strain involved:

$$a^2R = 2a/(\partial a_{TM}/\partial T)(\partial T/\partial p)_H$$
$$\approx 4.2 \times 10^{12} \text{ erg/cm}^3. \quad (A.1)$$

It would be good if this were known directly. From $a_F - a_{AF} = 3.4 \times 10^{-10}$ cm, we estimate

$$\rho = 2(a_F - a_{AF})R/9M^2 \approx 5.4 \times 10^{12} \text{ cm}^{-1}. \quad (A.2)$$

Note that ρ is positive. In terms of the strain dependence of the exchange integral, this value of ρ corresponds roughly to $\partial J/\partial e \approx 2 \times 10^{-13}$ ergs, which is quite plausible. We can check these estimates independently by looking at the difference in $\partial a/\partial T$ above and below the transition, which is given by

$$(\partial a_F/\partial T) - (\partial a_{AF}/\partial T) = (\Delta a/M^2)(dM^2/dT)$$
$$\approx -3.4 \times 10^{-12} \text{ cm/deg}. \quad (A.3)$$

The observed value of the left-hand side of (48) is -7×10^{-12} cm/deg, which is a partial check. It is not clear how all the discrepancy arises, although dM^2/dT is not too well known.

The paramagnetic data may be analyzed using the

machinery we have developed, but the comparison of the theoretical and experimental results are highly sensitive to the values chosen for $\partial a_{TM}/\partial T$ as defined by (27). It is not possible to get from available measurements a single value of the contribution of $\partial a_T/\partial T$ valid over the entire range of interest—such as at T_0, T_n, and up into the paramagnetic region. We suspect that the difficulty occurs either because the phase we have called AF or Δ may not be substantially ordered, or else because of magnetic effects on $\partial a_T/\partial T$—such effects could come quite naturally from interlattice interactions, and from short-range order in the paramagnetic region.

We note that the effect of substitutions in MnAs can be nontrivial. We know[19] that small amounts of Sb, an ion larger than As, depress the F/AF transition temperature, although the steric effect of the larger ion should be to raise T_0, because dT_0/dp is negative. It is perhaps not entirely surprising that the delicate balance of the interlattice interactions should be modified by changing anions, as these are the carriers of the superexchange part of the interaction.

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Kinetics of Magnetic Annealing in Cobalt-Substituted Magnetite*

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The time dependence of the magnetic annealing effect in single crystals of magnetite containing various amounts of substituted cobalt has been investigated by a technique which permits observation of the effect at the annealing temperature. The annealing kinetics in a particular crystallographic direction are determined by measuring the decay of the torque in the (001) plane following a preparatory anneal in a direction 45° removed. The directions chosen for study are the [100] and [110] directions, which are nodes of the cubic torque curve. The absence of a cubic torque in the directions of measurement allows precise observation of the anneal-induced uniaxial torque. The annealing kinetics observed in the two directions are different, and the nature of the torque decay in both directions depends upon the cobalt concentration of the sample. The torque decay in the [100] direction is attributed to the redistribution of single cobalt ions

and certain pairs of adjacent cobalt ions over the octahedral cation sites, whereas the decay in the [110] direction is attributed to the redistribution of cobalt ion pairs only. The results of a theoretical analysis of the annealing kinetics that would result from such ionic redistribution are in good agreement with the experimental observations. Comparison of the annealing behavior of samples in different states of oxidation indicates that ionic redistribution occurs by a vacancy diffusion mechanism, and the activation energy observed for this process is 1.05 ± 0.03 ev. In addition to the measurements performed at the annealing temperature, the torque in the [110] direction was determined as a function of temperature in a sample which had been quenched at the end of its preparatory anneal. These two measurements are used to show that there exists a repulsive interaction energy of 0.093 ± 0.04 ev between two adjacent cobalt ions.

I. INTRODUCTION

THE uniaxial anisotropy produced in ferrites containing cobalt by magnetic annealing has been the object of a number of investigations in recent years.[1-8] Penoyer and Bickford[4] have studied this effect

in single-crystal samples of cobalt-substituted magnetite as a function of both cobalt content and annealing direction. They have found that the noncubic aniso-

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* A preliminary account of this work was presented at the 1959 March Meeting of the American Physical Society at Cambridge, Massachusetts. See W. Palmer, Bull. Am. Phys. Soc. 4, 178 (1959).

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[5] S. Iida, H. Sekizawa, and Y. Aiyama, J. Phys. Soc. (Japan) 13, 58 (1958).

[6] J. C. Slonczewski, Phys. Rev. 110, 1341 (1959).

[7] L. R. Bickford, Jr., J. M. Brownlow, and R. F. Penoyer, J. Appl. Phys. 29, 441 (1958).

[8] S. Iida, J. Appl. Phys. 31, 251S (1960).

tropy energy density induced by magnetic annealing can be represented in the following functional form:

$$W_u = -F \sum_i \alpha_i^2 \beta_i^2 - G \sum_{i>j} \alpha_i \alpha_j \beta_i \beta_j, \qquad (1)$$

where α_i and β_i are the direction cosines of the magnetization during measurement and annealing, respectively, and F and G are positive constants. The value of G was observed to be approximately proportional to the concentration of cobalt. The value of F was found to vary roughly quadratically with cobalt concentration.

Penoyer and Bickford explained their results by postulating a fundamental uniaxial spin-lattice interaction energy which couples the spin of an individual cobalt ion and the axis of trigonal symmetry characteristic of the particular octahedral lattice site which the ion occupies. This trigonal axis results from the disposition of the six cations and six oxygen ions which surround each site of the octahedral lattice, and lies along one of the four [111] directions. Because of the spin-lattice interaction, the energy associated with a single cobalt ion on a given octahedral site depends upon the angle made by the magnetization with the appropriate trigonal axis. Thus, for a given direction of magnetization, the energies associated with cobalt ions on the four types of cation sites are not in general identical. During the annealing process the cobalt ions redistribute themselves, presumably by a vacancy diffusion mechanism, over the available lattice sites in such a way as to minimize the crystal free energy. The resulting equilibrium distribution is one which produces a uniaxial anisotropy energy with the symmetry of the term in Eq. (1) whose coefficient is G. Since the energy differences among cobalt ions on various types of cation sites were attributed to an interaction between individual cobalt ions and their surroundings, the linear variation of G with cobalt concentration was readily accounted for. However, the symmetry of the octahedral lattice sites does not allow individual cobalt ions to contribute to the value of F. Penoyer and Bickford suggested that pairs of cobalt ions on adjacent cation sites might be responsible for the energy term proportional to F, noting that this hypothesis would explain the quadratic dependence of its magnitude upon cobalt content.

Several more recent studies have tended to support the above model. Slonczewski[6] has studied the origin of the spin-lattice interaction energy and has proposed a one-ion model which yields the correct temperature dependence for G. In this theory the interaction results from a coupling of the cobalt spin to the residual orbital angular momentum, which is constrained by the crystalline field to lie along the trigonal axis. The role of cation vacancies in the annealing process has been qualitatively confirmed by Bickford, Brownlow, and Penoyer[7] by comparing the annealing rates of samples in different states of oxidation. Since an excess of oxygen is known to produce cation vacancies, more rapid annealing would be expected in more highly oxidized samples if the redistribution of cobalt ions occurs by a vacancy diffusion process. Such a relation between annealing rate and degree of oxidation was observed.

In the work reported here the time dependence of the magnetic annealing effect in single crystals is investigated. The experimental technique permits observation of the effect at the annealing temperature and allows the annealing kinetics in particular crystallographic directions to be determined. Samples of low cobalt concentration are used in order to make possible interpretation of the data in terms of the redistribution of single cobalt ions and cobalt ion pairs, and to insure the relevance of the results to the static measurements of Penoyer and Bickford. Previous determinations of annealing kinetics in single crystals of low cobalt concentration[7] have not been of sufficient precision to justify detailed analysis of the results, and more recent work of good precision in crystals of high cobalt concentration[8] is not amenable to the above type of interpretation. In the present study the time dependence of the magnetic annealing effect is investigated for two crystallographic directions. The kinetics observed for the two directions are different, and the results can be interpreted to yield information about the ionic diffusion processes responsible for the uniaxial anisotropy coefficients F and G.

