety owing to E_{ξ} of the exchange interaction within each sublattice, and so the sign of this term varies with each sublattice. The g -shift term is due to a variety of the interaction between an orbital magnetic moment and magnetic spins. In other words, this implies an aberration from steady state electrons which are localized at Cr^{3+} ions. The sign of this term is the same with respect to each sublattice.

By using the magnetization M_{ξ} for the case where H_{ξ} and E_{ξ} are in parallel with the c -axis, i.e.,

$$M_{\xi} = \chi_{\parallel} H_{\xi} + (\alpha_{\parallel}/4\pi) E_{\xi}, \quad (3)$$

and by calculating the free energy F by means of the molecular field approximation and second-order perturbation method, we can get the equation

$$\begin{aligned} (\alpha_{\parallel}/4\pi) &= \chi'_{me} \\ &= (\chi_{\parallel} - \chi_v) \left[(b'_{\parallel} + a_{\parallel} G_{\parallel}) \langle m \rangle - \frac{c_{\parallel}(u_{\parallel})^{-1} kT \langle m \rangle}{g_{\parallel} \beta (\langle m^2 \rangle - \langle m \rangle^2)} \right], \end{aligned} \quad (4)$$

where $\langle m \rangle = SB_s(-SE_m^{(0)}/mkT)$ is a dimensionless parameter denoting the Brillouin function B_s , the magnetic spin quantum number m and $E_m^{(0)}$ (an eigen function of the spin Hamiltonian in an absent state of E_{ξ} and H_{ξ}). In addition, the other parameters are given by

$$\begin{aligned} G_{\parallel} &= \frac{\langle m^3 \rangle - \langle m^2 \rangle \langle m \rangle}{\langle m \rangle (\langle m^2 \rangle - \langle m \rangle^2)}, \\ b'_{\parallel} &= \frac{1}{2} N g_{\parallel} \beta b_{\parallel}, \end{aligned} \quad (5)$$

$$u_{\parallel} = 1 - \frac{1}{2} (A + \Gamma) (\chi_{\parallel} - \chi_v),$$

and $\chi_v = 2N\beta^2 d$,

where A is a coefficient of the molecular magnetic field indicating an interaction between sublattices, and Γ is that within a sublattice. Then, χ_v is the well known Van-Vleck susceptibility, and a, b, c and d are arbitrary integral numbers, respectively. In view of Eq. (5), when $T=0^\circ\text{K}$ it is shown that the value of $\alpha_{\parallel}/4\pi$, i.e. the parallel component

of χ_{me} , tends to $-Ng_{\parallel}\beta c_{\parallel}S$ which corresponds to the g -shift term.

Next, we shall consider the condition where E and H are applied perpendicularly to the c -axis. The spin Hamiltonian of the Cr³⁺ ions corresponding to this case is given by

$$\begin{aligned} \mathcal{H}^{\pm} = & -g_{\parallel}\beta S_z H_z^{\text{eff}\pm} - g_{\perp}\beta S_x H_x^{\text{eff}\pm} \pm g_{\perp}\beta \left(\frac{a_{\perp}}{2}\right) (S_x S_z + S_z S_x) E_{\xi} \\ & \pm g_{\perp}\beta_{\perp} (S_x H_z^{\text{eff}\mp} - S_z H_x^{\text{eff}\mp}) E_{\xi} \\ & \pm g_{\perp}\beta c_{\perp} S_z H_{\xi} E_{\xi} + \mathcal{H}_a, \end{aligned} \quad (6)$$

where the first and the second terms given their Zeeman splitting terms, the third and the fourth are the single-ion and the double-ion ME terms, and then the fifth and the sixth are the g -shift terms arising from an electric field and the anisotropic energy term which is independent of the E and H fields.

Calculating the formular of $a_{\perp}/4\pi$, i.e., the transverse component of χ_{me} , in the manner of the former, we can get the solution

$$\chi_{me}^{\perp} = \chi_{\perp} \langle m \rangle (a_{\perp} G_{\perp} - b'_{\perp}), \quad (7)$$

where

$$\begin{aligned} G_{\perp} = & -\frac{3}{2} \left[\langle m^2 \rangle - \frac{1}{3} S(S+1) \right] / \langle m^2 \rangle, \\ b'_{\perp} = & [2b + c_{\perp}(u_{\perp})^{-1}(A - \Gamma)] \left(\frac{N}{2}\right) g_{\perp}\beta, \end{aligned}$$

and
$$u_{\perp} = 1 - \frac{1}{2} (A + \Gamma) \chi_{\perp},$$

respectively.

