reasonable to associate the diffuse neutron intensity with elastic scattering from the slightly disoriented spins which gradually change direction through the wall.

The crystallographic distortion of CoO has tetragonal symmetry and the anisotropy in the (111) plane is asymmetric. In agreement with this, the neutron diffraction data suggest a strong preference for a direction nearly parallel to the tetragonal axis. This suggests that the spin direction is a compromise between the dipole-dipole interactions which tend to hold the spins within (111) and the crystalline field energy arising from the deformation which favors a direction parallel to the tetragonal axis. In FeO the spin-orbit interactions apparently predominate, but since the crystallographic distortion is rhombohedral there is no conflict between the magnetic and crystalline anisotropies.

The alternative solution of the neutron diffraction data arrived at by considering only the sharp portion of the Bragg peaks is to maintain the spins coupled in a ferromagnetic sheet parallel to (111) but with the magnetic axis parallel to $[11\bar{1}]$. From symmetry considerations it seems unlikely that this is correct for MnO or NiO, although conceivably this result could be rationalized in the case of CoO as a consequence of the large spin-orbit interaction and crystalline deformation. A more likely explanation for the discrepancy in the intensity of the first magnetic peak is that the assumption of a common magnetic axis for all the magnetic moments is invalid, and in the case of CoO part of the discrepancy may be the consequence of an asymmetric magnetic form factor.

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Origin of Magnetic Anisotropy in Cobalt-Substituted Magnetite*

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The large part of the ferromagnetic anisotropy of $Co_xFe_{3-x}O_4$ attributed to the presence of Co^{2+} is explained, for small x, by means of a one-ion model. The residual orbital angular momentum $\alpha(\simeq 1)$ of Co^{2+} is constrained by the crystal electric field to lie parallel to the axis of trigonal symmetry. Spin-orbit energy $\lambda\mathbf{L}\cdot\mathbf{S}$ couples the spin to this axis, accounting for the anisotropy energy. By fitting the theory to cubic anisotropy data one finds $\alpha\lambda = -132$ cm^{-1}. The assumption that cations are mobile at higher temperatures leads to a quantitative explanation of the annealing-induced anisotropy energy. The mean orbital magnetic moment μ_L of Co^{2+} is predicted to be large ($\mu_L \simeq 0.5$ Bohr magneton) and anisotropic ($\Delta\mu_L \simeq 0.1$ Bohr magneton) at low temperatures.

1. INTRODUCTION

It has been shown[1] by means of torque measurements on single crystals that the substitution of a small amount of cobalt for iron in magnetite ($Co_xFe_{3-x}O_4$) causes a large change in the magnetic anisotropy energy. The cubic anisotropy parameters K_1 and K_2 were found to depend strongly on temperature and, at a given temperature, to be approximately linear in x for $0<x<0.15$.

It has been found also that the anisotropy energy in cobalt-iron ferrites is affected by magnetic annealing.[2,3] Suppose the temperature of the crystal is raised to an appropriate temperature T_a and the magnetization $\mathbf{M}$ is held for several minutes in a direction $\boldsymbol{\beta}$ by an applied magnetic field. If the crystal is then quenched to a temperature T, which is room temperature or lower, the free energy $\mathfrak{F}(T)$ is found to be a function of $\boldsymbol{\beta}$ as well as of the direction $\boldsymbol{\alpha}$ of $\mathbf{M}$ at T. In general $\mathfrak{F}$ does not have cubic symmetry in $\boldsymbol{\alpha}$, although the crystal is cubic. Penoyer and Bickford[2] have investigated in detail the dependence of $\mathfrak{F}$ on $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, and x for $0<x<0.15$.

It is the purpose of this paper to explain these effects. No attempt is made to explain the anisotropy energy of Fe_3O_4. Only the changes caused by substituting small amounts of cobalt are considered.

The basic assumption of the theory is that the lowest orbital level of Co^{2+} in the crystalline electric field is

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* A brief description of this theory has appeared [J. Appl. Phys. **29**, 448 (1958)].

[1] Bickford, Brownlow, and Penoyer, Proc. Inst. Elec. Engrs. London **104B**, Suppl. No. 5, 238 (1957).

[2] R. F. Penoyer and L. R. Bickford, Jr., Phys. Rev. **108**, 271 (1957).

[3] Bozorth, Tilden, and Williams, Phys. Rev. **99**, 1788 (1955).

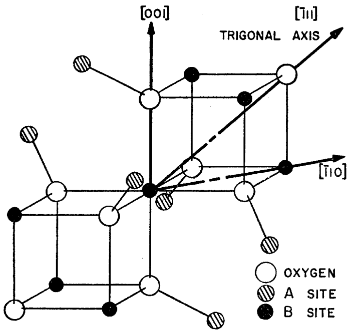

FIG. 1. A view of the spinel structure illustrating the trigonal symmetry of the central B site shown.

doubly degenerate. The residual angular momentum of each of these two states is constrained to lie parallel (in either direction) to an axis of trigonal symmetry. The spin of cobalt is coupled to the angular momentum in a first-order approximation of the spin-orbit energy. The consequent interaction of spin with the crystal axis results in anisotropy energy.†

This model differs from some previous models of anisotropy which assume that angular momentum is quenched in the ground orbital state.[4] In these models, the cubic anisotropy energy is given by a high order of perturbation by the spin-orbit coupling energy, or by magnetic dipole interactions. Consequently, the anisotropy energy per atom in these cases is very much smaller than that of the special model considered here. Two other crystals involving large antiferromagnetic coupling and large residual momentum are FeO and CoO.[5]

In this paper we will calculate the energy levels of Co^{2+} in a simple approximation. From these levels we will obtain the cubic anisotropy energy. We can then fit the theory to cubic anisotropy data for $Co_xFe_{3-x}O_4$ at all temperatures by a reasonable choice of a single parameter which is a measure of the spin-orbit interaction.

