

theoretical expression with  $m^* \sim 0.3m$ . This value of  $m^*$  is in reasonable agreement with the value of conductivity effective mass obtained from other measurements.<sup>7</sup>

<sup>7</sup> W. Spitzer and H. Y. Fan, Phys. Rev. **106**, 882 (1957).

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## Magnetic Annealing Effect in Cobalt-Substituted Magnetite Single Crystals\*

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The effect of magnetic annealing at 375°K on the room-temperature anisotropy of a series of six single crystals in the composition series  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ , in the range of  $x$  values between 0.0 and 0.15, is investigated. The anneal-induced anisotropy is shown to be represented by the equation  $W_U = -F \sum_i \alpha_i^2 \beta_i^2 - G \sum_{i>j} \alpha_i \alpha_j \beta_i \beta_j$ , where  $\alpha_i$  and  $\beta_i$  are direction cosines of the magnetization during measurement and during the annealing process, respectively.  $F$  and  $G$  are shown to vary with  $x$  in a regular fashion:  $F \approx 10.1 \times 10^6 x^2$  erg/cc and  $G \approx 9.25 \times 10^6 x$  erg/cc. These results cannot be explained by the Néel orientation-ordering model or by the precipitate model of magnetic annealing. A new model, involving cobalt ions individually rather than in pairs or larger agglomerates, is introduced.

## 1. INTRODUCTION

DURING the course of an investigation of the temperature dependence of the cubic anisotropy constants of some cobalt-substituted magnetite single crystals<sup>1</sup> it was found that measurements above about 400°K were greatly affected by magnetic annealing. The magnetic field applied during the torque measurements induced continuous changes in the anisotropy of the specimen, and thus masked the cubic anisotropy. This paper is a report of a systematic study of the anneal-induced anisotropy in these crystals and in others of the same composition series.

The effect of magnetic annealing on the anisotropy of ferrites containing large concentrations of cobalt has been investigated by Bozorth, Tilden, and Williams.<sup>2</sup> These authors found that the anisotropy of their crystals could be expressed by the equation

$$W_A = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_U \sin^2(\theta - \theta_U), \quad (1)$$

in which the  $\alpha$ 's are the direction cosines of the saturation magnetization ( $M_s$ ) with respect to the crystal axes;  $\theta$  is the angle between  $M_s$  and [001];  $\theta_U$  is the angle between the uniaxial preferred direction and [001]; and  $K_U$  is the uniaxial anisotropy constant. This equation was shown to be valid by experiments performed on (100) and (110) disks of  $\text{Co}_{0.32}\text{Zn}_{0.24}\text{Fe}_{2.18}\text{O}_4$ . Two characteristic features of their results were as follows: (1) The magnitude of  $K_U$  was the same for all

values of  $\theta_A$ , the angle between the annealing magnetic field and [001]; (2) The direction of the annealing field became the uniaxial preferred direction ( $\theta_U$  coincided with  $\theta_A$ ).

In this paper we report the results of similar experiments performed on crystals in the composition range from  $\text{Fe}_3\text{O}_4$  to  $\text{Co}_{0.15}\text{Fe}_{2.85}\text{O}_4$  and show that neither of the characteristic features referred to in the foregoing paragraph were observed. The magnitude of  $K_U$  and the deviation of  $\theta_U$  from  $\theta_A$  are both shown to be strongly dependent on  $\theta_A$ . The strength and symmetry of this dependence change systematically with increasing cobalt concentration. We discuss our experiments in the light of existing theories of magnetic annealing and show that our results are not entirely consistent with the predictions of these theories. Finally, we introduce a new model which is consistent with our experimental observations.

## 2. EXPERIMENTAL PROCEDURE

The six crystals studied in this investigation belong to the composition series  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ , and have the following values of  $x$ : 0.005, 0.01, 0.04, 0.07, 0.10, and 0.15. Details concerning the method of crystal growth (from the melt) have been published elsewhere.<sup>1</sup>

A spherical sample shape was chosen in order to minimize errors introduced by the fact that the cobalt concentration is not uniform throughout a given crystal growth. By using one and the same sample, measurements could then be carried out with the magnetization in each of the three crystal planes. The spheres were shaped by the abrasion technique of Bond<sup>3</sup> to a diameter

\* A preliminary account of this work was presented at the 1957 Annual Meeting of the American Physical Society [Bull. Am. Phys. Soc. Ser. II, **2**, 21 (1957)].

<sup>1</sup> Bickford, Brownlow, and Penoyer, Proc. Inst. Elec. Engrs. (London) **104**, Part B, Suppl. 5, 238 (1957).

<sup>2</sup> Bozorth, Tilden, and Williams, Phys. Rev. **99**, 1788 (1955).