In the following section the experimental technique is described, and in Sec. III the results of the annealing measurements are presented. In Sec. IV the kinetic behavior resulting from the anneal-induced redistribution of single cobalt ions and cobalt ion pairs in the magnetite lattice is analyzed, and the conclusions are used in Sec. V to explain the experimental annealing curves. The results are consistent with the known concentration dependence of F and G, and permit estimates to be made of the interaction energy and torque contribution of cobalt ion pairs.

II. EXPERIMENTAL PROCEDURE

Magnetic annealing of cobalt-substituted magnetite in certain crystallographic directions produces a uniaxial torque with a node in the direction of the annealing field. If a sample is previously annealed so that the torque in one of these directions has a nonvanishing value, then this torque will diminish from its initial value to zero if it is measured at a temperature sufficiently high that magnetic annealing can occur. From observations of the time dependence of this torque decay the kinetics of the annealing process for the direction can be determined.

Torque measurements are made in the (001) plane, and the directions chosen for preparatory annealing and for the measurement of torque decay are the [100] and [110] directions. For the (001) plane, Eq. (1) may

be rewritten as follows:

$$W_u = -F(\cos^2\vartheta \, \cos^2\vartheta_A + \sin^2\vartheta \, \sin^2\vartheta_A)$$
$$-\tfrac{1}{4}G(\sin2\vartheta \, \sin2\vartheta_A),$$

where ϑ and ϑ_A are the angles with the [100] axis formed by the magnetization during a torque measurement and during annealing, respectively. The torque L_u resulting from this angular energy dependence is given by

$$L_u = -\partial W_u/\partial\vartheta = -F \sin2\vartheta \, \cos2\vartheta_A + \tfrac{1}{2}G \cos2\vartheta \, \sin2\vartheta_A.$$

It is evident from this expression that an anneal in the [110] direction produces a uniaxial contribution to the torque whose maximum amplitude is measured in the [100] direction and is equal to $G/2$. Similarly, an anneal in the [100] direction produces a uniaxial torque whose maximum amplitude is measured in the [110] direction and is equal to $-F$. In both cases, the annealing direction is one in which no torque is observed.

The kinetics of the annealing process are studied in the following manner: A sample is first annealed to saturation at a suitable temperature in the [110] direction. The direction of magnetization is then abruptly changed to the [100] direction. The torque initially measured is $G/2$. After a long time, however, the torque must disappear, since at an elevated temperature the measuring direction becomes a new annealing direction and therefore a node of the uniaxial torque curve. The intervening period is thus one in which the torque $L_{[100]}(t)$ may be observed to decay from an initial value of $G/2$ to an ultimate value of zero. After this decay is achieved, the magnetization is abruptly shifted to the [110] direction. The torque $L_{[110]}(t)$ is then observed to decay from an initial value of $-F$ to zero.

The above procedure has a number of features which particularly suit it to the study of annealing kinetics. Of primary importance is the fact that all measurements are made at the annealing temperature and for only two specific field directions, thereby eliminating the need for determining complete torque curves and for the preparatory quenching of the sample required for such measurements. Moreover, the two field directions chosen are ones in which the torque associated with the cubic anisotropy is zero, thereby permitting an adjustment of the measuring apparatus to a sensitivity appropriate to the magnitude of the uniaxial anisotropy.

The samples studied were single-crystal spheres about 2 mm in diameter of $Co_xFe_{3-x}O_4$ for which the values of x were 0.01, 0.04, 0.07, and 0.10. With the exception of those for which $x=0.10$, they were the samples used by Penoyer and Bickford, and the method of preparation and orientation are described elsewhere.[9,4] Several samples of composition $x=0.10$ in various states of oxidation were made by the following

[9] L. R. Bickford, Jr., J. M. Brownlow, and R. F. Penoyer, Proc. Inst. Elec. Engrs. (London) 104, Part B, Suppl. 5, 238 (1957).

technique: A single crystal was first grown from the melt in an atmosphere of pure CO_2. One section, without subsequent treatment, yielded a slightly oxidized sample which was designated A. A second section (sample B) was treated at 1404°C in a reducing atmosphere (29 parts CO_2 to 1 part H_2) to yield as nearly as possible a stoichiometric ferrite. A third section (sample C) was heated at 1200°C in an atmosphere of CO_2 to produce a somewhat more oxidized sample than A. The above estimates of the relative degrees of oxidation are derived from the phase diagrams of the iron-oxygen system determined by Darken and Gurry[10] and Smiltens.[11] Following heat treatment, the samples were ground into spheres and oriented.

Torque measurements were made in a magnetic field of 10 400 oersteds provided by a 6-inch Varian electromagnet which could be rotated about the sample. To shift the direction of magnetization, the rate of rotation was adjusted so as to perform the required 45° rotation in approximately 3 seconds. The torque measurements were made with the self-balancing torque magnetometer described by Penoyer.[12] Annealing temperatures were measured by a copper-constantan thermocouple and were maintained constant to ±0.1°C by an electric heater.

III. RESULTS

Curves representing the decay of the torque[13] in the [100] direction following an anneal in the [110] direction are shown in Fig. 1 for samples of various cobalt concentration. The temperature, for both annealing and measuring, was 373.7°K. Curves of the decay of $L_{[110]}$ at this temperature for the samples in which it is measurable are shown in Fig. 2. It may be seen that $L_{[100]}(t)$ and $L_{[110]}(t)$ do not decay in the same sample at identical rates, $L_{[110]}(t)$ requiring somewhat longer than $L_{[100]}(t)$ to diminish to one-half its initial value. Moreover, the curves are seen to approach single decaying exponential functions as the concentration of cobalt is reduced. The curves for $L_{[100]}(t)$ have been analyzed with the aid of a computer into the sum of three decaying exponential functions and the curves for $L_{[110]}(t)$ have been decomposed into two decaying exponential functions. The constants of the expressions $L_{[100]}(t)=A_1e^{-\lambda_1t}+A_2e^{-\lambda_2t}+A_3e^{-\lambda_3t}$ and $L_{[110]}(t)=M_1e^{-\mu_1t}+M_2e^{-\mu_2t}$ are presented in Table I.

[10] L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. 68, 798 (1946).
[11] J. Smiltens, J. Am. Chem. Soc. 79, 4877 (1957).
[12] R. F. Penoyer, Rev. Sci. Instr. 30, 711 (1959).
[13] All torque values reported in this section have been corrected for the effect of incomplete magnetic saturation of the sample. If both the magnetization and applied field lie in the (001) plane and make angles with the [100] axis of ϑ and ϑ_H, respectively, then $L(\vartheta) = |\mathbf{H}\times\mathbf{M}| = HM \sin(\vartheta-\vartheta_H)$, and consequently $\vartheta \approx \vartheta_H + L(\vartheta)/HM$. Thus one finds $L(\vartheta_H)=L(\vartheta-L(\vartheta)/HM)=L(\vartheta)[1-(dL/d\vartheta)/HM]$. Values of $dL/d\vartheta$ can be obtained from the known values of K_1, $L_{[100]}(t)$, and $L_{[110]}(t)$. It has been found experimentally that $L_{[100]}(t)$ and $L_{[110]}(t)$ grow at approximately the same rate as they decay.
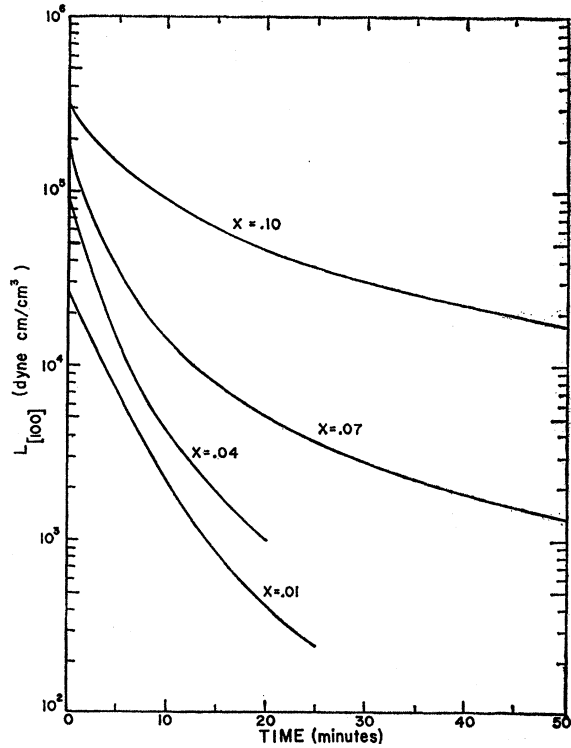
FIG. 1. Torque in the (001) plane measured in $Co_xFe_{3-x}O_4$ in the [100] direction at 373.7°K as a function of time, following a preparatory anneal in the [110] direction at the measuring temperature.

