# *HEXAGONAL ANISOTROPY AND MAGNETIZATION CURVES OF ANTIFERROMAGNETIC $CoCO_3$*

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The hexagonal anisotropy constant $K_3$ of antiferromagnetic $CoCO_3$ exhibiting weak ferromagnetism was measured with a magnetic torsion balance in conjunction with a photocompensator. The value of $K_3$ at 4.2°K is $K_3 = 656 \pm 10$ erg cm$^{-3}$. The temperature dependence of $K_3$ was investigated over a broad temperature range (1.8 to 20°K). It was found that at all investigated temperatures the directions of easy magnetization for the ferromagnetic moment were identical with the two-fold axes of the crystal. The magnetization curves along the axes of easy and difficult magnetization and the hysteresis loops in very weak fields were studied. The value $H_c \sim 1$ Oe and the saturation field strength of 600—800 Oe indicate that remagnetization occurs mainly as a result of rotation of the magnetization vector.

## 1. INTRODUCTION

THE existence of weak ferromagnetism in polycrystalline $CoCO_3$ was first discovered by Borovik-Romanov and Orlova.[1] Later Borovik-Romanov and Ozhogin[2] carried out a thorough investigation of the magnetic properties of this substance over a wide temperature range. In these investigations neither a magneto-crystalline anisotropy nor a hysteresis in the magnetic moment in the basal plane of the crystal (111) was detected.

Dzyaloshinskiĭ[3] has shown that the thermodynamic potential of rhombohedral antiferromagnetic crystals having weak ferromagnetism contains a term of the form $K_3 \sin 3\varphi$, where $\varphi$ is an angle measured in the (111) plane. This term describes the hexagonal anisotropy in the basal plane of the crystal. In a preliminary communication[4] it was shown that for $MnCO_3$ the value of $K_3 \sim 1$ erg/cm$^3$, i.e., it was shown that the hexagonal anisotropy was practically nonexistent. In contrast, a relatively large value for the hexagonal anisotropy constant was found for $CoCO_3$, namely, $K_3 = 634$ erg/cm$^3$, which corresponds to a value of the critical anisotropy field of $H_K = 228$ Oe. This value for the critical field is an order of magnitude less than the magnitude of the field for which saturation of the crystal was observed in the measurements of Borovik-Romanov and Ozhogin.[2]

The goals of the present work are the refinement of the values given in our preliminary report and an expansion of the investigation—the study of the temperature dependence of the hexagonal anisotropy constant, the magnetization curves, and the magnetic hysteresis in weak fields.

## 2. METHOD OF MEASUREMENT

The investigation of the hexagonal anisotropy and the measurement of the magnetic moment of the sample were carried out on a specially constructed magnetic balance of very high sensitivity employing photocompensation. A detailed description of the apparatus, which is very suitable for the measurement of very small samples, will be given in a separate paper.[5] The sensitivity of the balance was $9 \times 10^{-5}$ dyne-cm per 1 mm on the scale, and the maximum moment which could be measured was about 3 dyne-cm. Purely electrical means were used to change the sensitivity over a wide range—range-switching in the registering apparatus while providing critical damping in all ranges.

The maximum misalignment of the sample did not exceed 30′ and in the anisotropy measurements never exceeded 1′, so that the results did not require additional corrections. An automatic stop protected the delicate suspension during a sample

[1)]This work was completed as part of a scientific collaboration between the Academy of Sciences of Czechoslovakia and the Academy of Sciences of the USSR in the Institute for Physical Problems of the latter Academy.

change. The suspension constant was $1.82 \times 10^{-5}$ dyne cm/$\mu$A.

The measurements were made on a monocrystal grown by the hydrothermal method of Ikornikova[6] in the Crystallography Institute of the U.S.S.R. Academy of Sciences. The crystals were in the form of flat six-sided plates bounded by smooth growth surfaces. The crystallographic [111] axis (the Z axis) was perpendicular to the plate. The sample used for the measurements was cut from a well-faced crystal by means of a thin-walled tube in an ultrasonic drilling machine into the form of a disc 0.6 mm in diameter and 0.35 mm thick. The value obtained for the volume of the sample based on its dimensions as determined under a microscope and by weighing agreed within the limits of error and was

$$v = (1.14 \pm 0.01) \cdot 10^{-4} \text{ cm}^3$$

(The weight of the sample was 0.472 ± 0.005 mg, its density $\rho = 4.13$).