In addition, we can explain the annealing effect by assuming that cobalt is free to exchange places with iron at the annealing temperature T_a, but not at much lower temperatures. Thus the thermal distribution of cobalt ion positions at T_a is frozen in when the temperature is lowered. We are then able to fit the theoretical expression for the annealing-induced anisotropy to the data at all temperatures T by a reasonable choice of one additional energy-level parameter—the molecular exchange field.

Also, we predict a large and anisotropic orbital contribution to the magnetic moment of Co^{2+}. This is an immediate consequence of the model considered.

2. ENERGY LEVELS

In this section we calculate the energy levels of a Co^{2+} ion substituted for Fe^{2+} in the magnetite lattice. The crystal structure of Fe_3O_4 and $CoFe_2O_4$ is the same as for the mineral spinel.[6] There is considerable evidence that both of these crystals are inverse, meaning that the Co^{2+} and Fe^{2+} ions occupy octahedral or B sites rather than tetrahedral or A sites.[7] Therefore, it is reasonable to believe that the cation distribution of the mixed ferrite is represented by the formula $(Fe^{3+})[Co_x^{2+}Fe_{1-x}^{2+}Fe^{3+}]O_4$ where the ions in parentheses occupy A sites and the ions in brackets occupy B sites.

In a normal spinel $(A)[B_2]O_4$, each B site lies on an axis of threefold symmetry which is parallel to one of the body diagonals of the cubic crystal. This symmetry is illustrated in Fig. 1 which shows how a B site is surrounded by neighboring B and oxygen sites to form a configuration having trigonal symmetry about the $[\bar{1}11]$ axis. The B sites may be classified into four kinds; B_i lies on the ith trigonal axis ($i=111$, $\bar{1}11$, $1\bar{1}1$, $\bar{1}\bar{1}1$).

Suppose that one Fe^{2+} ion of a crystal of Fe_3O_4 is replaced by Co^{2+}. Then, if one neglects the distinction between Fe^{2+} and Fe^{3+}, the cobalt ion lies on an axis of threefold symmetry. The nearest-neighbor oxygens, 2.1 A distant from Co^{2+}, are close to the corners of a regular octahedron. The displacement in a $\langle 111\rangle$ direction from the regular positions has been found by x-ray diffraction to be 0.06 A ($u=0.379$) for Fe_3O_4.[8] Because the distortion of the octahedron from cubic symmetry is so small, we expect that the crystalline field has only a small trigonal distortion from cubic symmetry.

The energy levels of Co^{2+} in a paramagnetic crystal have been treated by Abragam and Pryce.[9] For the present problem we generalize their Hamiltonian to include the effect of exchange coupling. The Hamiltonian of the Co^{2+} ion, whose terms are arranged in decreasing order of magnitude, becomes

$$W=W_F+V_C+V_T+W_e+W_{LS}+W_m, \qquad (2.1)$$

where W_F is the Hamiltonian of the free ion (without spin-orbit energy), V_C is the cubic crystal field ($\sim 10^4$ cm^{-1}), V_T is the trigonal crystal field ($\sim 10^3$ cm^{-1}), W_e is the exchange energy ($\sim 10^3$ cm^{-1}) coupling the spin of Co^{2+} to other spins, W_{LS} is the spin-orbit energy ($\sim 10^2$ cm^{-1}), and W_m is the energy (~ 1 cm^{-1}) of interaction with magnetic fields. The quantities in parentheses

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† J. H. Van Vleck has proposed this explanation independently (contribution to the International Congress on Magnetism, Grenoble, July 2–5, 1958).

[4] F. Bloch and G. Gentile, Z. Physik **70**, 395 (1931); J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937); K. Yosida and M. Tachiki, Progr. Theoret. Phys. **17**, 331 (1957); W. P. Wolf, Phys. Rev. **108**, 1152 (1957).

[5] J. Kanamori, Progr. Theoret. Phys. (Japan) **17**, 177, 197 (1957).

[6] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Vol. II, Chap. 8.

[7] E. J. W. Verwey and E. L. Heilman, J. Chem. Phys. **15**, 174 (1947); E. Prince, Phys. Rev. **102**, 674 (1956); C. G. Shull, Phys. Rev. **81**, 626 (1951). A detailed description of the crystal structure of ferrites and its relationship to magnetic properties is given by E. W. Gorter, Philips Research Repts. **9**, 295, 321, 403 (1954).

[8] A. Claassen, Proc. Phys. Soc. (London) **38**, 482 (1925–1926).

[9] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951); **A206**, 173 (1951).

represent orders of magnitude of energy splittings caused by the respective terms.

We base our model of the cobalt ion on conclusions of Abragam and Pryce[9] concerning the effects of the crystal fields, as illustrated in Fig. 2. The electronic configuration of unfilled shells of the Co^{2+} free ion in its ground state is $3d^7$ and the total spin S is $\frac{3}{2}$. If V_C is not too large, it leaves S unchanged in the ground state. If the oxygen coordination is octahedral, the ground state under the influence of V_C is an effective P state with threefold orbital degeneracy. The wave functions belonging to this level are, in a first approximation, linear combinations of $(3d^7)\ {}^4F$ and $(3d^7)\ {}^4P$ functions of the free ion. The effect of V_T is to split the orbital triplet into a singlet and a doublet.

The last two terms in Eq. (2.1) are considerably smaller than the splitting due to V_C. Consequently we may, to a good approximation, calculate eigenvalues of W by using only the manifold of 3×4 eigenstates of the first four terms arising from the effective P state. In what follows, only this manifold is considered.

For purposes of calculation a fictitious angular momentum operator $\mathbf{l}$ ($\mathbf{l}'$ of Abragam and Pryce) is defined. The basic orbital states $|m\rangle$ satisfy the equation

$$l_z|m\rangle = m|m\rangle,\quad (m=-1, 0, 1), \tag{2.2}$$

where the z axis is the trigonal axis. The matrix representation of $\mathbf{l}$ in this manifold is the same as the usual representation for $\mathbf{L}$ in a P state. The phase of $|m\rangle$ is specified by the condition that the matrix elements of l_x are real and positive. The x axis may have any orientation perpendicular to the z axis.