The above is important for explaining the behavior of the ME effect as a function of temperature. As regards the temperature dependences of χ_{me}^{\parallel} and χ_{me}^{\perp} , it has been definitely shown by B. Hornreich¹⁴) that the parallel case mainly depended upon the double-ion ME term and the g -shift term, and that the perpendicular case mainly depended upon the single-ion ME term.

3. Experimental procedure for the (ME)_B and the (ME)_E effects in Cr₂O₃ single crystal

The sample used in this experiment was sliced off from the Cr₂O₃ single crystal which was grown by the Verneuil technique. The sample size was 2.65 × 5.50 × 5.95 mm³, whose cross section (2.65 × 5.50) was taken in parallel with the cleavage plane of this crystal. The measurement system for the (ME)_B and the sample arrangement are shown in Fig. 2. The sample and lead wires were suspended in a copper tube of a suitable diameter, in which they were electrically shielded by a few Teflon spacers.

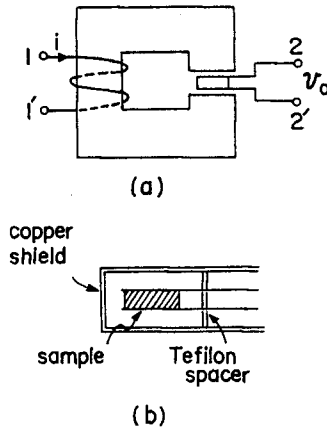


Fig. 2. The used measurement system for the $(ME)_B$ effect (a) and the sample arrangement (b).

Further, the measurement of the output voltage was made by using a high impedance voltmeter of a vibrating lead type, because the resistivity of the sample was of the high order of $\sim 10^{10} \Omega \text{ cm}$.

To give a full explanation in respect to the measured signal of the $(ME)_B$, an equivalent circuit for this system is shown in Fig. 3. Here, V_0 gives the voltage induced by an applied magnetic field, and C_s and R_s give a capacity and a resistivity corresponding to the sample. Then, C_0 and R_0 correspond to those of the Teflon spacers, but in practice, both $C_s \gg C_0$ and $R_0 \gg R_s$ are satisfied. On the other hand, the measuring circuit is able to be replaced by using the time constant RC , because the input part of a usual vibration-read type consists of an integral circuit having R_T and C_T .

The medium is electrically polarized according to Eq. (1a), i.e., $P = \chi_{em} B$ setting $E = 0$, when it is placed in a magnetic field. Hence, an electric charge corresponding to P is risen at both ends of the sample. In the equation $P = \chi_{em} B$, the flux density B and the contact area are known so that the susceptibility χ_{em} can be easily obtained from a measured value of an induced electric charge at the applied magnetic field of a rectangle pulse. To be concrete, an observable voltage $V(t)$ arises from a discharge

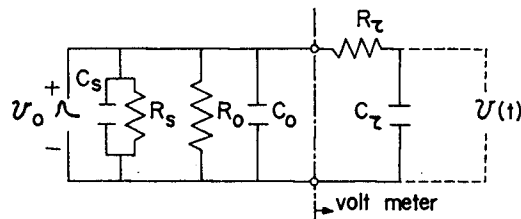


Fig. 3. Equivalent circuit for the measurement system.

of the induced electric charge through mainly the sample resistance R_s , and so $V(t)$ reduces to

$$V(t) = \frac{V_c C_s}{CC_r R_r} \frac{1}{2(b^2 - a)^{\frac{1}{2}}} e^{-bt} e^{(b^2 - a)^{\frac{1}{2}} t} - e^{-(b^2 - a)^{\frac{1}{2}} t}, \quad (8)$$

where $a \approx (CR_s C_r R_r)^{-1}$, $b \approx \frac{1}{2} (1/CR_r + 1/CR_s + 1/C_r R_r)$, $C = C_s + C_0$, and gives a voltage owing to the stored charge of C_s , respectively. From a peak value V_p which is obtained as a function of time, we are able to calculate the electric polarization P by substituting this value in

$$P = (V_p/A) \times 3.8 \times 10^{-11} \text{ coul/m}^2, \quad (9)$$

where A is the area of the electrode.

