associated with the ferroelectric transition. The discrepancy between theory and experiment is probably due to the lack of a more sophisticated theoretical treatment which would treat the complete problem of lattice dynamics of a distortable disordered dipolar lattice.

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Magnetoelectric Effect in Cr_2O_3 Single Crystal as Studied by Dielectric-Constant Method

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An anomaly in the dielectric constant of a single crystal of Cr_2O_3 in the neighborhood of the Néel temperature is studied with and without external magnetic fields up to a maximum value of 19 kOe. It is observed that the absolute value of the apparent change in the dielectric constant at the Néel temperature increases linearly with applied magnetic field and has a tendency to become constant at fields higher than 17 kOe. This effect is discussed on the basis of structure-sensitive magnetoelectric effects arising from changes in the domain pattern. Rado's spin-orbit atomic model is also considered as a possibility.

I. INTRODUCTION

UNTIL recently, the subjects of magnetostatics and electrostatics were considered to be independent. Landau and Lifshitz[1] first pointed out that magnetoelectric (ME) effects may, in principle, exist in spin-ordered materials. Their arguments were based on thermodynamics and symmetry considerations, and did not invoke any atomic mechanism for this effect. Dzyaloshinskii[2] gave more detailed arguments along similar lines and showed, in particular, that magnetoelectric effects could be observed in single crystals of chromium oxide. While Astrov[3,4] experimentally observed $(ME)_E$ (magnetic polarization produced by the application of an external electric field), Rado and Folen[5–7] observed both $(ME)_E$ and $(ME)_H$ (electric polarization produced by the application of an external magnetic field) independently. Similar effects were observed for antiferromagnetic Ti_2O_3 also.[8] Recently magnetoelectric effects have been observed also for the Cr_2O_3-Al_2O_3 system[9] and for the ferromagnetic $Ga_{2-x}Fe_xO_3$ system.[10] Shtrikman and Treves[11] have shown the existence of a magnetoelectric effect in polycrystalline chromium oxide, produced by cooling the sample through the Néel temperature in the presence of electric and magnetic fields, both applied in the same direction. O'Dell[12] has used a pulsed-magnetic-field technique to measure the magnetoelectric effect in ceramic disks of chromium oxide and has mentioned the possibility of using magnetoelectric materials as memory-device elements which, as he points out, should be independent of frequency below the antiferromagnetic resonance frequency (about 100 kMc/sec).

An atomic mechanism for explaining magnetoelectric effects was put forward by Rado[13,14] and is based on the spin-orbit interaction. Phenomenologically, the situation may be described as follows. At temperatures below

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[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. Dzyaloshinkii, Zh. Eksperim. i Teor. Fiz. **37**, 881 (1959) [English transl.: Soviet Phys.—JETP **10**, 628 (1960)].

[3] D. N. Astrov, Zh. Eksperim. i Teor. Fiz. **38**, 984 (1960) [English transl.: Soviet Phys.—JETP **11**, 708 (1960)].

[4] D. N. Astrov, Zh. Eksperim. i Teor. Fiz. **40**, 1035 (1961) [English transl.: Soviet Phys.—JETP **13**, 729 (1961)].

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

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

[7] G. T. Rado and V. J. Folen, J. Appl. Phys. Suppl. 33, 1126 (1962).

[8] V. I. Al'shin and D. N. Astrov, Zh. Eksperim. i Teor. Fiz. **44**, 1195 (1963) [English transl.: Soviet Phys.—JETP **17**, 809 (1963)].

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

[10] G. T. Rado, Phys. Rev. Letters **13**, 335 (1964); in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965).

[11] S. Shtrikman and D. Treves, Phys. Rev. **130**, 986 (1963).

[12] T. H. O'Dell, Phil. Mag. **10**, 899 (1964).

[13] G. T. Rado, Phys. Rev. Letters **6**, 609 (1961).

[14] G. T. Rado, Phys. Rev. **128**, 2546 (1962).

