

## Trigonal Magnetocrystalline Anisotropy in Hexagonal Oxides

L. R. BICKFORD, JR.

*International Business Machines Research Center, Yorktown Heights, New York*

(Received March 29, 1960)

Torque measurements of the magnetocrystalline anisotropy between 77°K and 300°K are reported for single crystals of two different ferrimagnetic oxides having structures related to that of the mineral magnetoplumbite. The compounds, with chemical compositions  $\text{Co}_2\text{Ba}_2\text{Fe}_{12}\text{O}_{22}$  and  $\text{Co}_2\text{Ba}_3\text{Fe}_{24}\text{O}_{41}$ , are known as  $\text{Co}_2Y$  and  $\text{Co}_2Z$ , respectively. Both compounds, after suitable magnetic field cooling treatment, display trigonal anisotropy in the basal plane at 77°K. The field cooling is shown to have the effect of placing the magnetization into one of two energetically equivalent orientations, each of which leads to a trigonal term of different sign. Examination of the crystal structures shows that in the case of  $\text{Co}_2Y$  an additional term  $K_3' \sin^3\theta \times \cos\theta \cos 3\varphi$  (where  $\theta$  and  $\varphi$  are the polar coordinates of the magnetization) should be added to the generally accepted phenomenological hexagonal anisotropy expression. The anisotropy constant  $K_3'$  is evaluated as  $6 \times 10^6$  erg/cm<sup>3</sup> at 117°K. In the case of  $\text{Co}_2Z$  this trigonal anisotropy term is not consistent with the crystal symmetry, although it is appropriate for structural subgroups of the unit cell. Its trigonal anisotropy is explained in terms of a "puckered" magnetization pattern whereby the sign of the  $c$ -axis component of magnetization is different for adjacent subgroups. The existence of this puckered pattern implies that the exchange coupling across the boundaries between subgroups is relatively weak. A new rotational hysteresis effect in  $\text{Co}_2Y$  is described and explained phenomenologically. An atomic theory assigning the origin of the trigonal anisotropy of both compounds to the cobalt ions is presented.

### I. INTRODUCTION

IN recent years, studies of the anisotropic properties of various members of the class of ferroxdure-type hexagonal ferrimagnetic oxides<sup>1</sup> have brought to light many new effects not previously observed or recognized in hexagonal ferromagnetic crystals. Such effects include the existence of planes<sup>1</sup> and cones<sup>2</sup> as loci of the preferred orientations for the magnetization. These phenomena are readily understandable in terms of the magnitudes and signs of the various constants of the hexagonal anisotropy expression. This paper concerns anisotropy phenomena which cannot be so explained.

The magnetocrystalline anisotropy energy  $W_A$  of hexagonal oxides is usually expressed in terms of the phenomenological equation

$$W_A = K_1 \sin^2\theta + K_2 \sin^4\theta + K_3' \sin^6\theta + K_3 \sin^6\theta \cos 6\varphi, \quad (1)$$

in which  $\theta$  and  $\varphi$  are the polar angles denoting the direction of the magnetization. Angle  $\theta$  is measured from the  $c$  axis. Angle  $\varphi$ , which lies in the basal plane, is most conveniently measured from a vertical mirror symmetry plane (i.e., from the hexagonal  $[\bar{1}10]$ ).  $K_3'$  and  $K_3$  are generally very small in comparison with the other two anisotropy constants. Therefore  $K_3'$  is usually neglected and  $K_3$  is only taken into account in describing the anisotropy in the basal plane.

The preferred orientation of the magnetization ( $\theta_0$ ) with respect to the  $c$  axis is found by setting the first  $\theta$  derivative of Eq. (1) equal to zero:

$$\partial W_A / \partial \theta = \sin 2\theta_0 (K_1 + 2K_2 \sin^2\theta_0) = 0, \quad (2)$$

and determining which of the three solutions to Eq. (2) [ $\theta_0 = 0$ ;  $\pi/2$ ;  $\sin^{-1}(-K_1/2K_2)^{1/2}$ ] has the lowest energy

<sup>1</sup> J. J. Went, G. W. Rathenau, E. W. Gorter, and G. W. van Oosterhout, *Philips Tech. Rev.* **13**, 194 (1951/2); G. H. Jonker, H. P. J. Wijn, and P. B. Braun, *Philips Tech. Rev.* **18**, 145 (1956/7).

for different combinations of magnitude and sign for  $K_1$  and  $K_2$ . One finds that the anisotropy is axial ( $\theta_0 = 0$ ) if  $K_1 + K_2 > 0$  and at the same time  $K_1 > 0$ ; and planar ( $\theta_0 = \pi/2$ ) if  $K_1 + K_2 < 0$  and  $-K_1 > 2K_2$ . If  $K_1 < 0$  and  $0 < -K_1/2K_2 < 1$ , the preferred directions lie on two cones for which  $\sin^2\theta_0 = -K_1/2K_2$ .

The two hexagonal oxide compounds known<sup>1</sup> as  $\text{Co}_2Y$  and  $\text{Co}_2Z$  (with chemical formulas  $\text{Co}_2\text{Ba}_2\text{Fe}_{12}\text{O}_{22}$  and  $\text{Co}_2\text{Ba}_3\text{Fe}_{24}\text{O}_{41}$ , respectively; and with crystal structures related to that of the mineral magnetoplumbite) have been reported<sup>2</sup> to possess cones of easy magnetization at temperatures below ca 215°K. In the case of  $\text{Co}_2Y$  the cone angle  $\theta_0$  is 68° at 90°K, and increases to 90° as the temperature increases to 215°K. Above this temperature the anisotropy remains planar. Corresponding numerical values of  $\theta_0$  for  $\text{Co}_2Z$  have not been reported. However, it is known<sup>2</sup> to have cones of easy magnetization below 220°K and planar anisotropy between 220°K and 480°K.

This paper reports the results of torque anisotropy measurements performed on single crystals of  $\text{Co}_2Y$  and  $\text{Co}_2Z$  at temperatures between 77°K and 300°K. The major emphasis is on the observation of anisotropy which is trigonal with respect to angle  $\varphi$  and therefore not consistent with Eq. (1). This trigonal anisotropy is observed at 77°K in crystals of both  $\text{Co}_2Y$  and  $\text{Co}_2Z$  which have been cooled in properly oriented magnetic fields. Various experiments show that it is an intrinsic property of the crystals, necessitating the addition of more terms to Eq. (1).

The complex crystal structures are examined and it is found that in the case of  $\text{Co}_2Y$  the trigonal anisotropy term is compatible with the crystal symmetry; whereas in the case of  $\text{Co}_2Z$  it is not. In the latter case, however,

<sup>2</sup> U. Enz, J. F. Fast, and H. P. J. Wijn; see H. B. G. Casimir *et al.*, *J. phys radium* **20**, 260 (1959).

the magnetic anisotropy is found to have the symmetry of the structural subgroups making up the crystal unit cell. The presence of the trigonal magnetocrystalline anisotropy indicates the existence of a "puckered" magnetization within the unit cell. This new phenomenon implies that the exchange coupling between the structural subgroups is relatively weak.

Finally, a brief discussion of the origin of the trigonal anisotropy is presented in terms of an existing theory<sup>3</sup> of the anisotropy introduced into oxides by cobalt.