For measurements of the hexagonal anisotropy constant the sample was affixed to the suspension of the balance such that the Z axis was parallel to the axis of the suspension. Measurements were made in a constant magnetic field lying in the (111) plane at every 10° of rotation. From the curves obtained in this manner, measured at different values of the magnetic field, the values of the angles $\varphi_i$ for twelve extrema were determined by harmonic analysis. Later measurements were made at only these twelve positions. The resulting moment $L_6$ was determined as the arithmetic mean of the absolute values $|L_i|$ measured at the aforementioned values of $\varphi_i$.

For measurement of the magnetization curves the sample was attached such that the Z axis was perpendicular to the axis of the suspension. The indications of the balance were recorded on an X-Y recorder as the field intensity was gradually changed. Voltage from a Hall probe was applied to the X axis, while a voltage proportional to the moment L was fed into the Y axis. The precise location of the Z axis was established by finding the angle at which L(H) = 0. The sensitivity of the apparatus could easily be changed by orienting the magnet differently with respect to the Z axis.

## 3. THE MAGNETIC ANISOTROPY

A typical result of the measurement of the dependence of the torque L on the angle of rotation of the magnet $\varphi_M$ together with its decomposition in a Fourier series at 4.2°K is presented in Fig. 1. From the figure it can be seen that the strongest

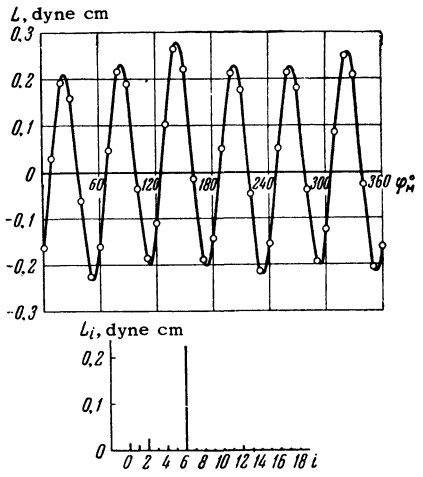


FIG. 1. Dependence of the torque L on the angle of rotation of the magnetic field $\varphi_M$ and the Fourier components for the given curve (T = 4.2° K).

harmonic is the sixth and that the twelfth harmonic is noticeable. The amplitude of the third harmonic was negligibly small in the majority of cases. The large magnitude of the even harmonics is probably explained partly by the fact that the sample is not completely circular in shape (shape anisotropy) and partly by inaccurate positioning of the sample in the field.

In order to determine the smallest field necessary for the saturation of the torque $L_6$, some measurements were made of the dependence of torque on magnetic field. Curve 1 in Fig. 2 shows this dependence for the case in which the crystal was cooled below its Neel temperature $T_N$ in the absence of an external field. Curve 2 was obtained after cooling the crystal in an external field of 1560 Oe. Upon repeated cooling in stronger fields the torque did not increase further, and the magnitude of the torque no longer changed upon repeated heating and cooling of the crystal (even without external field). Curve 3 is a theoretical curve

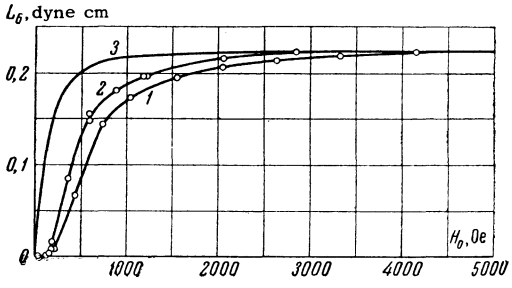


FIG. 2. Magnetic field dependence of the hexagonal torque $L_6$: 1 – crystal cooled below the temperature $T_N$ in the abscence of external field; 2 – crystal cooled below $T_N$ in a field of 1500 Oe; 3 – theoretical curve for zero demagnetization factor (T = 4.2° K).

calculated under the assumption that remagnetization proceeds only as a consequence of rotation of the magnetization vector. As Bozorth and Williams have shown,[7] such a discrepancy between the experimental and theoretical curves could be caused partly by the existence of domain structure and partly by the presence of a demagnetizing field $H_d$ that is not parallel to the external field $H_0$.

In this connection, we wish to remark that the method usually employed, in which the anisotropy constant is determined by an extrapolation of the curve L(1/H) as $H \to \infty$ (see, for example, [7]), is really not valid, since according to the theory of [8] the torque L for a simple rotation is an even function of 1/H. The inapplicability of this method is also seen from the fact that extrapolation of curves 1 and 2 (Fig. 2) yields different values for the hexagonal anisotropy constant, which is clearly nonsense.

The measurements were made up to almost 7000 Oe; above 4000 Oe no further increase in the torque $L_6$ was observed, within the limits of experimental error. From this it was concluded that above 3000 Oe (for curve 2) the torque was already saturated. Hence all the measurements of $L_6$ were carried out in a field of 6000 Oe.