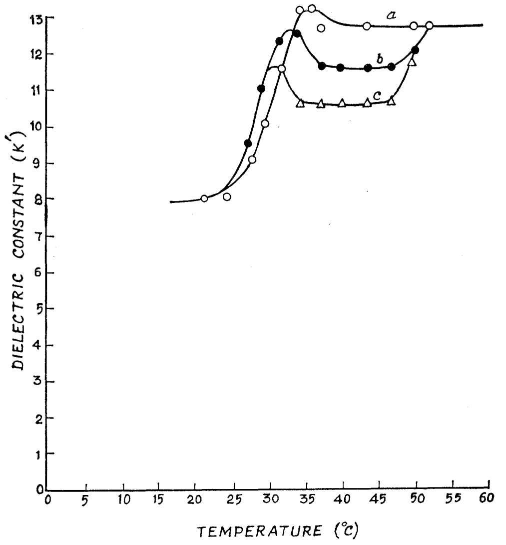

FIG. 1. The dielectric constant (K') of the single crystal of Cr_2O_3 as a function of temperature with and without impressed magnetic fields. (a) Magnetic field $=0$; (b) magnetic field $=3.5$ kOe; (c) magnetic field $=9$ kOe.

the Néel temperature, the magnetic moments of the ionic sublattices (M_A,M_B) are equal and opposite, the net magnetization thus being zero. By applying an electric field, the magnetic moment of each magnetic ion (for example, Cr^{+++} in chromium oxide) changes slightly because of the presence of spin-orbit interaction. If the symmetry is suitable (as it is for Cr_2O_3, etc.), then the changes in magnetization, ΔM_A and ΔM_B, are not equal. A net magnetization thereby results. On similar arguments, a net electric polarization can be shown to exist in the presence of a magnetic field. To explain magnetoelectric effects, Rado[10] further gave a theoretical model in which, in contrast to chromium oxide, two opposite fictitious magnetic-field components were postulated. This model, however, applies only to a weak ferromagnet.[15] He observed both linear and nonlinear magnetoelectric effects in Ga-Fe oxide.[10]

An alternative atomic explanation has been put forward by Kanamori, Date, and Tachiki,[16] who suggested that the intrasublattice exchange interaction is responsible for magnetoelectric effects.

Silverstein and Jacobs[17] have published an estimate which shows that the nonzero value of the parallel magnetic susceptibility for chromium oxide at low temperatures may be caused by Van Vleck–type temperature-independent paramagnetism.

Rado and Folen[6,7] and also Astrov[4] have observed structure-sensitive magnetoelectric effects in their investigations and explain them by the existence of antiferromagnetic domains. The explanation suggested is that there are two types of domains, the spin of each domain pointing either away from or towards the nearest oxygen plane which is perpendicular to the c axis. The different behavior due to the two kinds of domains results from the asymmetry of the Cr^{+++} sites with respect to oxygen planes.

Recently, Fang and Brower[18] carried out dielectric measurements on single crystals of chromium oxide, and qualitatively reported an anomaly in the neighborhood of the Néel temperature. A similar anomaly was also reported earlier by Samakhavalov.[19]

In order to look into the possibility that this anomaly arises from magnetoelectric effects, we have carried out dielectric measurements on a single crystal of chromium oxide in the presence of a magnetic field; the results are reported in this paper.

II. EXPERIMENTAL ARRANGEMENT

Samples in the form of disks were cut by diamond saw from a boule (grown by flame-fusion technique) of single-crystal chromium oxide obtained through the courtesy of Dr. W. S. Brower. The dimensions of the sample used in the present measurement are as follows:

$$\text{radius of the disk} \simeq 1\ \text{mm},$$
$$\text{thickness of the disk} \simeq 0.6\ \text{mm}.$$

The sample was thoroughly cleaned and dried as usual before applying electrodes (silver paint). It was then fixed tightly between two metallic plates insulated from each other by a low-loss Teflon piece. The two metallic plates were connected to the measuring apparatus by rigid leads of widely separated thick wires. The sample was placed in a glass tube over which a heating coil was wound. The above arrangement was placed between the pole pieces of an electromagnet (Polytronic, EM 100, Bombay, India). The direction of the applied magnetic field was altered by rotating the sample. Measurements were made with the magnetic field applied both parallel and perpendicular to the c axis. The strength of the magnetic field was varied up to a maximum of 19 kOe.

Dielectric measurements were made at 1 kc/sec by standard methods[20] with the help of a Muirhead Schering Bridge (Type D-98-A No. 134533 of Muirhead and Company, London) modified by us to suit our work. The source of power for the bridge was an audio-frequency oscillator (Toshniwal, EE0502, Bombay, India) and the balance point was observed with an amplifier detector (Toshniwal, EE07, Bombay, India) followed by a cathode-ray oscillograph (Toshniwal EE51, Bombay, India).

