

Observation of the Magnetolectric Effect in Cr₂O₃ Powders

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Measurements of the magnetolectric effect on Cr₂O₃ powders, after magnetolectric annealing are described. The experimental results are compared with theoretically derived relations between the magnetolectric effect in single crystals and powders. Reasonable agreement is found.

THE magnetolectric (ME) effect predicted by Landau and Lifshitz¹ and shown by Dzyaloshinski² to be allowed in Cr₂O₃, was recently observed by Astrov³ and by Folen *et al.*⁴ These investigators used single crystals for their measurements. We wish to report here measurements of this effect on polycrystalline powders.

Consider a polycrystalline powder which above the magnetic transition has the highest point symmetry possible. Its point group consists of all the proper and improper rotations, and time reversal *R*. Such a powder, if cooled below its transition temperature in the absence of a magnetic field will retain its high point symmetry. For such a powder the ME tensor and all tensors that reverse with *R* (*c* tensors in Birss⁵ notation) will vanish by symmetry even if they are allowed in a magnetically homogeneous single crystal of the same material.

In order to measure a *c* tensor on a powder it is necessary to eliminate *R* as a symmetry element. This can be done by inducing in the powder suitable remanent states. One can then obtain, from these, information that is usually obtained from measurements on single crystals. In the following we shall describe the evaluation of the ME tensor in Cr₂O₃ powder.

By applying simultaneous electric and magnetic fields, an antiferromagnetic remanent state is induced through the ME effect.⁶ Under practical fields, the energy available for reaching the lowest energy remanent state through the ME effect is very small. Therefore, in order to facilitate the approach to thermodynamic equilibrium, the powder is cooled through the Néel temperature under the applied fields. Below the Néel temperature the energy barriers are high and the system is frozen in.

Let us assume that the powder is of random distribution. Consider first the case of parallel electric and magnetic fields (i.e., $H_x = H_y = E_x = E_y = 0$), during heat treatment. If, as we assume, the antiferromagnetic remanence is induced through the ME effect the symmetry will be equal to (or higher than) the symmetry

of the tensor $E_i H_j$, where E_i and H_j are the fields present during the treatment. In the case discussed this symmetry is $\infty/m'm'm'$ so that the ME tensor for this case should have the form

$$\begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{xx} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix}.$$

α_{zz} is given by

$$\alpha_{zz} = \int_0^\vartheta (\alpha_{11} \cos^2\theta + \alpha_1 \sin^2\theta) \sin\theta d\theta - \int_\vartheta^{\pi/2} (\alpha_{11} \cos^2\theta + \alpha_1 \sin^2\theta) \sin\theta d\theta, \quad (1)$$

where θ is the polar angle around *z*; α_{11} and α_1 are the ME constants parallel and perpendicular to the *c* axis, respectively.

For every crystallite in the powder there are two possible remanent states^{3,7}; among other things the two states (which are related by time reversal) differ by the sign of the ME tensor. After the heat treatment each crystallite is assumed to be in the lowest energy state with respect to the applied fields. Those crystallites with *c* axis between $\theta = \vartheta$ and $\theta = \pi/2$ have lower energy if they are in a remanent state of opposite kind than the others, and, therefore, for them one takes $-\alpha$ instead of α . The value of ϑ is given by

$$\tan^2\vartheta = -(\alpha_{11}/\alpha_1)_0, \quad (2)$$

where the right-hand side is the value of the ratio in the neighborhood of the Néel temperature.

Integrating (1), one gets

$$\alpha_{zz} = \frac{\alpha_{11} + 2\alpha_1}{3} (1 - 2 \cos^3\vartheta) - 2\alpha_1 \cos\vartheta \sin^2\vartheta. \quad (3)$$

In order to find α_{xx} one can use the following argument: The trace $\alpha_{11} + 2\alpha_1$ of a single crystallite in the powder is the same for every crystallite but of opposite sign for the grains whose *c* axis lies between ϑ and $\pi/2$. The volume fraction that these occupy is

$$\int_\vartheta^{\pi/2} \sin\theta d\theta = \cos\vartheta; \quad (4)$$

therefore, the trace α_{ii} of α_{ij} for the treated powder is given by

$$\alpha_{ii} = 2\alpha_{xx} + \alpha_{zz} = (\alpha_{11} + 2\alpha_1) (1 - 2 \cos\vartheta). \quad (5)$$

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

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

² I. E. Dzyaloshinski, Soviet Phys.—JETP 10, 628 (1960).

³ D. N. Astrov, Soviet Phys.—JETP 13, 729 (1961).

⁴ V. J. Folen, G. T. Rado, and E. W. Stalder, Phys. Rev. Letters 6, 607 (1961).

⁵ R. R. Birss, Proc. Phys. Soc. (London) 79, 946 (1962).