The submatrix of true angular momentum $\mathbf{L}$ (in units of $\hbar$) is related[9] to $\mathbf{l}$ by

$$L_x=-\alpha' l_x,\quad L_y=-\alpha' l_y,\quad L_z=-\alpha l_z, \tag{2.3}$$

where α and α' are constants. This form of $\mathbf{L}$ may be deduced from the symmetry of the wave functions and the fact that they diagonalize a real Hamiltonian. In the special case in which the trigonal field is negligible, one has $\alpha=\alpha'$. If, in addition, the $|m\rangle$ are written as linear combinations of ${}^4F$ and ${}^4P$ free ion wave functions, it follows from the crystal-field matrix and equation for α given by Abragam and Pryce[9] that $1<\alpha<\frac{3}{2}$. The limit $\alpha=1$ is approached if V_C is large compared to the energy separation between ${}^4F$ and ${}^4P$ in the free ion. The limit $\alpha=\frac{3}{2}$ is approached in the opposite case. However, because of covalent effects, it is not clear that the wave functions may be written in this form, so that these limits on α are not rigorous.

Explicit representations for the terms in Eq. (2.1) will now be given. The term W_F+V_C is a constant, which we neglect. We may write V_T in the artificial form

$$V_T=\Delta(1-l_z^2), \tag{2.4}$$

where Δ is the energy difference between the singlet $m=0$ and the doublet $m=\pm1$.

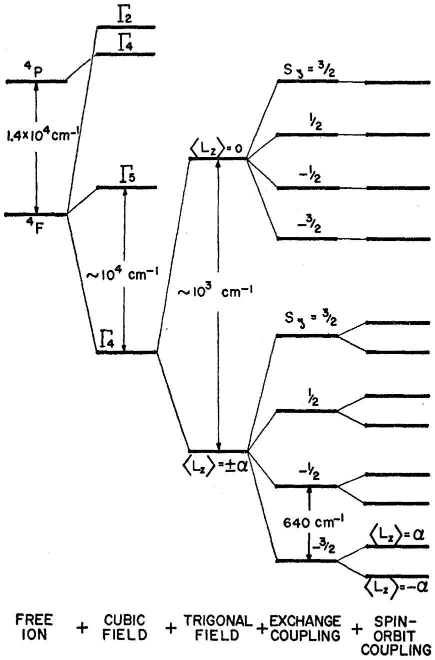

FIG. 2. Energy levels of Co^{2+} in $Co_xFe_{3-x}O_4$, illustrating the splitting of the free-ion levels by crystal effects. All levels at the extreme right are nondegenerate. The energy differences are not to scale.

For W_e we use the molecular field approximation. Since the magnetization of the B lattice exceeds the magnetization of the A lattice and the exchange energy is predominantly antiferromagnetic A–B coupling, the molecular field has the same sense as the total magnetization $\mathbf{M}$. In the absence of spin-orbit coupling, the degeneracy of the orbital doublet follows from the symmetry of the crystal field, so it must exist for each spin state, even in the presence of the exchange field. Therefore, the exchange field must have the same value H_e for both states of the orbital doublet. However, the exchange field H_e' for the singlet may be different.

We may write therefore

$$W_e=2\mu_\beta H_e l_z^2 S_\zeta + 2\mu_\beta H_e'(1-l_z^2)S_\zeta, \tag{2.5}$$

where μ_β is the Bohr magneton and the ζ axis is parallel to $\mathbf{M}$. For W_{LS} we have, from Eqs. (2.3),

$$W_{LS}=\lambda\mathbf{L}\cdot\mathbf{S}=-\alpha\lambda l_z S_z-\alpha'\lambda(l_xS_x+l_yS_y). \tag{2.6}$$

The magnetic energy is given by

$$W_m=\mu_\beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S}), \tag{2.7}$$

where $\mathbf{H}$ is the total magnetic field acting on the cobalt ion. Part of $\mathbf{H}$ is the field $\mathbf{H}_d$ caused by the magnetic dipoles distributed in the crystal. The part of W_m arising from $\mathbf{H}_d$ is small ($\sim1\ cm^{-1}$) compared to W_{LS}. The part of W_m arising from the applied fields ($\sim10^4$ oersteds) ordinarily obtained in the laboratory is also small ($\sim1\ cm^{-1}$). Therefore, neglecting W_m, and substituting (2.4), (2.5), and (2.6) into (2.1), we obtain

$$W=\Delta(1-l_z^2)+2\mu_\beta H_e l_z^2 S_\zeta+2\mu_\beta H_e'(1-l_z^2)S_\zeta \\ -\alpha\lambda l_z S_z-\alpha'\lambda(l_x S_x+l_y S_y). \quad (2.8)$$

The part of expression (2.8) proportional to λ will be treated as a perturbation. The unperturbed levels consist of 4 doublets and 4 singlets as illustrated in Fig. 2. (In Fig. 2 it is assumed that $\Delta>0$.) To a first approximation, matrix elements of W connecting the singlet to the doublet may be neglected. Since the nonzero elements of l_x and l_y occur only for $\Delta m=\pm 1$, the submatrix of $\mathbf{l}$ in the orbital doublet is diagonal and given by

$$l_x=l_y=\begin{pmatrix}0 & 0\\ 0 & 0\end{pmatrix},\quad l_z=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}. \quad (2.9)$$

