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A Theory of the Uniaxial Anisotropy Induced by Magnetic Annealing in Ferrites*

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Synopsis

In order to explain the magnetic annealing effect in ferrites, we have extended our theory of the ferromagnetic uniaxial anisotropy induced by magnetic annealing in metallic cubic solid solutions to cases of ferrites and derived a general expression for the uniaxial anisotropy induced in ferrites. It is shown that our theory of the magnetic annealing effect in ferrites can explain almost all of the available experimental results on the induced uniaxial anisotropy as dependent on the concentration, on the orientation of the magnetic field during annealing, and on the temperature of magnetic anneal. Thus, we conclude that the uniaxial anisotropy induced by magnetic annealing in ferrite is caused by an anisotropic distribution among cations and cation vacancies, namely, by a mechanism similar to that in ferromagnetic metallic solid solutions. In connection with the present study, a criticism has been made on the explanation of the effect proposed recently by Williams et al., and the concentration dependence of the magnetocrystalline anisotropy constant in binary ferrites composed of cobalt ferrite and other inverse ferrite has also been discussed briefly, based on the model given by Van Vleck and extended by Sugihara.

I. Introduction

Previously we⁽¹⁾ and, independently, Néel⁽²⁾ interpreted the uniaxial ferromagnetic anisotropy induced by magnetic annealing in metallic cubic solid solutions as the magnetocrystalline anisotropy resulted from the anisotropic distribution of atoms, and we developed theory which accords well with the experimental results as regards the magnitude of the induced uniaxial anisotropy and its dependence on the concentration of solute atoms, on the orientation of magnetic field applied during annealing and on the measuring temperature.

That ferrites also respond to magnetic anneal was discovered by Kato and Takei⁽³⁾ early in 1933 on solid solutions of cobalt ferrite and magnetite, and this property has been applied to the industrial production of O. P. magnets. Such a response, afterwards, was found in solid solutions of cobalt ferrite and nickel or magnesium ferrite⁽⁴⁾. Quite recently, Bozorth, Tilden and Williams⁽⁵⁾ studied the

* The 879th report of the Research Institute for Iron, Steel and Other Metals. Preliminary reports were published in *J. Phys. Soc. Japan*, **11** (1956), 604 and in *Nippon Kinzoku Gakkai-shi* (*J. Japan Inst. Metals*), **20** (1956), 503 and 507, in collaboration with M. Yamamoto.

(1) S. Taniguchi and M. Yamamoto, *Sci. Rep. RITU*, **A6** (1954), 330; S. Taniguchi, *ibid.*, **A7** (1955), 269.

(2) L. Néel, *J. de Phys.*, **15** (1954), 225.

(3) Y. Kato and T. Takei, *J. Inst. Elec. Engres. Japan*, **53** (1933), 408.

(4) L. Weil, *Compt. rend.*, **234** (1952), 1351.

(5) R. M. Bozorth, E. F. Tilden and A. J. Williams, *Phys. Rev.*, **99** (1955), 1788.

magnetic annealing effect in single crystals of a cobalt-zinc ferrite and showed that the magnitude of the induced uniaxial anisotropy *hardly* depends on the orientation of magnetic anneal and the direction of easy magnetization of the induced uniaxial anisotropy coincides with the direction of magnetic anneal. On the other hand, Iida, Sekizawa and Aiyama⁽⁶⁾ and Bozorth et al.⁽⁵⁾ found that, in solid solutions of cobalt ferrite and magnetite, the magnitude of the induced uniaxial anisotropy depends appreciably on the atmosphere during magnetic annealing and its maximum appear either at about 30 or 70 mole percent of cobalt ferrite in the solid solution, depending on the atmosphere of magnetic anneal.

Since these experimental results on the response of ferrites to magnetic anneal are considerably different from those of metallic solid solutions, one might expect an explanation quite different from that of the latter. Recently, Williams, Heidenreich and Nesbitt⁽⁷⁾ have found that the magnetic torque of some cobalt-zinc and cobalt-iron ferrite single crystals which respond to magnetic anneal changes its sign with an increase of measuring magnetic field strength when annealed without magnetic field, and that the ferrite crystals which can not respond to magnetic annealing do not show such a sign reversal of the magnetic torque. They⁽⁸⁾ discovered previously the similar phenomenon in Alnico 5 and in Fe₂NiAl single crystals and explained it in terms of the presence of precipitated thin particles, which can be observed in electron micrographs of Alnico 5 in the state slightly over-aged than that showing the maximum coercive force. The similarity of the phenomena, together with some evidence founded, as they claim, in electron diffraction patterns, has led them to the conclusion that the response of ferrites to magnetic anneal is due to the tendency of the precipitated particles of a second phase to grow preferentially along the direction of magnetic field present during heat-treatment, namely, due to quite the same mechanism as in Alnico 5, etc.

This conclusion, however seems doubtful to us, as shown later in Sec. II. Moreover, since even in *metallic solid solutions* the mode of the uniaxial anisotropy induced by magnetic annealing depends appreciably on the type of the crystal lattice concerned, as has already been shown by us⁽¹⁾, one can not expect that the experimental results on ferrites with the spinel or complicated cubic lattice may be discussed in direct comparison with the experimental and theoretical results for metallic solid solutions with simpler cubic lattices. Furthermore, Iida et al.⁽⁶⁾ have suggested, basing on their detailed magnetic, thermal, electrical and structural studies on iron-cobalt ferrites, that the metal ion vacancies may play an essential rôle for the response of ferrites to magnetic anneal.

In this paper, we shall extend generally our theory for the metallic solid solutions to cases of ferrites, apply it to each of special cases under a few

(6) S. Iida, H. Sekizawa and Y. Aiyama, J. Phys. Soc. Japan, **10** (1955), 907.

(7) H. J. Williams, R. D. Heidenreich and E. A. Nesbitt, J. Appl. Phys., **27** (1956), 85.

(8) E. A. Nesbitt, H. J. Williams and R. M. Bozorth, J. Appl. Phys., **25** (1954), 1014; E. A. Nesbitt and H. J. Williams, *ibid.*, **26** (1955), 1217.

reasonable assumptions, and show that our theory can interpret well the available experimental results. Before the development of our theory, we shall criticise the explanation offered by Williams et al. in Sec. II, and, for the need of the later development of the theory, discuss the magnetocrystalline anisotropy of ferrite in Sec. III.

II. Comments on the explanation based on the preferentially oriented precipitation of a second phase

As noted above, Williams et al.⁽⁷⁾ proposed an interpretation that the response of some ferrites to magnetic anneal may be due to the shape anisotropy of preferentially precipitated particles of a second phase. The experimental facts, on which their interpretation is based, are (1) the correlation between the sign reversal of magnetic torque and the response to magnetic anneal in single crystals of some cobalt-iron and cobalt-zinc ferrites, and (2) the electron diffraction patterns showing the presence of a second phase of a spinel structure with approximately the same lattice parameter as the matrix in single crystals of some cobalt-zinc ferrites which respond to magnetic anneal.

We note the following comments as to their conclusion:-

(a) The sign reversal of magnetic torque can not be related directly to a particular mechanism for the response to magnetic anneal, since the equations used by them for the explanation of the sign reversal of magnetic torque in Alnico 5, etc.⁽⁸⁾ hold for all ferromagnetic materials in which, when annealed without magnetic field, the uniaxial anisotropy can be induced by any mechanism along the directions of easy magnetization determined by the proper cubic anisotropy⁽⁹⁾. It is obvious, then, that the precipitated particles "apparently" shown by their electron diffraction patterns can not be related to the response to magnetic anneal and to the sign reversal of magnetic torque, unless it is shown by other means that the precipitated particles actually play an essential rôle.