b) A method of the measurement on the $(ME)_E$

This is an opposite effect of the $(ME)_B$, that is, the generation of the magnetization M by an applied electric field E . The block diagram for this measurement is illustrated in Fig. 4. The actual measurement of M is made by two pick-up coils holding the crystal, and the output signal is observed through a lock-in-amplifier. The output signal voltage V_0 for this case is given by

$$V_0 = \frac{V_a}{1 - \omega^2 L_0 C_0} \left(\frac{i\omega N A}{d} \right) \left(\frac{i\xi_{43}^{12}}{c} - i\omega\mu_0 N C_0 \right), \quad (10)$$

where ξ_{43}^{12} is the z -component of a general susceptibility tensor ξ_{ij}^{rs} which is defined ξ_{43}^{12} ($\mu_0 c/i$) χ_{me} (the magnetic permeability), c is the optical velocity and $i = \sqrt{-1}$. Then, L_0 and C_0 are the self inductance and the leakage capacitance of the pick-up coil having its turn N . Further, d and ω are the thickness and the angular frequency of the applied electric field V_a . In Eq. (10), if $\omega^2 L_0 C_0 \ll 1$, the absolute value of V_0 is simplified as

$$|V_0| = \omega |V_a| (X^2 + \omega^2 Y^2)^{\frac{1}{2}},$$

where

$$X = \left(\frac{NA}{d} \right) \frac{i\xi_{43}^{12}}{c} \quad \text{and} \quad Y = \left(\frac{NA}{d} \right) \mu_0 N^2 C_0. \quad (11)$$

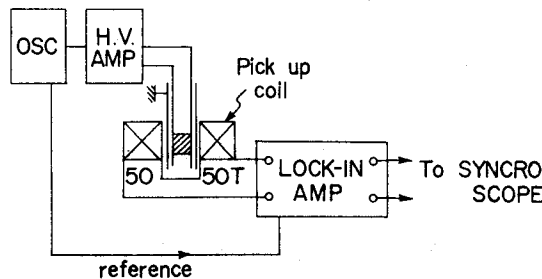


Fig. 4. The block diagram for the measurement of the $(ME)_E$ effect.

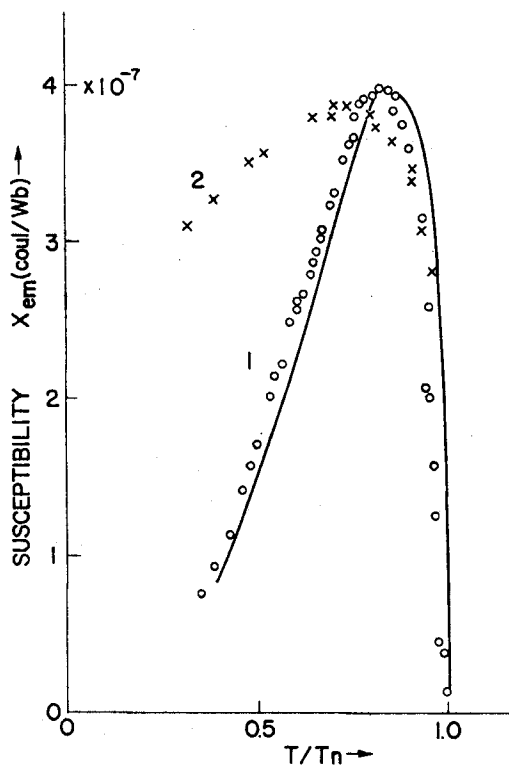


Fig. 5. The Temperature dependences of the magneto-electric susceptibilities corresponding to the $(ME)_B$ and the $(ME)_E$ effects: the experimental result for the former is plotted with the circle mark (1) and that for the latter is plotted with the cross mark (2). The solid curve indicates the temperature dependence for the theoretical susceptibility.

(c) Measurements of temperature dependences of the $(ME)_B$ and the $(ME)_E$

Out-put signals of two types in the magneto-electric effect were measured in various temperatures ranging from 77°K to 300°K. These results, in respect to the $(ME)_B$ and the $(ME)_E$, are shown with forms of the magneto-electric susceptibilities in Fig. 5. Yet, in the case of the $(ME)_B$, two electrodes were soldered to x - y planes, and in the $(ME)_E$ they were soldered to x - z planes. As a result, the curve of the $(ME)_B$ corresponds to a parallel effect to the c -axis, and that of the $(ME)_E$ corresponds to a perpendicular effect to this axis.

4. Determinations of anisotropic susceptibilities of the Cr_2O_3 single crystal

Anisotropic properties of a crystal in general arise from its asymmetric structure. Therefore, from the crystal structure, it is possible to determine a tensor formula for

anisotropic properties by using the well-known Neumann rule that a symmetric transformation for anisotropic properties belongs to that for a magnetic point group of its crystal.