## II. EXPERIMENT

### A. Experimental Details

The crystals were grown at the Philips Research Laboratories, under the direction of A. L. Stuijts. Chemical analysis indicated the presence of some divalent iron, so that the correct formulas of the two crystals are  $(\text{Co}_{1.88}^{\text{II}}\text{Fe}_{0.12}^{\text{II}})\text{Ba}_2\text{Fe}_{12}\text{O}_{22}$  and  $(\text{Co}_{1.92}^{\text{II}}\text{Fe}_{0.08}^{\text{II}})\text{Ba}_3\text{Fe}_{24}\text{O}_{41}$  for  $\text{Co}_2Y$  and  $\text{Co}_2Z$ , respectively.

The crystals were in the form of basal plane plates with volumes of approximately  $5 \times 10^{-3} \text{ cm}^3$ . The deviation of their shape from oblate ellipsoids introduced a small but measurable torque due to shape anisotropy. Suitable correction for this spurious torque could be made readily by graphical means.

Measurement of the basal plane anisotropy was accomplished by measuring the torque exerted on a crystal as a magnetic field rotates slowly in the basal plane ( $\theta = 90^\circ$ ). In terms of the anisotropy expression of Eq. (1) this torque  $L$  is given by

$$L = -\partial W_A / \partial \varphi = 6K_3 \sin^2 \theta \sin 6\varphi. \quad (3)$$

In the temperature region in which  $\theta_0 \neq \pi/2$  the amplitude of this sixfold torque should increase with increasing field strength, i.e., as the magnetization is pulled more closely from the equilibrium cone into the basal plane. From the published<sup>2</sup> values of  $K_1$  and  $K_2$  at  $77^\circ\text{K}$  it can be calculated that in the case of  $\text{Co}_2Y$  the torque curve should be saturated with respect to increasing field at  $H \approx 17\,000 \text{ oe}$ .

The torque curves were recorded automatically on an  $X-Y$  recorder, using the torque magnetometer described by Penoyer.<sup>4</sup> The crystals, which remained stationary during the measurement, were mounted with their  $c$  axis oriented vertically. The magnetic field strength was adjustable to a maximum value of  $10\,400 \text{ oe}$ ; its angular velocity of rotation in a horizontal plane, to a maximum value of  $6^\circ/\text{sec}$ ; and the sample temperature, from  $77^\circ\text{K}$  to  $300^\circ\text{K}$ .

For those field-cooling experiments which required a field to be applied along the  $c$  axis the crystal was transferred to a vertical air-core solenoid ( $10\,000 \text{ oe}$ ), cooled, and transferred back to the torque balance while still immersed in liquid nitrogen.

<sup>3</sup> J. C. Slonczewski, Phys. Rev. **110**, 1341 (1958).

<sup>4</sup> R. F. Penoyer, Rev. Sci. Instr. **30**, 711 (1959).

For some experiments, designed to detect changes in the  $c$ -axis component of magnetization during a torque measurement, the crystals were surrounded by a 100-turn winding and voltages induced therein were measured by means of a Liston-Becker chopper amplifier. Optimum conditions were achieved by varying the strength of the magnetic field and the velocity of its rotation.

## B. Results

### 1. $\text{Co}_2Y$

At room temperature the basal-plane torque curves have the expected shape, consisting of the superposition of a sixfold term ( $K_3 \approx -600 \text{ erg/cc}$ ) on a basically two-fold curve due to shape anisotropy.

At  $77^\circ\text{K}$  the predominant term in the torque curve becomes threefold if the crystal is cooled in a magnetic field. One of two torque curves ( $L = \pm C \sin 3\varphi$ ) is observed, depending on the orientation of the field which had been applied during cooling. Curve *A* of Fig. 1 results if the cooling field had been applied at orientations  $0^\circ < \varphi < 30^\circ$  or  $90^\circ < \varphi < 150^\circ$ . For other orientations of a cooling field in the basal plane between  $0^\circ$  and  $180^\circ$ , curve *B* of Fig. 1 results. In other words, the trigonal anisotropy at  $77^\circ\text{K}$  has its preferred direction as close as possible to the cooling field direction.<sup>5</sup> The magnitude of the cooling field need be only sufficiently large that domains are eliminated and the magnetiza-

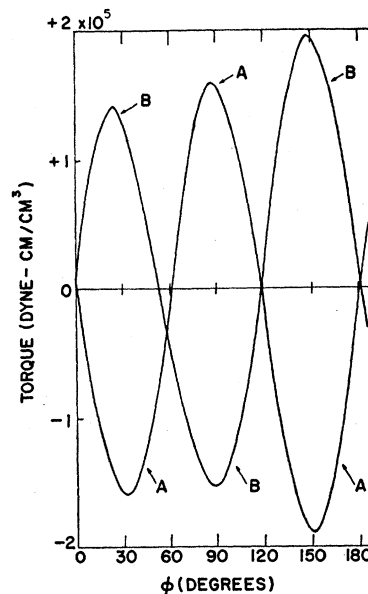


FIG. 1. Basal plane torque curves for  $\text{Co}_2Y$  single crystal, measured at  $77^\circ\text{K}$  in a field of  $10\,400 \text{ oe}$ . Curve *A* was obtained after the crystal had been cooled in a field of  $10\,000 \text{ oe}$  oriented at  $\varphi = 0^\circ$ ; curve *B* followed cooling at  $\varphi = 180^\circ$ .

<sup>5</sup> According to the sign convention utilized in the torque curves of this paper, the stable orientations of the magnetization exist where the torque curves pass through zero with a negative slope. A torque of negative sign signifies that the anisotropy tends to pull the magnetization back; i.e., decrease angle  $\varphi$ .

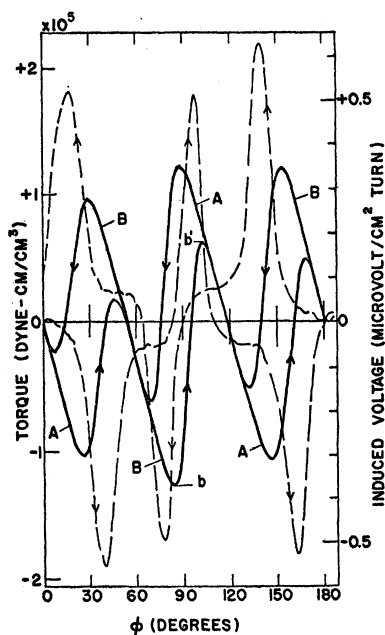


FIG. 2. Torque (solid curves) and voltage (dashed curves) recorded for a  $\text{Co}_2\text{Y}$  crystal at  $117^\circ\text{K}$  as a magnetic field of 3100 oe rotated clockwise and counterclockwise with a uniform angular velocity of  $2^\circ/\text{sec}$ . *A* and *B* designate segments of the torque curves corresponding with curves *A* and *B*, respectively, of Fig. 1. The voltage, induced in a stationary *c*-axis pickup coil surrounding the crystal, is a measure of the time rate of change in *c*-axis component of magnetization. Both curves show rotational hysteresis.

tion is oriented uniformly more or less parallel to the field direction. Once this condition is established (at ca 5000 oe) the amplitude of the trigonal torque curves is independent of the magnitude of the cooling field. If the crystal is cooled in the absence of an external field, there results an ill-defined state yielding torque curves which are an unstable combination of *A* and *B*.

