MAGNETOELECTRIC EFFECT IN CHROMIUM OXIDE

D. N. ASTROV

All-Union Institute for Physico-Technical and Radio-Engineering Measurements

The magnetization produced by an electric field in a Cr_2O_3 single crystal was investigated. The magnetization is proportional to the field, as predicted by theory.[2,3] The proportionality coefficient was measured to be 4.3×10^{-4} at 20° C. The magnetic moment along the threefold axis and the magnetic moment in the basal plane have opposite signs in the temperature range from 310° K to 80° K. Near the transition temperature the magnetic moment in the basal plane is well fitted by $\alpha_\perp \propto (T_N - T)^{1/2}$, in agreement with the theory of second-order phase transitions. The temperature dependence of the magnetic moment along the threefold axis is very complicated. Possible causes of the observed temperature dependence are discussed. A connection is established between the sign of the magnetic moment and the magnetic structure.

AN earlier communication[1] reported preliminary results of a study of the magnetoelectric effect in antiferromagnetic materials. It was established that when a single crystal of chromium oxide is placed in an electric field, it exhibits a magnetic moment proportional to the field. The possibility, in principle, of the occurrence of such an effect in substances with magnetic structure was first pointed out by Landau and Lifshitz.[2] Dzyaloshinskii, in a more detailed examination of this question, showed that at least one of the substances with known magnetic structure, namely, chromium oxide, ought to exhibit a magnetoelectric effect.

This conclusion was the result of an analysis of the behavior of the thermodynamic potential under all the symmetry transformations of the chromium oxide magnetic class. Dzyaloshinskii showed that the transformations of this class leave two expressions in the thermodynamic potential invariant; each is linear in **E** and **H** and the invariance corresponds to a linear relation between the inductions and field intensities in the substance:

$$D_{\|} = \varepsilon_{\|} E_{\|} + \alpha_{\|} H_{\|}, \qquad D_{\perp} = \varepsilon_{\perp} E_{\perp} + \alpha_{\perp} H_{\perp};$$

$$B_{\|} = \mu_{\|} H_{\|} + \alpha_{\|} E_{\|}, \qquad B_{\perp} = \mu_{\perp} H_{\perp} + \alpha_{\perp} E_{\perp}. \qquad (1)$$

The components marked $\|$ are directed along the crystal axis, those marked $\perp$ lie in the basal plane.

The present work gives the results of a more detailed investigation of the magnetoelectric effect in chromium oxide.

In reference 1, measurements were made on an irregularly shaped single crystal oriented arbitrarily relative to a highly inhomogeneous applied electric field. In order to show up the anistropy of the magnetoelectric effect and simplify the calculation of the internal field in the sample, the chromium oxide single crystal, grown by the Verneuil process,* was made spherical. The shaping of the single crystal was carried out with silicon carbide. A sample 6.4 ± 0.1 mm in diameter was oriented by means of an x-ray Laue pattern and was then attached to an appropriate holder with BF glue. The accuracy of orientation of the sample was 3 or 4 degrees.

Figure 1 shows the apparatus used to measure the exact value of $\alpha_{\|}$, the constant of proportionality between the magnetic moment and the electric field applied along the C_3 axis of the sample, 1. The magnetic moment thus produced was detected by an astatic pair of coils, 4; the output of the coils was fed through a symmetrizing transformer into an amplifier. The noise at the input of the circuit did not exceed 2×10^{-7}v. The measurements were carried out at 10^4 cps.

The special feature of the apparatus is that it makes possible a sufficiently uniform field in the sample. With this purpose, the diameter of the electrodes, 2, was made three times the diameter of the sample; the electrodes and the sample were placed in a teflon container, 3, filled with a liquid with dielectric constant as close as possible to 12,
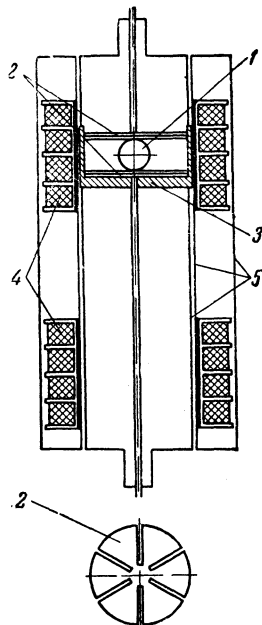
FIG. 1

the dielectric constant of chromium oxide,[4] in order that the electric field in the sample be uniform.