On the basis of 12 measurements made on different days the value of the hexagonal component of the torque at 4.2°K was found to be $L_6 = 0.224 \pm 0.001$ dyne cm. From this and the formula

$$K_3 = L_6 / 3V \qquad (1)$$

we obtain the hexagonal anisotropy constant $K_3 = 656 \pm 10$ erg $cm^{-3}$, which is within 3.5% of the value obtained earlier on the same crystal with a different apparatus.[4] The greatest source of error in this case is the determination of the volume V. The coefficient $L_{12}$ decreases as the field increases. By a linear extrapolation to infinite field we obtain for the value of the dodecagonal constant $K_6$ (on the basis of the determination of $E_K = K_6 \sin^2 6\varphi$) $K_6 \leq 5$ erg $cm^{-3}$.

The temperature dependence of the hexagonal anisotropy constant is shown in Fig. 3. In the range of temperatures 4.2 to 20.4°K the temperature was measured with a carbon thermometer; below 4.2°K the vapor pressure of helium was used. As a control the value of $K_3$ was measured at the triple point temperature of hydrogen (13.95°K). The limits of accuracy in determining the temperature were ± 0.1°K.

Above 4.2°K the anisotropy constant decreases very rapidly and becomes zero at the Neel point. In this temperature region our aim was to fit a

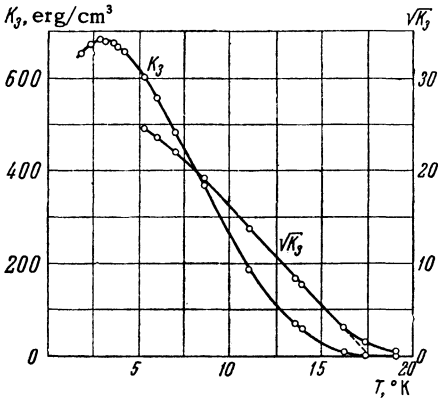


FIG. 3. Temperature dependence of the hexagonal anisotropy constant $K_3$.

suitable functional dependence for the description of the experimental data for $K_3(T)$.

The best fit is given by the function

$$K_3 \sim (T_N - T)^2, \qquad (2)$$

where $T_N = 17.6$°K. Figure 3 shows $\sqrt{K_3}$ as a function of T. It is seen that it is linear over a wide range of temperature.

The directions of easy magnetization lie at all measured temperatures along the two-fold axes. This means that the antiferromagnetic vector lies in the symmetry plane.

## 4. MAGNETIZATION AND HYSTERESIS CURVES

In measurements of the magnetization curves of $CoCO_3$ monocrystals Borovik-Romanov and Ozhogin [2] achieved saturation of the ferromagnetic moment in fields near 2500 Oe. Since this is approximately an order of magnitude greater than the critical field calculated by the author and Kreĭnes earlier,[4] the measurements of ferromagnetic moment as a function of external field $H_0$ were repeated with this apparatus. For this the sample was affixed to the suspension so that the Z axis was perpendicular to the line of the suspension. Since the ferromagnetic moment cannot be brought out of the (111) plane by a field,[2]

$$L = I(H) H_0 V \sin\varphi_M + \tfrac{1}{2} (\chi_\perp - \chi_\parallel) H_0^2 V \sin 2\varphi_M, \qquad (3)$$

where I(H) is the ferromagnetic moment per unit volume, $H_0$ is the external field, at an angle $\varphi_M$ with respect to the plane (111), V is the volume of the sample, $\chi_\perp$ and $\chi_\parallel$ are the susceptibilities perpendicular and parallel to the Z axis, and H is the component of the field in the (111) plane:

$$H = H_0 \cos\varphi_M. \qquad (4)$$

The advantages of this method of measuring the ferromagnetic moment of the sample are, first,

that the paramagnetism or diamagnetism of the suspension does not enter into the measurement (the cross-section of the suspension is circular and therefore isotropic) and, second, that the paramagnetic susceptibility of the sample itself plays a relatively small role in determining L, since it enters in Eq. (3) through the difference $\chi_\perp - \chi_\parallel$.

In a field of 2500 Oe, the value of the second term in Eq. (3) is only 3% of the first term, and in smaller fields it is much smaller. Typical magnetization curves taken at 4.2°K are shown in Fig. 4.