The trigonal torque occurs only in the temperature region in which the crystals have preferred cones, and the annealing field which establishes the phase of the torque curve need be applied only below ca  $215^\circ\text{K}$ , the temperature at which the equilibrium angle  $\theta_0$  departs from  $\pi/2$ .

The phase of the threefold torque curve is also affected by cooling the crystal in a field along the *c* axis. A field in one direction along the axis ( $\theta=\pi$ ) will produce curve *A* of Fig. 1, whereas a field in the opposite direction ( $\theta=0$ ) will produce curve *B*. The available cooling field (10 000 oe) was so small that the magnetization deviated from the *c* axis by a large angle. However, by carrying out cooling experiments at different values of  $\varphi$  it was demonstrated that it is the vertical and not the horizontal component of the magnetization during cooling which is effective in determining the phase of the threefold torque. This fact is a significant clue, leading to the assignment of the two torque curves to different states of magnetization of the crystal. One of the curves is associated with the cone of equilibrium

angle  $\theta_0$ ; and the other, with the cone of equilibrium angle  $\pi-\theta_0$ . Further evidence verifying this assignment is the direct observation of changes in *c*-axis component of magnetization. This effect will be described shortly.

The amplitude of the threefold torque curves at  $77^\circ\text{K}$  is a function of the field applied during its measurement. It was observed to have its maximum value at 5000 oe, and to decrease with increasing field. In 10 400 oe the amplitude had decreased 17% from its maximum value. The decrease in amplitude of the  $\sin 3\varphi$  torque curve with increasing field accompanies the approach of  $\theta$  to  $\pi/2$  from  $\theta_0$  or from  $\pi-\theta_0$ .

The two solid curves shown in Fig. 2 are torque curves recorded at  $117^\circ\text{K}$  as a magnetic field of 3100 oe rotated in the basal plane clockwise and counterclockwise, respectively. Each of these curves consists of labeled portions of the trigonal torque curves *A* and *B* of Fig. 1. The relatively steep portions of the curves (e.g., *b-b'*) correspond to transitions between the two trigonal torque curves. They occur at different values of  $\varphi$  for clockwise and counterclockwise rotation. In other words, a rotational hysteresis effect takes place.

The dashed curves of Fig. 2 illustrate the results of an experiment designed to verify the conclusion that curves *A* and *B* of Fig. 1 correspond to different *c*-axis components of the magnetization. They are recordings of the voltage induced in a stationary 100-turn *c*-axis pickup coil surrounding the sample as the magnetic field rotated with uniform angular velocity during the measurement. It can be seen that these curves consist of spikes of alternating sign which are centered about the transition regions of the corresponding torque curves. The integrated area under one of the spikes is a measure of the total flux change in the pickup coil during one transition (e.g., *b-b'*). This information, taken together with the dimensions of the sample, yields the change in *c*-axis component of magnetization. Assuming that these changes are symmetrical about the basal plane we calculate that angle  $\theta$  changes by ca  $8.0^\circ$  during each jump. In other words, the dashed curve of Fig. 2 is interpreted as indicating that  $\theta$  alternates between  $86.0^\circ$  and  $94.0^\circ$  by rather discrete jumps during the course of the torque measurement.

Since it was found that the width of the voltage spikes was relatively independent of temperature and magnetic field, the height of the spikes can be taken as a relative measure of the magnitude of the change in *c*-axis component of magnetization. The amount of rotational hysteresis is indicated by the difference between the values of  $\varphi$  corresponding to the voltage peaks of the clockwise and counterclockwise curves.

The height of the voltage spikes is determined by a number of parameters which can be adjusted to create optimum conditions. The speed of rotation of the magnet is limited by the response time of the amplifier. Increasing the magnetic field has the effect of increasing angle  $\theta$  and therefore decreasing the amount by which the *c*-axis component of magnetization changes during

each reversal. At the same time it increases the background voltage, which is essentially a  $\sin\theta$  curve due to stray pickup of the rotating horizontal magnetic field by the stationary coil. The magnetization switching effect persists, with only slightly less rotational hysteresis than that shown in Fig. 2, at fields up to 10 400 oe. At the larger fields it is more apparent that the observed torque curves consist of segments of the  $\pm C \sin 3\varphi$  torque curves separated by sharp transition regions.

In a field of 5000 oe the switching effect first appears at ca 90°K and it persists throughout the temperature region in which the crystal has cones of easy magnetization. With increasing temperature in this region the amount of rotational hysteresis steadily decreases. The amplitude of the voltage spikes also decreases, at first slowly and then more rapidly as the temperature approaches 215°K. Half of the decrease occurs in the last 20° (between 195° and 215°K). No voltage spikes are observed at temperatures above 215°K. Translated into terms of the sensitivity of the measurement, this means that the magnetization does not deviate from the basal plane by more than 0.2° during any 30° interval of angle  $\varphi$  in a field of 5000 oe.

A simple qualitative explanation of the switching effect is as follows. As the temperature increases from 77°K the equilibrium cone angle of  $\text{Co}_2\text{Y}$  increases from 68°, reaching 90° at 215°K. The magnetic field applied at  $\theta=90^\circ$  during the torque measurement pulls the magnetization more closely into the basal plane. At some temperature the magnetization is able to reverse its  $c$ -axis component of magnetization spontaneously as the magnetic field rotates in the basal plane, allowing the crystal to adopt the trigonal anisotropy corresponding to the lowest energy for a given value of  $\varphi$ . This process is characterized by rotational hysteresis. As the temperature increases the equilibrium values of  $\theta$  for a given field are closer to 90°, so that the amount of change during each reversal of  $c$ -axis component of magnetization becomes progressively smaller. At the same time the rotational hysteresis decreases. The effect disappears completely when the anisotropy becomes planar at 215°K. A quantitative treatment of the experiment of Fig. 2. will be presented in Sec. III B.

At temperatures in the vicinity of 215°K the rotational hysteresis just described becomes so small that the torque curves resemble the sixfold curves expected of a hexagonal crystal. Their amplitude decreases rapidly with increasing temperature between ca 195°K and 220°K. The determination of  $K_3$  from these torque curves [see Eq. (3)] leads to anomalously large apparent values for this anisotropy constant. The measured value of  $K_3$  at 230°K is  $-1890 \text{ erg/cm}^3$ .