It follows from Eqs. (2.8) and (2.9) that, in the first approximation, W commutes with l_z which may therefore be replaced by m, so that Eq. (2.8) becomes, for $m=\pm 1$,

$$W=2\mu_\beta H_e S_\zeta-\alpha\lambda m S_z. \quad (2.10)$$

The eigenvalues of the Hamiltonian (2.10) are obtained very simply since it represents a system in which the resultant of exchange and spin-orbit fields acts on the spin moment. Therefore the energy levels for $m=\pm 1$ are

$$\epsilon(\pm 1, m_s) \\ =m_s[4(\mu_\beta H_e)^2\mp 4\mu_\beta H_e\alpha\lambda\cos\theta_i+(\alpha\lambda)^2]^{\frac{1}{2}}, \quad (2.11)$$

where m_s is the projection of spin on the direction of the resultant field ($m_s=\pm\frac{1}{2}, \pm\frac{3}{2}$), and θ_i is the angle between the z and ζ axes. Equation (2.11) may be expanded to the form

$$\epsilon(\pm 1, m_s)=m_s[2\mu_\beta H_e\mp\alpha\lambda\cos\theta_i+(\alpha\lambda\sin\theta_i)^2/4\mu_\beta H_e \\ \pm(\alpha\lambda)^3\cos\theta_i\sin^2\theta_i/8(\mu_\beta H_e)^2+\cdots]. \quad (2.12)$$

In the first approximation, the $m=0$ levels are undisturbed by W_{LS} and are given by

$$\epsilon(0,m_s)=\Delta+2m_s\mu_\beta H_e'. \quad (2.13)$$

For all of the quantitative discussion in the remaining sections, the first approximation is found to be sufficient. However, we consider a second approximation which takes into account matrix elements connecting the singlet to the doublet, because this has the effect of removing the degeneracy of the doublet levels (2.11) occurring when $\theta_i=\frac{1}{2}\pi$. The ordinary second-order perturbation formula cannot be used because of this degeneracy in the first-order result. We may use, instead, a perturbation method of which a very direct demonstration has been given by Löwdin.[10]

The method consists of separating all the unperturbed states into a class A of degenerate states and a class B of all other states. To obtain the perturbed levels of class A to second order in the perturbing elements of W the following finite matrix is diagonalized:

$$U_{mn}{}^A=W_{mn}+\sum_q^B W_{mq}W_{qn}/(E_A-W_{qq}{}^0), \quad (2.14)$$

where m and n refer to class A states, W^0 is the unperturbed Hamiltonian, and E_A is the unperturbed energy of the A states. The summation is carried over all states q in class B.

We choose a spin representation in which S_ζ is diagonal. By letting the class A contain the doublet $m=\pm 1$, $S_\zeta=-\frac{3}{2}$, and class B contain the remaining 10 states, a quadratic secular equation is obtained from the Hamiltonian (2.8). Its solutions are

$$\epsilon(\pm 1, -\tfrac{3}{2})=-3\mu_\beta H_e+[-\alpha^2/\mu_\beta H_e-3\alpha'^2/X+\alpha'^2/Y] \\ \times(3\lambda^2/8)\sin^2\theta_i-3\alpha'^2\lambda^2/4Y \\ \pm[(3\alpha\lambda/2-3(\alpha'\lambda)^2/4Y)^2\cos^2\theta_i \\ +9(3X^{-1}-Y^{-1})^2(\alpha'\lambda\sin\theta_i)^4/64]^{\frac{1}{2}}, \quad (2.15)$$

where

$$X=\Delta+3\mu_\beta(H_e-H_e'), \quad (2.16)$$

and

$$Y=\Delta+\mu_\beta(3H_e-H_e'). \quad (2.17)$$

Thus the minimum separation between these two energy levels is

$$(3\alpha'^2\lambda^2/8)\,|3X^{-1}-Y^{-1}| \quad (2.18)$$

for $\theta_i=\frac{1}{2}\pi$. The terms $\mu_\beta H_e$ and $\mu_\beta H_e'$ should be only several times as large as $|\alpha\lambda|$. Then if Δ is sufficiently small, the correction given by the second approximation is appreciable near $\theta_i=\frac{1}{2}\pi$.

3. CUBIC ANISOTROPY ENERGY

If we take the orientation of $\mathbf{M}$ to be an extensive parameter, then the anisotropy energy, if measured isothermally, is a part of the Helmholtz free energy $\mathfrak{F}$. Since the energy levels of the cobalt ions are independent, the part of the free energy due to cobalt is given by

$$\mathfrak{F}_{\mathrm{Co}}=-kT\sum_i N_i\ln z_i, \quad (3.1)$$

where N_i is the cobalt population of the B_i sublattice, and z_i is the partition function given by

$$z_i=\sum_j\exp[-\epsilon_j(\theta_i)/kT], \quad (3.2)$$

where ϵ_j is an energy level of cobalt given in the previous section.

To proceed further we must choose a sign for Δ. We assume that $\Delta>0$ because we will see that this assumption leads to agreement with experiment. A good approximation to z_i is obtained by including only the two lowest levels of the first approximation given by (2.12). Terms of order λ^3 and higher may be neglected. Then the anisotropic part of $\mathfrak{F}_{\mathrm{Co}}$ is given by

$$\mathfrak{F}_{\mathrm{an}}=-kT\sum_i N_i\ln\cosh(3\alpha\lambda\cos\theta_i/2kT) \\ -(3\alpha^2\lambda^2/8\mu_\beta H_e)\sum_i N_i\sin^2\theta_i, \quad (3.3)$$

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[10] P.-O. Löwdin, J. Chem. Phys. **19**, 1396 (1951).