A general magneto-electric behaviour can be established by expressing the polarization tensor M_{ij} as a linear function of the field tensor F_{ij} , that is

$$\mu_0 c M_{ij} = \frac{1}{2} \xi_{ij}^{rs} F_{rs}, \quad (12)$$

where ξ_{ij}^{rs} is a general susceptibility tensor which is dimensionless and asymmetric in rs and ij . Both F_{ij} and M_{ij} are also asymmetric, and they can be represented by the following tensors, that is

$$[F_{ij}] = \begin{bmatrix} 0 & cB_z & -cB_y & -iE_x \\ -cB_z & 0 & cB_x & -iE_y \\ cB_y & -cB_x & 0 & -iE_z \\ iE_x & iE_y & iE_z & 0 \end{bmatrix}, \quad (13)$$

$$[M_{ij}] = \begin{bmatrix} 0 & M_z & -M_y & icP_x \\ -M_z & 0 & M_x & icP_y \\ M_y & -M_x & 0 & icP_z \\ -icP_x & -icP_y & -icP_z & 0 \end{bmatrix}. \quad (14)$$

Moreover, a transformation for ξ_{ij}^{rs} follows the general differential formula

$$\xi_{mn}^{kl} = \frac{\partial Y^k}{\partial X^r} \frac{\partial Y^l}{\partial X^s} \frac{\partial X^t}{\partial Y^m} \frac{\partial X^j}{\partial Y^n} \xi_{ij}^{rs}. \quad (15)$$

When we compare Eqs. (12)–(15) with the equations

$$\left. \begin{aligned} P^\alpha &= \chi_e^{\alpha\beta} E_\beta + \chi_{em}^{\alpha\beta} B_\beta \\ M^\alpha &= \chi_m^{\alpha\beta} E_\beta + \chi_m^{\alpha\beta} B_\beta \end{aligned} \right\}, \quad (16)$$

which are the general form in Eqs. (1a) and (1b), the matrixes $\chi_{em}^{\alpha\beta}$ and $\chi_m^{\alpha\beta}$ reduce to

$$[\chi_{em}^{\alpha\beta}] = \frac{i}{\mu_0 c} \begin{bmatrix} \xi_{41}^{23} & \xi_{41}^{31} & \xi_{41}^{12} \\ \xi_{42}^{23} & \xi_{42}^{31} & \xi_{42}^{12} \\ \xi_{43}^{23} & \xi_{43}^{31} & \xi_{43}^{12} \end{bmatrix}, \quad (17)$$

$$[\chi_m^{\alpha\beta}] = \frac{i}{\mu_0 c} \begin{bmatrix} \xi_{23}^{41} & \xi_{23}^{42} & \xi_{23}^{43} \\ \xi_{31}^{41} & \xi_{31}^{42} & \xi_{31}^{43} \\ \xi_{12}^{41} & \xi_{12}^{42} & \xi_{12}^{43} \end{bmatrix}. \quad (18)$$

As regards Cr₂O₃, the magnetic point group of this crystal is $\bar{3}m$ so that its symmetry element does indeed yield $\bar{1}$, $3z$, $\bar{3}z$, 2 , $\bar{2}$, when the z -axis lies along the c -axis as shown in Fig. 6. By using these results, in Cr₂O₃ it is found to take a diagonal matrix:

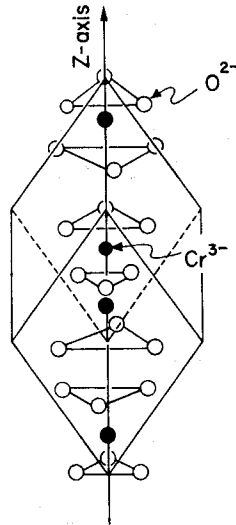


Fig. 6. The crystal structure of Cr₂O₃ which is of a rhombohedron and belongs in a magnetic point group $\bar{3}m$.