## 2. $\text{Co}_2\text{Z}$

The torque curves of  $\text{Co}_2\text{Z}$  at 77°K have threefold symmetry if the crystal is cooled in a magnetic field lying in the basal plane. The conditions establishing the

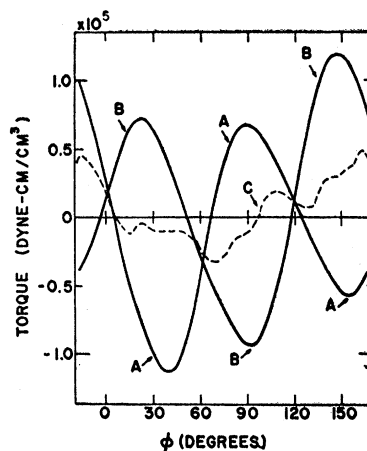


FIG. 3. Basal plane torque curves for  $\text{Co}_2\text{Z}$  crystal measured in a field of 10 400 oe. Curve A was obtained at 77°K after the crystal had been cooled in a field orientated at  $\varphi=0^\circ$ . Curve B (77°K) followed cooling at  $\varphi=180^\circ$ . Curve C was recorded at 216°K.

phase of the trigonal torque are identical to those in the case of  $\text{Co}_2\text{Y}$ . Figure 3 shows torque curves at 77°K following cooling in 10 400 oe oriented at  $\varphi=0^\circ$  (curve A) and at  $\varphi=180^\circ$  (curve B).

However, the similarity in behavior of  $\text{Co}_2\text{Z}$  and  $\text{Co}_2\text{Y}$  ends with this experiment of cooling in a basal plane field. If the Z compound is cooled in the absence of a magnetic field one observes a torque curve which is the superposition of a sixfold torque ( $K_3=-1450 \text{ erg/cm}^3$ ) on a term due to shape. If the crystal is cooled in a field oriented in either direction along the  $c$  axis one observes exactly the same torque curve at 77°K as was obtained by cooling in zero field; that is, no trigonal term is present.

If the crystal is warmed from the condition corresponding to curves A or B of Fig. 3, it passes through a transition region in which trigonal torque curves give way to hexagonal curves. Torque curves in this transition region have a very unusual shape bearing no similarity to the corresponding curves for  $\text{Co}_2\text{Y}$  (Fig. 2). Rotational hysteresis is present, but the torque curves include higher order harmonics—at least as high as twelfth order. This effect is illustrated by the dashed curve C in Fig. 3. Above 220°K the torque curves become smooth superpositions of  $\sin 2\varphi$  and  $\sin 6\varphi$  components. No change in  $c$ -axis component of magnetization is detectable at any temperature in the voltage experiment of Fig. 2.

## III. DISCUSSION OF EXPERIMENTAL RESULTS

In this section it will be shown that the behavior of the  $\text{Co}_2\text{Y}$  crystal is consistent with its crystalline structure, and all of the observed effects can be explained phenomenologically by adding suitable terms to the anisotropy equation; that in the case of  $\text{Co}_2\text{Z}$  a new and unusual anisotropic behavior has been observed;

and finally, that the anisotropy can be understood, at least qualitatively, on the basis of an atomic model.

### A. Crystalline Structure

The many hexagonal ferrimagnetic oxides have complex structures<sup>6</sup> which can be described in terms of basal plane oxygen layers with interstices between the oxygens occupied by metal cations. The oxygen layers, each containing four oxygens per unit cell, alternate between cubic and hexagonal close-packed arrangements. The cubic portions are layers of spinel structure, so oriented that a body diagonal of the cube coincides with the hexagonal  $c$  axis. The hexagonal portions have one of the four oxygens in at least one of the layers replaced by a barium cation.

It has been recognized<sup>7</sup> that all the structures can be constructed from three basic building blocks; one cubic and two hexagonal. Adopting the notation of Smit and Wijn<sup>7</sup> we label these blocks  $S$ ,  $R$ , and  $T$ .  $S$  is the cubic spinel block, consisting of two oxygen layers (8 oxygen ions and 6 cations).  $R$ , with three oxygen layers, has the formula  $BaFe_6O_{11}$ .  $T$  contains four oxygen layers, the center two of which each contains one Ba ion. Its formula is  $Ba_2Fe_8O_{14}$ .

Each of these structural units has its own symmetry elements, and the symmetry of the over-all structure

depends upon the way the basic elements are stacked together to fabricate the unit cell.  $R$ ,  $S$ , and  $T$  all have trigonal symmetry about the  $c$  axis.  $S$  and  $T$  both contain centers of symmetry.  $R$  is the only element containing a horizontal mirror symmetry plane. However, horizontal mirror symmetry planes are introduced into structures containing  $S$  and  $T$  if half of the blocks are rotated  $180^\circ$  about the  $c$  axis with respect to the other half. This operation occurs in most of the structures.

The structures of  $Co_2Y$  and  $Co_2Z$  are shown in Fig. 4(a) and 4(b), respectively. These figures show cross sections of the unit cells through a vertical mirror symmetry plane, with the  $c$ -axis vertical. The drawn vertical lines are axes of threefold symmetry. Any ion not lying on one of these lines in reality represents three ions. The unit cell is generated by performing this symmetry operation. Centers of symmetry are denoted by  $+$ ; and the horizontal mirror planes, by  $m$ . The asterisks indicate rotation of a block by  $180^\circ$  about the  $c$  axis.

Figure 4(a) shows that the  $Y$  structure is composed of alternating  $S$  and  $T$  blocks. There exist centers of symmetry in each of these blocks. However, there are no horizontal mirror planes, since none of the blocks has been rotated about the  $c$  axis with respect to the others. Although the smallest hexagonal elementary cell contains 18 oxygen layers, as shown here, it is possible to find an elementary cell of rhombohedral symmetry containing only six oxygen layers.<sup>7</sup>

Figure 4(b) shows that the  $Z$  structure has twenty-two oxygen layers per unit cell, and that the crystallographic buildup of blocks is  $STSR^*T^*S^*R^*$ . Centers of symmetry exist at the center of each block, and there are horizontal mirror planes through the middle of every  $R$  block.

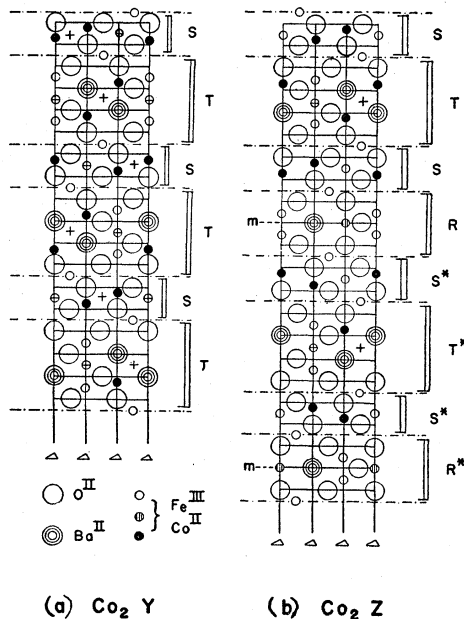


FIG. 4. Crystal structures of  $Co_2Y$  and  $Co_2Z$ , showing cross sections of the unit cells through vertical mirror symmetry planes. The  $c$  axes are vertical.  $S$ ,  $T$ , and  $R$  represent the basic structural subgroups. The drawn vertical lines are axes of threefold symmetry. Centers of symmetry are denoted by  $+$ ; and horizontal mirror planes by  $m$ . The asterisks indicate rotation of a block by  $180^\circ$  about the  $c$  axis.

<sup>6</sup> P. B. Braun, Philips Research Repts. 12, 491 (1957).

<sup>7</sup> J. Smit and H. P. J. Wijn, *Ferrites* (John Wiley & Sons, Inc., New York, 1959), Chap. IX.