FIG. 2. Torque in the (001) plane measured in $Co_xFe_{3-x}O_4$ in the [110] direction at 373.7°K as a function of time, following a preparatory anneal in the [100] direction at the measuring temperature.
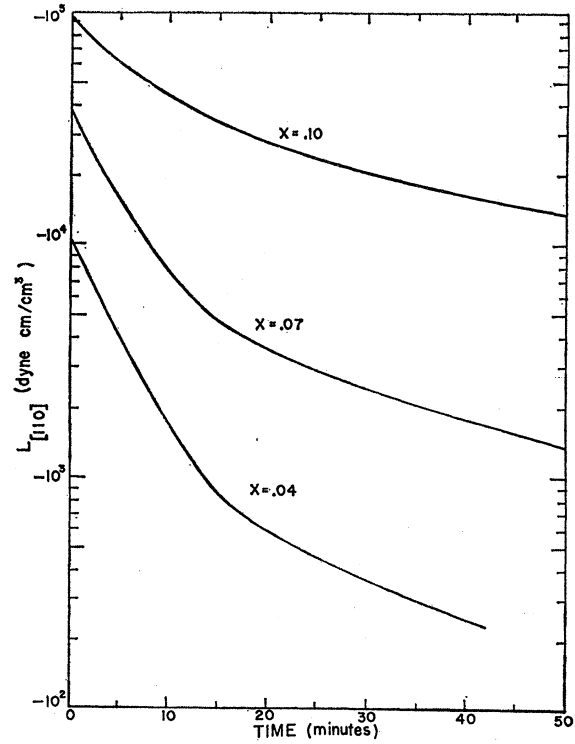
Decay curves at 351.9 and 394.7°K were obtained in addition to the ones shown in Figs. 1 and 2. The initial torque values $L_{[100]}(0)$ and $L_{[110]}(0)$, together with the half-lives of the decay processes $\tau_{\frac{1}{2}}$, are shown in Table II. Average activation energies for the decay processes were obtained by plotting $k \ln\tau_{\frac{1}{2}}$ as a function of the reciprocal of the absolute annealing temperature and determining the slope of the resulting curve. These activation energies are included in Table II. An approximately uniform value of 1.05 ± 0.03 ev is found for both annealing directions in all samples except 0.10 (B). The quantities $L_{[100]}(0)$, although obtained at higher temperatures, show the same types of concentration dependence as those found by Penoyer and Bickford for G and F, respectively. The results for samples 0.10 (A) and 0.10 (C) indicate that differences in the degree of oxidation produce differences in the

annealing rates but do not affect the magnitude of the anneal-induced anisotropy. In the stoichiometric sample 0.10 (B) a slow annealing rate together with an anomalously small anneal-induced anisotropy and activation energy are observed.

IV. THEORY OF ISOTHERMAL MAGNETIC ANNEALING

In this section the experimental rates compiled in Tables I and II are explained by assuming that the sources of the uniaxial anisotropy are various configurations of cobalt ions and determining the manner in which vacancy diffusion processes alter the concentrations of these configurations. Attention is restricted to single cobalt ions and cobalt ion pairs, since it win be shown that the important features of the data call be accounted for without considering the effects of

TABLE I. Analysis of torque decay curves.

	$L_{[100]}(t)=\Lambda_1 e^{-\lambda_1 t}+\Lambda_2 e^{-\lambda_2 t}+\Lambda_3 e^{-\lambda_3 t}$						$L_{[110]}(t)=M_1 e^{-\mu_1 t}+M_2 e^{-\mu_2 t}$			
	Λ_1	Λ_2	Λ_3	λ_1	λ_2	λ_3	M_1	M_2	μ_1	μ_2
x	(10^4 dyne cm/cm³)			(min⁻¹)			(10^4 dyne cm/cm³)		(min⁻¹)	
0.01	2.459	0.149		0.281	0.0768					
0.04	8.08	1.31		0.492	0.132		−1.009	−0.0885	0.232	0.0308
0.07	13.62	4.65	0.480	0.556	0.157	0.0228	−3.21	−0.564	0.236	0.0285
0.10(C)	18.85	9.24	2.80	0.257	0.0727	0.0123	−6.66	−2.84	0.119	0.0150
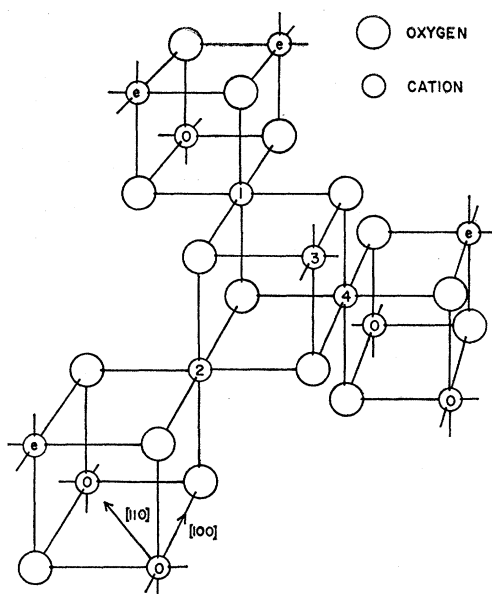
FIG. 3. The lattice of octahedrally coordinated cations and neighboring oxygen ions in a spinel.

TABLE II. Initial torque; half-lives and activation energies of torque decay.

x	T (°K)	$L_{[100]}(0)$ (10^4 dyne cm/cm³)	$\tau_{\frac{1}{2}}$ (min)	E (ev)	$L_{[110]}(0)$ (10^4 dyne cm/cm³)	$\tau_{\frac{1}{2}}$ (min)	E (ev)
0.01	351.9	3.44	18.6				
	373.7	2.60	2.58	1.02			
	394.7	1.805	0.491				
0.04	351.9	12.97	11.75		−1.42	24.6	
	373.7	9.39	1.54	1.06	−1.10	3.15	1.06
	394.7	6.12	0.268		−0.77	0.558	
0.07	351.9	26.48	12.5		−4.85	27.4	
	373.7	18.75	1.64	1.05	−3.77	3.55	1.06
	394.7	12.62	0.29		−2.84	0.62	
0.10(C)	351.9	41.0	32.0		−11.40	64.5	
	373.7	30.9	4.30	1.05	−9.51	8.40	1.06
	394.7	21.9	0.75		−7.40	1.45	
0.10(A)	373.7	31.2	17.3	1.08	−9.53	31.1	1.09
	394.7	22.6	2.89		−7.38	5.10	
0.10(B)	373.7	0.86	36.7		−0.23	45.0	
	394.7	0.73	9.2	0.87	−0.23	11.8	0.83
	415.2	0.62	2.5		−0.24	3.4	

larger agglomerations. The term "single cobalt ion" is used to denote those individual cobalt ions whose nearest cation neighbors consist entirely of iron ions. The term "cobalt ion pairs" is applied to similarly surrounded groups of two adjacent cobalt ions. The lattice of octahedral sites in a spinel is shown in Fig. 3.

a. The Annealing Kinetics

Case I. Magnetization in the [100] direction

To determine the torque in the (001) plane that one would measure with the magnetization in the [100] direction, the cobalt ion configurations which are capable of contributing a torque under these circumstances must be first ascertained. One observes that a 180° rotation about the [100] axis results in a reversal of the sign of the measured torque, since this is equivalent to a reversal of the sign of all components of a vector that are normal to the magnetization direction. The torque reversal resulting from the above operation extends to the individual torque contributions of any given cation or group of cations. It follows therefore that any cation configuration which retains its identity after a 180° rotation about the [100] axis is incapable of contributing a torque in this case.