(b) It has not yet been found by other investigators that any precipitable phase with spinel structure having almost the same lattice parameter as the matrix is present, for example, in iron-cobalt ferrite system. Even in wider system of γ -Fe₂O₃-Co₃O₄⁽¹⁰⁾, precipitable phases are α -Fe₂O₃ as well as CoO and Co₃O₄ containing some amount of iron ions, all of which can not appear so long as the composition deviates considerably from the stoichiometric composition of cobalt ferrite. Among these, only Co₃O₄ has the spinel structure, but its lattice parameter is considerably smaller than that of cobalt ferrite, and it can precipitate only when the concentration of cobalt ions in cations exceeds more than about 0.5, much greater than 0.33 for cobalt ferrite.

(c) According to Bozorth et al.⁽⁵⁾, a cobalt-zinc ferrite single crystal of the

(9) A mathematical formulation of this reasoning has been published recently by S. Chikazumi [J. Phys. Soc. Japan, **11** (1956), 719], after our paper written in Japanese was prepared.

(10) J. Robin and J. Benard, Compt. rend., **234** (1952), 734, 956; J. Robin, Ann. de Chim., **10** (1955), 389.

form of a hollow square shows the coercive force of only about 10 oersteds when annealed at 400°C for 15 minutes, though it responds to magnetic anneal, the induced uniaxial anisotropy being about 10^5 erg/cm^3 at this annealing temperature^(5,11). This coercive force may probably be far smaller than that of polycrystalline specimen, in view of the fact that a polycrystalline cobalt ferrite, which show the induced uniaxial anisotropy of the same order of magnitude, has the very high coercive force of the order of several hundreds oersteds both in annealed and in quenched states. Thus, the high coercive force of this cobalt ferrite or of other ferrites may be explained not by the precipitated particles but by the single domain behavior of crystallites composing the polycrystalline specimen.

(d) Ferrites which respond to magnetic anneal do not show any over-aging phenomenon which is observed in nearly all precipitable materials. For example, Bozorth et al.⁽⁵⁾ have studied the induced uniaxial anisotropy as dependent on the duration of magnetic anneal at various temperatures using a cobalt-zinc ferrite single crystal and found that, at every annealing temperature, the induced uniaxial anisotropy increases exponentially with time and reaches a finite value, showing no decrease at all. They have shown, further, that if the direction of magnetic field applied during annealing at 300°C is rotated from the [100] to the [010] direction in the (001) plane after kept for about 20 hours, the uniaxial anisotropy amounting to about the same magnitude as mentioned before is induced along the new direction within a negligibly short time.

(e) Even if preferentially precipitated particles were present, their volume fraction may be considered, from the preceding remarks (b)~(d), to be very small. Then, it can be said at once that the shape anisotropy due to them is far smaller than the experimental value, as the following consideration shows:- The induced uniaxial anisotropy constant, K_u , due to the preferential precipitation of elongated or thin particles is given by⁽¹²⁾

$$K_u = (1/2) \Delta N (\Delta I_s)^2 V (1 - V),$$

where ΔN is the difference in the demagnetizing factor of precipitated particles along longitudinal and transversal directions, ΔI_s the difference in saturation magnetization between the matrix and precipitates, and V the volume fraction of the *oriented* precipitates. The possible highest value of K_u given by this formula can not exceed about $2 \times 10^5 \text{ erg/cm}^3$ obtained by taking $\Delta N = 2\pi$, $\Delta I_s = 500$ and $V = 0.5$ which are considerably over-estimated, since, for example, the highest saturation magnetization of ferrite at room temperature is about 500 for magnetite. Even this over-estimated value of K_u , is smaller than the experimental value of about 10^6 erg/cm^3 .

Thus, it seems that the precipitated particles which have been found by

(11) Cf. Fig. 5 and Sec. IV.

(12) L. Néel, *Compt. rend.*, **225** (1947), 109; L. A. Subina and J.S. Shur, *J. Tech. Phys. USSR*, **19** (1949), 88; C. Kittel, E. A. Nesbitt and W. Shockley, *Phys. Rev.*, **77** (1950), 839.

Williams et al. fail to interpret the response of ferrites to magnetic anneal. In order to interpret the response by the precipitated particles, it is necessary to show that the shape of precipitated particles is highly anisotropic, and that their orientational distribution depends on the direction of magnetic anneal as expected from the measurement of the induced uniaxial anisotropy. It should be added, further, that it is very regrettable that the electron diffraction pattern of cobalt-zinc ferrite single crystals in magnetically annealed state must be taken with the incident electron beam perpendicular to the direction of magnetic anneal, in order to avoid the disturbance due to the stray magnetic field.

III. The magnetocrystalline cubic anisotropy of ferrite

The response to magnetic anneal has been found very conspicuous in ferrites containing cobalt ferrite, which has largest cubic anisotropy and magnetostriction among ferrites⁽⁵⁾. This may be due to the presence of Co^{2+} ions in cobalt ferrite. Although it is considered now that the main and general origins of the magnetocrystalline anisotropy of ferrites are the anisotropy of crystalline field and the anisotropic exchange interaction⁽¹³⁾, the former can not be the origin of the proper cubic anisotropy of cobalt ferrite, since Co^{2+} ion has the spin quantum number $S = 3/2$ ⁽¹⁴⁾. The orbital degeneracy of ${}^4\text{F}$ state of free Co^{2+} ion is not removed completely by the cubic crystalline field of surrounding oxygen ions in ferrite, but the small crystalline field of surrounding cations having symmetry lower than cubic can remove the degeneracy so that the orbital angular momentum in the degenerated ground state is quenched. The anisotropy due to the anisotropic exchange interaction comes from the spin-orbit coupling and isotropic exchange interaction through the excited states where the orbital angular momentum is not quenched. Van Vleck⁽¹⁵⁾ has shown that such anisotropic exchange interaction can be expressed as the presence of an anisotropic coupling between spins. If $S = 1/2$, the only one possible anisotropic coupling is the dipole-dipole type coupling and if $S > 1/2$ the quadrupole-quadrupole type coupling must be considered, but the latter is neglected in the following. The perturbational calculation of the anisotropic exchange interaction shows that the coefficient of such a dipole-dipole coupling is inversely proportional to the square of energy separation between the ground state and excited ones⁽¹³⁾, so that it may be very large for a pair of Co^{2+} ion and any other magnetic ion owing to the relatively small level separation of Co^{2+} ion caused by the crystalline field⁽¹⁴⁾.

Van Vleck⁽¹⁵⁾ assumed that the anisotropy of ferromagnetic metal crystal is originated solely from the anisotropic exchange interaction, and employs the following Hamiltonian H :

$$H = H_0 + \sum_{j>i} w(i:j), \quad (1)$$

(13) See for example, T. Nagamiya, K. Yosida and R. Kubo, *Advances in Phys.*, **4** (1955), 1.

(14) K. Yosida, *Busseiron Kenkyu*, No. 93 (1956), 169; No. 94 (1956), 145 (in Japanese).

(15) J. H. Van Vleck, *Phys. Rev.*, **52** (1937), 1178; *J. de phys.*, **12** (1951), 262.