### B. Phenomenological Description of Anisotropy

#### 1. $Co_2Y$

A careful analysis of the structure of  $Co_2Y$ , as described in the last section, leads one to the conclusion that Eq. (1) is not a complete phenomenological expression for its anisotropy. The absence of horizontal mirror symmetry planes, coupled with the presence of centers of symmetry, permits the inclusion of two additional terms:  $K_2' \sin^3\theta \cos\theta \cos 3\varphi$  and  $K_3'' \sin^3\theta \cos^3\theta \cos 3\varphi$ . The first of these terms has been mentioned previously by Dzyaloshinsky<sup>8</sup> in a thermodynamic theory of the "weak" ferromagnetism of antiferromagnetic  $\alpha$ - $Fe_2O_3$ . However, its existence has not been directly verified experimentally in that material or in any ferro- or ferrimagnetic crystal.

Most of the experimental results obtained with the  $Co_2Y$  crystal can be explained in terms of the anisotropy expression containing terms no higher than fourth order in the direction cosines of the magnetization:

$$W_A = K_1 \sin^2\theta + K_2 \sin^4\theta + K_2' \sin^3\theta \cos\theta \cos 3\varphi. \quad (4)$$

<sup>8</sup> I. Dzyaloshinsky, J. Phys. Chem. Solids 4, 241 (1958).

The torque in the basal plane is given by

$$L = -\partial W_A / \partial \varphi = 3K_2' \sin^3 \theta \cos \theta \sin 3\varphi. \quad (5)$$

This torque decreases in magnitude as  $\theta$  approaches  $\pi/2$ , a fact which explains the decrease in amplitude with increasing field measurement. The sign of the coefficient of  $\sin 3\varphi$  becomes negative when  $\theta$  exceeds  $\pi/2$ . Therefore, one of two threefold torque curves is possible. The phase is determined by the  $c$ -axis component of the magnetization. The effect of the magnetic field cooling for fields applied both in the basal plane and perpendicular thereto is merely to orient the magnetization. The field induces the magnetization to lie in the particular cone which corresponds to the lowest energy of the system under the field cooling conditions.

Evaluation of the constant  $K_2'$  from the amplitude of a  $\sin 3\varphi$  torque curve requires a knowledge of angle  $\theta$ . It was shown in Sec. IIB that the experiment illustrated in Fig. 2 involved changes in  $\theta$  between  $86^\circ$  and  $94^\circ$ . Using this information it is estimated that  $K_2'$  has the approximate value  $6 \times 10^5$  erg/cm<sup>3</sup> at  $117^\circ\text{K}$ .

The spontaneous change of the  $c$ -axis component of magnetization and the rotational hysteresis which accompanies it in the experiment of Fig. 2 can also be explained, at least semiquantitatively, by means of Eq. (4). We find the equilibrium values of  $\theta$  by minimizing the total energy with respect to changes in  $\theta$ ; thus

$$\partial(W_A - \mathbf{M} \cdot \mathbf{H}) / \partial \theta = 0, \quad (6)$$

where  $\mathbf{M}$  and  $\mathbf{H}$  are vectors indicating the magnetization and magnetic field, respectively. It is convenient to carry out the calculations in terms of angle  $\gamma$ , which measures the angular deviation of  $\mathbf{M}$  from the basal plane ( $\gamma = \pi/2 - \theta$ ).

Noting that  $\gamma$  is a small angle, we can approximate  $\sin \gamma$  and  $\cos \gamma$  as power series containing terms of no higher order than  $\gamma^4$ . We assume that  $\mathbf{H}$  is sufficiently strong with respect to anisotropy in the basal plane that the projection of  $\mathbf{M}$  on the basal plane has the same orientation as  $\mathbf{H}$ ; i.e.,  $\mathbf{M} \cdot \mathbf{H} = MH \cos \gamma$ . Under these conditions, Eq. (6) becomes:

$$\gamma^3 + (a/2b)\gamma + (c/4b) \cos 3\varphi = 0. \quad (7)$$

where

$$\begin{aligned} a &= -(K_1 + 2K_2) + (\frac{1}{2})MH, \\ b &= (\frac{1}{3})(K_1 + 5K_2) - MH/24, \\ c &= K_2'. \end{aligned} \quad (8)$$

This cubic expression of equilibrium values of  $\gamma$  as a function of  $\varphi$  is most easily handled by graphical means. In Fig. 5 are plotted the two parametric equations:

$$y = \gamma^3,$$

and

$$y = -(a/2b)\gamma - (c/4b) \cos 3\varphi. \quad (9)$$

The second equation represents a family of straight lines of constant slope  $(-a/2b)$  with a  $y$ -axis intercept

$(-c/4b) \cos 3\varphi$  which oscillates up and down as  $\varphi$  increases. The equilibrium values of  $\gamma$  correspond to the intersections of the straight lines with the other curve. The parameters used in the plots of Fig. 5 were obtained from the values of  $K_1$  ( $-11.7 \times 10^6$  erg/cm<sup>3</sup>),  $K_2$  ( $+6.7 \times 10^6$  erg/cm<sup>3</sup>) and  $M$  (210 cgs) reported by Enz et al.<sup>2</sup>; taken together with  $K_2'$  ( $6 \times 10^5$  erg/cc) and  $H$  (10 400 oe) determined from the present experiments.

The variation of  $\gamma$  as  $\varphi$  increases from  $0^\circ$  to  $120^\circ$  is indicated in Fig. 5 by numerical sequence. As  $\varphi$  increases from  $0^\circ$  to ca  $33^\circ$ ,  $\gamma$  follows the path 1, 2, 3, 4. At point 4 the second derivative of energy with respect to  $\gamma$  is zero, and the magnetization spontaneously changes sign, moving to point 4'. As  $\varphi$  continues to increase, the equilibrium point moves out to 5', then returns along the path 5', 4', 3', 2'. Again the magnetization spontaneously changes sign to 2 (at  $\varphi \approx 93^\circ$ ), then continues to point 1 as  $\varphi$  increases to  $120^\circ$ .

Rotational hysteresis occurs because the spontaneous change in sign of  $\gamma$  from positive to negative (at point 2') takes place at a value of  $\cos 3\varphi$  different from that at which the change from negative to positive (at point 4) occurs. Therefore, if  $\varphi$  were to change in the opposite direction (i.e., decrease from  $120^\circ$  to  $0^\circ$ ) the reversals would occur at  $27^\circ$  and  $87^\circ$ , rather than at  $33^\circ$  and  $93^\circ$ .

Increasing the magnetic field strength has the effect of first reducing the slope of the straight line to zero, then reversing its sign. The amount of rotational hysteresis would decrease, then disappear.