The majority of organic liquids with sufficiently high values of ϵ either strongly absorb moisture from the air (alcohols, acetone) and acquire an observable conductivity ($\geq 10^{-7}$) which makes them difficult to work with, or have a significantly frequency-dependent dielectric constant at room temperature (cresols), or, finally, mix poorly with nonpolar liquids with small ϵ (carbon tetrachloride, xylylols), thus making difficult the preparation of a mixture with the necessary value of the dielectric constant. The most suitable liquid proved to be dichlorethane, with a dielectric constant of 10.4 at 25° C.[5] Dichlorethane absorbs practically no moisture from the air and has a conductivity $\leq 5 \times 10^{-9}$ after double distillation. Because of the difference between the dielectric constants of chromium oxide and dichlorethane, the field in the sample is not perfectly uniform; its intensity is somewhat less than the field intensity between the electrodes.

Estimating the magnitude of the actual field in the sample is very complicated; a solution to the problem of the field distribution in a dielectric sphere pressed between two conducting planes has not been attained. One can only calculate that if the difference between the dielectric constants of the sphere, ϵ_i, and the medium, ϵ_e, is not large, the field inside the sphere will differ from a uniform field by a factor of order $(\epsilon_i - \epsilon_e)/\epsilon_i$.

In preparing the apparatus for determining an accurate value of $\alpha_{||}$, steps were taken to avoid short-circuited loops in the electrostatic screens,

5, and to lessen the losses in the electrodes; the latter were two slit discs, one rotated through a small angle relative to the other, with electrical connections only at their centers.

In calculating the magnetic flux, one must take into account the fact that a significant fraction of the lines of magnetic induction from the sphere magnetized by the electric field are closed inside the detecting coil and give no contribution to the voltage produced on the coil. The magnetic flux outside the coil which contributes to the measured voltage is given by the formula

$$\Phi = 4\pi v \int_0^{l/2} \int_R^\infty H(\rho, z)\, \rho\, d\rho\, dz, \qquad (2)$$

where $H(\rho, z)$ is the projection on the z axis (axis of the coil) of the magnetic field intensity at any point due to the magnetized sphere, and R, l, and v are the radius, length, and number of turns per unit length of the detecting coil, respectively.

After evaluating the integral, we have

$$\Phi = (2\pi l v m/R)(1 + l^2/4R^2)^{-1/2}; \qquad (3)$$

here m is the magnetic moment produced by the magnetoelectric effect in the sample.

The value of m can be calculated as follows. The connection between the field inductions and intensities in the magnetoelectric substance is given by Eqs. (1). For a dielectric sphere in an external electric field $\mathscr{E}_i$ and no external magnetic field, we have[2]

$$E_i = \frac{3\varepsilon_e}{2\varepsilon_e + \varepsilon_i}\mathscr{E}_i, \qquad (4)$$

$$2H_i + B_i = 0. \qquad (5)$$

By using Eq. (1), we obtain (for Cr_2O_3, $\mu_i \approx 1$)

$$B_i = \frac{2}{3}\alpha_i E_i = \frac{2\varepsilon_e \alpha_i}{2\varepsilon_e + \varepsilon_i}\mathscr{E}_i. \qquad (6)$$

The magnetic moment of a sphere of radius a is

$$m = \frac{1}{4\pi}(B_i - H_i)\frac{4}{3}\pi a^3 = \alpha_i a^3 \frac{\varepsilon_e}{2\varepsilon_e + \varepsilon_i}\mathscr{E}_i. \qquad (7)$$

Finally, for the induced flux we obtain

$$\Phi = 2\pi n \frac{\alpha_i \varepsilon_e}{2\varepsilon_e + \varepsilon_i}\frac{a^3}{R}\left(1 + \frac{l^2}{4R^2}\right)^{-1/2}\mathscr{E}_i, \qquad (8)$$

where n is the number of turns on the detecting coil.