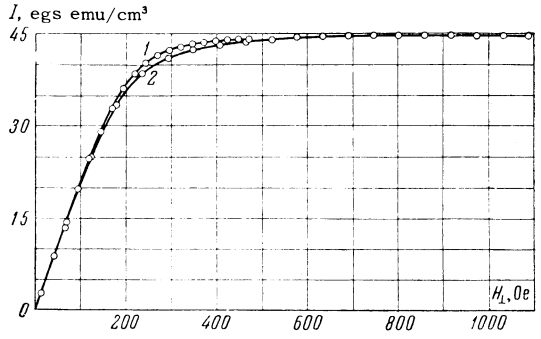


FIG. 4. Magnetization curves, measured at 4.2° K: 1 – measurements along a two-fold axis (direction of easy magnetization); 2 – measurement in a direction perpendicular to a two-fold axis (direction of hard magnetization).

The curves have been corrected for the paramagnetic moment, which in maximum field is about 1.5% of the ferromagnetic moment. By extrapolation to the case of infinite field the value $I_S = 45.3 \pm 1$ cgs emu/cm³ was obtained for the saturation ferromagnetic moment. This is in good agreement with the value given by Borovik-Romanov and Ozhogin,[3] viz., $I_S = 48.6 \pm 2.6$ cgs emu/cm³. In distinction with their results, saturation in our case was attained in much smaller fields, 600—800 Oe. Our curve was not corrected for the finite demagnetization factor, which for a disc is difficult to calculate and which we estimate to be N = 3.5. Thus, we obtain for the demagnetization field at saturation $H_d = 160$ Oe. For the critical field in the direction of difficult magnetization we have $H_C = 18K_3/I_S = 260$ Oe. Curve 1 of Fig. 4 is obtained from magnetization measurements in a field applied along a two-fold axis (direction of easy magnetization) and curve 2 in a field applied in the symmetry plane (direction of hard magnetization). The area between curves 1 and 2 should be equal to $K_3$, and it is, approximately.

Because of the high sensitivity of the apparatus it was found possible to measure hysteresis loops in weak fields. Figure 5 shows two hysteresis

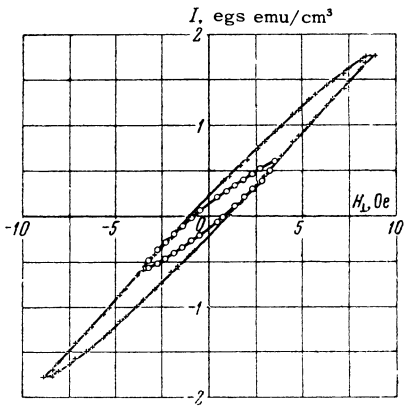


FIG. 5. Hysteresis loops measured in weak fields in the direction of easy magnetization (T = 4.2° K).

loops measured in maximum fields of 3.5 and 9 Oe. The coercive force $H_C$ equals 0.8 and 1 Oe, and the hysteresis losses are respectively 1.3 and 5.2 erg/cm³. The residual magnetization is small because of the large demagnetization factor, and so its actual value could not be determined accurately.

As a control additional measurements of the difference $\chi_\perp - \chi_\parallel$ were made at room temperature. The value obtained, $1.04 \times 10^{-4}$ cgs emu/cm³ was found to be in good agreement with that obtained by Borovik-Romanov and Ozhogin,[2] viz., $1.08 \times 10^{-4}$ cgs emu/cm³.

## 5. DISCUSSION OF THE RESULTS

The results of measurements of the anisotropy constant $K_3$ at 4.2°K were found to be in good agreement with the preliminary measurements. The difference amounted to about 3.5%, which can be explained by the inaccuracies in the preliminary experiment, which was carried out in a simpler apparatus. The anisotropy field of 260 Oe is somewhat larger than the value of 200 Oe that Borovik-Romanov and Ozhogin[2] obtained as an estimate of the upper limit to this quantity. We shall see that the primary reason these authors did not observe this anisotropy is that the Faraday method is not particularly suitable for the determination of relatively small values of this quantity.

As can be seen from Fig. 2, which shows the field dependence of the torque, the discrepancy between the experimental and theoretical curves is rather marked. In weak fields this discrepancy is attributable to the presence of a relatively large demagnetization factor and the existence of domain structure. However, above 1000 Oe the crystal, as can be seen from Fig. 4, is already saturated, and the domains have probably disappeared. According to theoretical calculations $L_6$ should approach

saturation according to an $H^{-2}$ law. If the experimental data are plotted as a function of $H^{-1}$, we obtain very straight lines in fields above 600—800 Oe. As Brown[9] has shown, the approach to saturation is influenced by lattice defects as well as by inhomogeneous demagnetizing fields. In part, an inhomogeneous demagnetizing field acts here, because of the ellipsoidal shape of the sample. As a result of this effect, regions of the crystal lying close to sharp edges are saturated later than the interior regions of the sample. Another factor which apparently predominates occurs as a consequence of microscopic defects (precipitates, dislocations, grain boundaries) which cause greater or smaller deviations of the magnetization from the equilibrium direction, i.e., a definite disorder in the spin system of the antiferromagnetic lattice. All of this leads to a diminution in the average value of the magnetization.