In principle, this switching effect could be observed during the course of torque measurements in the (111) plane of cubic crystals such as ferrites, since the constants of Eqs. (7) and (8) all have their counterparts in terms of cubic anisotropy constants. Certainly the small component of magnetization normal to the (111) plane reverses its sign periodically during the measurement of a (111) torque curve. However, no cases of

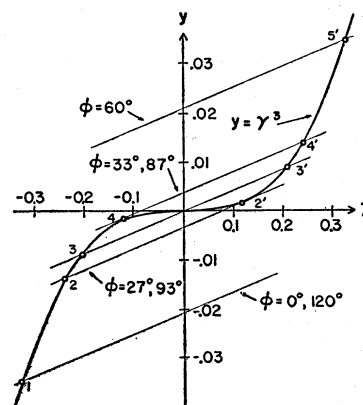


FIG. 5. Equilibrium values of  $\gamma$  as a function of  $\varphi$  at  $117^\circ\text{K}$  for  $\text{Co}_2\text{Y}$ , represented by the numbered intersections of the two parametric curves of Eq. (9). The straight lines each correspond to a different value of  $\varphi$ . Rotational hysteresis is illustrated by the possibility of the change in sign of  $\gamma$  occurring via the path 4-4' or via the path 2'-2.

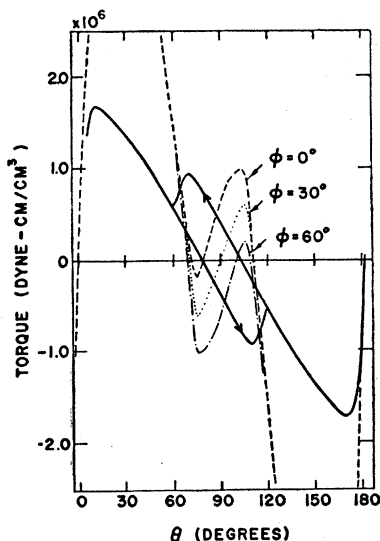


FIG. 6. Torque curves (solid lines) recorded for  $\text{Co}_2\text{Y}$  at  $77^\circ\text{K}$  in mirror plane ( $\varphi=0^\circ$ ) containing the  $c$  axis. Angle  $\theta$  represents the orientation of the magnetic field (10 400 oe), and no correction has been made for the angular deviation between magnetization and field. The broken curves represent theoretical curves for three different values of  $\varphi$ , calculated from the experimental values of the anisotropy constants of Eq. (4), assuming alignment of magnetization and field.

rotational hysteresis during such measurements have been reported to date.

Finally, brief mention will be made of the shape of torque curves to be expected in planes containing the  $c$ -axis. The inclusion of  $K_2'$  leads to the prediction of the torque curves shown by the dashed curves in Fig. 6, for three different values of  $\varphi$ . An attempt was made to observe the torque curve corresponding to  $\varphi=0^\circ$ , with the results shown in the solid curve of Fig. 6. A curve for  $\varphi=90^\circ$  had a similar shape. Unfortunately, the magnetic field is small compared to the major anisotropy fields. Moreover, the platelike structure of the crystals necessitated the use of specimens with unfavorable shape. For these reasons the torque curves are distorted considerably from their true shape. The solid curves of Fig. 6 have not been corrected for lack of alignment of the magnetization with the magnetic field. Some rotational hysteresis is shown, and it was determined that the sudden breaks in the torque curves are accompanied by changes in the component of magnetization normal to the plane swept out by the magnetic field. Angle  $\varphi$  thus changes during the measurement. About all that can be said for the experimental curves of Fig. 6 is that they have roughly the expected shape. This experiment should be repeated in a larger field with crystals of more favorable geometry.

## 2. $\text{Co}_2\text{Z}$

Since the  $Z$  structure contains horizontal mirror symmetry planes the trigonal anisotropy terms introduced in the previous section are not appropriate for  $\text{Co}_2\text{Z}$ .

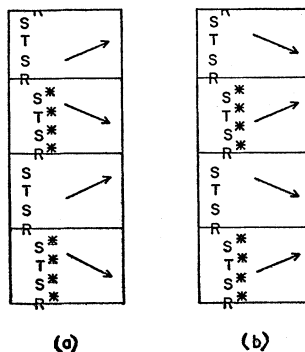


FIG. 7. Representation of the puckered magnetization patterns within a unit cell of  $\text{Co}_2\text{Z}$  which result in trigonal anisotropy at  $77^\circ\text{K}$ . The magnetized state is shown, with the net magnetization lying in the basal plane.  $R, S, T$ , etc., refer to the structural subgroups shown in Fig. 4(b). Curves  $A$  and  $B$  of Fig. 3 correspond to patterns  $a$  and  $b$ , respectively.

Equation (1) should provide an adequate description of the anisotropy.

Nevertheless, as shown in Fig. 3, trigonal torque curves were observed at  $77^\circ\text{K}$  in  $\text{Co}_2\text{Z}$  crystals which were cooled in the presence of a magnetic field lying in the basal plane. One very significant difference in the behavior of the  $Y$  and  $Z$  crystals is that a field applied along the  $c$  axis failed to produce trigonal anisotropy in  $\text{Co}_2\text{Z}$  at  $77^\circ\text{K}$ .

Examination of the  $Z$  structure [Fig. 4(b)] reveals that it consists of the stacking of the different building blocks along the  $c$  axis in the sequence  $STSR S^*T^*S^*R^*$ . The unit cell is made up of two identical subgroups ( $STSR$  and  $S^*T^*S^*R^*$ ), one of which is rotated  $180^\circ$  about the  $c$  axis with respect to the other.<sup>9</sup> Equation (4), including the trigonal  $K_2'$  term, is appropriate within each subgroup. It is the operation of rotation of one subgroup with respect to the other which eliminates the  $K_2'$  term from the anisotropy expression of the unit cell, since the  $K_2'$  terms from alternate subgroups cancel each other.

If the  $c$ -axis component of magnetization were to reverse its sign in alternate subgroups, as indicated in Fig. 7, the  $K_2'$  terms for all subgroups would add together, and the crystal would display trigonal anisotropy. We explain the observed trigonal anisotropy shown in Fig. 3 on the basis of this model.

Cooling the crystal in a magnetic field in the basal plane causes the magnetization within each subgroup to lie in whichever cone corresponds to the lowest energy for the value of  $\varphi$  determined by the magnetic field. One of the magnetization patterns represented by Fig. 7 is created and remains when the field is removed. These patterns are very stable at  $77^\circ\text{K}$ , surviving demagnetization and the application of a field of at least 10 400 oe for prolonged periods of time in any direction in the basal plane.

If the crystal is cooled to  $77^\circ\text{K}$  in a field along the  $c$  axis, the magnetization will be forced to have the same  $c$ -axis component in all regions of the crystal. The puckered magnetization pattern will not be established,

<sup>9</sup> Actually the dividing line between subgroups runs through the center planes of the  $R$  and  $R^*$  blocks, since these planes are mirror symmetry planes.

and no trigonal term should appear in the torque curves. One would also predict no trigonal torque in crystals cooled in the absence of a magnetic field. Both of these predictions agree with experiment. The existence of the puckered pattern also explains the failure to observe any net changes in *c*-axis component of magnetization during torque measurements in the transition region in which cones disappear. Any change in magnetization in one of the subgroups is matched by an equal and opposite change in the other subgroup.

The basal-plane field-cooling treatment has the effect of setting up an unusual "domain" structure in the crystal. The boundaries between these domains are stationary and lie between the structural subgroups. The existence of such domains implies that the exchange coupling across certain basal planes in the structure must be relatively weak. The anisotropy energy gained by establishing the magnetization pattern illustrated in Fig. 7 must exceed the work which must be done against exchange forces to maintain that pattern. It is not clear whether the boundary region is sharp or whether it is spread over the entire *R* block, creating a "domain wall" five magnetic atom layers thick.