where H_0 is the Hamiltonian of the unperturbed system, that is, the ordinary exchange term expressed in terms of the molecular field approximation as

$$H_0 = -g\beta H \sum_i S_{zi} \tag{2}$$

where H is the molecular field supposed to be directed along the z axis, S_{zi} is the z component of spin of atom i , g is Lande's factor and β is Bohr's magneton. The second term of Eq. (1) is the perturbing energy, in which $w(i:j)$ is the interaction energy between atoms i and j . In the case of dipole-dipole coupling, the interaction is expressed as

$$w(i:j) = \sum_{q,q'=x,y,z} a(i:j)^{qq'} S_{qi} S_{qj}, \tag{3}$$

where $a(i:j)^{qq'}$ is the coefficient of the interaction energy between S_{qi} and S_{qj} . Then, the partition function, Z , is given by

$$Z = Z_0(1 + A + B + \dots), \tag{4}$$

where

$$A = - (kT)^{-1} \langle \sum w(i:j) \rangle_{AV}, \tag{5a}$$

$$B = (1/2)(kT)^{-2} \langle (\sum w(i:j))^2 \rangle_{AV}, \tag{5b}$$

Z_0 is the partition function of the unperturbed system, and $\langle \rangle_{AV}$ denotes the quantum-mechanical average. The anisotropy energy is obtained by calculating the free energy by the formula:-

$$F = -kT \log Z = -kT \log Z_0 - kTA + (1/2)kTA^2 - kTB + \dots \tag{6}$$

$\langle w(i:j) \rangle_{AV}$ is written down as:

$$\langle w(i:j) \rangle_{AV} = \sum_{q,q'} a(i:j)^{qq'} \langle S_{qi} S_{qj} \rangle_{AV} = a(i:j)^{zz} B^2(\theta), \tag{7}$$

where $B(\theta) = \{(2S + 1)/2\} \coth\{(2S + 1)\theta/2\} - (1/2) \coth(\theta/2)$, \tag{8a}

and

$$\theta = g\beta H/kT. \tag{8b}$$

To obtain anisotropy, it is, however, necessary to express $\langle w(i:j) \rangle_{AV}$ in terms of $A(i:j)$, instead of $a(i:j)$, for a system of axes fixed relative to the crystal, which are denoted by X , Y , and Z . The relation between $a(i:j)$ and $A(i:j)$ is given by

$$a(i:j)^{qq'} = \sum_{p,p'=X,Y,Z} \lambda_{qp} \lambda_{q'p'} A(i:j)^{pp'}, \tag{9}$$

where λ_{qp} 's are the direction cosines of q axes relative to p axes, and because of dipole-dipole coupling,

$$A(i:j)^{pp'} = C(i:j) (\delta_{pp'} - 3n_{ij}^p n_{ij}^{p'}), \tag{10}$$

where $C(i:j)$ is the constant of dipole-dipole coupling and n_{ij}^p 's are the cosines of angles between the pair direction and p axes. Then, from Eqs. (7), (9) and (10),

$$\langle w(i:j) \rangle_{AV} = C(i:j) B^2(\theta) (1 - 3 \cos^2 \phi), \tag{11}$$

where ϕ is the angle between the pair and spin directions.

Sugihara⁽¹⁶⁾ have applied the method of Van Vleck to the case of ferrite and discussed the temperature dependence of its cubic anisotropy. Ferrite is the ferrimagnetic oxide having spinel lattice, in which the cations are distributed on its 16c and 8f sites, the spins of cations on 16c sites being directed antiparallel to those on 8f sites. Then, the Hamiltonian of unperturbed system in this case is, instead of Eq. (2),

$$H_0 = -g\beta H_c \sum_i S_{zi} - g\beta H_f \sum_j \sigma_{zj} \quad (2a)$$

where H_c and H_f are the molecular fields acting on the ions in 16c sites and on those in 8f sites, whose spins are S_i and σ_j , respectively, regarding as the same for ions in each of 16c and 8f sublattices. According to the kind of sites, on which ions i and j exist, the interaction energy is specified as $w_{cc}(i:j)$, $w_{cf}(i:j)$ and $w_{ff}(i:j)$.

The term A (Eq. (5a)) can not give any anisotropy in ferrite because of cubic symmetry, but we give its explicit form, since we use it in the calculation of the induced uniaxial anisotropy. $\langle w_{kl}(i:j) \rangle_{AV}$ is, after Eq. (11), written as

$$\langle w_{kl}(i:j) \rangle_{AV} = \varepsilon_{kl} C_{kl}(i:j) B(\theta_k) B(\theta_l) (1 - 3 \cos^2 \phi), \quad (k, l = c, f), \quad (12)$$

where $\varepsilon_{kl} = +1$ for $k = l$ and -1 for $k \neq l$ and suffix k and l denotes the quantity for 16c- and 8f- site ions. The summation of Eq. (11) or (12) over all pairs of spins in cubic crystal gives a constant independent of the direction of magnetization vector.

The term B (Eq. (5b)) gives a cubic anisotropy and if we employ the nearest neighbor assumption, the cubic anisotropy constant of ferrite at 0°K , K_c° , is given by

$$K_c^\circ = -(9/8)(kT\theta_c)^{-1} N S^2 C_{cc}^2(i:j) + (1872/121) \{kT(\theta_c - \theta_f)\}^{-1} N S \sigma C_{cf}^2(i:j) + (kT\theta_f)^{-1} N \sigma^2 C_{ff}^2(i:j), \quad (13)$$

where N is the number of molecules in unit volume.

Now, we consider cobalt ferrite, in which 16c sites are occupied by Co^{2+} and Fe^{3+} ions with equal probability, while 8f sites are occupied by Fe^{3+} ions only. Since C_{cc}^2 etc. are the mean value for various kinds of ion pairs,

$$C_{cc}^2(i:j) = (1/4)C_{cc}^2(\text{Co}:\text{Co}) + (1/2)C_{cc}^2(\text{Co}:\text{Fe}) + (1/4)C_{cc}^2(\text{Fe}:\text{Fe}), \quad (14a)$$

$$C_{cf}^2(i:j) = (1/2)C_{cf}^2(\text{Co}:\text{Fe}) + (1/2)C_{cf}^2(\text{Fe}:\text{Fe}), \quad (14b)$$

$$\text{and } C_{ff}^2(i:j) = C_{ff}^2(\text{Fe}:\text{Fe}). \quad (14c)$$

We assume here that

$$C_{cc}(\text{Co}:\text{Co}) = 2C_{cc}(\text{Co}:\text{Fe}) = 2C_{cf}(\text{Co}:\text{Fe}), \quad (15a)$$

$$\text{and } |C_{kl}(\text{Fe}:\text{Fe})| \ll |C_{cc}(\text{Co}:\text{Co})|, |C_{kl}(\text{Co}:\text{Fe})|, \quad (15b)$$

which may be reasonable, since C 's come from the anisotropic exchange interaction which plays between one excited and one unexcited ions through the

(16) K. Sugihara, *Busseiron Kenkyu*, No. 59 (1953), 39 (in Japanese).

spin-orbit coupling and isotropic exchange interaction, and very large value of C results from the small level separation of Co^{2+} ions. Further, when the anisotropic distribution of M and N ions can not occur by magnetic anneal, which, as will be seen in Sec. IV, may be the case of cobalt ferrite, the following relation holds:-

$$C(M:M) + C(N:N) - 2C(M:N) = 0. \quad (16)$$

Then, from Eq. (13), (14) and (15), K_c° for cobalt ferrite, $K_c^\circ(\text{Co})$, becomes

$$K_c^\circ(\text{Co}) \sim 3.1 \times 10^{13} NC_{cc}^2(\text{Co:Co}) \text{ erg/cm}^3, \quad (17)$$

using $\sigma = 5/2$, $S = 2$, and $kT\theta_c \sim -kT\theta_f \sim 10^{-13} \text{ erg}^{(17)}$.