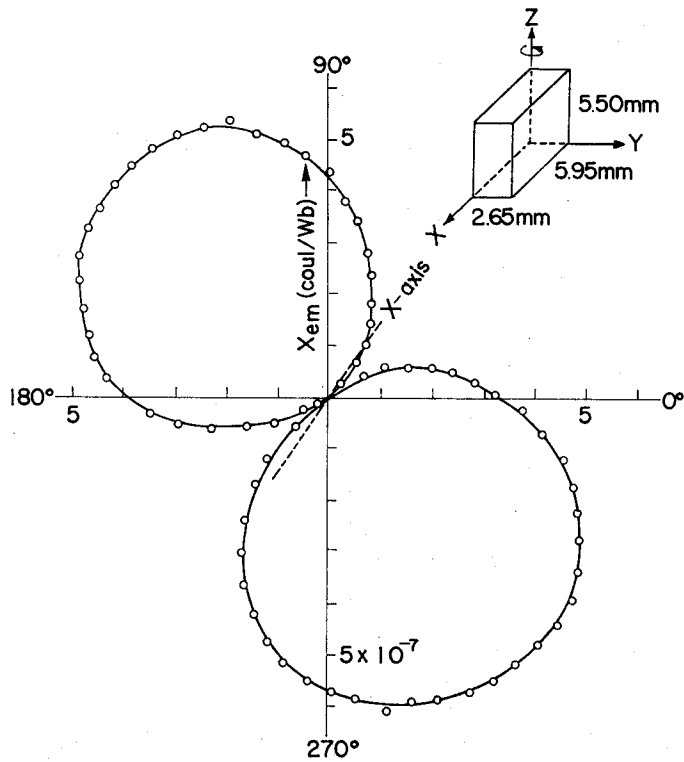


Fig. 7. Anisotropic dependence of the magneto-electric susceptibility χ_{em} when electrodes are soldered along the x -axis and a magnetic field encircles the x - y plane.

$$[\chi_{em}^{a\beta}] = \begin{bmatrix} \chi_{11} & 0 & 0 \\ 0 & \chi_{22} & 0 \\ 0 & 0 & \chi_{33} \end{bmatrix}, \quad (19)$$

but $\chi_{11} = \chi_{22}$ for such a crystal.

An actual measurement on the matrix $\chi_{em}^{a\beta}$ in Cr₂O₃ was first made. It is fairly easy to get the value of $\chi_{em}^{a\beta}$ from measurements on the electric polarization which varies with an angle between a crystal axis and an applied magnetic field. Fig. 7 shows an experimental result for the anisotropic values of χ_{em} which was measured at 273 °K by a rotation of the magnetic field about the x - y plane. In this figure, the arrangement of two electrodes and three co-ordinate axes of the crystal are added to the result. From this result, we can first obtain the respective components corresponding to the tensor χ_{em} with respect to the co-ordinate axes. They are then rewritten as a form of the following diagonal matrix

$$[\chi_{em}^{a\beta}] = \begin{bmatrix} -8.56 & 0 & 0 \\ 0 & -8.56 & 0 \\ 0 & 0 & 112 \end{bmatrix} \times 10^{-8} \text{ coul}/W_b. \quad (20)$$

This experimental value is quite satisfactory to explain the theoretical estimation indicated in Eq. (19).

5. Domain switching in the Cr₂O₃ single crystal

As regards the observation of magnetic domains in a magnetic medium, the methods by means of a neutron diffraction or an electron beam diffraction are usually known. For the case of the Cr₂O₃ single crystal, however, it was suggested by D. N. Astrov¹⁵⁾ that the existence of the magnetic domain might be confirmed, from which a value of the ME susceptibility varies with a condition of heat-treatments. As shown in Fig. 8, two anti-parallel domains in this crystal have relations with an inversion of each spin in azimuth by 180°. This relation, therefore, can be also represented by using the $(t) \rightarrow (-t)$ transformation, so that the general susceptibility tensor is written as

$$\xi_{ij}^{rs} = -\xi_{ij}^{rs}. \quad (21)$$

This practically amounts to the condition that the ME coefficient is antisymmetry under the $(t) \rightarrow (-t)$ transformation, and each ME susceptibility of two magnetic domains has reciprocally an opposite sign with its value as it is. Consequently, the observable susceptibility in practice is determined by a rate of these two domains, which changes with a condition for the heat treatment. For example, if the rate of these domains are the same order, the ME susceptibility becomes zero, and if the crystal is aligned with a single domain, the ME susceptibility becomes a maximum value.

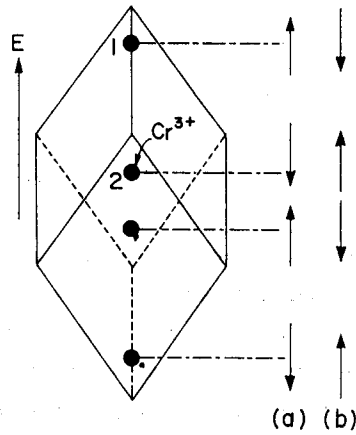


Fig. 8. View of the inversion of spins of respective Cr^{3+} ions which belong to different sublattices. Under an application of high voltage electric field in the direction of the directed line, spins in each sublattice invert from a stabilized state (a) to (b).

As mentioned above, although a normal anti-magnetic medium consists of two different partial lattices, spins in these lattices connect with one another because of a spin-spin interaction as a boundary between two domains or at an exchange energy coming into existence. For the case of the normal anti-magnetic medium, however, both the net magnetization and the static magnetic energy are zero so that the inevitability of having the multi-domain structure does not appear in the least. Rather, this structure is unfavorable enough to have the energy of the magnetic energy rather than a single domain structure. On the other hand, the evidence of the multi domain has been virtually confirmed in the experiment by D. N. Astrov. This seems probably because such an obstruction as crystal vacancies or dislocations becomes a barrier to motions of the domain wall. Consequently, an alignment to the single domain can not be expected, unless an applied energy is enough to vault over the barrier.