Suppose all $N_i=\frac{1}{4}N$ ($N=1.35\times10^{22}x$ cobalt ions per cc). Then the second term in (3.3) is isotropic and the cubic anisotropy energy is given by

$$\mathfrak{F}_c=-\tfrac{1}{4}kTN\sum_i \ln\cosh(3\alpha\lambda\cos\theta_i/2kT). \quad (3.4)$$

We wish to compare Eq. (3.4) with the anisotropy determined by torque measurements. The results of measurements have been expressed in terms of the parameters K_1 and K_2 in the phenomenological energy expression

$$W_A=K_0+K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_1^2\alpha_3^2)+K_2\alpha_1^2\alpha_2^2\alpha_3^2, \quad (3.5)$$

where α_k are the direction cosines of **M** with respect to the cubic axes. However, Eq. (3.4) cannot be written accurately in the form (3.5) except at large T.‡ We shall therefore make an approximate comparison by equating $\mathfrak{F}$ to Eq. (3.5) at the three symmetry directions [100], [110], and [111]. The following relations are obtained:

$$K_1=4(\mathfrak{F}[110]-\mathfrak{F}[100]), \quad (3.6)$$

$$K_2=27\mathfrak{F}[111]-36\mathfrak{F}[110]+9\mathfrak{F}[100]. \quad (3.7)$$

Since the theory considers only the anisotropy due to cobalt, we introduce the quantity ΔK_i, which represents the excess of K_i for $Co_xFe_{3-x}O_4$ over that for Fe_3O_4:

$$\Delta K_i(x)=K_i(x)-K_i(0). \quad (3.8)$$

Empirically, the anisotropy of one cobalt ion in $Co_xFe_{3-x}O_4$ is more than 100 times as large as that of one iron ion. Therefore, it is reasonable to attribute all of ΔK_i to the presence of cobalt. From Eqs. (3.4), (3.6), (3.7), and (3.8), we obtain

$$\Delta K_1=kTN[4\,f(3^{-\frac{1}{2}})-2\,f(2/\sqrt{6})], \quad (3.9)$$

$$\Delta K_2=kTN[18\,f(2/\sqrt{6})-(27/4)\,f(1)-(81/4)\,f(1/3)-9\,f(3^{-\frac{1}{2}})], \quad (3.10)$$

where

$$f(s)=\ln\cosh(3\alpha\lambda s/2kT). \quad (3.11)$$

Equations (3.9), (3.10), and (3.11) are compared with the experimental results in Fig. 3.

The only atomic parameter in the theory is $\alpha\lambda$. A value $|\alpha\lambda|=2.63\times10^{-14}$ erg (or 132 cm^{-1}) was determined by fitting the theory to the data of reference 1 for $\Delta K_1(0.01)$. In the ground state of the free ion, the value of λ as obtained by means of the interval rule from spectroscopic tables[11] is about -176 cm^{-1}. As observed in Sec. 2, α should lie in the approximate interval $1<\alpha<\frac{3}{2}$. The agreement is satisfactory, considering the effect covalence may have on λ.[12] Since λ is negative in the free ion, we may assume that it is also negative when the ion is in a crystal. The measured parameters ΔK_1 and ΔK_2 are approximately linear in x for $x<0.15$, which must follow from any one-atom model.

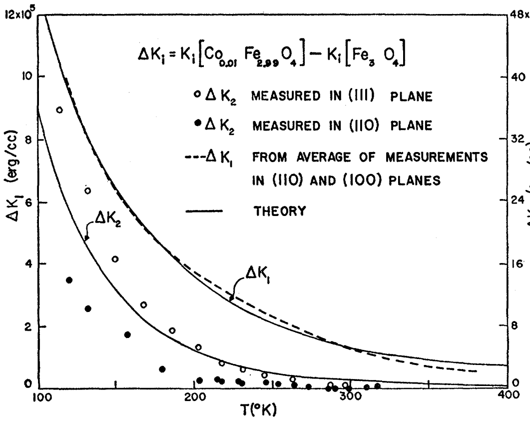

FIG. 3. Temperature dependence of the difference in anisotropy between $Co_{0.01}Fe_{2.99}O_4$ and Fe_3O_4. The values of ΔK_2 measured in the (110) plane were communicated privately. All other experimental results were obtained by multiplying the results of reference 1 by the correction factor 1.19 explained in reference 2. In all ΔK_2 data, K_2 for Fe_3O_4 was neglected. The theoretical curves are based on the value $|\alpha\lambda|=132$ cm^{-1}, obtained by fitting the ΔK_1 curve to experiment.

If the same value of $\alpha\lambda$ is used, the theoretical ΔK_2 has the right order of magnitude and a temperature dependence resembling the experimental dependence. The quantitative discrepancy for ΔK_2 is due at least in part to experimental error.

4. THE ANNEALING EFFECT

We shall now show how our model can explain the annealing effect. Let **M** be held in a direction $\boldsymbol{\beta}$ at an elevated temperature T_a. Suppose that at this temperature the cobalt ions are free to jump from one B site to another by exchanging places with iron ions. For small x we may assume that the cobalt ions are distributed independently of each other. Then Boltzmann statistics lead to the equilibrium distribution given by

$$N_i=N\{\textstyle\sum_j \exp[-\epsilon_j(\theta_i')/kT_a]\}/\textstyle\sum_{ij}\exp[-\epsilon_j(\theta_i')/kT_a] \quad (4.1)$$

where θ_i' is the value of θ_i at T_a. If, after equilibrium at T_a has been reached, the crystal is quenched to a lower temperature T at which the ions remain fixed in position,

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‡ *Note added in proof.*—This follows from the fact that the coefficients of an expansion of Eq. (3.4) in powers of α_1, α_2, and α_3 contain powers of (λ/kT) so that convergence does not occur for small T. In fact, at $T=0$, discontinuities appear in the torque derived from Eq. (3.4), owing to the degeneracy in energy at $\theta_i=\frac{1}{2}\pi$. In Sec. 6 several perturbing effects are discussed which remove this degeneracy. We anticipate that these effects may smooth the angular dependence of $\mathfrak{F}_c$ so that it will resemble (3.5) more closely without causing a great change in the magnitude of the anisotropy as determined by the values of $\mathfrak{F}_c$ along axes of symmetry. A similar consideration holds for the component of free energy induced by magnetic annealing, which is discussed in Sec. 4.

[11] *Atomic Energy Levels*, edited by Charlotte E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1952), Vol. II, p. 85. (Analyzed by A. G. Shenstone.)