If a single cobalt ion is placed on any of the odd-numbered sites or those marked o, a possibly nonvanishing torque L_I^o will be produced in the (001) plane, since the rotation described above would transfer the ion to a site with an even number or marked e. The odd sites are all equivalent, since their surroundings are either identical or differ only by a reflection through the measuring plane. The even sites are similarly equivalent. A single ion on an even site will contribute a

torque $-L_I^o$, since the ion could be transferred to an odd site by a 180° rotation of the crystal about the [100] axis.

Cobalt ion pairs can assume the six orientations possessed by all possible pairs of numbered sites in Fig. 3. Cobalt pairs 14 and 23 can make no torque contribution in case I since they retain their identity under the 180° rotation described above. Pairs 12 and 34 make no contribution for the following reason: a 180° rotation about the magnetization direction transforms a 12 pair into a 34 pair, and thus, the torque contribution of a 12 pair must be the negative of that of a 34 pair. However, the torque of a 12 pair is unchanged by a reversal of the magnetization direction, and since the torque contributed by a 12 pair following such a reversal is the same as that of a 34 pair before the reversal, the torque contributions of a 12 pair and a 34 pair must be identical. These two requirements can be met only if the torque contributions are zero.

13 pairs do not retain their identity following a 180° rotation of the crystal about the [100] axis and can thus contribute a possibly nonvanishing torque L_I^{13}. Since 24 pairs are transformed into 13 pairs by the rotation, the torque of a 24 pair is $-L_I^{13}$.

The torque per unit volume in the (001) plane for the magnetization in the [100] direction can now be written

$$L_{[100]} = \frac{N\rho}{M}[(c_o - c_e)L_I^o + (c_{13} - c_{24})L_I^{13}], \qquad (2)$$

where c_o and c_e are the molar concentrations of single cobalt ions on odd and even sites, respectively, c_{13} and c_{24} are the concentrations of cobalt ion pairs of the type designated by the subscript, N is Avogadro's number, ρ is the density, and M is the molecular weight.

The presence of vacancies on the octahedral cation sites will allow the various cobalt ion configurations to

change their identity, since there is a finite probability that any given configuration will have a vacancy on a neighboring lattice site and that this vacancy will interchange sites with a cobalt ion. Since the concentration of vacancies is fixed, this probability will remain constant throughout the course of an anneal. It is evident from Fig. 3 that the jumps of cobalt ions from one site to an adjacent one can convert any cobalt ion configuration, whether a single cobalt ion or a cobalt ion pair, into any other configuration. These jumps not only allow single cobalt ions to change the type of site on which they are located, but permit them to combine to form pairs of all possible orientations. Similarly, cobalt ion pairs cannot only change their orientation, but can break up to form two single cobalt ions. Thus, there is a finite probability that within a given time any configuration will lose its identity and contribute to the concentration of any other type of configuration. The rate of change of the concentration of any given type of configuration will consequently depend upon the concentration of all other configurations.

The rate of change of the concentration of cobalt ions on odd sites can be written as follows:

$$\frac{dc_o}{dt} = -c_o[p_o{}^e(1-2c_o-c_e) + \sum_{i>j} (2c_o p_{o,o}{}^{ij} + c_e p_{o,e}{}^{ij})]$$
$$+ c_e p_e{}^o(1-2c_e-c_o) + \sum_{ij} c_{ij}p_{ij}{}^o. \quad (3)$$

$p_o{}^e$ is the probability per unit time that a single cobalt ion on an odd site jumps to an adjacent even site, and the factor $(1-2c_o-c_e)$ approximates the probability that the adjacent even site has no other cobalt neighbors. $p_e{}^o$ is the corresponding transition probability for the reverse process. $c_o{}^2 p_{o,o}{}^{ij}$ is the rate at which ij pairs are formed as a result of the combining of two cobalt ions on odd sites. $c_o c_e p_{o,e}{}^{ij}$ is the corresponding rate for ij pair formation resulting from the combination of an odd-site and an even-site cobalt ion. $p_{ij}{}^o$ is the probability per unit time that an ij cobalt ion pair produces a single cobalt ion on an odd site as a result of breaking up.

The rate of change of the concentration of cobalt ions on even sites can be similarly written

$$\frac{dc_e}{dt} = -c_e[p_e{}^o(1-2c_e-c_o) + \sum_{i>j} (2c_e p_{e,e}{}^{ij} + c_o p_{o,e}{}^{ij})]$$
$$+ c_o p_o{}^e(1-2c_o-c_e) + \sum_{i>j} c_{ij}p_{ij}{}^e. \quad (4)$$

The symmetry of the lattice, however, is such that

$$p_o{}^e = p_e{}^o,$$
$$\sum_{i>j} p_{o,o}{}^{ij} = \sum_{i>j} p_{e,e}{}^{ij},$$
$$p_{12}{}^o = p_{12}{}^e = p_{34}{}^o = p_{34}{}^e,$$
$$p_{14}{}^o = p_{14}{}^e = p_{23}{}^o = p_{23}{}^e,$$
$$p_{13}{}^o = p_{24}{}^e,$$

and
$$p_{13}{}^e = p_{24}{}^o.$$

One thus obtains

$$\frac{d(c_o-c_e)}{dt} = -2(c_o-c_e)p_o{}^e - (c_o{}^2-c_e{}^2)(\sum_{i>j} 2p_{o,o}{}^{ij} - 4p_o{}^e)$$
$$+ \sum_{i>j} c_{ij}(p_{ij}{}^o - p_{ij}{}^e)$$
$$= -2(c_o-c_e)[p_o{}^e + (c_o+c_e)(\sum_{i>j} p_{o,o}{}^{ij} - 2p_o{}^e)]$$
$$+ (c_{13}-c_{24})(p_{13}{}^o - p_{13}{}^e). \quad (5)$$

The rate of change of the concentration of 13 cobalt ion pairs is given by

$$\frac{dc_{13}}{dt} = -c_{13}\left[\frac{p_{13}{}^o + p_{13}{}^e}{2} + \sum_{i>j}' p_{13}{}^{ij}\right] + c_o c_e p_{o,e}{}^{13}$$
$$+ c_o{}^2 p_{o,o}{}^{13} + c_e{}^2 p_{e,e}{}^{13} + \sum_{i>j}' c_{ij}p_{ij}{}^{13}, \quad (6)$$

where $p_{ij}{}^{mm}$ is the probability per unit time that an ij pair becomes an mm pair, and the prime signifies exclusion of the specified pair from the summation indices.