In attempting to consider the transition of the domain from the one side to the other, i.e., the domain switching, it seems first inevitable that a free energy in the crystal has to be considered. This free energy can be expanded by using an exponent progression:

$$F = F_0 + \sigma_i H_i + \rho_i E_i + \frac{1}{2} \chi_{ij} H_i H_j + \frac{1}{2} \chi'_{ij} E_i E_j + \alpha_{ij} E_i H_j + \dots, \quad (22)$$

where the tensors σ_i , ρ_i , χ_{ij} , χ'_{ij} and α_{ij} are a piezomagnetic coefficient, a piezoelectric coefficient, the magnetic susceptibility, the electric susceptibility and the magneto-electric susceptibility, respectively. For the case of the Cr_2O_3 single crystal, it is easily certified that all components for σ_i and ρ_i lead to zero on the basis of the Neumann rule. Besides, both χ_{ij} and χ'_{ij} represent symmetry under the $(i) \rightarrow (-i)$ transformation, and then α_{ij}

is asymmetry as shown in Eq. (21).

In the present problem, we have in view two antiferro magnetic domains in which one consists of the $(t) \rightarrow (-t)$ transformation for the other. Therefore, these free energies of the respective domains can be written as

$$F^+ = F_0 + \frac{1}{2} \chi_{ij} H_i H_j + \frac{1}{2} \chi'_{ij} E_i E_j + \alpha_{ij} E_i H_j, \quad (23a)$$

$$F^- = F_0 + \frac{1}{2} \chi_{ij} H_i H_j + \frac{1}{2} \chi'_{ij} E_i E_j - \alpha_{ij} E_i H_j. \quad (23b)$$

From these equations, it is found that when both electric and magnetic fields are in existence the energy difference between these domains reduces to

$$F^+ - F^- = 2\alpha_{ij} E_i H_j. \quad (24)$$

This is an energy required to give rise to the inversion of the domain, that is, the domain switching.

The behavior of the domain switching can be expected likewise in a magneto-electric annealing which is known by way of a heat treatment effect under the application of both E_i and H_j . To be concrete, when the Cr_2O_3 crystal is rapidly cooled from a temperature above the Néel point 306°K to below $\sim 100^\circ\text{K}$ under the application of a reasonable amount of E_i and H_j , the crystal does indeed yield the single domain. It is necessary to keep the multi-domain unless the external energy depending on E_i and H_j is applied to the crystal.

6. Experimental results for the domain switching and the ME annealing

6.1 Observations of the domain switching

The inversion of domains of a Cr_2O_3 single crystal was examined in various amounts of E and H , ranging from zero to $3 \times 10^5 \text{ W}_b \cdot \text{V}/\text{m}^3$. Fig. 9 shows one example of the result which was measured at 288°K on an unannealed sample of Cr_2O_3 . This result, however, does not give full play to the domain switching so great as to be expected from a similar experiment by T. J. Martin.¹⁶⁾ Namely, a sign of χ_{em} essentially ought to change with a EH energy, whereas the change of the sign does not occur and only the amplitude changes. This is probably due to a cause that an irregularity contained in the crystal, e.g. dislocation, was responsible for a partial inversion of domains, because the single crystal of Cr_2O_3 was used as it was unannealed. However, if we could apply it to a higher electric field than the present field $5 \times 10^5 \text{ V}/\text{m}$, the complete inversion might possible occur. This confirmation in practice could not be done on account of the difficulty of an electrical insulation.

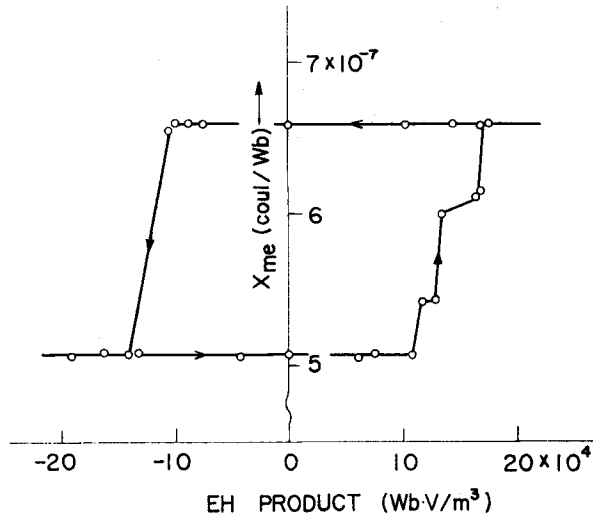


Fig. 9. Variations of the magneto-electric susceptibility χ_{me} illustrating the domain switching.