According to Shenker⁽¹⁸⁾, K_c of $\text{Co}_{1.12}\text{Fe}_{2.11}\text{O}_4$ is about $3.8 \times 10^6 \text{ erg/cm}^3$ at 20°C , while about $17.5 \times 10^6 \text{ erg/cm}^3$ at -196°C . Then, taking $2 \times 10^7 \text{ erg/cm}^3$ as $K_c^\circ(\text{Co})$,

$$NC_{cc}^2(\text{Co:Co}) \sim 6.4 \times 10^{-7} \text{ erg}^2/\text{cm}^3 \quad (18)$$

and $NC_{cf}^2(\text{Co:Fe}) \sim NC_{cf}^2(\text{Co:Fe}) \sim 1.6 \times 10^{-7} \text{ erg}^2/\text{cm}^3. \quad (19)$

Now, we shall consider the concentration dependence of the cubic anisotropy constant in solid solution of cobalt ferrite and any other inverse ferrite, which will be denoted as M ferrite. Since C 's of ion pairs containing Co^{2+} ion is very larger than those of other ion pairs, the concentration dependence of K_c° results primarily from the concentration dependence of C_{cc}^2 etc., then the coefficient of C^2 's in Eq. (13) can be regarded as constant. Denoting the mole concentration of cobalt ferrite in the solid solution as n , Eq. (13) may be rewritten as

$$K_c^\circ(n) = -\alpha C_{cc}^2(n) + \beta C_{cf}^2(n) - \gamma C_{ff}^2(n), \quad (20)$$

where α , β and γ are constants and, as in Eq. (14),

$$\begin{aligned} C_{cc}^2(n) &= (n^2/4)C_{cc}^2(\text{Co:Co}) + \{n(1-n)/2\}C_{cc}^2(\text{Co:M}) \\ &+ \{(1-n)^2/4\}C_{cc}^2(\text{M:M}) + (n/2)C_{cc}^2(\text{Co:Fe}) \\ &+ \{(1-n)/2\}C_{cc}^2(\text{M:Fe}) + (1/4)C_{cc}^2(\text{Fe:Fe}), \end{aligned} \quad (21a)$$

$$\begin{aligned} C_{cf}^2(n) &= (n/2)C_{cf}^2(\text{Co:Fe}) + \{(1-n)/2\}C_{cf}^2(\text{M:Fe}) \\ &+ (1/2)C_{cf}^2(\text{Fe:Fe}), \end{aligned} \quad (21b)$$

and $C_{ff}^2(n) = C_{ff}^2(\text{Fe:Fe}). \quad (21c)$

Considering about the relation given by Eq. (14) and similar relation for M ferrite, $K_c^\circ(n)$ becomes

$$K_c^\circ(n) = nK_c^\circ(\text{Co}) + (1-n)K_c^\circ(\text{M}) + (1/4)n(1-n)K', \quad (22a)$$

where $K' = \alpha\{C_{cc}^2(\text{Co:Co}) + C_{cc}^2(\text{M:M}) - 2C_{cc}^2(\text{Co:M})\}. \quad (22b)$

(17) This value is obtained by using the numerical values of exchange integrals for magnetite as obtained by L. Néel (Ann. de Phys., 3 (1948), 137), which may be approximately valid for cobalt ferrites.

(18) H. Shenker, thesis, University of Maryland, 1955, cited by Bozorth et al. in reference (5).

Eq. (22a) shows that the concentration dependence of K_c° in solid solution of cobalt ferrite and inverse M ferrite can be expressed schematically by a curve (1) or (2) in Fig. 1, according to whether the sign of K' (Eq. (22b)) is positive or negative. If the relation like that given by Eq. (16) holds, which may be the case of solid solution of cobalt ferrite and magnetite, as will be seen in Sec. IV, Eq. (22b) becomes

$$K' = (\alpha/2)\{C_{cc}(\text{Co:Co}) - C_{cc}(\text{M:M})\}^2 > 0. \quad (23)$$

Since $|C_{cc}(\text{Co:Co})| \gg |C_{cc}(\text{M:M})|$, we obtain

$$K' \sim 15 \times 10^6 \text{ erg/cm}^3$$

using the value of $|C_{cc}(\text{Co:Co})|$ as given by Eq. (18), which is comparable as $K_c^\circ(\text{Co})$.

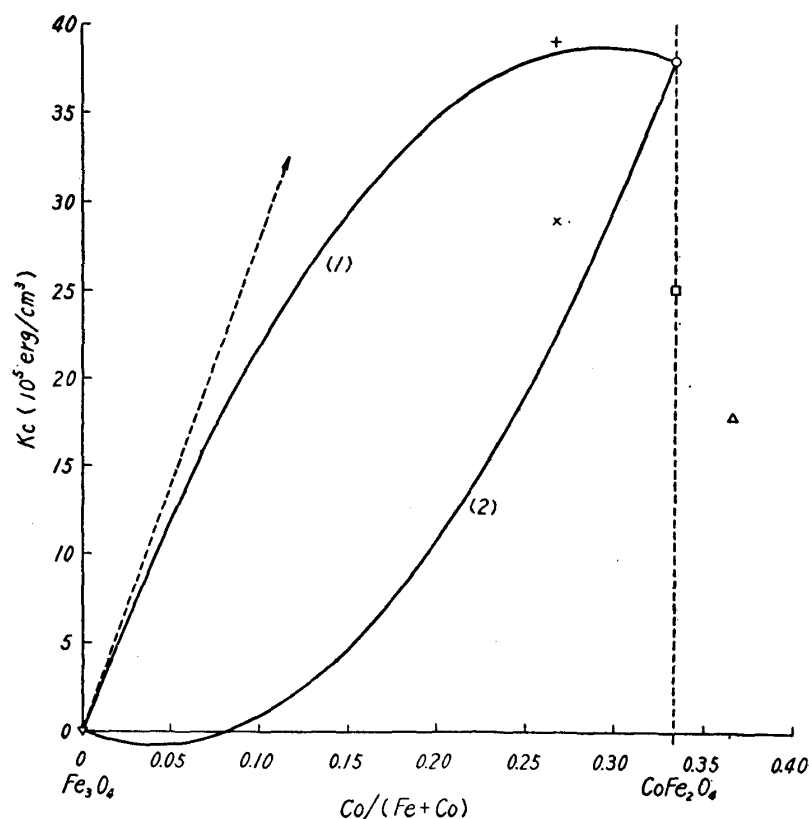


Fig. 1. Concentration dependence of the magnetocrystalline cubic anisotropy constant, K_c , in solid solution of magnetite and cobalt ferrite. \square : Fujimura⁽²⁰⁾, cobalt ferrite; \circ : Shenker⁽¹⁸⁾, $\text{Co}_{1.12}\text{Fe}_{2.21}\text{O}_4$; ∇ : Bickford, Jr.⁽²¹⁾, Fe_3O_4 ; \triangle : Bozorth et al.⁽⁵⁾, $\text{Co}_{1.1}\text{Fe}_{1.9}\text{O}_4$; $+$: Bozorth et al.⁽⁵⁾, $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$, air-quenched from 400°C ; \times : Bozorth et al.⁽⁵⁾, $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$, aged at 150°C for 3 days; ---: Bickford et al.⁽¹⁹⁾.

Bickford et al.⁽¹⁹⁾ have found that the K_c changes its sign from negative to positive by a very small addition of cobalt ferrite to magnetite, but the linear extrapolation of the relation to the stoichiometric cobalt ferrite gives the value of K_c far larger than that obtained experimentally as shown by a broken line in Fig. 1. Further, Bozorth et al.⁽⁵⁾ have also stated that ferrite having the concent-

(19) L. R. Bickford, Jr., J. Pappis and J. L. Stull, Phys. Rev., **99** (1955), 1210.

ration nearer to that of stoichiometric cobalt ferrite has smaller value of K_c . These facts may be interpreted by the discussion given above. The datas^(5,18,19,20,21) on K_c of solid solution of cobalt ferrite and magnetite measured at room temperature are also given in Fig. 1, but the quantitative comparison between the theoretical curve and experimental results can not be expected, since the above discussion has been done on the values at absolute zero and also the temperature dependence of cubic anisotropy given by the theory of Van Vleck is not so drastic as that found experimentally because of its molecular field approximation⁽²²⁾.

IV. The uniaxial magnetic anisotropy induced by magnetic annealing

Now, we consider solid solutions of an inverse ferrite and other normal or inverse ferrite, which contain generally more than two kinds of cations both on 16c and 8f sites. However, we assume, at first, that only two kinds of cations are present on each of k and l sites ($k, l = (16)c, (8)f$) and denote the ferrite as $N_{n_f}^f M_{1-n_f}^f (N_{n_c}^c M_{1-n_c}^c) O_4$. Then, the anisotropic coupling energy between a M^k ion and a N^l ion at the temperature θ is given by Eq. (12) :-

$$w_{kl}(M^k : N^l) = \varepsilon_{kl} C_{kl}(M^k : N^l) B_k(\theta) B_l(\theta) (1 - 3 \cos^2 \phi_\theta), \quad (24)$$

where $B_k(\theta)$, $B_l(\theta)$ and ϕ_θ are the same as in Eq. (12), but they are rewritten in order to indicate explicitly the temperature concerned, the simbol $\langle \rangle_{AV}$ being omitted for simplicity.