The rate of change of the concentration of 24 pairs is given by

$$\frac{dc_{24}}{dt} = -c_{24}\left[\frac{p_{24}{}^o + p_{24}{}^e}{2} + \sum_{i>j}' p_{24}{}^{ij}\right] + c_o c_e p_{o,e}{}^{24}$$
$$+ c_o{}^2 p_{o,o}{}^{24} + c_e{}^2 p_{e,e}{}^{24} + \sum_{i>j}' c_{ij}p_{ij}{}^{24}. \quad (7)$$

The symmetry of the lattice requires further that

$$\sum_{i>j}' p_{24}{}^{ij} = \sum_{i>j}' p_{13}{}^{ij},$$
$$p_{12}{}^{13} = p_{12}{}^{24} = p_{34}{}^{13} = p_{34}{}^{24},$$
$$p_{14}{}^{13} = p_{14}{}^{24} = p_{23}{}^{13} = p_{23}{}^{24},$$
$$p_{o,e}{}^{13} = p_{o,e}{}^{24},$$

and
$$p_{o,o}{}^{13} = p_{e,e}{}^{24}.$$

Since the processes represented by the probabilities $p_{13}{}^{24}$, $p_{24}{}^{13}$, $p_{o,o}{}^{24}$ and $p_{e,e}{}^{24}$, and $p_{e,e}{}^{13}$ cannot occur by single jumps, they may be taken as zero. Upon subtracting Eq. (7) from Eq. (6), one obtains

$$\frac{d(c_{13}-c_{24})}{dt} = -(c_{13}-c_{24})\left[\frac{p_{13}{}^o + p_{13}{}^e}{2} + \sum_{i>j}' p_{13}{}^{ij}\right.$$
$$\left. + (c_o-c_e)(c_o+c_e)p_{o,o}{}^{13}\right]. \quad (8)$$

Equation (5) may be rewritten

$$dy/d\delta = -\alpha y + \beta z, \quad (9)$$

where

$$y = (c_o - c_e),$$

$$z = (c_{13} - c_{24}),$$

$$\alpha = 2[p_o{}^e + (c_o + c_e)(\sum_{i>j} p_{o,o}{}^{ij} - 2p_o{}^e)],$$

$$\beta = p_{13}{}^o - p_{13}{}^e.$$

Equation (8) may be rewritten

$$dz/dt = -\gamma z + \delta y, \qquad (10)$$

where

$$\gamma = \frac{p_{13}{}^o + p_{13}{}^e}{2} + \sum_{i>j} p_{13}{}^{ij},$$

$$\delta = (c_o + c_e) p_{o,o}{}^{13}.$$

Since $(c_o + c_e)$ is essentially constant during the annealing process, the quantities α, β, γ, and δ can also be taken as constants. Equations (9) and (10) thus constitute a pair of ordinary differential equations with constant coefficients and can be solved by well-known techniques. Solution of these equations yelds the following expression for the torque:

$$L_{[100]}(t) = \frac{N\rho}{M}(\Lambda_1 e^{-\lambda_1 t} + \Lambda_2 e^{-\lambda_2 t}), \qquad (11)$$

where

$$\lambda_1 = \frac{\alpha + \gamma}{2} + \left[\left(\frac{\alpha + \gamma}{2}\right)^2 - (\alpha\gamma - \beta\delta)\right]^{\frac{1}{2}} \approx \alpha + \frac{\beta\delta}{\alpha - \gamma}, \qquad (12)$$

$$\lambda_2 = \frac{\alpha + \gamma}{2} - \left[\left(\frac{\alpha + \gamma}{2}\right)^2 - (\alpha\gamma - \beta\delta)\right]^{\frac{1}{2}} \approx \gamma - \frac{\beta\delta}{\alpha - \gamma}, \qquad (13)$$

$$\Lambda_1 = \frac{[(\lambda_2 - \alpha)y_o + \beta z_o]L_I{}^o + [(\lambda_2 - \gamma)z_o + \delta y_o]L_I{}^{13}}{\lambda_2 - \lambda_1}, \qquad (14)$$

and

$$\Lambda_2 = \frac{[-(\lambda_1 - \alpha)y_o - \beta z_o]L_I{}^o + [-(\lambda_1 - \gamma)z_o - \delta y_o]L_I{}^{13}}{\lambda_2 - \lambda_1}. \qquad (15)$$

y_0 and z_0 are the initial values of y and z, respectively. Equations (11)–(15) show that torque decay in the [100] direction results from the liquidation of any differences of c_o and c_e and of c_{13} and c_{24} which may have initially existed.

Case II. Magnetization in the [110] direction

In order to obtain an expression for the torque, under the conditions of case II, the contributing configurations must be determined as for case I. The torque-reversing operation chosen for this purpose will be a reflection of the crystal through the (110) plane. All single cobalt ions retain their identity following this operation and thus do not contribute to the torque. 13 and 24 pairs are similarly unaffected. 12 and 14 pairs interchange identities, and thus $L_{II}{}^{12} = -L_{II}{}^{14}$. Sim-

ilarly, one finds $L_{II}{}^{23} = -L_{II}{}^{34}$. The torque of a 12 pair is unchanged by a reversal of the magnetization direction, and thus $L_{II}{}^{12} = L_{II}{}^{34}$. The total torque under the conditions of case II can now be written

$$L_{[110]} = \frac{N\rho}{M}(c_{12} + c_{34} - c_{14} - c_{23})L_{II}{}^{12}. \qquad (16)$$

The rate of change of the concentration of 12 pairs is given by

$$\frac{dc_{12}}{dt} = -c_{12}\left[\frac{q_{12}{}^o + q_{12}{}^e}{2} + \sum_{i>j}{}' q_{12}{}^{ij}\right] + c_o{}^2 q_{o,o}{}^{12}$$
$$+ c_e{}^2 p_{e,e}{}^{12} + c_o c_e p_{o,e}{}^{12} + \sum_{i>j}{}' c_{ij} p_{ij}{}^{12},$$

where the q's denote quantities appropriate to the conditions of case II which correspond to those designated by p's for the conditions of case I. Similar expressions can be written for the rates of change of the concentrations c_{14}, c_{23}, and c_{34}. Symmetry requires that

$$q_{12}{}^o = q_{14}{}^o = q_{23}{}^o = q_{34}{}^o,$$

$$q_{12}{}^e = q_{14}{}^e = q_{23}{}^e = q_{34}{}^e,$$

$$q_{o,o}{}^{12} = q_{o,o}{}^{23} = q_{o,o}{}^{14} = q_{o,o}{}^{34},$$

$$q_{e,e}{}^{12} = q_{e,e}{}^{23} = q_{e,e}{}^{14} = q_{e,e}{}^{34},$$

$$q_{o,e}{}^{12} = q_{o,e}{}^{23} = q_{o,e}{}^{14} = q_{o,e}{}^{34},$$

$$q_{12}{}^{14} = q_{14}{}^{12} = q_{23}{}^{34} = q_{34}{}^{23},$$

$$q_{12}{}^{23} = q_{23}{}^{12} = q_{14}{}^{34} = q_{34}{}^{14}.$$

Upon applying these conditions, one obtains

$$d(c_{12} + c_{34} - c_{14} - c_{23})/dt = -(c_{12} + c_{34} - c_{14} - c_{23})$$
$$\times [\tfrac{1}{2}(q_{12}{}^o + q_{12}{}^e) + 2(q_{12}{}^{14} + q_{12}{}^{23}) + q_{12}{}^{13} + q_{12}{}^{24}].$$

The solution of the above equation is

$$(c_{12} + c_{34} - c_{14} - c_{23}) = (c_{12} + c_{34} - c_{14} - c_{23})_{t=0}e^{-\mu t}, \qquad (17)$$

where

$$\mu = \tfrac{1}{2}(q_{12}{}^o + q_{12}) + 2(q_{12}{}^{14} + q_{12}{}^{23}) + q_{12}{}^{13} + q_{12}{}^{24}.$$

Substituting Eq. (17) into Eq. (16), one obtains

$$L_{[110]}(t) = L_{[110]}(0)e^{-\mu t}. \qquad (18)$$

It is evident from Eq. (17) that torque decay in the [110] direction results from the liquidation of any differences of c_{12} and c_{14} and of c_{23} and c_{34} which may have initially existed.

b. The Equilibrium Configuration Concentrations

In order to determine the initial torque in a given crystallographic direction, the configuration concentrations resulting from an infinitely long magnetic anneal in the preparatory annealing direction must be specified. To do this, one must first find the energy contribution of

each cobalt ion configuration. From these energies the configuration concentrations existing under conditions of thermal equilibrium can be determined by the methods of statistical mechanics.