When the sample is cooled in a magnetic field, it is obvious that a more regular ordering of the antiferromagnetic system takes place, leading to an increase in the spontaneous moment (curve 2, Fig. 2). The difference between the saturation of the torque L (Fig. 2) and the magnetic moment (Fig. 4) is partially caused by the circumstance that the magnetic moment curves were measured in the directions of easy and hard magnetization, whereas the torque curves were taken at an angle of 15° to these directions. However, the main reason is that the magnitude of the torque is determined by the expression $L = HI_n$, where $I_n$ is the perpendicular component of the magnetization vector. As $I_n$ changes with field, I varies as $\sqrt{I_S^2 - I_n^2}$ in large fields, i.e., much more slowly. The source of the discrepancy between our magnetization curve and those of Borovik-Romanov and Ozhogin (who obtained saturation only in fields of about 2500 Oe) can be the difference in crystal quality.

A consideration of the magnetic symmetry of the crystal leads us to the conclusion that the terms representing the trigonal symmetry[3] for the ferromagnetic moment cannot appear in the thermodynamic potential. This result is confirmed by the very small values for the amplitude of the third harmonic $L_3$ in the Fourier expansion (see Fig. 1).

Our result that the antiferromagnetic vector lies in the symmetry plane agrees with the neutron diffraction studies of Alikhanov[10] on samples from the same preparation.

The temperature dependence of the hexagonal anisotropy (Fig. 3) is not monotonic and indicates that the anisotropy constant in the vicinity of the Neel point approaches zero as $(T_N - T)^x$, where $x > 1$. The existence of such a dependence does not allow the accurate determination of the temperature of the phase transition from our data. It is interesting, however, that the transition temperature determined by extrapolation of a function of the form $\sqrt{K_3}$ (which best fits the measurements) equals 17.6°K, and this is found to be in agreement with the value obtained by Borovik-Romanov and Orlov[1] for polycrystalline $CoCO_3$. If we use the later value 18.1°K,[2] we get $x = 2.25$. For the temperature dependence of the critical field $H_C = 18K_3/I_S$ [where $I_S(T)$ is taken from [2]] over a wide temperature range (higher than $0.4\,T_N$) we have the relation

$$H_c = 485\,(T_N - T)^{1.75}.$$

The hysteresis loops (Fig. 5) are evidence for the presence of domain structure. As a result of the small value of the hexagonal anisotropy constant, the boundary energy is very small, and the boundaries are therefore very mobile. Evidence for this is also given by the small value for the coercive force (~ 1 Oe). Attempts to observe the domains by means of the Faraday effect, however, were unsuccessful. The small value for the coercive force and the relatively large magnitude of the field for saturation are evidence that homogeneous rotation is the basic mechanism for remagnetization.

## 6. CONCLUSION

Using a photocompensated magnetic torsion balance, the hexagonal anisotropy constant, its temperature dependence, magnetization curves, and hysteresis loops of a disc-shaped sample of $CoCO_3$ were measured. The following principal results were obtained:

1. During measurements of the field dependence of the hexagonal torque component $L_6$ it was found that the properties of the crystal were improved irreversibly by cooling the sample in a magnetic field.

2. A better value for the hexagonal anisotropy constant at 4.2°K was obtained ($K_3 = 656 \pm 10$ erg/cm$^3$), and the directions of easy magnetization, which lie along the two-fold axes of the crystal, were established.

3. The temperature dependence of the hexagonal anisotropy constant was measured and found not to be monotonic. The relation

$$H_c = 485\,(T_N - T)^{1.75}.$$

was obtained for the temperature dependence of the critical field (above $0.4\,T_N$). At 4.2°K, $H_C = 260$ Oe.

4. The magnetization curves in the directions of easy and hard magnetization were measured; the saturation moment $I_S = 45.3$ cgs emu/cm$^3$ at 4.2°K.

5. The hysteresis loops were measured in very weak fields, and the presence of a domain structure was thus demonstrated. The coercive force of the crystal $H_c \sim 1$ Oe.

6. The difference between the susceptibilities perpendicular and parallel to the Z axis was measured at room temperature and was found to be $\chi_\perp - \chi_{||} = 1.04 \times 10^{-4}$ cgs emu/cm$^3$.

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