By replacing $C_{kl}(M^k : N^l)$ in Eq. (24) by C_{kl} written as

$$C_{kl} = C_{kl}(M^k : M^l) + C_{kl}(N^k : N^l) - C_{kl}(M^k : N^l) - C_{kl}(N^k : M^l), \quad (25)$$

we may obtain the change in the coupling energy between k and l sites caused by the interchange between a M^k ion and a N^k ion or between a M^l ion and a N^l ion at the temperature θ , as

$$w_{kl}(\theta) = \varepsilon_{kl} C_{kl} B_k(\theta) B_l(\theta) (1 - 3 \cos^2 \phi_\theta). \quad (26)$$

Then, if we hold the ferrite at the temperature θ for a long time, keeping the magnetization vector along a crystallographic direction, ions may redistribute so as to make the coupling energy as low as possible. Then the probability, $\omega_{kl}(\theta)$, finding a M^l ion in one of the nearest neighbor directions of a M^k ion, which make an angle ϕ_θ with the direction of magnetization vector, is given approximately by

$$\omega_{kl}(\theta) = (1/z_{kl})(1 - w_{kl}(\theta)/k\theta), \quad (27)$$

where z_{kl} is the number of nearest neighbors in l site of a cation in k site. Here, we assume that $w_{kl}(\theta)/k\theta \ll 1$ and neglect terms containing more than the

(20) T. Fujimura, *Kyojisei Sankakinzoku no Kenkyu*, No. 3 (1955), 20 (in Japanese).

(21) L. R. Bickford, Jr., *Phys. Rev.*, **78** (1950), 449.

(22) C. Zener, *Phys. Rev.*, **96** (1954), 1335; F. Keffer, *Phys. Rev.*, **100** (1955), 1692; T. Kasuya, *Busseiron Kenkyu*, No. 92 (1956), 7 (in Japanese).

second degree of $w_{kl}(\theta)$. And further, we assume that the tendency of ionic ordering, which means that cations of a specific kind inclined to occupy a particular lattice site, and also the correlation between the distribution of cations can be neglected. Furthermore, the transition of the cations between different sublattices may not occur, since the kinds of cations present on 16c and 8f sites may be determined by the Madelung energy, size effect, etc., which are far decisive than the magnetic energy concerned. Then, the uniaxial anisotropy, F , induced at the temperature T is given by

$$F = \sum_{k,l} z_{kl} n_l w_{kl}(\theta) w_{kl}(T) = (1/2) \sum_{k,l} F_{kl}, \quad (28a)$$

$$\text{and } F_{kl} = -\{9N_k n_k n_l C_{kl}^2 B_k(\theta) B_l(\theta) B_k(T) B_l(T) / k\theta\} \sum' \cos^2 \phi_\theta \cos^2 \phi_T, \quad (28b)$$

where N_k is the total number of cations per unit volume for k sites and \sum' denotes the summation over all of the nearest neighbors belonging to l sites of a cation on k site, and n_k and n_l , both of which are assumed to be small, are the concentrations of N^k ions and N^l ions, respectively.

If we consider two molecules in a octant of a unit cell of ferrite as a unit, 4 cations on 16c site have doubly occupied 24 nearest neighbor cations on 16c site in all of $\langle 110 \rangle$ directions and 24 nearest neighbor cations on 8f site in all of $\langle 113 \rangle$ directions, while 2 cations on 8f site have 24 nearest neighbor cations on 16c site in all of $\langle 113 \rangle$ directions and 8 nearest neighbor cations on 8f site in all of $\langle 111 \rangle$ directions. Then, by calculating $\sum' \cos^2 \phi_\theta \cos^2 \phi_T$ in Eq. (28b), F can be rewritten as

$$F = F_{cc} + F_{cf} + F_{ff}, \quad (29a)$$

$$F_{cc} = -\{(9/2) N n_c^2 n_c'^2 C_{cc}^2 B_c^2(\theta) B_c^2(T) / k\theta\} (S_1 + 4S_2), \quad (29b)$$

$$F_{cf} = -\{(2304/121) N n_c n_c' n_f n_f' C_{cf}^2 B_c(\theta) B_f(\theta) B_c(T) B_f(T) / k\theta\} \\ \times \{S_1 + (19/16) S_2\}, \quad (29c)$$

$$F_{ff} = -\{4 N n_f^2 n_f'^2 C_{ff}^2 B_f^2(\theta) B_f^2(T) / k\theta\} S_2, \quad (29d)$$

$$S_1 = \sum_i \alpha_i^2 \beta_i^2, \quad S_2 = \sum_{j>i} \alpha_i \alpha_j \beta_i \beta_j, \quad (29e)$$

where α_i 's and β_i 's are the direction cosines of magnetization vector at the temperatures T and θ , respectively. In Eq. (29), we have replaced n_c^2 , $n_c n_f$ and n_f^2 in Eq. (28) with $n_c^2 n_c'^2$, $n_c n_c' n_f n_f'$ and $n_f^2 n_f'^2$, respectively, so as to remove the restriction that n_c and n_f are small, and to extend to the cases where more than two kinds of cations are present both in 16c and 8f sites but the main contribution to the uniaxial anisotropy comes from the anisotropic distribution of two kinds of cations among those present on each of 16c and 8f sites, whose concentrations are n_c , n_c' , n_f and n_f' .

As seen from Eq. (29), the induced uniaxial anisotropy depends complicatedly on the kind and concentration of cations which play main rôle, so that we can not develop further the theory in a general way. So, we shall discuss some special cases and compare with the experimental results.

1. Magnitude and the concentration dependence

Iida et al.⁽⁶⁾ have studied the response to magnetic anneal in solid solutions of cobalt ferrite and magnetite, and found that the magnitude of induced uniaxial anisotropy depends appreciably on the atmosphere during magnetic annealing. Their results are reproduced in Fig. 2. The specimens were heated, at first, at 1,000°C for 5 hours and furnace-cooled with the presence of magnetic field of about 4,000 Oe in a high vacuum (curve (1)). Next, they were heated again up to 400°C and then furnace-cooled with magnetic field of the same strength as before in the oxygen atmosphere of about 0.7 mmHg (curve (2)). The same procedure was repeated with increasing pressure of oxygen atmosphere up to 765 mmHg, and the induced uniaxial anisotropy was measured after each heat-treatment. In connection with this study, they have carried out extensive thermal, electrical, X-ray, and magnetic studies and suggest that the uniaxial anisotropy in these ferrites is induced by the directional short range order between Co²⁺ ions and cation vacancies.