⁶ At the U. S. Naval Research Laboratory magnetolectric annealing experiments have been previously carried out on Cr₂O₃ single crystals [G. T. Rado (private communication)].

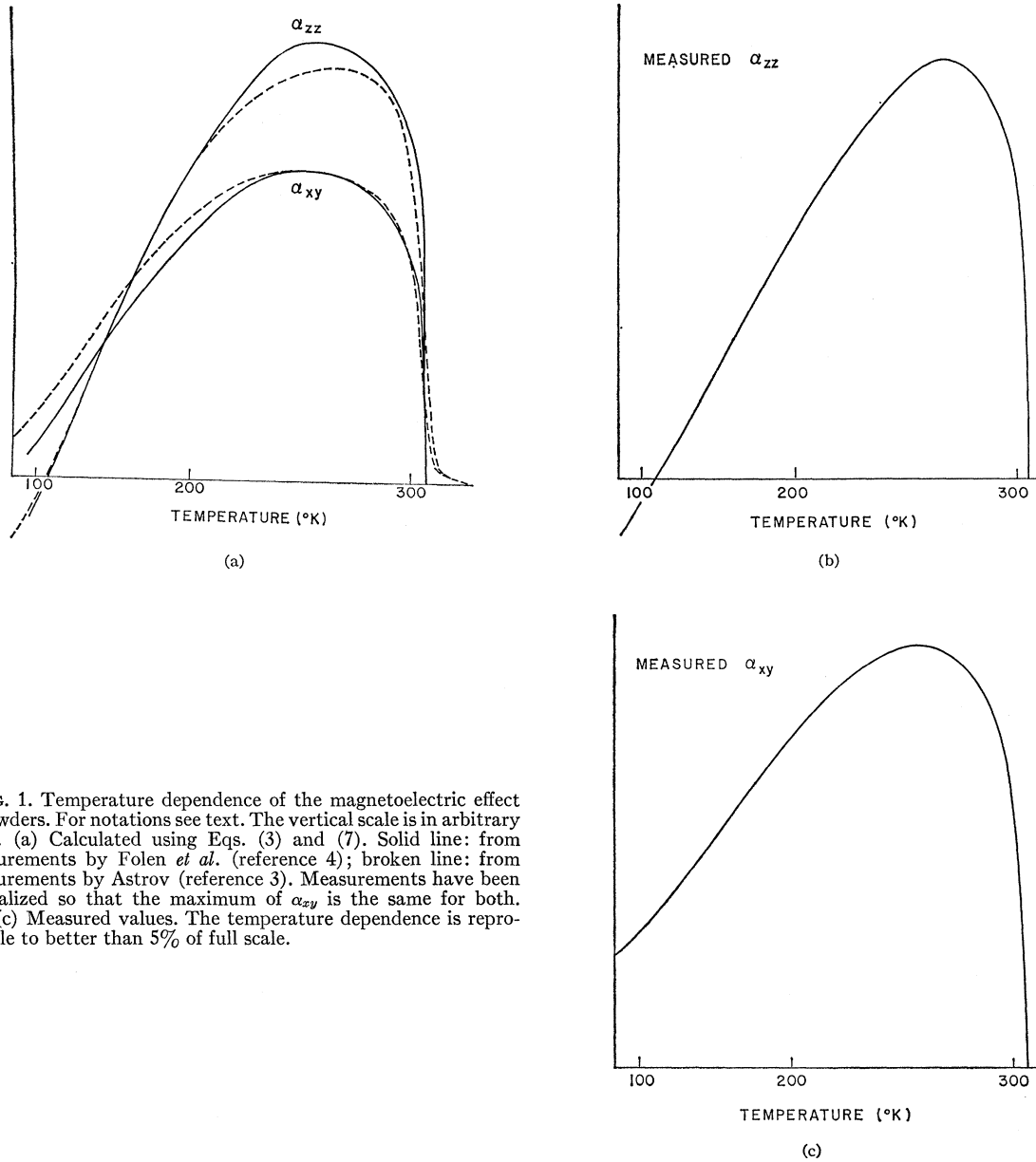


FIG. 1. Temperature dependence of the magnetoelectric effect in powders. For notations see text. The vertical scale is in arbitrary units. (a) Calculated using Eqs. (3) and (7). Solid line: from measurements by Folen *et al.* (reference 4); broken line: from measurements by Astrov (reference 3). Measurements have been normalized so that the maximum of α_{xy} is the same for both. (b), (c) Measured values. The temperature dependence is reproducible to better than 5% of full scale.

From (5) and (3) one finds

$$\alpha_{xx} = \frac{\alpha_{11} + 2\alpha_1}{3}(1 + \cos^3\vartheta) - [\alpha_{11} + \alpha_1(1 + \cos^2\vartheta)] \cos\vartheta. \quad (6)$$

For $\alpha_{11}/\alpha_1 > 0$, $\vartheta = \pi/2$ with the result that $\alpha_{xx} = \alpha_{zz} = (\alpha_{11} + 2\alpha_1)/3$ and the ME effect is isotropic.