[12] A review of covalent effects in octahedral complexes is given by J. Owen, in *Microwave and Radio-Frequency Spectroscopy*, Disc. Faraday Soc. **19**, 127 (1955).

the distribution (4.1) will remain. Then Eqs. (3.3) and (4.1) express the effect of annealing on $\mathfrak{F}_{\mathrm{an}}$ which is now a function of T_a and $\boldsymbol{\beta}$ as well as T and $\boldsymbol{\alpha}$.

The results of annealing experiments on $\mathrm{Co}_x\mathrm{Fe}_{3-x}\mathrm{O}_4$ have been expressed[2] in terms of the parameters F and G appearing in the following phenomenological expression for the anisotropy energy minus its cubic part:

$$W_U = -F\sum_i \alpha_i^2\beta_i^2 - G\sum_{i>j}\alpha_i\alpha_j\beta_i\beta_j. \tag{4.2}$$

This expression is the function of lowest degree in $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, aside from terms depending on $\boldsymbol{\alpha}$ alone or $\boldsymbol{\beta}$ alone, which is symmetric with respect both to simultaneous cubic symmetry operations on $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, and to inversion of $\boldsymbol{\alpha}$ or $\boldsymbol{\beta}$ separately. It is essentially the same as the "two constant" phenomenological expression for magnetostriction.[13] The second condition on W_U is not in general necessary and would not hold if an "exchange anisotropy"[14] were present. However, it does hold for the mechanism of the present theory, and appears to hold in the annealing experiments.

We may show that the model described here leads to $F=0$, by letting $\boldsymbol{\beta}=[100]$. Then Eq. (4.2) becomes

$$W_U = -F\alpha_1^2. \tag{4.3}$$

But in this case all of the θ_i' are equal. It follows from (4.1) that all N_i are equal and therefore that $\mathfrak{F}_{\mathrm{an}}$ has cubic symmetry. This conclusion is consistent with Eq. (4.3) only if $F=0$. It is easily seen that G is not zero for our model.

The experimental results for $T_a=375$°K and $T=301$°K have been expressed[2] by the empirical relations

$$F = (10.1\times 10^6)x^2, \tag{4.4}$$

and

$$G = (9.25\times 10^6)x, \tag{4.5}$$

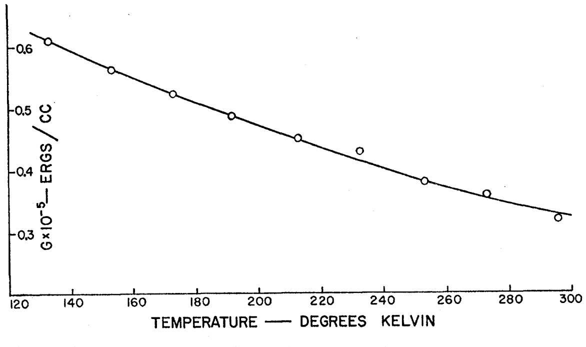

FIG. 4. Temperature dependence of the induced anisotropy parameter G for $\mathrm{Co}_{0.005}\mathrm{Fe}_{2.995}\mathrm{O}_4$. Measurements were made by Penoyer and Bickford.[15] The theoretical curve is based on the values $|\alpha\lambda|=132\ \mathrm{cm}^{-1}$, $\mu_\beta H_e=320\ \mathrm{cm}^{-1}$, and $n=0.0273$. The values of the last two parameters were adjusted to fit the data for G.

which hold in the range $0.0<x<0.15$. Thus, experimentally F/G approaches zero as x approaches zero, in agreement with the model.

In comparing the theoretical dependence of G on T with experiment, we again have the difficulty that the theoretical expression for the annealing effect cannot be written accurately in the phenomenological form (4.2) for small T. We can make an approximate check by comparing the maximum annealing torque in the (001) plane for the case $\boldsymbol{\beta}=[110]$.

From symmetry it follows that if $\boldsymbol{\beta}=[110]$, then

$$N_{1\bar{1}1} = N_{\bar{1}11} \tag{4.6}$$

and

$$N_{111} = N_{\bar{1}\bar{1}1}. \tag{4.7}$$

We let

$$n = (N_{1\bar{1}1}+N_{\bar{1}11}-N_{111}-N_{\bar{1}\bar{1}1})/N. \tag{4.8}$$

Then the torque in the (001) plane, calculated by differentiating Eq. (3.3), has, at $\boldsymbol{\alpha}=[010]$, its maximum value of

$$\mathcal{L}[010] = nN[(\sqrt{3}\alpha\lambda/2)\tanh(\sqrt{3}\alpha\lambda/2kT) - (\alpha\lambda)^2/4\mu_\beta H_e]. \tag{4.9}$$

In the absence of an annealing effect this torque would be zero. If we set $F=0$, the same torque from (4.2) is

$$\mathcal{L}[010] = \tfrac{1}{2}G. \tag{4.10}$$

Combining (4.9) and (4.10), we obtain

$$G = 2nN[(\sqrt{3}|\alpha\lambda|/2)\tanh(\sqrt{3}|\alpha\lambda|/2kT) - (\alpha\lambda)^2/4\mu_\beta H_e]. \tag{4.11}$$

To the parameter $|\alpha\lambda|$ we assign the previously determined value of 2.63×10^{-14} erg. Instead of using the value of n given by Eqs. (4.1) and (4.8), we can determine experimental values of n as well as H_e by fitting (4.11) to data of Penoyer and Bickford[15] shown in Fig. 4. The temperature dependence of H_e may be neglected for temperatures much smaller than the Curie temperature.

The theoretical curve in Fig. 4 is for the values $n=0.0273$ and $\mu_\beta H_e=320\ \mathrm{cm}^{-1}$. This value of $\mu_\beta H_e$ is not very critical because the term in (4.11) containing H_e is merely a correction ($\simeq 20\%$) to the main term. It is reasonably consistent with the Curie temperature of 993°K[16] for $\mathrm{CoFe}_2\mathrm{O}_4$. If this value of $\mu_\beta H_e$ is accepted, the term in the energy expression (2.12) containing $(\alpha\lambda)^3$ changes the splitting by less than 2% and is justifiably neglected, as we have done.