Now, we may see from Fig. 2 that the uniaxial anisotropies of these ferrites are very small when magnetically annealed in a high vacuum, indicating, surely, that the main origin of the uniaxial anisotropy is not the anisotropic distribution of Fe²⁺, Fe³⁺ and Co²⁺ ions alone on 16c sites. Heating in oxygen atmosphere, unstable Fe²⁺ ions are oxydized, at first, into Fe³⁺ ions, producing cation vacancies probably in 16c sites as in the case of γ -Fe₂O₃⁽²³⁾. Then, from Eq. (25) and by taking into considerations of the relations (15),

$$C_{cc} = C_{cc}(Co:Co) + C_{cc}(V:V) - 2C_{cc}(Co:V) \sim C_{cc}(Co:Co), \quad (30)$$

where V denotes the cation vacancy. The induced uniaxial anisotropy of polycrystalline specimen is given by averaging Eq. (29b) for polycrystals, as:

$$F = -(36/5)(Nn_V^2 n^2 C_{cc}^2 B_c^2(\theta) B_c^2(T)/k\theta) \cos^2\psi, \quad (31)$$

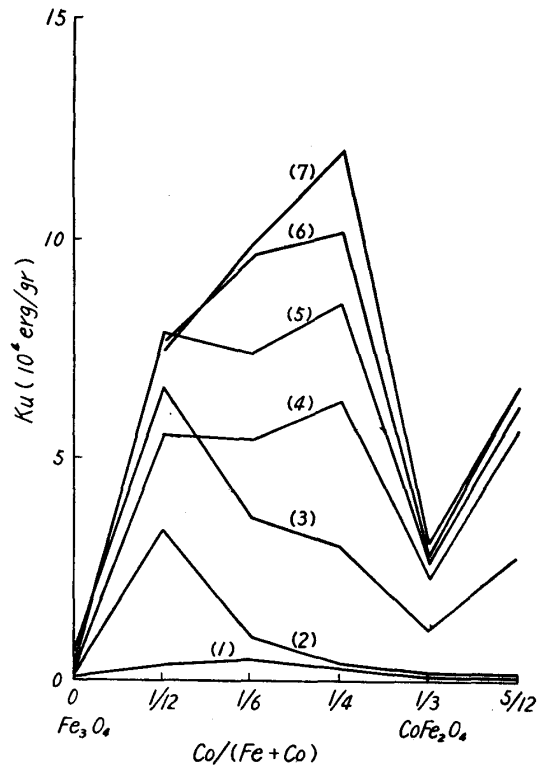


Fig. 2. Induced uniaxial anisotropy constant, K_u , as functions of the composition and pressure of oxygen atmosphere during heat-treatment in solid solution of magnetite and cobalt ferrite. The composition is indicated in atom ratio of cobalt to cobalt+iron, $Co/(Fe+Co)$. The pressure of oxygen atmosphere during magnetic annealing is 0, 0.7, 1.7, 6.5, 28, 160 and 765 mmHg for curves (1), (2), (3), (4), (5), (6) and (7), respectively (After Iida et al.⁽⁶⁾).

(23) E. J. Verwey, Z. Krist., **91** (1935), 65; E. J. Verwey and E. L. Heilman, J. Chem. Phys., **15** (1947), 174; L. Néel, Ann. Phys., (12) **3** (1948), 137; W. P. Osmond, Proc. Phys. Soc., **65** (1952), 121; W. E. Henry and M. J. Boehm, Phys. Rev., **101** (1956), 1253.

where n_V and n are the concentrations of cation vacancies and cobalt ions, respectively, and ψ is the angle between the direction of magnetization vector and that of magnetic field applied during annealing. Since $NC_{cc}^2(\text{Co}:\text{Co}) \sim 6.4 \times 10^7 (\text{erg})^2/\text{cm}^3$ (Eq. (18)), the induced uniaxial anisotropy constant, K_u , for $n = 3/4$ becomes about $6n_V^2 \times 10^8 \text{ erg/cm}^3$, taking $B_c^2(\theta) \sim B_c^2(T) \sim S^2 \sim 4$, $k\theta \sim 7 \times 10^{14} \text{ erg}$. For the ferrite having n larger than $3/4$, we can change all Fe^{2+} ions to Fe^{3+} ions preventing the precipitation of $\alpha\text{-Fe}_2\text{O}_3$ ⁽¹⁰⁾, and then, for $n = 3/4$, n_V can reach

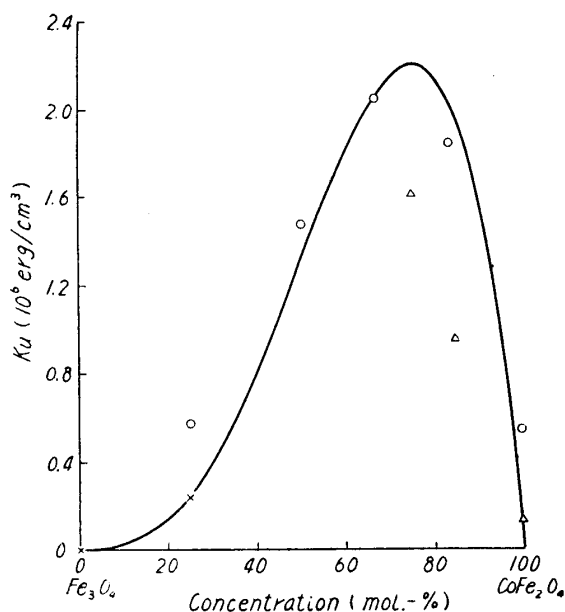


Fig. 3. Theoretical concentration dependence of the induced uniaxial anisotropy constant, K_u , in solid solution of magnetite and cobalt ferrite as compared with the experimental results obtained by Bozorth et al.⁽⁵⁾

about 0.05. Accordingly, for this case, $K_u = 1.5 \times 10^6 \text{ erg/cm}^3$. Bozorth et al.⁽⁵⁾ found that K_u for $n = 3/4$ is about $2 \times 10^6 \text{ erg/cm}^3$ when fired at 1250°C in O_2 , as shown in Fig. 3.

Eq. (31) shows that the concentration dependence of the induced uniaxial anisotropy in these ferrites is expressed by $n_V^2 n^2$, since the other quantities can be regarded as being nearly constant. As for the relation between the concentration of cation vacancies, n_V , and the concentration of cobalt ions, n , after the ferrite has been heat-treated in the same pressure of oxygen atmosphere, the following three cases may be probable:-

(a) When the pressure of oxygen during heat-treatment is relatively

low, n_V may be large in magnetite side and it may decrease rapidly with the increase in molar concentration of cobalt ferrite in solid solution,

(b) when the pressure of oxygen increases, n_V also increases but, in magnetite side, the precipitation of $\alpha\text{-Fe}_2\text{O}_3$ occurs. Then, n_V , which actually contributes to the induced uniaxial anisotropy is smaller in magnetite side as well as in cobalt ferrite side than in the intermediate region between them, and

(c) when we can change all Fe^{2+} ions to Fe^{3+} ions preventing the precipitation of $\alpha\text{-Fe}_2\text{O}_3$, n_V decreases nearly in proportion to the increase in n . This is also the case of solid solution of $\gamma\text{-Fe}_2\text{O}_3$ and cobalt ferrite.

The most simple expressions for the relations between n_V and n in these three cases are

$$(a) \quad n_V^2 \propto (1-n)^3/n, \quad (b) \quad n_V^2 \propto n(1-n) \quad \text{and} \quad (c) \quad n_V^2 \propto (1-n)^2, \quad (32)$$

and then the concentration dependence of the induced uniaxial anisotropy for these cases are

$$(a) \quad K_u \propto n(1-n)^3, \quad (b) \quad K_u \propto n^3(1-n) \quad \text{and} \quad (c) \quad K_u \propto n^2(1-n)^2. \quad (33)$$

According to the experimental results of Iida et al.⁽⁶⁾ shown in Fig. 2, K_u

increases, at first, with increasing oxygen pressure but shows a decrease in magnetite side, indicating probably that the precipitation of $\alpha\text{-Fe}_2\text{O}_3$ occurs at the annealing temperature of 400°C employed by them. Then, the case (c) can not hold, and the concentration dependence of K_u may be given by Eq. (33a) or (33b) according to the pressure of oxygen during annealing being either low or high. Eqs. (33a) and (33b) show that K_u becomes maximum at $n = 1/4$ for the case (a) and $n = 3/4$ for the case (b), which may correspond to the maxima of K_u appeared at the two compositions in Fig. 2. Further, Fig. 3 indicates that a theoretical curve given by Eq. (33b) agrees well with the experimental results obtained by Bozorth et al.,⁽⁵⁾ considering the simplifying assumptions and approximations used in the present theory as well as difficulties of experiment.

Here it is to be noted that K_u becomes maximum at about $n = 3/4$ or near the composition of OP magnet, when heat-treated in such a relatively high pressure of oxygen as usually employed. On the other hand, the magnetocrystalline cubic anisotropy constant, K_c , is also very large near this composition, being, at least, comparable with that of cobalt ferrite as shown in Fig. 1 and in Sec. III. These facts indicate that the high coercive force of OP magnet may be interpreted by the rotation of magnetization vector against these high anisotropies, each of crystal grains behaving as a single domain. Then, the coercive force may depend appreciably on the grain size, and accordingly, on the sintering temperature and time.