Consider now the case of perpendicular electric and magnetic fields (i.e., $H_x = H_z = E_y = E_z = 0$) during the heat treatment: The symmetry of the powder in the remanent state will be the symmetry of the term $E_x H_y$, that is, the group $m'mm$. The magnetoelectric tensor has in this case only the two components α_{xy} and α_{yx} .

By integrating the contribution of different crystallites, one finds

$$\alpha_{yx} = -(\alpha_{11} - \alpha_1) \int_0^{\pi/2} \cos\theta \sin^2\theta d\theta = \frac{2}{3\pi}(\alpha_{11} - \alpha_1) = \alpha_{xy}. \quad (7)$$

From Eqs. (3), (6), and (7) one can deduce the following: If $\alpha_{11}/\alpha_1 > 0$, then from a "parallel" heat treatment one can obtain only one relation between α_{11} and α_1 ; the other relation can then be obtained by a perpendicular heat treatment. It is interesting to note that with this treatment only one relation between α_{11} and α_1 is obtained independently of the value of $(\alpha_{11}/\alpha_1)_0$ and

also for nonrandom distributions of the powder. Also $\alpha_{xy}=0$ for $\alpha_{11}=\alpha_1$; if, however, $(\alpha_{11}/\alpha_1)_0 < 0$, then, at least in principle, one can obtain both constants from the parallel heat treatment by measuring α_{xx} and α_{zz} .

EXPERIMENTAL

Samples were prepared from Baker's (analytically pure) Cr_2O_3 . The powder was pressed into cylinders of 15-mm diam and from 2- to 5-mm height, under pressure of 8500 atm. In some samples a few drops of very diluted crystal cement was added as a binder, while in others no binder was used. The samples were coated with silver paint on the flat ends that served as the condenser plates. The cylinders were very fragile so that few runs of measurements could be done on one sample. To overcome this difficulty and in order to increase the grain size⁸ of the samples, some slugs were sintered at 1500°C. There was a considerable increase in grain size and mechanical strength; however, it was found that conduction between the condenser plates increased considerably. No attempt was made to reduce the conductance by controlling the atmosphere during sintering.

A dc voltage of the order of kilovolts was applied to the condenser and a magnetic field of a few kilogauss applied either parallel or perpendicular to the electric field. Under these applied fields the samples were slowly cooled through the Néel temperature. They were then introduced in an electrode system for the application of a 2000-cps voltage, of usually 1 kV rms. The electrode system was cylindrically symmetric in order to minimize conduction current effects, which were particularly strong in the sintered samples. A pair of pickup coils with 38 000 turns each, connected back to back measured the magnetic moment.

The electrode system was cooled to liquid air temperature, and the voltage versus temperature recorded during heating. The temperature sensing element was

a copper constantan thermocouple in direct contact with the sample. Care was taken to heat up very slowly in order to minimize temperature gradients.

Typical voltage versus temperature curves for parallel and perpendicular heat treatment are shown in Fig. 1. After heating above the Néel temperature, the ME effect was destroyed.

In Fig. 1 are also given theoretical curves derived from the values of α_{11} and α_1 measured by Astrov and by Folen *et al.* and Eqs. (3) and (7). $(\alpha_{11}/\alpha_1)_0$ is taken from Rado⁹ and the powder is assumed of random distribution. The results show that the picture used above is a reasonable approximation to the actual behavior.

The determination of the absolute value of α from measurements in powders is a hard problem. The determination of the electric field in the material is difficult because of the heterogeneous nature of the sample. By taking the internal field as the applied voltage divided by the thickness of the sample one gets a maximum value of α_{11} as a function of temperature between 0.2 and 0.5 times the value obtained by Folen *et al.* from single crystals.

The lower value obtained here could be in part due to nonsaturation of the remanence. A series of heat treatments was done with the same magnetic field but different electric fields. It was found that in the absence of an electric field no ME effect could be detected. Also that the effect still increased slightly up to the highest electric fields applied (about 15 kV/cm).

Calibration of the pickup coils was carried out by replacing the sample with an equivalent coil.

In the above, use of powders for the measurements of the ME effect was described. It should be noted that similar techniques can be used in order to measure other c tensors in antiferromagnetic materials.¹⁰

ACKNOWLEDGMENT

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⁸ The crystallite size has to be large enough in order to eliminate the damaging coupling between the magnetic field and the weak ferromagnetism due to uncompensated antiferromagnetism that exists in very small crystallites.

⁹ G. T. Rado, Phys. Rev. Letters **6**, 529 (1961).

¹⁰ S. Shtrikman, Bull. Am. Phys. Soc. **7**, 279 (1962).