In respect to the temperature dependence of the energy required for the domain switching, an experiment was performed. This result is shown in Fig. 10. From this result, it is found that the required energy, denoted by $\chi_{em}(EH)$, decreases monotonically at a temperature above 260°K and, that it becomes constant at a lower temperature. This property is able to be explained in terms of an energy change of magnetic domain walls.

With the purpose to make more clear the physical property of domain inversions,

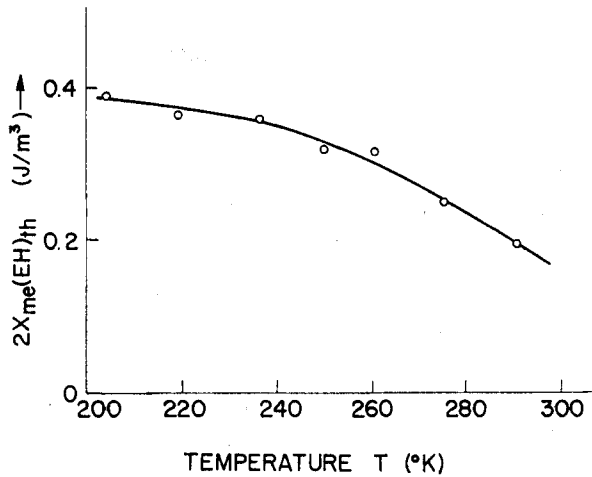


Fig. 10. The temperature dependence of the ME energy density which is required to occur the domain switching.

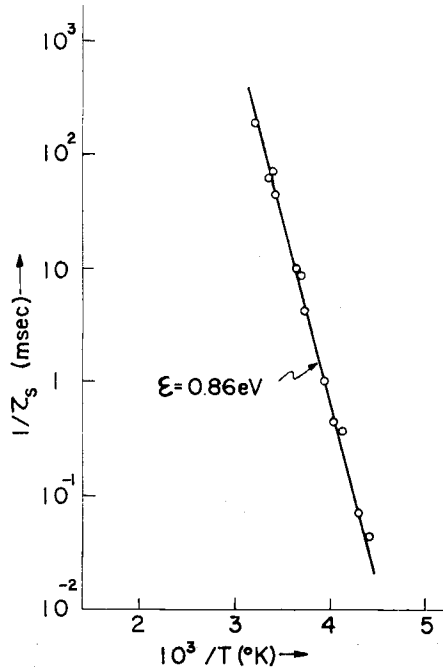


Fig. 11. The temperature dependence of the reciprocal switching time ($1/\tau_s$) as a function of the reciprocal temperature ($1/T$).

a measurement on a switching time of multi-domains was made in various temperatures. We define it as the time required from the application of an external EH field until the close of the domain inversion. This actual switching time was measured by the application of a high voltage pulse, having its sharp rising in the direction of the x -axis of the Cr_2O_3 single crystal whose c -axis was parallel with the direction of an applied static field. A temperature dependence of the switching time obtained in the vicinity of the threshold energy $\chi_{em}(EH)$ corresponding to respective temperatures is shown in Fig. 11.

6.2 Observations of the magneto-electric annealing

The procedure of this experiment was that a sample was rapidly cooled from 100°C to 0°C under the application of E and H after it was held for ~ 1 hr. at a temperature above 100°C . Then, the observation is also made by way of a measurement of the $(ME)_B$ in the sample, which was treated with heat in different amounts of the EH product and in its both signs. In Fig. 12, evidence of the output signal in the $(ME)_B$ is shown as a function of an applied EH energy. This result satisfactorily accounts for the domain switching as well as in the former case. However, the required energy for the ME annealing is by far the lower of these two cases. On the other hand, indicating a different output signal between two saturation regions can be attributed to a case that some spins, polarized in a direction of the negative χ_{em} , may stay for the sake of their