If the magnetization is in the (001) plane, the free energy of a cobalt ion configuration can be written as a Fourier series composed of functions of multiples of 2ϑ. Experimental results and the theoretical work of Slonczewski indicate that the coefficients of functions of 4ϑ and higher multiples of 2ϑ are negligible relative to the coefficients of 2ϑ, and the free energy change resulting from the replacement of an iron ion on an odd site by a cobalt ion can therefore be written in the following useful form:

$$\mathfrak{F}_o = \nu_s - \tfrac{1}{2}L_I{}^o \sin 2\vartheta. \tag{19}$$

In the above expression the symmetry of the lattice is used to exclude a function of $\cos 2\vartheta$, and the coefficient of $\sin 2\vartheta$ is made to correspond to the torque designation of the previous section. The free energies of the other configurations are as follows:

$$\mathfrak{F}_e = \nu_s + \tfrac{1}{2}L_I{}^o \sin 2\vartheta, \tag{20}$$

$$\mathfrak{F}_{12} = \mathfrak{F}_{34} = \nu_p + \tfrac{1}{2}L_{II}{}^{12} \cos 2\vartheta, \tag{21}$$

$$\mathfrak{F}_{14} = \mathfrak{F}_{23} = \nu_p - \tfrac{1}{2}L_{II}{}^{12} \cos 2\vartheta, \tag{22}$$

$$\mathfrak{F}_{13} = \nu_p + \tfrac{1}{2}L_{II}{}^{12} - \tfrac{1}{2}L_I{}^{13} \sin 2\vartheta, \tag{23}$$

$$\mathfrak{F}_{24} = \nu_p + \tfrac{1}{2}L_{II}{}^{12} + \tfrac{1}{2}L_I{}^{13} \sin 2\vartheta. \tag{24}$$

In the derivation of Eqs. (23) and (24), use is made of the fact that for $\vartheta = 0$, $\mathfrak{F}_{13} = \mathfrak{F}_{12}$.

The above energies can now be used to calculate the equilibrium configuration concentrations. By using the results of Yvon,[14] the probability of finding two adjacent cobalt ions can be shown for small cobalt concentrations x to be

$$n_p = \frac{1 + x(w-1) - [(1-x)^2 + 2x(1-x/2)w]^{\frac{1}{2}}}{2(w-1)}. \tag{25}$$

where

$$w = \exp(-\Delta \mathfrak{F}_{ij}/kT),$$

and $\Delta \mathfrak{F}_{ij}$ is the energy required to bring an odd and an even cobalt ion together to form an ij pair. One may may write $\Delta \mathfrak{F}_{ij}$ as follows:

$$\Delta \mathfrak{F}_{ij} = \mathfrak{F}_{ij} - (\mathfrak{F}_0 + \mathfrak{F}_e) = \Delta \nu + \zeta_{ij},$$

where

$$\Delta \nu = \nu_p - 2\nu_s,$$

and

$$\zeta_{ij} = \mathfrak{F}_{ij} - \nu_p.$$

As was shown by Néel,[15] the right-hand side of Eq. (25) can be expanded about the point $\zeta_{ij} = 0$, and if $\zeta_{ij} \ll \Delta \nu$, one obtains the approximation

$$n_p(\Delta \nu, \zeta_{ij}) = n_p(\Delta \nu, 0) - S\zeta_{ij}/kT, \tag{26}$$

[14] J. Yvon, Cahiers phys. 28, 1 (1945).
[15] L. Néel, J. phys. radium 15, 22 (1954).

where

$$S = \frac{dn_p}{d(-\zeta/kT)} = \frac{x^2(1-x/2)^2 e^{-\Delta\nu/kT}}{(1+\Omega)^{\frac{1}{2}}[1+(1-\Omega)^{\frac{1}{2}}]^2}, \tag{27}$$

and

$$\Omega = 2x(1-x/2)(e^{-\Delta\nu/kT} - 1). \tag{28}$$

After all pair concentrations have been determined by this procedure, the total concentration of single cobalt ions can be found by subtracting twice the pair concentrations from the total cobalt ion concentration, since it has been assumed that the concentration of agglomerations larger than pairs is negligible. The relative concentration of odd and even cobalt ions can then be determined from the single ion energies by statistical mechanics.

After a long anneal in the [100] direction at temperature T, the configuration concentrations are the following:

$$c_{12} = c_{34} = c_{13} = c_{24} = n_p(\Delta\nu, 0) - SL_{II}{}^{12}/2kT,$$

$$c_{14} = c_{23} = n_p(\Delta\nu, 0) + SL_{II}{}^{12}/2kT,$$

$$c_0 = c_e = \tfrac{1}{2}x - [6n_p(\Delta\nu, 0) - SL_{II}{}^{12}/kT].$$

These concentrations, being the ultimate ones for Case I, are the initial concentrations for Case II. From Eqs. (16) and (17), the initial torque measured after the magnetization is rotated to the [110] direction is

$$L_{[110]}(0) = -2(N\rho/MkT)S(L_{II}{}^{12})^2. \tag{29}$$

The ultimate concentrations resulting from a long anneal in the [110] direction are the following:

$$c_{13} = n_p(\Delta\nu, 0) - S(L_{II}{}^{12} - L_I{}^{13})/2kT,$$

$$c_{24} = n_p(\Delta\nu, 0) - S(L_{II}{}^{12} + L_I{}^{13})/2kT,$$

$$c_{12} = c_{34} = c_{14} = c_{23} = n_p(\Delta\nu, 0),$$

$$c_0 = \{\tfrac{1}{2}x - [6n_p(\Delta\nu, 0) - SL_{II}{}^{12}/kT]\}(1 + L_I{}^o/2kT),$$

$$c_e = \{\tfrac{1}{2}x - [6n_p(\Delta\nu, 0) - SL_{II}{}^{12}/kT]\}(1 - L_I{}^o/2kT).$$

These concentrations are the initial ones for Case I. The torque initially measured with the magnetization direction in the [100] direction is thus

$$L_{[100]}(0) = (N\rho/MkT)\{[\tfrac{1}{2}x - (6n_p(\Delta\nu, 0) + SL_{II}{}^{12}/kT)](L_I{}^o)^2 + S(L_I{}^{13})^2\}. \tag{30}$$

The concentration dependence of $L_{[100]}(0)$ observed at low concentration can be used to determine $L_I{}^o$. Using the data of Table II, one obtains for $T = 373.7°K$ the value $L_I{}^o = 4.46 \times 10^{-15}$ dyne cm.

V. THE CORRESPONDENCE OF THEORY WITH EXPERIMENT

The theory of the magnetic annealing effect presented in the two preceding sections explains many of the results summarized in Tables I and II. Equation (11) indicates that the torque decay in the [100] direction can be represented by the sum of two exponential functions of initial magnitudes Λ_1 and Λ_2 and rate coefficients λ_1

and λ_2. From Eqs. (12) and (13) it can be seen that, since δ is proportional to x, at sufficiently low cobalt concentrations $\lambda_1 = \alpha$ and $\lambda_2 = \gamma$. Since α becomes independent of concentration as the cobalt content is reduced, the ratio λ_1/λ_2 should be a constant at sufficiently low cobalt concentrations. From Eq. (14) it can be seen that at low concentrations, $\Lambda_1 \approx y_0 L_{\mathrm{I}}^\circ$. Since for small values of x, y_0 is proportional to x, Λ_1 is also proportional to x. Moreover, since $[(\lambda_1-\alpha)L_{\mathrm{I}}^\circ + \delta L_{\mathrm{I}}^{13}]y_0$ and $[\beta L_{\mathrm{I}}^\circ + (\lambda_1-\gamma)L_{\mathrm{I}}^{13}]z_0$ are proportional to x^2, the ratio Λ_2/Λ_1 approaches zero as x is reduced. These features of the theoretically expected low-concentration annealing behavior are observed in the experimentally determined curves of $L_{[100]}(t)$ throughout the concentration range studied. It may be seen in Table I that the ratio λ_1/λ_2 has the approximately uniform value of 3.6. The value of Λ_1 is observed to have a nearly linear dependence on x, and Λ_2 is roughly proportional to x^2. The magnitude of the third decaying exponential function, when it appears at all, is small and probably reflects the presence of clusters of three or more adjacent cobalt ions, the effects of which are not taken into account by the theory.