<sup>3</sup> W. L. Bond, Rev. Sci. Instr. **22**, 344 (1951).

of approximately 2.5 mm. Their volume was determined from their mass, by assuming their density was the same as that of a synthetic magnetite crystal (5.19 g/cm<sup>3</sup>).<sup>4</sup> They were oriented by x-ray diffraction, using the Laue back-reflection technique.

Curves of torque *versus* orientation of the magnetization ( $\theta$ ) were obtained by means of an automatic torque balance.<sup>5</sup> They were plotted on an X-Y recorder as the magnetic field rotated at a uniform angular velocity ( $\sim 1$  rpm) in one of the principal crystallographic planes of the spherical specimen. The procedure for annealing the specimens and measuring their anisotropy was as follows: The specimen, while mounted in the torque balance, is heated to  $375 \pm 1^\circ\text{K}$  in a continuous stream of dry nitrogen by means of a non-inductively wound cylindrical heater. The annealing magnetic field (about 10 000 oersted) is applied in a particular direction  $\theta_A$  for a time sufficiently long (about 30 min) to insure that the maximum annealing effect has been induced. The specimen is then cooled rapidly to room temperature with the magnetic field still applied. A torque curve is recorded at  $301 \pm 0.5^\circ\text{K}$  in a field of 10 000 oersted. This procedure was repeated for different values of  $\theta_A$ , varying in ten degree steps from  $0^\circ$  to  $90^\circ$ . All angles are measured from  $[001]$  in the (100) and (110) planes, and from  $[\bar{1}10]$  in the (111) plane.

As a result of the large cubic anisotropy at room temperature in the four samples of highest cobalt concentration, the magnetization was not aligned with the magnetic field at all orientations of the latter. Therefore, the torque curves for these crystals were corrected in the following way<sup>2</sup> prior to analysis. For a given point on the curve, the angular deviation  $\gamma$  between the applied field  $H$  and the magnetization  $M$  can be calculated from the equation  $L = MH \sin\gamma$ , where  $L$  is the measured torque. The correction consists of changing the  $\theta$  coordinate of the point in the direction of decreasing anisotropy energy by the amount  $\gamma$ . This correction is obviously valid only if the magnetization remains in the plane defined by the magnetic field. The use of spherical samples rather than oblate ellipsoids has the disadvantage that no demagnetizing fields are present to constrain the magnetization to remain in the desired plane. However, it can be shown that for the magnetic fields used the magnetization does not deviate from the correct plane in the (100) and (110) torque curves. Since the deviation becomes appreciable in the (111) plane, we have not attempted to analyze these curves for  $x$  values larger than 0.04. The cubic anisotropy at the annealing temperature is only approximately one-third as large as the room-temperature value. Therefore the largest deviation of  $M$  from the direction of  $H$  during annealing (for  $x=0.15$ ) was only four degrees.

<sup>4</sup> J. Smiltens, *J. Chem. Phys.* **20**, 990 (1952).

<sup>5</sup> R. F. Penoyer, *Proceedings of the A.I.E.E. Conference on Magnetism and Magnetic Materials* (1956), p. 365.

The equation of the torque curve is obtained by taking the negative derivative of Eq. (1) with respect to angle  $\theta$ , and can be written:

$$-L = K_1 f_1(\theta) + K_2 f_2(\theta) + K_U \sin 2(\theta - \theta_U), \quad (2)$$

where  $L$  is the torque per unit volume (dyne/cm<sup>2</sup>) and  $f_1(\theta)$  and  $f_2(\theta)$  are well known functions of  $\theta$  which are characteristic of the different crystallographic planes [see, for example, Eqs. (2), (3), and (4) of reference 1]. The method used here to obtain the anisotropy constants from the torque data has been described for the (100) plane by Bozorth, Tilden, and Williams<sup>2</sup> (hereinafter referred to as BTW). For all planes Eq. (2) can be written in the form of a Fourier expansion

$$-L = \sum (a_n \cos n\theta + b_n \sin n\theta). \quad (3)$$

The torque curves were analyzed into the coefficients  $a_n$  and  $b_n$  (through the twelfth-order term) by means of an electronic computer. The constants  $K_1$ ,  $K_2$ ,  $K_U$ , and  $\theta_U$  were then calculated from these coefficients.