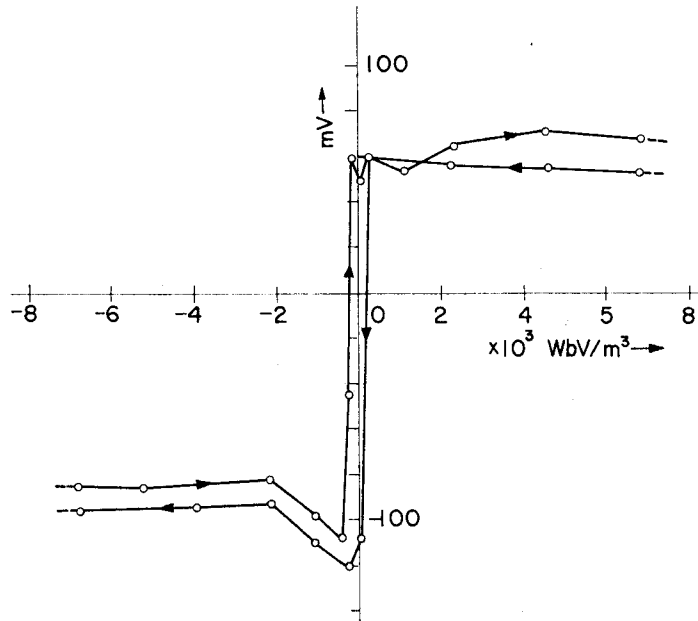


Fig. 12. Variations of the out-put voltage by means of the $(ME)_B$ with applied energies of EH product. The magnetic annealing was carried out under the application of respective EH energies.

restriction due to lattice defects.

7. Discussions and conclusion

The major results concerning a threshold value $(EH)_{th}$ for the magnetic domain switching and its relaxation time τ_s are as follows:

(1) It may possibly invert anti-parallel domains contained in a Cr_2O_3 single crystal in the direction of an external magnetic field H , if an electric field E is applied with H to the crystal. A choice of a good quality single crystal, however, seems to be inevitable because an irregularity of the lattice or microscopic crack would be an obstacle to such a magnetic domain switching.

(2) An external applied energy over a threshold value $(EH)_{th}$ is needed for the occurrence of the domain switching. This threshold value is decided upon by an energy difference between two anti-parallel domain walls, i.e., $2\alpha_{ij}E_iH_j$.

(3) The $(EH)_{th}$ has a temperature dependency such that the magnetoelectric energy $\chi_{me}(EH)_{th}$, corresponding to the domain switching, keeps constant at a lower temperature than the Néel point T_N , and it decreases exponentially above T_N .

(4) The relaxation time in the process of the domain switching becomes short with an increase of an applied energy. Besides, it is found that a temperature dependence of

this relaxation time approximately follows $\tau_s^{-1} \propto \exp(-\epsilon/kT)$, where k is the Boltzmann constant and probably has relations with a potential energy between magnetic domain walls. From the result of $1n(\tau)^{-1}$ was $1/T$ shown in Fig. 11, the inverse relaxation time approximates $\tau_s^{-1} \approx 1.6 \times 10^{17} \exp(-9550/T)$, and so we get $\epsilon = 0.86$ eV. This result suggests clearly that a transition probability for the domain inversion follows the Boltzmann statistics, because τ_s^{-1} denotes the transition probability.

In view of our data concerning the magnetic-electric annealing, a simple model is considered to explain a possible cause of the domain switching in the *ME* annealing. Now, we deal with a case where the *c*-axis of the Cr₂O₃ single crystal is taken along the *z*-axis and the crystal is cooled across the Néel temperature under the application of both energies E_z and H_z . In this situation, the magneto-electric susceptibility tensor of interest is χ_{me}^{33} , i.e., $i \xi_{43}^{12}$ or $i \xi_{12}^{43}$ and this value gives rise to a magnetic moment M_z and an electric dipole moment P_z corresponding to

$$\begin{aligned} M_z &= \frac{i \xi_{12}^{43}}{\mu_0 c} E_z \Delta V, \\ P_z &= \frac{i \xi_{43}^{12}}{\mu_0 c} H_z \Delta V, \end{aligned} \quad (25)$$

with the applied E_z and H_z , respectively. Here, ΔV is a rate of polarized domains taking the total volume of the crystal. From Eq. 25, therefore, it is found that an $E_z H_z$ product does indeed yield a total *ME* energy written as

$$\begin{aligned} G_{me} &= -\frac{i \xi_{12}^{43}}{\mu_0 c} E_z H_z \Delta V - \frac{i \xi_{43}^{12}}{\mu_0 c} H_z E_z \Delta V \\ &\quad - \frac{2i \xi_{43}^{12}}{\mu_0 c} E_z H_z \Delta V, \end{aligned} \quad (26)$$

by using the relation $\xi_{12}^{43} = \xi_{43}^{12}$.

This equation suggests that when both E_z and H_z point in a parallel direction, the *ME* annealing leads to a positive susceptibility, and that when they point in the opposite direction, its sign goes into reverse. In order to make a quantitative comparison between this model and the experimental result, more detailed studies on a good quality single crystal have to be carried out.

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