Since the amplification of the amplifier, the impedance and mutual inductance of the detecting coils, and the impedance of the symmetrizing transformer were all known, it was easy to compute the voltage produced on the detecting coil as a result of the magnetoelectric effect due to an applied field of known intensity, and from this the
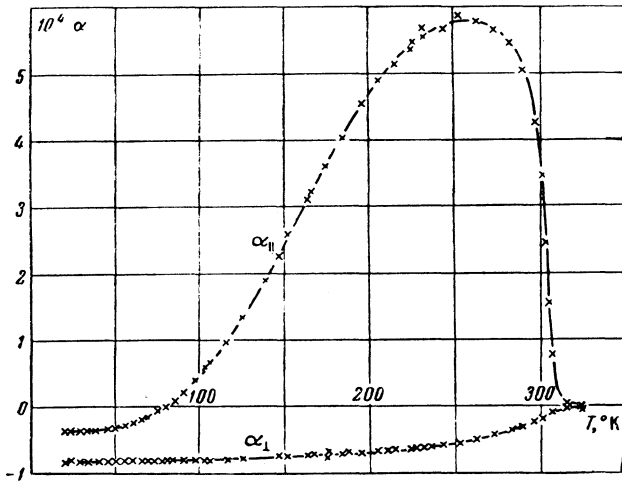
FIG. 2

constant $\alpha_{||}$ characterizing the effect along the C_3 axis. The electric field intensity varied within the limits 1700 and 90 v/cm; $\alpha_{||}$ did not vary within the experimental accuracy. The corresponding voltages on the detecting coil were about 6.6 and 0.35 μv.

The constant $\alpha_{||}$ was measured to be 4.3×10^{-4} at 20° C. Curves giving the temperature dependence of $\alpha_{||}$ and $\alpha_{\perp}$ were normalized to this value. These curves were measured in a separate apparatus which allowed the dependence of the coefficient α on the angle of rotation of the sample to be determined throughout the temperature interval from the antiferromagnetic transition point (310° K) to hydrogen temperature. This apparatus differed from that shown in Fig. 1 in that its basic detecting coil consisted of two identical parts separated by a distance of 10 mm. The sample was oriented perpendicular to the axis of these coils and placed in the electric field in such a way that it was possible to rotate it about any direction lying in the basal plane of the crystal. The apparatus was placed in a vacuum chamber in a Dewar flask with liquid nitrogen or hydrogen. The temperature was measured with a copper-constantan thermocouple
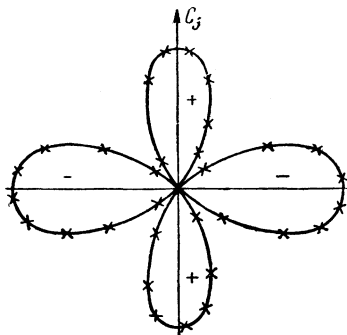
and regulated with a heater. The electrical circuits were the same as those described above.

Figure 2 shows the temperature dependence of the coefficients $\alpha_{||}$ and $\alpha_{\perp}$. A preliminary measurement at room temperature established that the coefficient $\alpha_{\perp}$ is the same, within the experimental accuracy, for all directions lying in the basal plane of the crystal; the corresponding rotation curves were circles.

It should be noted that the curves given for the temperature dependence were obtained with the sample placed in a very nonuniform electric field. With the special apparatus we obtained rotation curves with the sample placed between electrodes whose dimensions were three times the diameter of the sample (and with the space between filled with dichlorethane) and established that at room temperature the rotation curves are the same in the uniform and in the nonuniform field. Figure 3 shows a typical rotation curve taken in the nonuniform field at the arbitrarily chosen temperature 103° K; the axis of rotation is perpendicular to the plane of the figure.

