EFFECT OF DOMAIN STRUCTURE ON THE MAGNETIC PROPERTIES OF CHROMIUM OXIDE

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Results of investigation of the properties of antiferromagnetic Cr_2O_3, presented in a number of papers,[1-12] are considered. It is shown that the observed peculiarities in the behavior of the magnetic susceptibility $\chi_{||}$ at $T \to 0°K$ and of the constant of the magnetoelectric effect in a magnetic field can be explained qualitatively by the influence of a domain structure of the material. The existence of a "perpendicular" magnetoelectric effect, due to the influence of interdomain boundaries, is detected experimentally.

NEW results of experimental investigations of the properties of antiferromagnetic Cr_2O_3 have been published recently. The results of these researches in many cases contradicted the experimental data obtained earlier on the study of the properties and on the determination of the magnetic structure of chromium oxide; some newly obtained experimental dependences, in particular the form of the dependence of the magnetoelectric-effect coefficient on the applied magnetic field, seemed incomprehensible. In the present paper, an attempt is made to explain the observed discrepancies of the experimental data by the presence of domains in the structure of antiferromagnetic Cr_2O_3, and by processes that occur in the interdomain boundary regions. Furthermore, it follows from our investigation that the magnetoelectric effect in an interdomain boundary region in Cr_2O_3 should differ from the usual one in that the magnetic moment that arises should have a component perpendicular to the applied electric field. This hypothesis was confirmed experimentally: in a fine-grained polycrystalline specimen, a magnetoelectric moment perpendicular to the applied field was observed.

As is known, the magnetic structure of Cr_2O_3 was determined by Brockhouse,[1] by neutron-diffraction measurements made on polycrystalline specimens. Brockhouse determined the order of alternation of the chromium spins in the elementary cell, but he did not establish the distribution of spins with respect to the crystallographic axes. McGuire and collaborators,[2] by measuring the magnetic susceptibility of single-crystal specimens, showed that the susceptibility along the C_3 axis decreases on lowering of the temperature below T_N, whereas in the perpendicular direction it is practically unchanged.

Thus the magnetic structure of Cr_2O_3 was determined: its chief distinctive feature was the existence in the magnetic point group not of simple inversion I, but of inversion combined with the operation R, consisting of a simultaneous change of direction of all magnetic fields and spins.

The presence of the symmetry element IR determined the existence of a magnetoelectric effect in this material. In Foner's[3] however, it was shown that the magnetic susceptibility of single-crystal Cr_2O_3 parallel to the C_3 axis, $\chi_{||}$, approaches a constant nonvanishing value at low temperatures; the value of $\chi_{||}(T \to 0)$ changes greatly from specimen to specimen. To explain this phenomenon, Pratt and Bailey[4] supposed that the direction of the spins of the chromium ions makes an angle of 30° with the C_3 axis and that the magnetic structure itself is helicoidal. In the opinion of Pratt and Bailey, this is corroborated also by the results of their investigations of the optical spectra of Cr_2O_3. It should be mentioned at once that the conclusion about helicoidal structure is to all appearances wrong, since with it there could be no magnetoelectric effect.[5,6]

Another explanation of Foner's results was proposed by Silverstein and Jacobs,[7] who suggested that the form of the susceptibility curve $\chi(T)$ can be explained by Van Vleck temperature-independent paramagnetism, connected with virtual transitions between orbital levels; they obtained satisfactory agreement of the results of the calculation with Foner's experimental data.

We should like to call attention to another pos-

sible explanation of this phenomenon: namely, to attribute it to the influence of interdomain boundaries in the Cr_2O_3 single crystal.

There have been earlier communications[8, 10] about experimental indications of the existence of antiferromagnetic domains in Cr_2O_3, obtained during investigation of the magnetoelectric effect. The existence of domains was revealed by the different signs of the magnetic moments that appear in an applied electric field.