Equation (18) indicates that the torque decay in the [110] direction should occur by a single exponential process. At low cobalt concentrations the magnitude of $L_{[110]}(0)$ should be proportional to x^2, and the rate coefficient μ_1 should be independent of concentration, making the ratio of μ_1/λ_2 a constant. These characteristics are observed in the experimentally determined annealing curves. The value of M_1 is roughly proportional to x^2. The second decaying exponential function probably results from the presence of cobalt ion clusters. A ratio μ_1/λ_2 of 1.6 which is constant to within $\pm 7\%$ is observed. Although the decay processes governed by λ_2 and μ_1 result from the breakup or reorientation of cobalt ion pairs, their values are not approximately equal because the four pairs adjacent to a *13* pair do not contribute to $L_{[100]}(t)$, and thus λ_2 contains only four reorientation probabilities; on the other hand, two of the four pairs adjacent to a *12* pair contribute the negative of L_{II}^{12} during the decay of $L_{[100]}(t)$, and consequently two reorientation probabilities must be doubly weighted, yielding a total of six reorientation probabilities for μ_1.

It should be noted that in the preceding section no restrictions have been placed on the form of the energy of a cobalt ion pair other than those which can be inferred from the symmetry of the lattice. Equations (22) – (24) indicate that the pair energy can be approximated by an ellipsoid. One of the semi-axes lies along the line joining the two cobalt ions and has a length $\nu_p + \frac{1}{2}(L_{\mathrm{II}}^{12} - L_{\mathrm{II}}^{13})$. Of the two orthogonal semiaxes, one is perpendicular to a cube face and has a length $\nu_p - \frac{1}{2}L_{\mathrm{II}}^{12}$; the other is parallel to a face diagonal and has a length $\nu_p + \frac{1}{2}(L_{\mathrm{II}}^{12} + L_{\mathrm{I}}^{13})$. The assumption that the interaction between cobalt ions is direct requires that the energy be an ellipsoid of revolution about the axis joining the

cobalt ions, or that $L_{\mathrm{I}}^{13} = -2L_{\mathrm{II}}^{12}$. Equations (29) and (30) show that such a relation implies that the contribution of pairs to the torque in the [100] direction is twice that of pairs to the torque in the [110] direction and, if the depletion of the single ion concentrations by the formation of pairs is negligible, that $L_{[100]} + 2L_{[110]}$ (or $\frac{1}{2}G - 2F$) would be proportional to the cobalt concentration. The results of Penoyer and Bickford and the values of Table II both show that such a proportionality does not exist. However, the absence of such a proportionality does not indicate that the exchange between cobalt ions takes place exclusively *via* adjacent oxygen ions, as has been proposed by Smit and Wijn.[16] Such an assumption would require that L_{I}^{13} be zero. The data in this paper, unfortunately, do not allow an evaluation of this quantity.

If the magnetic annealing effects are attributed to vacancy diffusion processes, one would expect that the magnitude of all jump probabilities and hence all rate coefficients should be proportional to the vacancy concentration, but that the magnitude of the anneal-induced anisotropy should be independent of the vacancy content. Such behavior is observed for the samples A and C of $Co_{0.10}Fe_{2.90}O_4$ in which the rate of annealing corresponds roughly to the degree of oxidation, but the values of $L_{[100]}(0)$ and $L_{[110]}(0)$ are essentially uniform. The small torque magnitude observed in sample B, which was heated in a reducing atmosphere to produce a stoichiometric sample, cannot be explained by the theory of Secs. IV *a* and *b*, and in view of the anomalously low activation energy observed, the possibility must be considered that the observed torque changes do not result from the vacancy diffusion of cobalt ions.

VI. THE COBALT ION PAIR INTERACTION

In this section the cobalt ion pair interaction energy $\Delta\nu$ will be evaluated by determining the temperature dependence of the pair concentrations from observations of the dependence of the torque in the [110] direction on the preparatory annealing temperature.

If a sample of magnetite containing a small amount of substituted cobalt is annealed in the [100] direction at temperature T, the torque initially measured in the [110] direction at the same temperature is given by Eq. (29). Values of $L_{[110]}$ obtained for a number of temperatures will determine a curve whose slope is

$$\frac{dL_{[110]}}{dT} = L_{[110]}\left[\frac{2}{L_{\mathrm{II}}^{12}}\frac{dL_{\mathrm{II}}^{12}}{dT} + \frac{kT}{S}\frac{d}{dT}\left(\frac{S}{kT}\right)\right].$$

If the sample is annealed at temperature T_Q and then quenched to prevent further ionic diffusion, the configuration concentrations characteristic of thermal equilibrium at T_Q will be retained. If the torque in

[16] J. Smit and H. P. J. Wijn, *Ferrites* (John Wiley & Sons, Inc., New York, 1959), Chap. VIII, p. 168.

the [110] direction is then measured at a temperature T which is different from T_Q, it will no longer be given by Eq. (29), but by the expression

$$L_{[110]Q} = -(2N\rho/MkT_Q)S(T_Q)L_{II}{}^{12}(T_Q)L_{II}{}^{12}(T).$$

$L_{[110]Q}$ is also the maximum amplitude of the uniaxial torque in the (001) plane and can be determined from a torque curve measured at a temperature which is sufficiently low to prevent magnetic annealing. Values of $L_{[110]Q}$ measured at a number of temperatures will determine a curve whose slope is

$$\frac{dL_{[110]Q}}{dT} = \frac{L_{[110]Q}}{L_{II}{}^{12}(T)} \frac{dL_{II}{}^{12}}{dT}.$$

The curve of values of $L_{[110]Q}$ can be extrapolated to make the required intersection with the curve of values of $L_{[110]}$ at $T = T_Q$. At this temperature

$$\left(\frac{dL_{[110]}}{dT}\right)_{T_Q} = \left[2\frac{dL_{[110]Q}}{dT} + L_{[110]}\frac{kT}{S}\frac{d}{dT}\left(\frac{S}{kT}\right)\right]_{T_Q}. \quad (31)$$

If $\Delta\nu \geqslant 0$ and the concentration of cobalt is small, one finds from Eqs. (27) and (28) that

$$S \approx \tfrac{1}{4}x^2(1 - \tfrac{1}{2}x)^2 e^{-\Delta\nu/kT}. \quad (32)$$

$\Delta\nu$ is therefore given by

$$\Delta\nu = kT_Q\left[1 + \frac{T}{L_{[110]}}\left(\frac{dL_{[110]}}{dT} - 2\frac{dL_{[110]Q}}{dT}\right)\right]_{T_Q}. \quad (33)$$