Finally, if the uniaxial anisotropy were induced in the solid solution of cobalt ferrite and any other inverse ferrite by the anisotropic distribution of Co ions and divalent ions, the concentration dependence of K_u should be expressed by Eq. (33c). The response to magnetic anneal of cobalt-nickel and cobalt-magnesium ferrites, which contain relatively stable divalent cations, seem to indicate such a possibility and, also in cobalt-iron ferrite annealed magnetically in a high vacuum, K_u becomes maximum, though its magnitude being negligibly small, at equi-concentration of cobalt ferrite and magnetite as seen from Fig. 2 (curve (1)). It is to be noted, however, that, in the present theory, the formation of cation vacancies due to the oxidation of divalent cobalt ion into high-valent ion is not taken into consideration, and accordingly, the induced uniaxial anisotropy is zero for stoichiometric cobalt ferrite, as seen from the theoretical curve in Fig. 3. The experimental results of Iida et al. and of Bozorth et al. indicate that K_u for cobalt ferrite is very small but not zero, and, further, K_u of ferrite containing more cobalt ions than that of stoichiometric cobalt ferrite is far larger than that of cobalt ferrite as shown by Iida et al. (Fig. 2). These facts seem to indicate that the divalent cobalt ion has a tendency to form the cation vacancy by being oxidized and that the stability of divalent cobalt ion depends probably on the concentration, although naturally the possibilities, that K_u of ferrite containing more cobalt ion than cobalt ferrite is due to the anisotropic distribution of divalent and higher-valent cobalt ions and that practically the preparation of stoichiometric cobalt ferrite containing none of Fe^{2+} ions may be difficult, can not completely be

excluded. Thus, even if the uniaxial anisotropy can be induced mainly by the anisotropic distribution of divalent cations in ferrite having relatively stable divalent cations, the concentration dependence of K_u may deviate from that given by Eq. (33c) because of the oxidation of divalent cobalt ions.

2. Orientational dependence

As stated in the introduction, Bozorth et al. have found that the induced uniaxial anisotropy, F , in a single crystal of cobalt-zinc ferrite can be expressed almost completely as

$$F = -K_u(\sum_i \alpha_i \beta_i)^2. \quad (34)$$

The cobalt-zinc ferrite studied by them has the analysed composition of $\text{Co}_{0.32}\text{Zn}_{0.24}\text{Fe}_{2.18}\text{O}_4$, which can be rewritten as $\text{Zn}_{0.24}\text{Fe}_{0.76}(\text{Co}_{0.32}\text{V}_{0.26}\text{Fe}_{1.42})\text{O}_4$, since zinc ferrite is normal ferrite. Here, cation vacancies, V, may be present on 16c sites as in cobalt-iron ferrite. Then, the C_{kl} 's which have large values are, from Eq. (25),

$$C_{cc} = C_{cc}(\text{Co}:\text{Co}) + C_{cc}(\text{V}:\text{V}) - 2C_{cc}(\text{Co}:\text{V}) \sim C_{cc}(\text{Co}:\text{Co}), \quad (35a)$$

and

$$C_{cf} = C_{cf}(\text{Co}:\text{Fe}) + C_{cf}(\text{V}:\text{Zn}) - C_{cf}(\text{Co}:\text{Zn}) - C_{cf}(\text{V}:\text{Fe}) \sim C_{cf}(\text{Co}:\text{Fe}), \quad (35b)$$

and, moreover, from Eq. (15a),

$$C_{cc}^2 \sim 4C_{cf}^2. \quad (35c)$$

Now, the induced uniaxial anisotropy, F , for this case is given, from Eq. (29), by

$$F = -A_1\{1 + (512/121)A_2\}S_1 - A_1\{4 + (512/121)(19/16)A_2\}S_2, \quad (36a)$$

where

$$A_1 = (9/2)Nn_V^2n^2C_{cc}^2B_c^2(\theta)B_c^2(T)/k\theta, \quad (36b)$$

$$A_2 = n_f(1-n_f)C_{cf}^2B_f(\theta)B_f(T)/n_VnC_{cc}^2B_c(\theta)B_c(T), \quad (36c)$$

and n and n_f are the concentration of Co ions and of Zn ions, respectively. Since $B_f(\theta)B_f(T)/B_c(\theta)B_c(T) \sim 1$, A_2 becomes approximately 2 using the relation (35c) and the values of the concentrations $n_f = 0.24$, $n_V = 0.13$ and $n = 0.16$ as given by the composition of ferrite concerned. So, if we take A_2 as 2, we obtain from Eq. (36a),

$$F = -A\{(\sum_i \alpha_i \beta_i)^2 - (590/1145)\sum_{j>i} \alpha_i \alpha_j \beta_i \beta_j\}, \quad (37)$$

where A is the uniaxial anisotropy constant when magnetically annealed in $\langle 100 \rangle$ directions. Since the second term in $\{ \}$ of Eq. (37) is far smaller than the first term, we have the same formula as Eq. (34) by neglecting the second term. The relative magnitude of the induced uniaxial anisotropy constant in (001) plane, calculated from Eq. (37), is shown as a function of the angle between the direction of magnetic field applied during annealing and [100] direction by a solid curve in Fig. 4, where circles show the experimental results of Bozorth et al.⁽⁵⁾ Since

the magnitude of induced uniaxial anisotropy constant in (001) plane must be symmetric in regard to the [110] direction, the corresponding experimental values among them may be averaged. The averaged values are shown by squares in the figure. The fluctuation in the experimental values may naturally due to the difficulties involved in experiment, that is, those of the accurate shaping of single

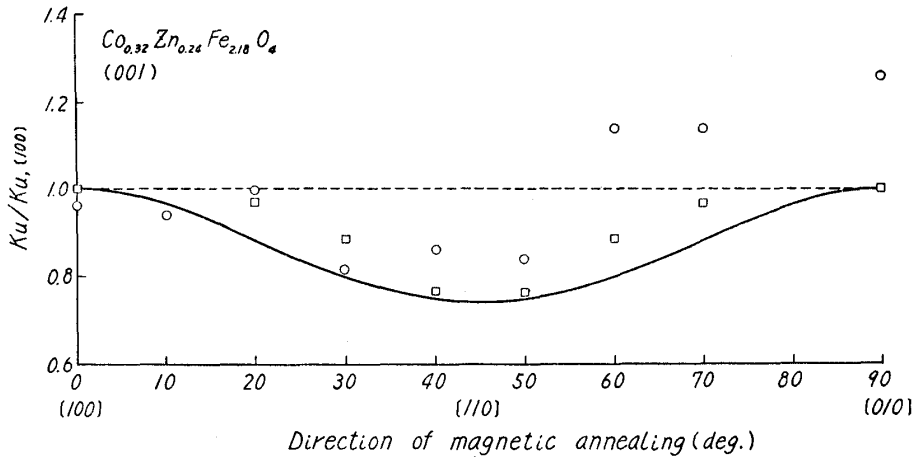


Fig. 4. Induced uniaxial anisotropy constant, K_u , as dependent on the orientation of magnetic field applied during heat-treatment in $\text{Co}_{0.32}\text{Zn}_{0.24}\text{Fe}_{2.18}\text{O}_4$; — theoretical curve, \circ experimental results obtained by Bozorth et al.⁽⁵⁾.

crystal disks, of the accurate separation between the cubic anisotropy and uniaxial one from the experimental torque curves, etc., but, according to the present author's view, it may also be due to the slight change in the composition caused probably by sublimation of zinc, oxydation, etc. during the repetition of anneal. The averaged values clearly agree well with Eq. (37) than with Eq. (34) which is a horizontal broken line in the figure and has been proposed by Bozorth et al.⁽⁵⁾

Further, according to Eq. (37), the direction of easy magnetization of the induced uniaxial anisotropy deviate from that of magnetic field applied during annealing to a $\langle 100 \rangle$ direction nearest to it, but the deviation never exceeds about 4 degrees in (001) plane, being smaller than in the case of ferromagnetic metallic solid solutions with face-centered cubic lattice. This deviation, however, is too small to be detected by magnetic torque measurements, because the ferrites concerned have relatively high cubic anisotropy energy.