This circumstance is also easily explained by the thermodynamic theory developed by Dzyaloshinskiĭ;[6] in it, the sole vector for the magnetic structure of Cr_2O_3, which takes naturally the form $\mathbf{l}_{2Z} = \mathbf{s}_1 - \mathbf{s}_2 + \mathbf{s}_3 - \mathbf{s}_4$ ($\mathbf{s}_i$ = spins of the chromium ions in the elementary cell), changes sign on inversion of all spins, i.e., on transition to another domain. The vector $\mathbf{l}_{2Z}$ is linearly related to the constants $\chi_{\parallel}$ and $\chi_{\perp}$ that describe the magnetoelectric effect according to the formula[5] for the induction and intensity of the fields in the material,

$$D_{\parallel} = \varepsilon_{\parallel}E_{\parallel} + \alpha_{\parallel}H_{\parallel}, \qquad \mathbf{D}_{\perp} = \varepsilon_{\perp}\mathbf{E}_{\perp} + \alpha_{\perp}\mathbf{H}_{\perp},$$
$$B_{\parallel} = \mu_{\parallel}H_{\parallel} + \alpha_{\parallel}E_{\parallel}, \qquad \mathbf{B}_{\perp} = \mu_{\perp}\mathbf{H}_{\perp} + \alpha_{\perp}\mathbf{E}_{\perp}$$

(here $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the dielectric constants along the C_3 axis and in the basal plane of the crystal, and $\mu_{\parallel}$ and $\mu_{\perp}$ are the corresponding magnetic permeabilities). Thus different domains correspond to different signs of $\alpha_{\parallel}$ and $\alpha_{\perp}$.

In investigation of the magnetoelectric effect, we observed that an increase of the number of domains in a single-crystal specimen occurs very easily. In fact, a specimen that has been at temperature 25° C for a month becomes multidomain to such an extent that in general no magnetoelectric effect can be observed in it, because of the different signs of the constants α of the effect in domains of different types.[8-10] In this process, naturally, there also occurs a growth of the volume in the specimen that is occupied by interdomain boundaries, in which there is a gradual rotation of the antiferromagnetic vector through an angle π over a distance of some hundreds of atomic distances. Thus spins lying in the interdomain region have nonvanishing projections on the basal plane and show, qualitatively, the same sort of effect on the temperature dependence of the susceptibility $\chi_{\parallel}$ as does the Van Vleck paramagnetism. In the immediate vicinity of impurity atoms and lattice defects, the configuration of the field that acts on the spins of the chromium ions and forces them to orient in a definite manner is different from that for a homogeneous material in which the spins also have a projection on the basic plane. Such a situation occurs on the external surface of a specimen, and this can evidently explain the results of Pratt and Bailey, who investigated optical spectra obtained by Wickersheim[11] on thin specimens.

In an investigation of the magnetoelectric effect in a single crystal of Cr_2O_3 in a magnetic field, applied parallel to the C_3 axis, Foner[12] obtained a smooth dependence of the coefficient α of the effect on the value of the applied field. When the value of H reached critical values H_c, corresponding to a transformation of the spins into an antiferromagnetic state with the spins perpendicular to the C_3 axis, the coefficient α underwent a large change. But over the whole interval of applied fields from zero to H_c, the function $\alpha(H)$ was described by a smooth curve, on which there was no indication of a sudden transformation of the spins into the basal plane of the crystal, as might have been expected; the form of the function $\alpha(H)$ was like the usual magnetization curve of ferromagnets.

Such a form of the $\alpha(H)$ curve, obtained by Foner, can evidently be explained by the fact that as the increase of the applied magnetic field progresses, there occurs not a sudden transformation of the spins, but a gradual increase of the dimensions of the interdomain regions by rotation of the spins, and the appearance in them of a projection on the basal plane; thus there is realized in a whole large volume of the crystal a configuration of spins which, at $H = 0$, occurred in the interdomain region. Upon attainment of the value $H = H_c$, this configuration is realized in the whole volume of the crystal.

The general picture of the phenomenon described above explains qualitatively the results enumerated in the investigation of the properties of Cr_2O_3; and it enables us to make still another suggestion, which it is relatively easy to test experimentally. It can be shown that for the magnetic structure of Cr_2O_3 in the interdomain regions and near the specimen boundaries, where the spins of the ions have projections on the basal plane (under the condition of retention in the magnetic class of the symmetry element IR), the form of the part of the thermodynamic potential that corresponds to appearance of a magnetoelectric effect is quite different from that considered earlier by Dzyaloshinskiĭ.[5] The basic difference of interest to us consists in the fact that in the thermodynamic potential of the crystal in this case, there appear terms (invariants) of the form $\gamma E_i H_j$ ($i \neq j$). A consequence should be the existence of a "perpendicular" magnetoelectric effect, i.e., the occurrence of