### 3. RESULTS AND DISCUSSION

The first- and second-order cubic anisotropy constants at  $301^\circ\text{K}$ , which were extracted from our data, are plotted as a function of  $x$  in Fig. 1. The dashed curve joining the  $K_1$  points is the expression  $K_1 = A + Bx + Cx(1-x)$  previously suggested<sup>1</sup> for the dependence of  $K_1$  on  $x$ .<sup>6</sup>

Figure 2 shows  $K_U$  and  $\theta_U$  as functions of  $\theta_A$  for

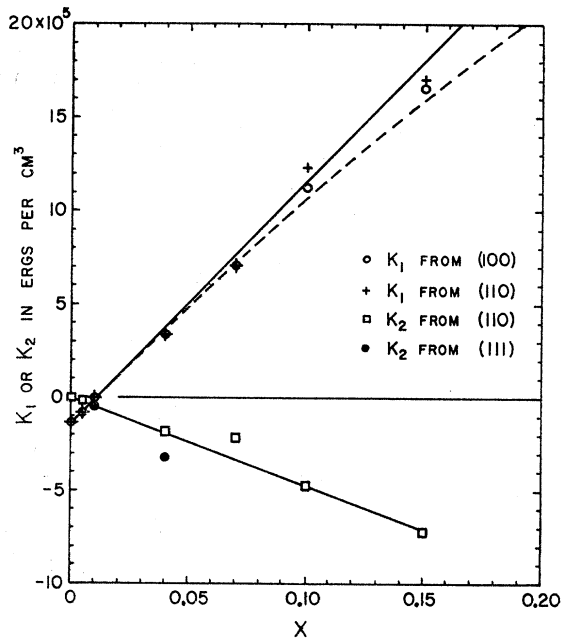


FIG. 1. First- and second-order anisotropy constants at  $301^\circ\text{K}$ .

<sup>6</sup> Because of a calibration error the numerical results of reference 1 are all too small and should be multiplied by the factor 1.19 to give the correct values. The corrected values of  $A$ ,  $B$ , and  $C$  are  $-1.3 \times 10^6$ ,  $3.6 \times 10^6$  and  $9.3 \times 10^6$  erg/cm<sup>3</sup>, respectively.

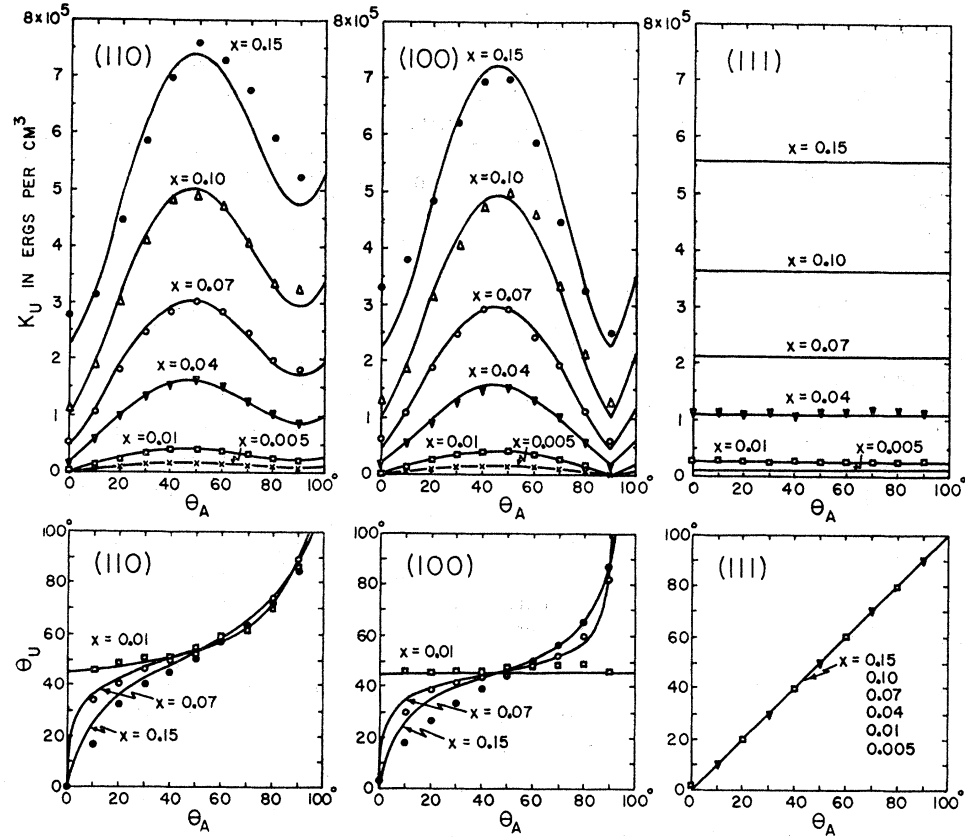


FIG. 2.  $K_U$  and  $\theta_U$  versus  $\theta_A$  at 301°K following annealing at 375°K, obtained from (100), (110), and (111) torque curves.