To obtain a theoretical value of n, the energy levels given by Eq. (2.12) are substituted into Eq. (4.1), which is in turn substituted into Eq. (4.8). If we use the experimental value $T_a=375$°K, we find that more than the two lowest levels given by (2.12) contribute per-

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[13] See, for example, R. M. Bozorth, *Ferromagnetism* (D. van Nostrand Company, Inc., Princeton, New Jersey, 1951), p. 650.

[14] W. H. Meiklejohn and C. P. Bean, Phys. Rev. **102**, 1413 (1956); **105**, 904 (1957).

[15] R. F. Penoyer and L. C. Bickford (private communication). The experimental methods used are described in reference 2.

[16] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), Section 5, p. 211.

ceptibly to the sums in Eq. (4.1), and that the theoretical value of n is 0.061, or a factor of 2.2 greater than the empirical value. This discrepancy may be explained by recent work[17] showing that the annealing effect in $Co_xFe_{3-x}O_4$ is a function of the state of oxidation. In that work, it was concluded that appreciable migration of cobalt ions at 100°C occurs only if cation vacancies are present, and that the number of vacancies is proportional to the concentration of oxygen in excess of the stoichiometric concentration. Only those cobalt ions which happen to lie near vacancies participate in the annealing effect, so that n is smaller than theory predicts. We may conclude that our model gives an accurate account of the temperature dependence of the anneal-induced anisotropy and gives the correct order of magnitude of the effect.

5. MAGNETIC MOMENT

A consequence of the model considered here is that the orbital contribution to the magnetic moment of Co^{2+} is large and anisotropic. The statistical mean of the total moment of cobalt, averaged over all B_i, is, in Bohr magnetons,

$$\mu=-\sum_i \frac{N_i}{N}\left[\frac{\sum_j\langle j|\mathbf{L}+2\mathbf{S}|j\rangle \exp[-\epsilon_j(\theta_i)/kT]}{\sum_j \exp[-\epsilon_j(\theta_i)/kT]}\right]. \tag{5.1}$$

We shall consider the energy eigenstates in the first approximation. Since L_z is diagonal, we have, for the projection of $\mathbf{L}$ on the direction of the molecular field,

$$\langle m|L_\zeta|m\rangle=-m\alpha\cos\theta_i. \tag{5.2}$$

The expectation value of spin may be calculated directly from the eigenstates. For the two lowest states ($m=\pm1$, $m_s=-\frac{3}{2}$) we find, to the order of λ^2,

$$\langle m|S_\zeta|m\rangle=\tfrac{3}{2}-\tfrac{3}{16}(\alpha\lambda\sin\theta_i)^2/(\mu_\beta H_e)^2. \tag{5.3}$$

To illustrate, we calculate $\boldsymbol{\mu}$ along axes of symmetry for the case $N_i=\frac{1}{4}N$. We assume that T is low compared to the Curie temperature so that only the populations of the two lowest levels need to be considered. From symmetry we need to consider only ζ components of $\mathbf{L}$ and $\mathbf{S}$. Then from Eq. (5.3) and the fact that the average of $\sin^2\theta_i$ is $\frac{2}{3}$, the spin part of μ is given by

$$\mu_S=3-(\alpha\lambda)^2/(2\mu_\beta H_e)^2, \tag{5.4}$$

and is, to order λ^2, the same for all three axes and independent of temperature. The deviation of μ_S from 3 is very small. For the numerical parameters $(\alpha\lambda)=-132$ cm^{-1} and $\mu_\beta H_e=320$ cm^{-1}, deduced previously, $\mu_S=2.96$.

To illustrate the orbital contribution to μ, we consider the case where $\mu_\beta H_e\gg|\lambda|$, so that Eq. (2.11) becomes, for $m_S=-\frac{3}{2}$,

$$\epsilon(m,-\tfrac{3}{2})=-3\mu_\beta H_e+\tfrac{3}{2}m\alpha\lambda\cos\theta_i. \tag{5.5}$$

Then from Eqs. (5.5) and (5.1) we obtain, for the orbital part of μ, when the magnetization is saturated along the axes indicated,

$$\mu_L\langle100\rangle=(\alpha/\sqrt{3})\tanh(-\sqrt{3}\alpha\lambda/2kT), \tag{5.6}$$

$$\mu_L\langle110\rangle=(\alpha/\sqrt{6})\tanh(-(\sqrt{\tfrac{3}{2}})\alpha\lambda/kT), \tag{5.7}$$

$$\mu_L\langle111\rangle=\tfrac{1}{4}\alpha\tanh(-3\alpha\lambda/2kT)+\tfrac{1}{4}\alpha\tanh(-\alpha\lambda/2kT). \tag{5.8}$$

The temperature dependence of μ_L is plotted in Fig. 5. We observe that, for small T, the anisotropy of μ_L is of the order of 0.1 Bohr magnetons and conceivably could be measured. It should be observed that these curves are not accurate for the values of $\alpha\lambda$ and $\mu_\beta H_e$ given above, except near $T=0$. The higher order terms of Eq. (2.11) might be required for actual comparison with experiment.

The calculated moments are roughly consistent with the total moment of 3.7 to 3.9 Bohr magnetons reported for polycrystalline $CoFe_2O_4$.[16] Precise agreement could not be expected even if α were known because the one-atom model may not be accurate in the case of large x.

6. DISCUSSION

There is sufficient agreement between the theory and the anisotropy measurements to justify confidence in the basic model. It is worth while to discuss effects which would alter the energy levels as given in the first approximation. Any effect which splits the energy level for $\theta_i=\frac{1}{2}\pi$ by an amount comparable to $|\alpha\lambda|$ (=132 cm^{-1}) should cause an appreciable change in the anisotropy energy.