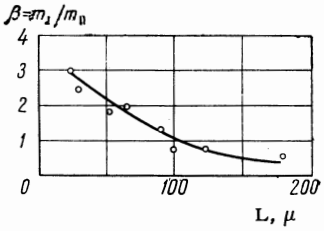
magnetization perpendicular to the applied electric field. For observation of this phenomenon, of course, the specimen should possess a sufficiently extended surface, in order that the volume of the boundary layer may be comparable with the volume of the whole specimen. It was mentioned earlier[9, 13] that when a sufficiently homogeneous applied electric field is insured, it is possible to observe a magnetoelectric effect in polycrystalline specimens at the moment of magnetic ordering.

To record the "perpendicular" magnetoelectric effect, we used a method little different from that described earlier. What was measured was the ratio of the value of the magnetic moment $m_\perp$ of the specimen, induced by an applied electric field in a direction perpendicular to the field E, to the value of the magnetic moment $m_\parallel$ induced in the parallel direction. The measurements were made on powders with various mean particle dimensions. The specimens were made by the method of Schiff and Ditte[14] from preparations of qualification ChDA, with subsequent sifting through a screen. The mean dimensions of the particles of the specimen were determined by means of an MIM-8 microscope.

Eight different specimens were observed, with the mean particle dimension from 20 to 200μ. The specimens were placed in a teflon container, filled with dichloroethane; this made it possible to insure a satisfactorily homogeneous electric field in the process of antiferromagnetic transition and in the measurements. All measurements were made at room temperature. The results obtained on specimens with a single mean particle diameter showed good reproducibility.

The figure shows the dependence of the ratio of the values of the "perpendicular" and "ordinary" magnetoelectric effects, $\beta = m_\perp/m_\parallel$, upon the mean dimension L of the particles in the specimen. It is clear that the size of the magnetic moment induced perpendicular to the applied electric field increases with diminution of the particle dimensions, i.e., with increase of the volume occupied by the domain boundary layer.

On the basis of the data obtained, we did not succeed in answering definitely the question: how are the spins that have projections on the basal plane oriented with respect to the x and y axes



Dependence of the ratio of the magnetic moments induced by an electric field in directions perpendicular ($m_\perp$) and parallel ($m_\parallel$) to the field E upon the dimensions of the particles.

(the z axis is parallel to the C_3 axis)? A difference in the arrangement of spins lying in the basal plane along the x or y axis leads to the consequence that in one of the cases of orientation, as can be shown, the "longitudinal" magnetoelectric effect in general vanishes. To determine the answer, it is necessary to make measurements both on specimens with smaller particle dimensions and on specimens of different purity.

[1] B. N. Brockhouse, J. Chem. Phys. **21**, 961 (1953).

[2] T. R. McGuire, E. J. Scott, and F. H. Grannis, Phys. Rev. **98**, 1562 (1955); **102**, 1000 (1956).

[3] S. Foner, Phys. Rev. **130**, 183 (1963).

[4] G. W. Pratt, Jr., and P. T. Bailey, Phys. Rev. **131**, 1923 (1963).

[5] I. E. Dzyaloshinskiĭ, JETP **37**, 881 (1959), Soviet Phys. JETP **10**, 628 (1960).

[6] I. E. Dzyaloshinskiĭ, JETP **32**, 1547 (1957), Soviet Phys. JETP **5**, 1259 (1957).

[7] S. P. Silverstein and I. S. Jacobs, Phys. Rev. Letters **12**, 670 (1964).

[8] D. N. Astrov, JETP **40**, 1035 (1961), Soviet Phys. JETP **13**, 729 (1961).

[9] D. N. Astrov, Dissertation, Moscow, 1963.

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

[11] K. A. Wickersheim, J. Appl. Phys. **34**, 1224 (1963).

[12] S. Foner and M. Hanabusa, J. Appl. Phys. **34**, 1246 (1963).

[13] B. I. Al'shin and D. N. Astrov, JETP **44**, 1195 (1963), Soviet Phys. JETP **17**, 809 (1963).

[14] Yu. V. Karyakin, Chistye khimicheskie reaktivy (Pure Chemical Reagents), ONTI, 1936.

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