(100), (110), and (111) planes, respectively. The (111) curves characterize the behavior reported by BTW:  $K_U$  is independent of  $\theta_A$  and  $\theta_U$  coincides with  $\theta_A$ . In the (100) and (110) curves, however, the magnitude of  $K_U$  and the deviation of  $\theta_U$  from  $\theta_A$  are each strongly dependent on  $\theta_A$ . The magnitude and shape of the  $K_U$  curves and the shape of the  $\theta_U$  curves change in a continuous manner with increasing cobalt concentration.

Our data will be discussed in terms of the following general mathematical expression of the noncubic anisotropy energy density,  $W_U$ :

$$W_U = -F \sum_i \alpha_i^2 \beta_i^2 - G \sum_{i>j} \alpha_i \alpha_j \beta_i \beta_j, \quad (4)$$

where  $\alpha_i$  and  $\beta_i$  are the direction cosines of the magnetization during the torque measurement and during the annealing process, respectively; and  $F$  and  $G$  are positive constants. It will be shown later (Sec. IV) that several different physical models lead to Eq. (4) in their mathematical formulation.

Equation (4) can be reduced to the form  $W_U = K_U \sin^2(\theta - \theta_U)$  in case the magnetization lies in one of the three principal crystallographic planes. Expressions for  $K_U$  and  $\theta_U$  in terms of  $F$ ,  $G$ , and  $\theta_A$  are given for the (100), (110), and (111) planes in Table I. By using these expressions, values of  $F$  and  $G$  for each of the (100) and (110) planes were obtained from a Fourier

analysis of the experimental data ( $K_U^2$  versus  $\theta_A$ ). The appropriateness of Eq. (4) to express the results can be seen in Fig. 2, where the solid curves are plots of the equations of Table I using the average values of  $F$  and  $G$  obtained by the harmonic analysis.

The principal results of this investigation are summarized in Table II, where the individual values of  $F$  and  $G$  at 301°K following annealing at 375°K are tabulated. The average of the two values of each constant obtained from different crystallographic planes is plotted as a function of composition in Fig. 3. It can

TABLE I. Equations for  $K_U$  and  $\theta_U$  in terms of  $\theta_A$  as determined for the three principal planes from Eq. (4).

Plane	Equations
(110)	$K_U^2 = a_0 + a_1 \cos 2\theta_A + a_2 \cos 4\theta_A,$ $a_0 = (1/128)(44F^2 + 4FG + 19G^2),$ $a_1 = (1/32)(12F^2 - 4FG - G^2),$ $a_2 = (3/128)(12F^2 + 4FG - 5G^2),$ $\cot 2\theta_U = \left(\frac{F}{2G} - \frac{1}{4}\right) \csc 2\theta_A + \left(\frac{3F}{2G} + \frac{1}{4}\right) \cot 2\theta_A.$
(100)	$K_U^2 = \frac{1}{3}[4F^2 + G^2 + (4F^2 - G^2) \cos 4\theta_A],$ $\tan 2\theta_U = (G/2F) \tan 2\theta_A,$
(111)	$K_U = \frac{1}{3}(F + G),$ $\theta_U = \theta_A.$

TABLE II.  $F$  and  $G$  constants, as determined from (110) and (100) planes, for various values of cobalt concentration in magnetite ( $x$ ).

$x$	$10^{-5}F(110)$	$10^{-5}F(100)$	$10^{-5}G(110)$	$10^{-5}G(100)$
0.005	0.03	0.03	0.31	0.32
0.01	0.00	0.05	0.80	0.83
0.04	0.16	0.22	3.17	3.04
0.07	0.37	0.55	5.89	5.90
0.10	0.99	1.09	9.77	9.88
0.15	1.94	2.67	14.80	13.95

be seen that the variation of  $F$  with concentration is approximately quadratic ( $F \approx 10.1 \times 10^6 x^2$  erg/cc), whereas the variation of  $G$  is approximately linear ( $G \approx 9.25 \times 10^6 x$  erg/cc). The ratio of  $F$  to  $G$  therefore increases approximately linearly with  $x$  ( $F/G \approx 1.1x$ ) in this composition region.