$\alpha_{\perp}$ has the temperature dependence characteristic of ferromagnetic susceptibilities near the Curie point. Near the transition the temperature dependence of $\alpha_{\perp}$ is well fitted by $\alpha_{\perp} \propto (T_N - T)^{1/2}$ with T_N the transition temperature. This is in agreement with the theory of second-order phase transitions (if we assume that the anisotropy constant is independent of temperature). The fit is shown graphically in Fig. 4, which shows the dependence of $\alpha_{\perp}^2$ on $T_N - T$. It is clear that $\alpha_{\perp} \propto (T_N - T)^{1/2}$ up to values of $T_N - T$ of about 80°.

The temperature dependence of $\alpha_{||}$ is much more complex. $\alpha_{||}$ has a broad maximum at about 250° K and then decreases with decreasing temperature; at 80° K it changes sign and then tends to a constant value. Near the transition temperature $\alpha_{||}$ varies in a very complicated way, and we could not find a simple formula to fit its temperature dependence.

The causes of this temperature dependence of $\alpha_{||}$ are still not clear. A possible hypothesis would be that the magnetic structure of chromium
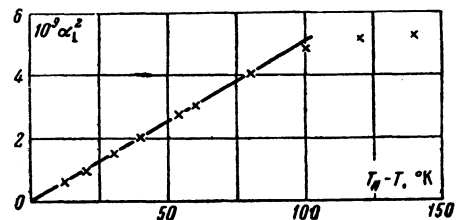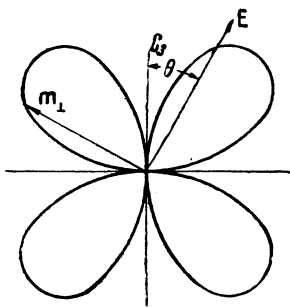

FIG. 3

FIG. 4

FIG. 5

FIG. 6

oxide, determined by the measurements of Brock-
house[6] and McGuire et al.,[7,8] somehow changes
with temperature and as a result of this change the
spins of the magnetic ions have a non-zero projec-
tion on the basal plane. Then terms of the type
$\alpha_1 E_x H_y$, $\alpha_2 E_x H_z$, etc. appear in the thermody-
namic potential and Eq. (1), which describes the
magnetoelectric effect when the spins are along
the threefold axis, must be materially changed.
For example, a component of the magnetic moment
along one of the axes in the basal plane will arise
from electric field components along the other two
axes. Therefore, one should observe a magnetic
moment in a direction perpendicular to the applied
electric field, and the temperature dependence of
the effect can be very complex.

An attempt was made to measure this "perpen-
dicular" effect. Figure 5 shows the rotation curve
obtained; the axis of rotation is perpendicular to
the plane of the figure. It is clear that when the
electric field vector lies in the basal plane the
magnetic moment along the C_3 axis is zero. Cor-
respondingly, when the field is along C_3, there is
no moment in the basal plane. It is easy to see
that such a diagram is obtained by using Eq. (1)
for the component of the magnetic moment perpen-
dicular to the applied electric field; this compo-
nent is $\frac{1}{2}(\alpha_\perp - \alpha_\parallel) \sin 2\theta$, where θ is the angle
between the electric field direction and the crystal
axis. If the hypothesis about the change in magnetic
structure were correct, then a non-zero magnetic
moment in the basal plane should have been ob-
served with the field applied along the crystal axis.
Thus, the hypothesis that the magnetic structure
of chromium oxide is incorrectly determined by
the measurements of Brockhouse[6] and McGuire et
al.[7,8] is not supported by the experiment and must
be rejected.

Along with the peculiarities in the temperature
dependence of $\alpha_\parallel$, the anomalous temperature de-
pendence of the antiferromagnetic resonance in
chromium oxide, observed by Foner,[9] should be
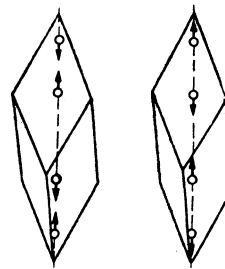noted. The curve given in his paper for the tem-

perature dependence of the resonance field for
fixed frequency has a broad maximum at about
250° K. It is possible that the anomaly observed
by Foner is related to the presence of a magneto-
electric effect in chromium oxide.