The above experiment was performed with the sample of $Co_{0.04}Fe_{2.96}O_4$. A sample of low cobalt concentration was chosen to insure that the effects of clusters of three or more cobalt ions would be negligible, and the small departure of $L_{[110]}(t)$ in $Co_{0.04}Fe_{2.95}O_4$ from a simple exponential decay indicates that this requirement is largely satisfied. The sample was first annealed to saturation in the [100] direction at 373.7°K and then quenched with liquid nitrogen. Torque curves were then determined at temperatures between 158°K and 288°K. The magnitude of the uniaxial component of these curves is $L_{[110]Q}$, and the results are plotted as the open circles of Fig. 4. The data of Table II are plotted as the solid dots and determine the curve of $L_{[110]}$. The curve of $L_{[110]Q}$ is extrapolated to give a common torque value of -1.10×10^4 dyne cm/cm³ at $T = 373.7°K$. The value of $dL_{[110]Q}/dT$ at this temperature is $(1.04 \pm 0.01) \times 10^2$ dyne cm/cm³ °K and the value of $dL_{[110]}/dT$ is $(1.52 \pm 0.03) \times 10^2$ dyne cm/cm³ °K. The value of $\Delta\nu$ is found from Eq. (33) to be 0.093 ± 0.04 ev. This value of $\Delta\nu$ can be used in Eq. (32) to evaluate $S(T_Q)$, which can in turn be used in Eq. (29) to calculate $L_{II}{}^{12}(T_Q)$. The value obtained for $L_{II}{}^{12}$ at 373.7°K is $(3.14 \pm 0.20) \times 10^{-14}$ dyne cm.
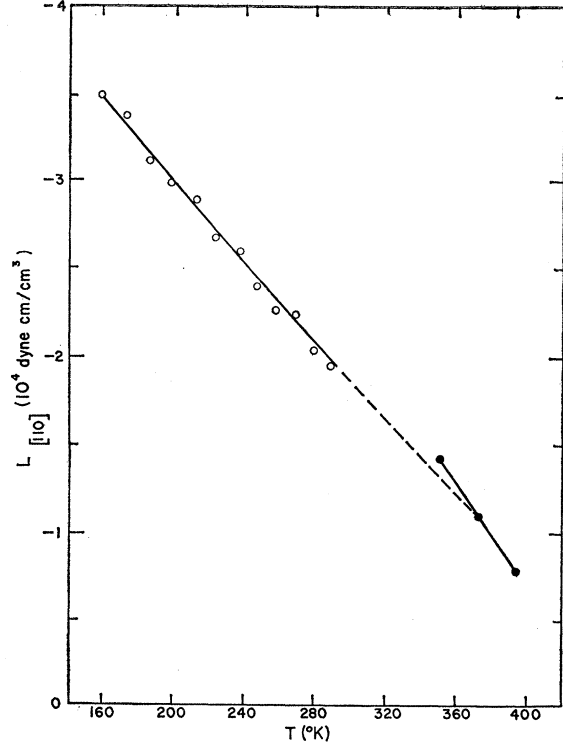

FIG. 4. The torque in $Co_{0.04}Fe_{2.96}O_4$ measured in the [110] direction following a preparatory anneal in the [100] direction at 373.7°K which is terminated by quenching the sample (open circles), and the torque in the [110] direction following a preparatory anneal in the [100] direction at the measuring temperature (solid dots).

The two types of measurements described above can be performed also for an anneal in the [110] direction. Following such an anneal, the initial torque in the [100] direction at the annealing temperature can, from Eq. (30), be approximated at low concentrations by

$$L_{[100]Q} = (N\rho x/2MkT)[L_I{}^0(T)]^2.$$

Following an anneal in the [110] direction at temperature T_Q which is terminated by quenching the sample, the torque measured in the [100] direction at temperature T is

$$L_{[100]Q} = (N\rho x/2MkT_Q)L_I{}^0(T_Q)L_I{}^0(T).$$

The relationship between the slopes of $L_{[100]}$ and $L_{[100]Q}$ at temperature T_Q can be shown to be

$$\left(\frac{dL_{[100]}}{dT}\right)_{T_Q} = \left(2\frac{dL_{[100]Q}}{dT} - \frac{L_{[100]}}{T}\right)_{T_Q}. \quad (34)$$

In contrast to the slope relationship of Eq. (31), which contains an unknown interaction energy $\Delta\nu$ and can be used for the determination of this energy, Eq. (34) for an anneal in the [110] direction contains only directly measurable quantities. The two types of torque measurements have been made for the sample of
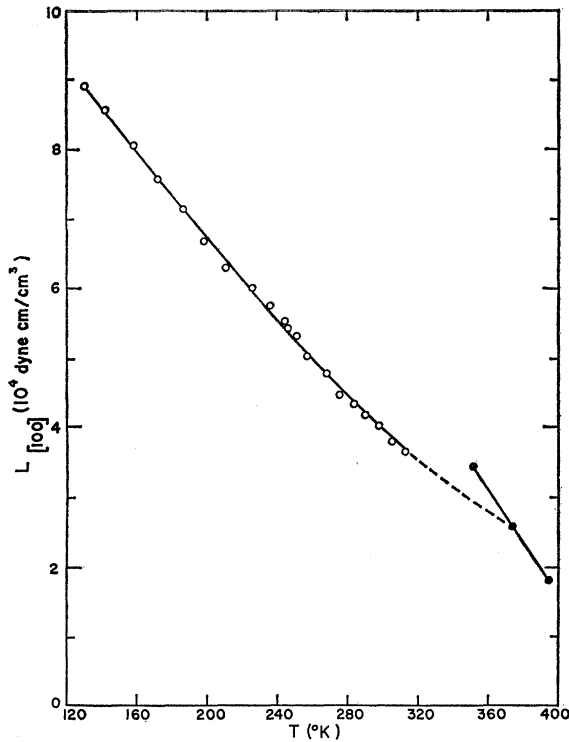
FIG. 5. The torque in $Co_{0.01}Fe_{2.99}O_4$ measured in the [100] direction following a preparatory anneal in the [110] direction at 373.7°K which is terminated by quenching the sample (open circles), and the torque in the [100] direction following a preparatory anneal in the [110] direction at the measuring temperature (solid dots).

$Co_{0.01}Fe_{2.99}O_4$, which was chosen to insure a small concentration of cobalt ion pairs. The results are shown in Fig. 5. A quench temperature of 373.7°K was used, and values of $dL_{[100]Q}/dT = -1.59 \times 10^2$ dyne cm/cm^3 °K, and $L_{[100]} = 2.60 \times 10^4$ dyne cm/cm^3 at this temperature were obtained. By using the experimental values of $dL_{[100]Q}/dT$ and $L_{[100]}$ in Eq. (34), one obtains a value for $dL_{[100]}/dT$ of -3.78×10^2 dyne cm/cm^3 °K, which is in good agreement with the observed value of -3.82×10^4 dyne cm/cm^3 °K.

VII. CONCLUSIONS

The satisfactory correspondence of the experimental observations with the theory of Sec. IV probably justifies the following inferences regarding the nature of the annealing effect:

1. Magnetic annealing in the [110] direction produces differences in the numbers of single cobalt ions on odd and even octahedral sites and in numbers of 13 and 24 pairs, thereby giving rise to the noncubic energy term proportion to G. The decay of the torque in the (001) plane observed at elevated temperatures with the magnetization in the [100] direction results from the liquidation of these concentration differences. This decay occurs largely by two exponential processes, the rate coefficient of the first process being determined primarily by the probability that single cobalt ions change the type of site on which they are located and that of the second process being determined primarily by the rate of reorientation and breakup of cobalt ion pairs.

2. Magnetic annealing in the [100] direction produces differences in the number of 12, 34, 14, and 23 pairs, thereby giving rise to the noncubic energy term proportional to F. The torque decay in the [110] direction results from the liquidation of these concentration differences and can be approximated by a single exponential process whose rate coefficient depends upon the rate of reorientation and breakup of pairs.

3. The increased rate of annealing corresponding to higher degrees of sample oxidation indicates that the annealing effect results from vacancy diffusion processes. The absence of a large annealing effect in a stoichiometric sample further supports the vacancy diffusion hypothesis. The origin of the extremely small annealing effect observed in this sample is unknown.

4. A repulsive interaction between adjacent cobalt ions in excess of that which exists between cobalt ions and iron ion neighbors is observed. The value of the interaction energy is found to be 0.093 ± 0.04 ev.

VIII. ACKNOWLEDGMENTS