We first examine these results to determine whether they are compatible with the observation of BTW that  $K_U$  is independent of  $\theta_A$  in cobalt-zinc ferrite, and perhaps also in a cobalt-iron ferrite corresponding to an  $x$  value of 0.77. Equation (4) reduces to the form  $W_U = F \cos^2(\alpha, \beta)$  when the ratio  $F/G$  equals one-half. The magnitude of  $K_U$  is therefore independent of  $\theta_A$ , and  $\theta_U$  coincides with  $\theta_A$  for all crystallographic planes. The variation of  $K_U$  with  $\theta_A$  remains invariant within the limits  $\pm 20\%$  when  $F/G$  lies between 0.41 and 0.61. If the linear trend of  $F/G$  observed in our experiments were to continue at larger  $x$ , these limits would correspond to  $x$  values between 0.37 and 0.56. These 20% limits correspond to  $K_U$  fluctuations observed by BTW (see Fig. 19 of reference 2). It is difficult to compare with the cobalt-zinc ferrite, since it is not known whether zinc has any additional effect on the annealing process. The composition of their crystal was given as  $\text{Co}_{0.32}\text{Zn}_{0.24}\text{Fe}_{2.18}\text{O}_4$ . If we assign a comparative value of  $x$  to this composition equal to three times the ratio of cobalt to total metal, we obtain  $x=0.35$ , which is just outside the limits mentioned above. The value of  $x=0.77$  for the cobalt-iron ferrite studied by BTW is well outside these limits. However, there are two factors which must be taken into account. First of all, extrapolation of the  $F$  and  $G$  concentration dependence to very high cobalt concentrations is not feasible since the magnitude of the anneal-induced anisotropy reduces to zero at cobalt ferrite. Secondly, BTW did not definitely establish that  $K_U$  is independent of  $\theta_A$  in the cobalt-iron ferrite crystal. We conclude that our observations and those of BTW are not necessarily incompatible.†

#### 4. ANALYSIS OF RESULTS

We shall now analyze our data in the light of existing theories and then proceed to a discussion of another possible interpretation.

† Note added in proof.—Wijn, van der Heide, and Fast [Proc. Inst. Elec. Engrs. (London) 104, Part B Suppl. 7, 412 (1957)] have deduced from measurements on polycrystalline samples

#### (a) Néel's Orientation Ordering Model

Angular variations of  $K_U$  and  $\theta_U$  similar to those illustrated in Fig. 2 have been observed in  $\text{FeNi}_3$  single crystals by Chikazumi.<sup>7</sup> He interpreted his experimental results in the light of the theory of orientation ordering as proposed by Néel<sup>8</sup> and independently by Taniguchi and Yamamoto.<sup>9</sup>

Stated very briefly, the essential idea of this theory is as follows: A pseudo-dipolar interaction is assumed to exist between nearest-neighbor atom pairs (iron, in the case of  $\text{FeNi}_3$ ) with the interaction energy varying as the cosine squared of the angle between the magnetization and the line joining the neighbors. During the annealing process at an elevated temperature the atoms redistribute themselves among the lattice sites available to them in order to minimize this energy. At the elevated temperature the atom pair directions assume a Boltzmann distribution which is essentially "frozen in" at lower temperatures.

The mathematical formulation of the orientation-ordering model leads to Eq. (4), with a particular relationship existing between  $F$  and  $G$ . Both constants are proportional to the product of the interaction energy per atom pair, the number of pairs per unit volume and the reciprocal of the annealing temperature. The values of the proportionality constants, which are different for the two terms, depend upon the symmetry of the lattice occupied by the magnetic ions.  $F$  equals zero for a body-centered cubic lattice (bcc), and  $G$  equals zero for a simple cubic lattice. The ratio  $F/G$  equals

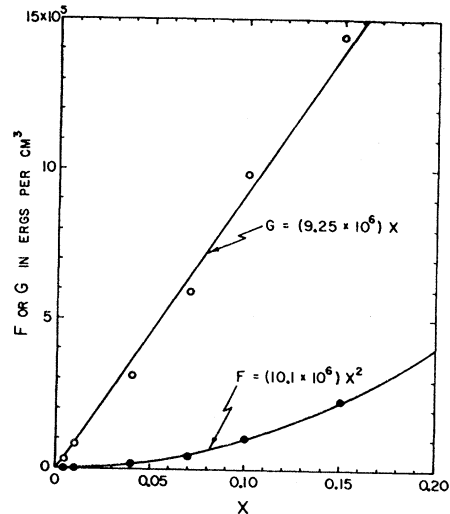


FIG. 3. Average experimental values of  $F$  and  $G$  versus  $x$ .

that the axis of the anneal-induced anisotropy is not necessarily in the direction of the applied magnetic field but is rather along a crystallographic direction nearest to it.

<sup>7</sup> S. Chikazumi, J. Phys. Soc. Japan 11, 551 (1956).

<sup>8</sup> L. Néel, J. phys. radium 15, 225 (1954).

<sup>9</sup> S. Taniguchi and M. Yamamoto, Science Repts. Research Inst. Tôhoku Univ. A6, 330 (1954).

one-fourth for a face-centered cubic lattice (fcc) and one-half for an isotropic distribution of nearest neighbors.