Gorter<sup>10</sup> has worked out the spin arrangements in the various structural hexagonal oxide blocks, making use of the various principles of superexchange interaction which had been applied successfully to the spinel ferrites. In this way he was able to account for the observed saturation magnetization of the various structures. The coupling between the *R* and *S* blocks was shown to be possible through one of two different metal-oxygen-metal interactions, each of which would lead to a different spin arrangement. The interaction which was judged to be stronger led to the correct magnetization. It is possible that the presence of the opposing interaction is the influence which weakens the exchange interaction across the boundary.

Whatever the details of the interactions involved, it is clear that field-cooled  $\text{Co}_2\text{Z}$  at 77°K demonstrates an unusual type of anisotropy which has lower symmetry than that of the crystalline structure. The magnetic anisotropy has the symmetry of a subgroup of the crystalline symmetry. It is a real rather than apparent anisotropy in the sense that it occurs when the orientation of the net magnetization coincides with that of the applied magnetic field.

Other known cases in which the magnetic symmetry is lower than that of the overall crystalline symmetry usually involve some kind of magnetic annealing process at elevated temperatures. This treatment in some way creates localized conditions (e.g., precipitates, ionic disorder) whereby the crystalline symmetry is lowered in certain regions of the crystal. These structural elements contribute their own appropriate anisotropy to the intrinsic anisotropy of the crystal, which then appears to have a magnetic symmetry of lower order than that of

the crystalline symmetry. Such effects would not occur in a perfect crystal.

The effect of magnetic field cooling in  $\text{Co}_2\text{Z}$  has been merely to orient the magnetization. No structural imperfections or disorder have been introduced. The unusual anisotropy would exist in a perfect crystal.

### C. Atomic Considerations

In view of the complexity of the crystalline structures involved it is not possible to place the results of this investigation on a sound theoretical foundation based on existing crystal field models of magnetic anisotropy of oxides. However, several aspects of the situation make it possible to present a crude molecular model for the origin of the trigonal anisotropy of  $\text{Co}_2\text{Y}$  and  $\text{Co}_2\text{Z}$ .

First of all, the existence of cones of easy magnetization in these compounds is associated with the presence of cobalt. Secondly, it has been demonstrated<sup>11</sup> that the cobalt ions are located for the greater part on the octahedral sites of the spinel portion of the hexagonal oxide lattices, where they contribute to anisotropy in much the same way as they do in the cubic spinels. Finally, the theory developed by Slonczewski<sup>3</sup> to explain the exceptionally large anisotropy introduced into magnetite by small additions of cobalt can, with certain simplifying approximations, be adapted readily to the present situation. This approach has already been used by Smit et al.<sup>12</sup> in describing certain anisotropy characteristics of some cobalt-substituted ferroxidure compounds.

In this section we apply Slonczewski's theory in its simplest classical form to  $\text{Co}_2\text{Y}$  and  $\text{Co}_2\text{Z}$ , and show that it leads to the prediction of a trigonal anisotropy which is too large by an order of magnitude. Consideration of the simplifying assumptions made in this approximation shows that in principle the agreement is satisfactory.

Slonczewski has considered the case of a cobalt ion located on an octahedral spinel site surrounded by identical nearest neighbor ions. The electrostatic crystalline field, of trigonal symmetry, leaves the cobalt ion in a doubly degenerate orbital ground state with the residual angular momentum constrained to lie parallel (in either direction) to the trigonal axis of the site. Because of the degeneracy of the ground state the spin of the cobalt ion is coupled to its angular momentum in a first-order approximation of the spin-orbit energy. The fact that the spin of the cobalt ion is thus strongly coupled to the crystal lattice explains the exceptionally large contribution of the cobalt ion to the magnetocrystalline anisotropy of ferrites. Any influence which lowers the symmetry of the crystalline field acting on the cobalt (e.g., introducing different kinds of ions on neighboring sites) will remove the degeneracy of the ground orbital state and reduce the effectiveness of the spin-orbit coupling.

<sup>11</sup> L. R. Bickford, Jr., *J. Appl. Phys.* **31**, 259S (1960).

<sup>12</sup> J. Smit, F. K. Lotgering, and U. Enz, *J. Appl. Phys.* **31**, 137S (1960).

<sup>10</sup> E. W. Gorter, *Proc. Inst. Elec. Engrs. (London)* **104B**, Suppl. **5**, 255 (1957).



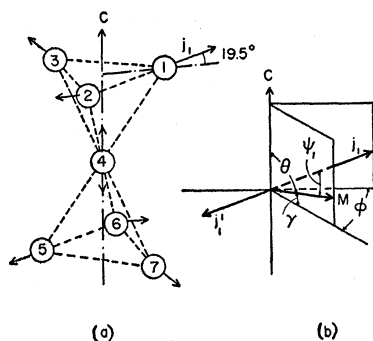


FIG. 8 (a) Orientation of the trigonal axes of the seven octahedral cation sites per spinel block of the  $Y$  and  $Z$  structures. The trigonal axis for atom 4 is aligned with the  $c$  axis. All others make an angle of  $19.5^\circ$  with the basal plane. (b) Relationship between the various angles used in calculating spin-orbit energy for atom 1. Angle  $\psi_1$  is the deviation of the spin (assumed to be aligned with the macroscopic magnetization) from the direction of the orbital moment; that is, from the trigonal axis of the site it occupies. Following Slonczewski, we assign the value  $2.63 \times 10^{-14}$  erg as representing the upper limit of the effective spin-orbit parameter  $\alpha\lambda$ .

We will calculate the anisotropy expected in the experiments described in this paper by assuming that it is due entirely to the cobalt ions, each of which contributes the spin-orbit energy  $\frac{2}{3}\alpha\lambda \cos\psi$ . Angle  $\psi$  measures the separation of the spin (assumed to be aligned with the macroscopic magnetization) from the direction of the orbital moment; that is, from the trigonal axis of the site it occupies. Following Slonczewski, we assign the value  $2.63 \times 10^{-14}$  erg as representing the upper limit of the effective spin-orbit parameter  $\alpha\lambda$ .

The orientation of the trigonal axes of the seven octahedral sites per spinel block of the  $Y$  and  $Z$  structures is shown in Fig. 8(a). These axes coincide with the body diagonal directions of the cubic spinel. In the case of atom 4 the trigonal axis coincides with the  $c$  axis; whereas in the case of the other atoms the axes make angles of  $19.5^\circ$  with the basal plane, and their projections on the basal plane are  $60^\circ$  apart. Figure 8(b) illustrates the variation of angle  $\psi$  with angle  $\varphi$  in the case of atom 1. The positive and negative trigonal axis directions are represented by  $\mathbf{j}_1$  and  $\mathbf{j}'_1$ , respectively. It is assumed in this approximation that as the magnetic field is applied in the basal plane at angle  $\varphi$  the magnetization deviates from the basal plane by the small angle  $\gamma$  which remains constant with respect to changes in  $\varphi$ . Under these conditions the relationship between  $\cos\psi_1$  and  $\varphi$  is approximately

$$\cos\psi_1 = \pm\gamma/3 \pm (2 - \sqrt{2}/3) \cos\varphi, \quad (10)$$

where the  $+$  and  $-$  signs refer to the positive and negative trigonal axis directions, respectively. It is further assumed that for all values of  $\varphi$  the orbital moment of the cobalt ion will lie in whichever direction ( $\mathbf{j}_1$  or  $\mathbf{j}'_1$ ) leads to the minimum value of  $\cos\psi_1$ . Similar expressions for atoms 2 and 3 are obtained by replacing  $\varphi$  by  $(\varphi - 2\pi/3)$  and  $(\varphi - 4\pi/3)$ , respectively.