There are several effects which remove this degeneracy:

(1) In Sec. 2 we showed that inclusion of the excited orbital singlet ($m=0$) in the manifold of the perturbation calculation (second approximation) has the effect

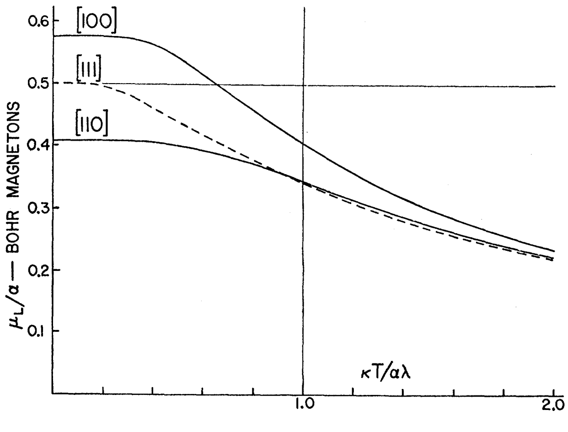

FIG. 5. Theoretical temperature dependence of the mean orbital magnetic moment μ_L of Co^{2+} in $Co_xFe_{3-x}O_4$ with the saturation magnetization directed along the axes indicated. It is assumed that all N_i are equal and that $\mu_\beta H_e\gg|\lambda|$. The constant α is of the order of unity, and $|\alpha\lambda|/k=190$°K.

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[17] Bickford, Brownlow, and Penoyer, J. Appl. Phys. **29**, 441 (1958).

of removing the degeneracy. The fact that the anisotropy energy calculated from the energy levels of the first approximation could be fitted to the experimental data implies that the trigonal splitting Δ is much greater than $|\alpha\lambda|$.

(2) According to an ionic model of cubic Fe_3O_4, the B sublattice would have a disordered distribution of equal numbers of Fe^{2+} and Fe^{3+} ions. A cobalt ion substituted into such a crystal would not be in a field of trigonal symmetry, so that the degeneracy of the orbital doublet would be removed. Part of this asymmetric crystal field would be caused by the direct action of the asymmetric charge distribution of the iron ions on B sites, whose effect would be partially shielded by the oxygen electrons. Another part, generally believed to be larger, would be caused by the asymmetric distortion of the arrangement of the neighboring oxygen ions. The difference between the ionic radius of 0.83 A for Fe^{2+} and 0.67 A for Fe^{3+} gives an indication of the amount of this distortion. Since the trigonal distortion of the oxygen arrangement is about 0.06 A we expect the splitting due to the asymmetric field to be about as large as Δ. Since we find that $\Delta \gg |\alpha\lambda|$, the asymmetric splitting should also be larger than $|\alpha\lambda|$. Since we find that it is much less than $|\alpha\lambda|$, we are led to the belief that electron charge is transferred from one iron ion to another at a frequency larger than $|\alpha\lambda|/h$, so that the cobalt atom is effectively in a symmetric field produced by the average charge distribution. This result suggests that the iron electrons of highest energy occupy Bloch states in a band whose width is greater than $|\alpha\lambda|$, rather than disordered ionic states.

Although this line of reasoning is not rigorous, it is supported by evidence, discussed in reference 1, that addition of cobalt to ferrites containing two different elements on B sites causes much smaller changes in anisotropy energy. The asymmetric fields in these ferrites apparently split the orbital doublet of Co^{2+}, causing a further quenching of orbital angular momentum. This in turn decreases spin-orbit energy so that the anisotropy is decreased.

(3) There is a general principle[18] which states that if the electronic orbital state of a molecular system is symmetry-degenerate, then the nuclear configuration is unstable, unless all of the nuclei are colinear. In the "static" treatment of this effect,[18,19] the nuclei assume equilibrium positions which destroy the symmetry responsible for the degeneracy, thereby removing the degeneracy. The more complicated "dynamic" treatment, which takes into account motion of the nuclei, has also been considered.[20] This effect must alter the energy levels of our model, but apparently by an amount less than $|\alpha\lambda|$.

(4) There is a phase transition in Fe_3O_4 at approximately 120°K. Below this temperature the crystal symmetry is orthorhombic rather than cubic.[21] The trigonal symmetry of a B site is destroyed and the orbital doublet of a substituted Co^{2+} should be split. The anisotropy energy of cobalt-iron ferrite in the orthorhombic phase has not been measured.

It would be of interest to study the anisotropy of $Co_xFe_{3-x}O_4$ further, particularly at lower temperatures, to seek evidence of some of the effects described above, which would appear as departures from the theory given here. In comparing experiment with theory it will be best to compare experimental torque curves directly with torque curves calculated from the theory, because the theoretical anisotropy energy cannot be written accurately in the phenomenological form (3.5) at low temperatures. Observation of the anisotropy of the moment would also be of interest.

The fact that the annealing parameter F is not zero for higher cobalt concentration deserves discussion. From the symmetry argument given in Sec. 4, the existence of a nonzero value of F is inconsistent with any theory which assumes that the energy levels of the cobalt ion depend only on θ_i. Experimentally, F is proportional to x^2. Therefore it seems likely, as has been suggested,[2] that pairs of Co^{2+} interact to change the energy levels. Another possible explanation is that cation vacancies or some other imperfections exert fields on Co^{2+}, and that the concentration of these increases with x.

Measurement[22] of cubic anisotropy as a function of temperature in $CoFe_2O_4$ also shows that the theory given here cannot apply to cases of high cobalt concentration. Only the anisotropy energy in the neighborhood of the (easy) $\langle 100\rangle$ axis was measured.[22] The theoretical anisotropy, using the value of $\alpha\lambda$ given here, is as much as 8 times as large as the experimental anisotropy. Also, adjustment of the value of $\alpha\lambda$ cannot bring about agreement over the whole temperature range.

ACKNOWLEDGMENTS

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