Chikazumi<sup>7</sup> obtained the constants of Eq. (4) from his  $\text{FeNi}_3$  data by a harmonic analysis of curves of  $K_U^2$  and  $\theta_U$  versus  $\theta_A$  for a (110) specimen. The ratio  $F/G$  was found to have a value intermediate between zero and one-fourth. This fact was interpreted as an indication that both fcc and bcc interactions were present. Since  $\text{FeNi}_3$  has a fcc structure and since a bcc interaction can be synthesized by adding the interactions of three iron atoms occupying mutually adjacent sites on a (111) plane of the crystal, the orientation-ordering model was regarded as a satisfactory explanation of the effect in  $\text{FeNi}_3$ .

We shall now predict the behavior which would result if the magnetic annealing effect in the cobalt-iron ferrites were due to the orientation ordering of cobalt-cobalt nearest-neighbor pairs. Since cobalt ferrite itself is an inverse spinel,<sup>10,11</sup> we assume that all the cobalt ions are on the octahedral cation sites. Figure 4 shows the environment of a cation on an octahedral site. The lines joining this cation to its six nearest-neighbor cations are all  $\langle 110 \rangle$  directions. In fact, the octahedral sites make up a face-centered cubic lattice with half of the positions empty. Accordingly, the fcc form of Eq. (4) should apply. Following the reasoning of Chikazumi<sup>7</sup> it might be expected that a relatively small amount of body-centered cubic interactions could result from cobalt "triplets" on these sites. The number of cobalt-cobalt pairs should be proportional to  $x^2$  at small values of  $x$ ; accordingly the amplitude of the fcc interaction should have a quadratic concentration dependence. The number of cobalt triplets and therefore the amplitude of the bcc interaction should be proportional to  $x^3$ .

We can check these predictions of the orientation-ordering model against our experimental values of  $F$  and  $G$ . Since the first term of Eq. (4) is zero for a bcc

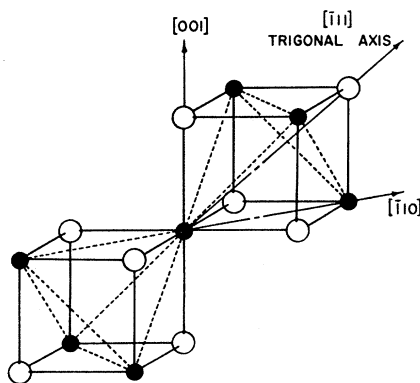


FIG. 4. Environment of a cation in an octahedral site of the ferrite spinel lattice. Solid circles represent octahedral site cations; open circles, oxygen ions.

<sup>10</sup> E. J. W. Verwey and E. L. Heilman, *J. Chem. Phys.* **15**, 174 (1947).

<sup>11</sup> E. Prince, *Phys. Rev.* **102**, 674 (1956).

interaction,  $F$  represents the amplitude of the fcc interaction. The amplitude of the bcc interaction is given by  $G-4F$ . By making use of these simple conversion factors it can be seen from Fig. 3 that most of our results disagree with the predictions of the orientation-ordering model. As a matter of fact, the only observation which bears out prediction is that the fcc interaction has a quadratic concentration dependence. However, the bcc term is overwhelmingly predominant for small  $x$ . Its concentration dependence is linear rather than cubic (or even quadratic, as might be expected if it were due to cobalt ion pairs on the tetrahedral sites).

### (b) Precipitate Model

Williams, Heidenreich, and Nesbitt<sup>12</sup> have demonstrated that fine precipitates of a second phase are formed in cobalt-zinc ferrites which respond to magnetic annealing. These authors have suggested that the annealing mechanism is the tendency of the precipitated particles to grow along the field direction. A precipitate model is capable of yielding the orientation dependence given in Eq. (4). One specific example which leads to the condition that  $F=0$  is that of ellipsoidal precipitates (either oblate or prolate) of a second phase with a different magnetization than that of the matrix, and with the symmetry axes along  $\langle 111 \rangle$  directions of the cubic matrix crystal. In this case the source of the uniaxial energy and the motivation for the selection of different axes is the shape demagnetization energy of the precipitates.

Several experimental observations provide evidence that the precipitate model does not apply in the case of the cobalt-iron ferrites which we have investigated. First of all, we have not observed torque reversals of the type reported by Williams *et al.*<sup>12</sup> as evidence of the presence of a precipitate. Second, the changing ratio of  $F$  to  $G$  as a function of  $x$  would indicate that the symmetry axis of the precipitates is changing its crystallographic orientation. The precipitate most likely to occur in these materials is  $\text{Fe}_2\text{O}_3$ . Crystals grown or slowly cooled under oxidizing conditions develop visible plates of  $\text{Fe}_2\text{O}_3$  with a definite crystal orientation; presumably with the normal parallel to  $\langle 111 \rangle$  directions of the spinel [an epitaxial fit occurs<sup>13</sup> between the basal (0001) plane of  $\alpha\text{Fe}_2\text{O}_3$  and the (111) plane of  $\text{Fe}_3\text{O}_4$ ]. We have no evidence that the orientation of the precipitates changes with composition; indeed it is doubtful that such a change occurs, in view of the fact that the lattice constant changes only very gradually with cobalt content. Finally, according to the precipitate model the changes in symmetry of the uniaxial anisotropy induced by annealing with the field along different crystal directions is brought about by a growth of some of the precipitates at the expense of

<sup>12</sup> Williams, Heidenreich, and Nesbitt, *J. Appl. Phys.* **27**, 85 (1956).