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[15] G. T. Rado, J. Appl. Phys. **37**, 1403 (1966).

[16] M. Date, J. Kanamori, and M. Tachiki, J. Phys. Soc. Japan **16**, 2589 (1961).

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

[18] P. H. Fang and W. S. Brower, Phys. Rev. **129**, 1561 (1963).

[19] A. A. Samakhavalov, Fiz. Tverd. Tela **3**, 3593 (1961) [English transl.: Soviet Phys.—Solid State **3**, 2613 (1962)].

[20] A. von Hippel, *Dielectric Materials and Applications* (John Wiley & Sons, Inc., New York, 1954).

III. RESULTS AND DISCUSSION

The dielectric loss (K'') was observed to be fairly small ($<10^{-2}$) and no reliance could be placed on this parameter in our experimental measurements. The dielectric constant (K') varied from 7 to 13 in this work and could be measured with an accuracy of ±0.5. The temperature measurements had an accuracy of ±0.5°C.

The results for K', as a function of temperature in the absence and presence of magnetic fields of different strengths, are given in Fig. 1. No detectable change in the data plotted in Fig. 1 could be observed upon changing the direction of the applied magnetic field.

As seen from curve (a) of Fig. 1, the dielectric constant K' shows an anomaly in the neighborhood of the Néel temperature (34°C). This anomaly is similar to that reported by Samakhvalov[19] and Fang[18] *et al.*, and is of a high order (i.e., not λ-type).

When a magnetic field is applied, the dielectric constant decreases in the anomalous region and the change $|\Delta K'|$ increases as the magnetic field is increased. In Fig. 2, values of $|\Delta K'|$ at the Néel temperature are plotted as a function of the applied magnetic field. It is observed that $|\Delta K'|$ first changes linearly with field and that at fields higher than 17 kOe it has a tendency to become constant.

We also observe that the peak of the anomalous change in the dielectric constant continuously shifts towards lower temperatures as the magnetic field is increased. However, the temperature range of anomalous behavior is almost unaffected when the strength of the magnetic field is varied.

It appears to us that the apparent change in dielectric constant reported above is due to domain effects (structure-sensitive magnetoelectric effects).[6,4,7] We observe that the results are repeatable in successive measurements. The effect of domains on the magnetoelectric coefficient has been studied in detail by Martin and Anderson,[21,22] who found that switching between substantially single-domain states is possible with the simultaneous impression of electric and magnetic fields of the order of 10 kV/cm and 5 kOe, respectively. The magnetic fields used in our investigation were rather higher than the above value, but since the electric field on our sample was fairly small, being of the order of a few volts per centimeter, we cannot be sure that domain patterns were altered in our measurements.

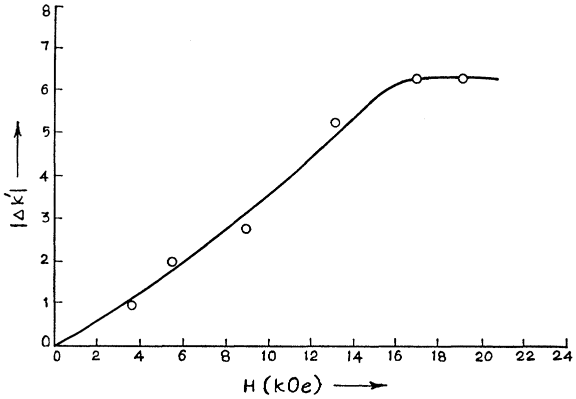

FIG. 2. Apparent change in the dielectric constant ($\Delta K'$) at the Néel temperature of Cr_2O_3 single crystal as a function of applied magnetic field (H).

If these changes in the dielectric constant have a direct connection with changes on the atomic scale, we would conclude that Rado's spin-orbit interaction model is more applicable than the intrasublattice-exchange interaction model of Date *et al.*[16] We are led to the above conclusion for the following reasons. Firstly, according to Date[16] *et al.*, the intrasublattice-exchange-interaction model cannot give rise to the magnetoelectric effect when the external field is perpendicular to the trigonal axis of the Cr_2O_3 single crystal. However, we observe that the change in the dielectric constant is independent of the direction of the external magnetic field. Secondly, the magnetic fields used in this investigation are possibly not high enough to modify the intrasublattice interaction.

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[21] T. J. Martin and J. C. Anderson, Phys. Letters **11**, 109 (1964).

[22] T. J. Martin, Phys. Letters **17**, 83 (1965).