It may readily be seen from Eq. (29) and above discussions that the orientational dependence of K_u depends not only on the kind and composition of ferrite but also on the condition of heat-treatment, so that the results obtained by Bozorth et al. for a single crystal of cobalt-zinc ferrite may not necessarily hold for other ferrites which respond to magnetic anneal. For example, if the uniaxial anisotropy were induced by the anisotropic distribution of cations or of cations and cation vacancies on 16c sites alone, the orientational dependence may be the same as in the case of ferromagnetic metallic solid solutions with face-centered cubic lattice, as seen from Eq. (29). This may probably be the case of solid solutions of cobalt ferrite and other inverse ferrite.

3. Temperature dependence

The change in the magnitude of the induced uniaxial anisotropy constant with measuring temperature has not yet been studied. Bozorth et al.⁽⁵⁾ have

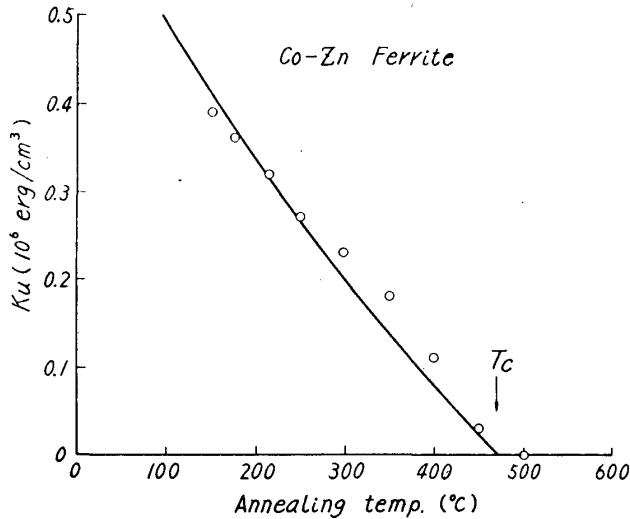


Fig. 5. Induced uniaxial anisotropy constant, K_u , as dependent on the temperature of magnetic anneal in $\text{Co}_{0.32}\text{Zn}_{0.24}\text{Fe}_{2.18}\text{O}_4$; — theoretical curve, \circ calculated from the experimental results obtained by Bozorth et al.⁽⁵⁾.

measured the induced uniaxial anisotropy of a cobalt zinc ferrite at room temperature as a function of the duration of magnetic anneal at various temperatures and expressed their results in terms of the ratio L_1/L_2 , where L_1 and L_2 are, respectively, the first minimum and the first maximum values of the magnetic torque of (001) disk single crystal when magnetically annealed along [100] direction. The equilibrium values of K_u at various temperature of magnetic anneal, which have been calculated by the present author from the values of L_1/L_2 given by them,

are shown in Fig. 5 by circles. For the cobalt-zinc ferrite, the temperature dependence is given, from Eq. (37), as

$$K_u \propto B^2(\theta)B^2(T)/\theta \quad (38)$$

where θ and T are the temperature of magnetic anneal and measuring temperature, respectively. The solid curve in Fig. 5 is the theoretical temperature dependence given by Eq. (38), taking the Curie temperature as 470°C and K_u at 100°C as 0.5×10^6 erg/cm³ and using Brillouin function for $S = 1/2$. It is to be noted that the use of Brillouin functions for $S > 1/2$ hardly alter the theoretical results.

Summary

It has been pointed out, in the first place, that the uniaxial anisotropy induced by magnetic annealing in ferrites, especially in those containing cobalt ferrite can not be interpreted by the shape anisotropy of preferentially precipitated particles of a second phase proposed by Williams et al.⁽⁷⁾ Since the large magnetocrystalline cubic anisotropy of cobalt ferrite may be resulted from the anisotropic exchange interaction between ion pairs containing cobalt ion and this circumstance is similar in ferromagnetic metal crystals, we have extended the theory of the induced uniaxial anisotropy in metallic solid solutions, proposed previously by the present author and Yamamoto, to cases of ferrites and obtained a general expression for the induced uniaxial anisotropy energy.

In order to compare with the experimental results, the general expression has been specialized using a few reasonable assumptions and the following results have been obtained:-

(1) In solid solutions of cobalt ferrite and magnetite, the concentration dependence of the induced uniaxial anisotropy constant can be explained satisfactorily using the experimental fact that the uniaxial anisotropy is hardly induced when magnetically annealed in a high vacuum, together with assumptions that cation vacancies, produced by the oxydation of unstable Fe^{2+} ions, are present only on 16c sites as in $\gamma\text{-Fe}_2\text{O}_3$ and that their concentration depends in a relatively simple manner on both the molar concentration of cobalt ferrite in solid solution and the atmosphere during magnetic annealing. The induced uniaxial anisotropy in this case is due to the anisotropic distribution of Co ions and cation vacancies both present on 16c sites.

(2) The maximum observed value of about 2×10^6 erg/cm³ for the induced uniaxial anisotropy constant in solid solution of cobalt ferrite and magnetite having the molar concentration of cobalt ferrite of about 3/4 can be explained using the anisotropic coupling constant for a cobalt ion pair deduced from the magnetocrystalline cubic anisotropy constant of cobalt ferrite and the concentration of cation vacancies expected by oxydizing Fe^{2+} ions in preventing the precipitation of $\alpha\text{-Fe}_2\text{O}_3$.

(3) For $\text{Co}_{0.32}\text{Zn}_{0.24}\text{Fe}_{2.18}\text{O}_4$ single crystal, the experimental results that the induced uniaxial anisotropy constant *hardly* depends on the orientation of magnetic field applied during annealing and the direction of its easy magnetization almost coincides with that of magnetic field applied during annealing, have been interpreted using assumptions that cation vacancies, whose concentrations is expected from the above analytical composition, are present on 16c sites alone, and that not only the anisotropic distribution of cobalt ions and cation vacancies on 16c sites but also the iron and zinc ions on 8f sites contribute to the induced uniaxial anisotropy through the anisotropic interaction between 16c and 8f sites.

(4) The experimentally found relation between the temperature of magnetic anneal and the magnitude of the uniaxial anisotropy constant induced in a (001) disk single crystal of cobalt-zinc ferrite by the isothermal anneal with magnetic field applied along [100] direction agrees well with the theoretical relation.

Thus, the theoretical results have been shown to agree well with almost all of the experimental results available at present. We are, then lead to conclude that the induced uniaxial anisotropy of ferrite is essentially a magnetocrystalline anisotropy appeared due to the anisotropic distribution of cations and cation vacancies.

In connection with the above-mentioned, the concentration dependence of magnetocrystalline cubic anisotropy constant in solid solution of cobalt ferrite and other inverse ferrite has been discussed briefly and it has been pointed out that the cubic anisotropy constant can become larger by the addition of magnetite. Since the composition of OP magnet corresponds approximately to the concentration,

where the induced uniaxial anisotropy shows a maximum and the cubic anisotropy is, at least, as large as that of cobalt ferrite, the rotation of magnetization vector in each crystal grain composed of polycrystalline OP magnet against these very large anisotropies may result a very high coercive force, that is, the high coercive force of OP magnet may not be due to the presence of precipitated particles as in the cases of Alnico 5 etc.

In conclusion, the present author expresses his sincere thanks to Prof. M. Yamamoto who guided and encouraged him and to Mr. T. Iwata who gave him valuable discussions throughout the present investigation. It is to be added that this work was supported in part by the Grant in Aid for Fundamental Scientific Researches of the Ministry of Education.