<sup>13</sup> Davies, Simnad, and Birchenall, *J. Metals* **3**, 889 (1951).

others which are less favorably oriented with respect to the magnetization direction. This process would involve a mass migration of metal ions through the crystals. The relaxation time associated with the annealing process seems to be much too short to be associated with this process. We observed a considerable amount of variation in relaxation time from sample to sample with no apparent trend as a function of composition. However, the relaxation time for the annealing process at 375°K was less than ten minutes for all of our crystals. This time is shorter by approximately four orders of magnitude than what one obtains by extrapolation of the data of BTW to this temperature.

### (c) Directional Ordering Involving Cation Vacancies

It has been suggested by Iida and co-workers<sup>14</sup> that the uniaxial anisotropy is induced by directional order between divalent cobalt ions and cation vacancies. These authors have demonstrated that the magnitude of the annealed anisotropy is lowered when the ferrite is heated to 1000°C in vacuum, and is increased on subsequent reheating to 400°C in controlled oxygen pressure. It is well known that ferrite spinel lattice can be oxidized and that the oxidized lattice can be regarded as a complete oxygen lattice with some cation vacancies. It is not clear, however, to what degree the oxidation procedure of Iida *et al.*<sup>14</sup> has introduced cation vacancies. It is difficult to analyze our data in terms of a model of vacancy-cobalt ordering because this idea has not yet been worked into a specific quantitative model. However, we can raise objections on the basis of symmetry to the concept that some such mechanism is the primary cause of annealed anisotropy. We have observed that the anneal-induced anisotropy is characteristic of body-diagonal symmetry at low values of  $x$  and that the symmetry changes with increasing cobalt concentration. If the cobalt ions are on octahedral sites the vacancy-cobalt axis is not a  $[111]$  direction, and there is no apparent way that the symmetry can change with increasing cobalt concentration.

On the other hand, it is very likely that cation vacancies and other types of lattice defects do play an important role in the annealing process. For example, the puzzling rapidity with which the annealing takes place may be due to their presence. We are in the process of growing crystals with various controlled oxidation states for a systematic study of the cation-vacancy effect.

### (d) New Outlook on the Annealing Process

It can be seen from Fig. 4 that each octahedral-site cation is surrounded by six nearest-neighbor octahedral cations and that the combination forms two tetrahedra. Consider that the cobalt ion occupies the center posi-

tion. Its immediate environment has a trigonal symmetry axis along the body diagonal joining the two tetrahedra of which it is a member. The corresponding symmetry axes of the four cations in any one tetrahedron constitute the four body diagonals of a cube. The essential features of the annealing process can be explained if one hypothesizes the existence of a fundamental uniaxial spin-lattice interaction energy ( $W = A \cos^2\theta$ ), the axis of which coincides with the symmetry axis referred to above. The mechanism of the annealing process is then the migration of the cobalt ion to whichever of the adjacent cation sites has the symmetry axis which would minimize this energy. According to this model the anneal-induced anisotropy is due to cobalt ions acting individually rather than in pairs or larger agglomerates.

To be sure, this model is similar in many respects to the orientation-ordering model. The only difference between the two models lies in the origin of the fundamental interaction energy. In our model it is due to an interaction between a single cobalt ion and its surroundings, rather than between two adjacent cobalt ions. This one difference, however, eliminates the two major objections to the orientation-ordering model which we have cited. It leads to the condition  $F=0$  in Eq. (4) and to a linear dependence of  $G$  on  $x$  at low cobalt concentrations, in accordance with our experimental observation.

The observation that the  $F/G$  ratio increases with increasing cobalt concentration can be interpreted as an indication that the interaction symmetry axis deviates more and more from a body diagonal. The first term of Eq. (4) represents that portion of the total interaction which does not have body-diagonal symmetry. Since  $F$  varies quadratically with  $x$ , it is very likely that the effective change in symmetry axis is brought about by the presence of two cobalt ions on the same tetrahedron of lattice sites (see Fig. 4). This situation could either result in a change in symmetry of the fundamental spin-lattice interaction or introduce separate cobalt-cobalt interactions of the Néel type.

