SOVIET PHYSICS JETP VOLUME 17, NUMBER 4 OCTOBER, 1963

MAGNETOELECTRIC EFFECT IN TITANIUM OXIDE Ti_2O_3

B. I. AL'SHIN and D. N. ASTROV

Institute for Physico-technical and Radio-engineering Measurements

Submitted to JETP editor November 27, 1962

J. Exptl. Theoret. Phys. (U.S.S.R.) 44, 1195-1198 (April, 1963)

The magnetoelectric effect has been discovered in polycrystalline Ti_2O_3. Crystallographically this compound is isomorphous with Cr_2O_3, in which the effect has been previously observed.[1,2] The most probable type of the magnetic structure of Ti_2O_3 was determined.

An experimental observation of the magnetoelectric effect in chromium oxide Cr_2O_3 has been reported earlier.[1,2] The magnetoelectric effect [3,4] is manifest in the appearance of magnetization in a sample placed in an electric field, or in the appearance of electric polarization in a magnetic field. This effect arises from the fact that a magnetic structure of IR type (here I is an inversion transformation and R is an operation consisting of simultaneous change of the directions of magnetic fields and spins) allows the existence of terms proportional to EH in the thermodynamic potential. The magnetic symmetry of Cr_2O_3 includes an element of IR type, in contrast to other substances with known magnetic structure having the symmetry element I which forbids the magnetoelectric effect.

It was of interest to investigate the magnetic properties, and in particular the magnetoelectric effect, of substances with unknown magnetic structure, but having crystal structure similar to Cr_2O_3. V_2O_3 and Ti_2O_3 were selected for the tests. Their crystal structures are the same as Cr_2O_3; the unit cell parameters are close to the parameters of Cr_2O_3.[5] The magnetic properties of V and Ti atoms are similar to the properties of Cr. From the work of Hoshek and Klemm[6] and Foëx[7] it is known that a phase transition, presumably antiferromagnetic, occurs in V_2O_3 at 170°K. The existence of the antiferromagnetic state in Ti_2O_3 with a transition at 250°K was first noted in the work of Adler and Selwood[8] and Naylor,[9] but it was not detected by Pearson.[10]

MEASUREMENTS ON V_2O_3

For these tests we used single-crystal samples grown by the Verneuil method and kindly supplied by A. A. Popova, a member of the staff of the Crystallography Institute. The samples were made spherical by grinding with carborundum. The sample diameter was 2—5.5 mm. Debye diffraction patterns were used to check stoichiometry. The deviation from the stoichiometric composition did not exceed 1%.[1)]

The susceptibility of V_2O_3 was investigated using magnetic balances described earlier.[11] It was found that the temperature dependence of the magnetic susceptibility differed from the curve described by Hoshek and Klemm[6] by a much stronger discontinuity and by the susceptibility below the transition point being independent of temperature within the experimental error right down to 14°K. A marked hysteresis was found during the measurements, which definitely indicated a first-order transition. At this transition there was apparently a discontinuous change of the volume since, on rapid variation of temperature in this region, the single crystal cracked or even transformed into a coarse powder.

An attempt to detect the magnetoelectric effect by the technique used for Cr_2O_3 gave a negative result. After these measurements the authors became acquainted with the work of Paoletti and Pickart[12] on the determination of the magnetic structure of V_2O_3 by neutron diffraction. It became clear that at the phase transition V_2O_3 changes its crystal symmetry and the magnetoelectric effect should no longer exist in it.

MEASUREMENTS ON Ti_2O_3

Measurements were carried out on polycrystalline samples of Ti_2O_3 prepared by reduction of the oxide TiO_2.[2)] Foreign impurities in the samples did not exceed 0.1% and the deviation from

---

[1)] The authors are grateful to M. A. Gurevich for obtaining and interpreting the Debye diffraction patterns.

[2)] The authors take this opportunity to thank L. A. Mikhel'son for preparing the oxide.

stoichiometry was also less than 0.1%. Polycrystalline samples were used because of the difficulties in preparing single crystals. Titanium easily forms compounds with oxygen with a great variety of compositions. Using the Verneuil method one can hardly obtain a single crystal of Ti_2O_3 which melts at ≈1900°K and transforms into other oxides even at 1300—1400°C.

The technique for detecting the magnetoelectric effect was very simple.[2] However, it should be remembered that the first attempt[2] to detect this effect in polycrystalline Cr_2O_3 ended in failure, because of the presence of two possible orders of spin distribution in the unit cell, corresponding to opposite signs of the magnetoelectric effect. Nevertheless when the antiferromagnetic transition of polycrystalline Cr_2O_3 took place in electric and magnetic fields, it was possible to detect a magnetoelectric effect equal in magnitude to about one-third of the effect in a single crystal along the three-fold axis. The electric-field uniformity was ensured by placing the sample in a teflon bath filled with dichloroethane. This result for Cr_2O_3 suggested that it should be feasible to investigate a polycrystalline sample of Ti_2O_3.

To detect the magnetoelectric effect in Ti_2O_3 we used the method of applying an alternating magnetic field and measuring the potential difference at the ends of the sample. The choice of this technique was dictated by the considerable electrical conductivity of Ti_2O_3,[13] which made it difficult to establish a strong electric field in the sample.