At this point it should be noted that atom 5 adds its

contribution to the anisotropy in phase with that of atom 1; and that atoms 6 and 7 act in unison with atoms 2 and 3, respectively. In order to see this we perform the successive operations of reversing the  $c$ -axis component of magnetization (which changes the sign of  $\gamma$ ), then increasing  $\varphi$  by  $180^\circ$  (which changes the sign of  $\cos\varphi$ ). Equation (10) is thus appropriate for atom 5. Atom 4 does not contribute to the anisotropy provided the magnitude of  $\gamma$  does not change.

We now add the contributions of atoms 1, 2, and 3 at various values of  $\varphi$ . At  $\varphi = 0, 2\pi/3$ , and  $4\pi/3$  we obtain  $\frac{2}{3}\alpha\lambda(\gamma/3 - 4\sqrt{2}/3)$ ; while at  $\varphi = \pi/3, \pi$ , and  $5\pi/3$  we obtain  $\frac{2}{3}\alpha\lambda(-\gamma/3 - 4\sqrt{2}/3)$ . Relating the difference between these two quantities to the amplitude of the threefold term in the anisotropy equation, we find that the trigonal term per three cobalt ions is

$$w_A = (\frac{2}{3}\alpha\lambda)\gamma \cos 3\varphi. \quad (11)$$

This equation has the same form as the  $K_2'$  term of Eq. (4) in the limit as angle  $\theta$  approaches  $90^\circ$ . The calculated value of  $K_2'$  for  $\text{Co}_2Y$  is therefore

$$K_2' = (\frac{2}{3}\alpha\lambda)N/3 = 4.39 \times 10^{-15} N \text{ erg/cm}^3, \quad (12)$$

where  $N$  is the number of cobalt ions per cubic centimeter of the crystal which are located on sites other than 4. We assume that for electrostatic reasons the divalent cobalt ions have a preference for the central sites (atom 4), so that for  $\text{Co}_{1.98}Y$ ,  $N$  has the value  $2.4 \times 10^{22}$ . The calculated value of  $K_2'$  is thus  $1.07 \times 10^7$  erg/cm<sup>3</sup>, a number 17 times as large as the experimental value of  $6 \times 10^5$  erg/cm<sup>3</sup> determined at  $117^\circ\text{K}$ .

The numerical agreement between the calculated and measured values of  $K_2'$  can scarcely be called satisfactory. However, the several refinements necessary in order to make a more accurate calculation would each serve to reduce the theoretical value considerably. First and most important, the cobalt ions which contribute to the threefold anisotropy experience electrostatic crystalline fields which are distorted from trigonal symmetry. They lie on the border between cubic and hexagonal blocks of the structure. One of the six nearest neighbor octahedral cation sites surrounding each of them is distorted from the normal position and is occupied by a barium ion. As a result of this distortion the effectiveness of the spin-orbit coupling would be significantly reduced from the magnitude used in this calculation. Secondly, the conditions assumed in making the calculation correspond to absolute zero of temperature. The anisotropy becomes smaller as temperature increases. Other considerations which would tend to diminish the calculated anisotropy include the possibility that some of the cobalt ions are located in the hexagonal portions of the structure, and the fact that  $\gamma$  does not remain constant during the rotation of  $H$ .

Nevertheless, the calculation has served to demonstrate that the cobalt ions are fully capable of contributing the observed trigonal anisotropy.

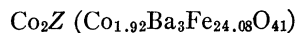
In principle this model could be applied also to  $\text{Co}_2\text{Z}$ . However, a quantitative comparison is not possible for that compound in the absence of any information concerning the value of  $\theta$  within each structural subgroup.

#### IV. SUMMARY

The existence of trigonal anisotropy in single crystals of



and



has been demonstrated experimentally by means of basal plane torque curves. This phenomenon is observed in the low-temperature region in which the crystals have cones of easy magnetization. A field-cooling treatment is necessary in order to observe the effect. The only influence of such treatment is to saturate the crystal magnetically (i.e., remove domain structure) and leave it in one of the two energetically stable conditions. One of these states yields a trigonal anisotropy of phase opposite to that of the other.

Examination of the crystalline structures of the two compounds showed that in the case of the *Y* compound the trigonal anisotropy is consistent with the crystalline symmetry, whereas in the case of the *Z* compound it is not.

The *Y* compound has trigonal symmetry about the *c* axis and a phenomenological trigonal term ( $K_2' \sin^3\theta \cos\theta \cos 3\varphi$ ) is one of many terms allowed by the crystal symmetry (a fact which had been overlooked in previous work). An interesting new phenomenon has been observed in the transition region as the *Y* crystal warms up to the temperature (ca 215°K) at which the cones of easy magnetization merge into the basal plane and the trigonal anisotropy in basal plane torque curves disappears. This phenomenon amounts to a spontaneous periodic reversal of the *c*-axis component of mag-

netization as the magnetic field rotates in the basal plane during a torque measurement. A phenomenological explanation for this effect, which involves rotational hysteresis, has been presented. Measurement of the *c*-axis component of magnetization during one of its reversals, combined with the amplitude of the trigonal torque has permitted an evaluation of  $K_2'$  ( $6 \times 10^5$  erg/cm<sup>3</sup> at 117°K). The hexagonal anisotropy constant  $K_3$  was found to have the values  $-600$  and  $-1890$  erg/cm<sup>3</sup> at 300 and 230°K, respectively.

$\text{Co}_2\text{Z}$  has been shown to display an unusual type of intrinsic anisotropy having a symmetry which is lower than that of the crystal structure, but consistent with the symmetry of a subgroup thereof. Observation of trigonal anisotropy in this compound was interpreted as indicating that the puckered magnetization pattern shown in Fig. 7 had been established by the magnetic field in which the crystal had been cooled. The existence of this pattern implies that the exchange interaction across certain layers normal to the *c* axis must be relatively weak. The value of  $K_3$  for  $\text{Co}_2\text{Z}$  at 77°K was found to be  $-1450$  erg/cm<sup>3</sup>.

Finally, the atomic origin of the trigonal anisotropy was explored by applying in its simplest form the Slonczewski theory of the anisotropy of divalent cobalt ions in octahedral cation sites of oxide structures. It was shown that this theory is in principle capable of accounting for the observed anisotropy.

#### V. ACKNOWLEDGMENTS

The experimental assistance of C. F. Aliotta and H. R. Lilienthal is gratefully acknowledged. The author also benefited from discussions with J. C. Slonczewski and B. A. Calhoun. The single crystals were grown under the direction of A. L. Stuijts, and kindly supplied to the author during his sojourn at the Philips Research Laboratories, Eindhoven, Netherlands.