Since the annealing process according to this model as well as to the orientation-ordering model involves the movement of cobalt ions from one site to another, the activation energy characterizing the annealing mechanism should bear some relationship to the activation energy for diffusion of cobalt through the lattice. We do not know the value of this activation energy. Lindner<sup>15</sup> has reported that the activation energies for the self-diffusion of zinc and iron in zinc ferrite are 3.7 and 3.6 electron volts per ion, respectively. We have not measured the activation energies for all our crystals. However, those we did measure and the value reported by BTW are approximately one-fourth as large as the values quoted above. It is possible that the activation energy for the short-range migration of

<sup>14</sup> Iida, Sekizawa, and Aiyama, *J. Phys. Soc. Japan* **10**, 907 (1955).

<sup>15</sup> R. Lindner, *J. Chem. Phys.* **23**, 410 (1955).

cobalt in iron-cobalt ferrites is significantly smaller than that for the diffusion of zinc and iron in zinc ferrite because in the former case iron is present in both divalent and trivalent states. In this situation electrons can move about quite readily to maintain local charge neutrality. Cation vacancies could also lower the activation energy.

At first sight it is surprising that cobalt ions should have symmetry axes for the anneal-induced anisotropy along body diagonals whereas it establishes the cube edges as preferred directions of magnetization with respect to the cubic anisotropy. However, on closer inspection it can be seen that no basic inconsistency exists. Jonker, Wijn, and Braun<sup>16</sup> have compared the behavior of cobalt in ferrites with its behavior in the hexagonal barium-iron oxide ferroxplana materials. These authors pointed out that the body-diagonal direction in the cubic ferrite is equivalent to the  $c$  axis of the hexagonal structures, and that these axes are "abhorred" directions of the magnetization when cobalt is present. According to the model for the annealing process which we have described, the results are the same whether the body diagonals are preferred or "abhorred" directions for the magnetization.<sup>17</sup> It should be pointed out, however, that the cubic anisotropy does not result from the same order of interaction as the uniaxial anisotropy. If the expression for the spin-lattice interaction is written as a power series of the direction cosine of the magnetization with respect to the symmetry axis:

$$W = A \cos^2\theta + B \cos^4\theta + \dots, \quad (5)$$

the first term does not contribute to the cubic anisotropy if the four types of octahedral sites are equally populated by cobalt ions.

Finally, we shall mention very briefly one possible origin of the spin-lattice interaction energy represented by Eq. (5). Slonczewski<sup>18</sup> is in process of considering this problem on the basis of the one-ion approximation with the exchange interaction represented by a molecular field. When the effects of the crystalline field and spin-orbit coupling on the energy levels of the cobalt ion are taken into account, an energy expression having the form of Eq. (5) results. The details of this work, including a comparison between this theory and our experimental results will be published at a later date.

<sup>16</sup> Jonker, Wijn, and Braun, Philips Tech. Rev. 18, 145 (1956).

<sup>17</sup> This fact was pointed out to one of us (LRB) by J. Smit during a discussion of our preliminary results.

<sup>18</sup> J. C. Slonczewski, Bull. Am. Phys. Soc. Ser. II, 2, 238 (1957).

## 5. SUMMARY

The angular dependence of the response of cobalt-iron ferrite single crystals to a magnetic anneal was found to be adequately represented by Eq. (4). This equation can be fitted to a number of different physical models, all of which have three things in common: first, a source of uniaxial energy the magnitude of which depends on the cosine squared of the angle between the magnetization and a particular symmetry axis; second, the possibility that the symmetry axis can lie along different equivalent crystallographic directions in different regions of the crystal; and third, a mechanism whereby the different equivalent symmetry axes are selected by the magnetic field present during annealing according to a  $\cos^2\theta'$  preference law, where  $\theta'$  is the angle between the magnetization during annealing and a specific symmetry axis.

Our data show that the constants of Eq. (4) have a definite trend with increasing cobalt concentration; that is,  $F$  varies quadratically and  $G$  varies linearly with  $x$ . The observation of Bozorth, Tilden, and Williams<sup>2</sup> that the magnitude of the anneal-induced anisotropy is independent of crystal orientation with respect to the annealing field in a cobalt-zinc ferrite was found to be not inconsistent with our results. The two major models of the magnetic annealing process, orientation ordering and second-phase precipitate, were found to be inadequate to fully explain our results. The former model fails to give the correct symmetry and cobalt concentration dependence; whereas the latter fails to explain the change in symmetry with increasing cobalt concentration and also fails to account for the very short relaxation times. A new model, involving cobalt ions acting individually rather than in pairs or larger agglomerates, was introduced and shown to be consistent with the essential features of our results.

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