In selecting the alternating-field frequency we took into account the fact that the electrical conductivity of the substance would cause rapid neutralization of the electric charge appearing at the ends of the sample under the action of the magnetic field H. At low frequencies, when the sample dimensions are small compared with the depth of the skin layer and the magnetic field in the sample is uniform, we can obtain the following dependence for the voltage V at the poles of a sphere: $V \propto (a\omega/\sigma)\alpha H$ where a is the radius of the sphere, σ is the electrical conductivity, α is the magnetoelectric effect constant, and ω is the frequency. From this dependence it is evident that to obtain high voltages one should use high frequencies. However, with increase of the frequency the skin-layer depth becomes smaller than the sample dimensions, and the magnetic field begins to act only in a surface layer of thickness decreasing rapidly with increasing frequency. This reduces the voltage V. The selected frequency was 4 Mc and corresponded to a skin-layer depth of ≈3 mm. The high-frequency magnetic field intensity was 1 Oe.

The sample, compacted by a pressure of ≈2500 atm into a cylinder of 5 mm diameter and 8—10 mm length, was provided with electrodes at its end and placed in a coil so that the sample axis coincided with the coil axis. The electrical resistance of the samples depended strongly on the compacting technique and varied within the limits of one order of magnitude at room temperature.

The temperature dependence of the voltage at the sample ends was measured in the temperature interval from 20°K to room temperature. The required temperatures were obtained by placing the whole device into a test tube surrounded by a vacuum jacket placed in turn in a Dewar flask. Provision was made to take the sample through the antiferromagnetic point in a magnetic field; for this purpose a solenoid was used which produced a constant field of up to 3000 Oe intensity. The sample temperature was measured with a copper—constantan thermocouple.

The tuned amplifier used in this work had a noise level of 1.5 μV at the input. To obtain the highest possible high-frequency field the solenoid was constructed in a special way. It was wound with one layer of ribbon 0.1 mm thick and 2.2 mm wide. The plane of the ribbon was perpendicular to the solenoid axis.

The results of the measurements are given in Fig. 1. Curve 1 represents the temperature dependence of the signal at the sample electrodes at a constant amplitude of the alternating magnetic field. Throughout the test range of temperatures the dc electrical resistance was also recorded (curve 2). The figure shows clearly a singularity on curve 2 at a temperature corresponding to the antiferromagnetic transition in the sample. It is also seen that the voltage at the sample electrodes at 250°K begins to increase smoothly, reaching a maximum at 165°K. The position of the electrical signal maximum and the transition temperature were identical within the experimental error for all four samples used in tests, irrespective of the ohmic resistance of these samples.

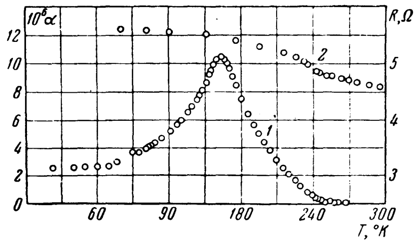

FIG. 1

It should be noted that because of a stray capacitance between the solenoid and the sample there was a certain induced noise signal at the amplifier input, which usually did not exceed 50% of the difference between the signals at the maximum and at the transition point. In some measurements the induced noise signal at room temperature was compensated by a device which allowed variation in the required way of the amplitude and phase of the voltage of the oscillator which supplied the coil. In other measurements the magnitude of the induced noise signal at room temperature was simply subtracted from the total voltage. The resultant curves coincided within the experimental error. From our measurements the value of α, the coefficient of proportionality between the electric polarization and the applied magnetic field, was found to be $\alpha_{\max} = 10^{-5}$.

Six tests were carried out in which the sample was taken through the transition temperature in an external magnetic field with several volts applied across the sample electrodes. It was found that the amplitude of the signal at the electrodes (curve 1) was always the same irrespective of the parallel or antiparallel orientation of **E** and **H**, and that it was identical with the value obtained at the transition when no external electric or magnetic field was applied to the sample. It should be noted that the sign of the electric signal was always the same and that the crystal behaved as a single domain.

On the basis of these tests we may conclude that the magnetoelectric effect exists in Ti_2O_3 but that it is weaker than in chromium oxide. Thus the thermodynamic potential of Ti_2O_3 contains terms with the product of **E** and **H**, and the order of alternation of the spin directions of the Ti ions in a unit cell is that shown in Fig. 2. As regards the spin orientation with respect to the crystallographic axes, we can only say that it is much more probable that the spins in a single-domain crystal lie in the basal plane than along a three-fold axis (as occurs in chromium oxide).

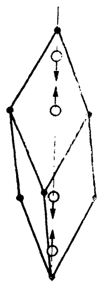

FIG. 2

The authors are very grateful to I. E. Dzyaloshinskiĭ for his interest in this work and valuable advice.

---

[1] D. N. Astrov, JETP **38**, 984 (1960), Soviet Phys. JETP **11**, 708 (1960).

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

[3] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Gostekhizdat, 1957.

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

[5] B. F. Ormont, Struktury neorganicheskikh veshchestv (Structures of Inorganic Substances), Gostekhizdat, 1950.

[6] E. Hoshek and W. Klemm, Z. anorg. allgem. Chem. **242**, 66 (1939).

[7] M. Foëx, Compt. rend. **223**, 1126 (1946).

[8] S. F. Adler and P. W. Selwood, J. Am. Chem. Soc. **76**, 346 (1954).

[9] B. F. Naylor, J. Am. Chem. Soc. **68**, 1077 (1948).

[10] A. D. Pearson, J. Phys. Chem. Solids **5**, 316 (1958).

[11] Astrov, Novikova, and Orlova, JETP **37**, 1197 (1959), Soviet Phys. JETP **10**, 851 (1960).

[12] A. Paoletti and S. J. Pickart, J. Chem. Phys. **32**, 308 (1960).

[13] F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).

Translated by A. Tybulewicz
197