From the curves, it is also clear that the signs
of $\alpha_\parallel$ and $\alpha_\perp$ are different in the temperature
range from 80° K to the antiferromagnetic transi-
tion. The signs of $\alpha_\parallel$ and $\alpha_\perp$ were fixed by meas-
uring the phase difference between the voltage on
the electrodes and the voltage at the output of the
detecting amplifier. Moreover, it turned out that
the sign of $\alpha_\parallel$, for example, can be negative as
well as positive, i.e., the magnetic moment pro-
duced can be parallel or antiparallel to the applied
field, while the magnitude of $\alpha_\parallel$ does not change,
but, as mentioned above, the signs of $\alpha_\parallel$ and $\alpha_\perp$
always remain opposite. The sign of $\alpha_\parallel$ observed
in any particular case depends on the history of
the sample. If the sample is heated to a tempera-
ture above the transition point and then cooled
slowly, the sign of $\alpha_\parallel$ can be positive or negative,
and is independent of its value before the sample
was heated. If the sample is cooled rapidly, so
that the transition occurs as irreversibly as pos-
sible, the sign of $\alpha_\parallel$ is again arbitrary, but its
magnitude is sharply decreased. The different
signs of the magnetoelectric effect can be most
naturally explained by the existence of two elec-
trically equivalent possibilities for the spin orien-
tations in the magnetic unit cell of chromium ox-
ide, as shown in Fig. 6.

From the thermodynamic theory of the magneto-
electric effect it can be shown[2] that each of the
two possibilities shown leads to a definite sign for
α, but it is impossible to say which sign corre-
sponds to each structure. After a reversible anti-
ferromagnetic transition one of the two types of
magnetic orderings shown is realized in the single
crystal. In an irreversible transition, the differ-
ent types of order corresponding to opposite signs
for the effect, are realized in different regions of
the single crystal; this leads to a sharp decrease
in the magnitude of the total magnetic moment and
even to its disappearance. The failure of attempts

to observe the magnetoelectric effect in polycrystalline sample where definite, but arbitrary, signs are realized in each single-crystal grain can also be understood on this basis. The presence of a large number of grains leads to complete cancellation of the effect in the sample.

While the sign changes in the magnetoelectric effect after antiferromagnetic transitions were being studied, the following effect was discovered. If the transition described above is carried out with the sample in a magnetic field of about 500 oe parallel to the C_3 axis, then the effect has the same sign every time. If the direction of the applied field is reversed without changing the orientation of the sample, then the sign of the effect also reverses, and this same sign is obtained every time the sample is cooled below the transition point. At the same time, it is easy to see that both structures shown in Fig. 6 remain energetically equivalent in an external magnetic field. The above effect of the magnetic field on the magnetoelectric effect was verified in twenty trials with transitions in the sample.

In conclusion, the author takes this opportunity to convey his profound gratitude to Academician

[1] D. N. Astrov, JETP 38, 984 (1960), Soviet Phys. JETP 11, 708 (1960).
[2] L. D. Landau and E. M. Lifshitz, Электродинамика сплошных сред, (Electrodynamics of Continuous Media), Gostekhizdat 1957.
[3] I. E. Dzyaloshinskii, JETP 37, 881 (1959), Soviet Phys. JETP 10, 628 (1960).
[4] A. Güntherschulze and F. Keller, Z. Physik 75, 78 (1932).
[5] Weissberger, Proskauer, Riddik, and Tups, Organic Solvents, (Russian translation) IIL 1958.
[6] B. N. Brockhouse, J. Chem. Phys. 21, 961 (1953).
[7] McGuire, Scott, and Gronmis, Phys. Rev. 98, 1562 (1955).
[8] T. R. McGuire, Phys. Rev. 102, 1000 (1956).
[9] S. Foner, J. Phys. radium 20, 336 (1959).

Translated by M. Bolsterli
173