MAGNETIC ANISOTROPY OF COBALT-NICKEL FERRITE

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The temperature-dependence of the anisotropy constants K_1 and K_2 of ferrite $Co_xNi_{1-x}Fe_2O_{4\mp y}$ are determined at $0.075 \leqslant x \leqslant 1$. The anisotropy measurements were performed[1] with an anisometer and the anisotropy constants calculated from magnetic torque curves. On applying Tachiki's theory to the results,the following conclusions were reached:

1. There is no need to distinguish the two types of cobalt ion configurations assumed by Tachiki.

2. If the parameters $\alpha\lambda$ and a are assumed constant, their values cannot be adjusted in a way to bring the theoretical K_1-curve obtained from Tachiki's theory to agree with the temperature-dependence of K_1 obtained in experiment.

3. Agreement between theory and experiment can be achieved on assuming: a. that the product $\alpha\lambda$ varies with temperature like the magnetization and internal field; this is equivalent to assuming temperature-dependent spin-orbit coupling. b. The constant a defining the lower symmetry field also varies with temperature, but falls to zero already about 0.4 T_N.

4. At 0°K, the product $\alpha\lambda$ should amount to 91.5 cm^{-1}. On the other hand $a = 141$ cm^{-1}, suggesting Slater's wave function as the most suitable for describing the $3d$ electrons in NiCo-ferrite with which Tachiki obtained theoretically $a = 123$ cm^{-1}.

1. Introduction

The very large anisotropy constant of cobalt ferrite and other cobalt-doped ferrites has attracted the attention of numerous authors [1, 2, 3, 4]. Theoretically, the magnetic anisotropy of ferrites is explained on the basis of the one-ion model proposed by Nagoyama, Yosida and Kubo [6]. The model was used by Slonczewski [5] for elucidating the influence of cobalt on the magnetic anisotropy of cobalt-substituted magnetite. He assumed the Hamiltonian of the Co^{2+} ion in the ferrite crystal to be of the form:

$$H = W_F + V_c + V_T + W_{ex} + W_{LS}, \tag{1}$$

where W_F is the Hamiltonian of the free ion, and the other terms are successive contributions, thus V_c from the electrostatic cubic crystalline field due to the oxygen nearest neigh-

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[1] The magnetic anisotropy measurements were carried out at the Zentralinstitut für Festkörperphysik und Werkstoff-Forschung, Institutsteil für Magnetische Werkstoffe, DAV Jena.

bours, V_T from the electrostatic trigonal crystalline field of nearest octahedral neighbours, W_{ex} from exchange energy, and W_{LS} from spin-orbit coupling, and succeeded in calculating the anisotropic part of the free energy, which was equal to the energy of crystalline anisotropy contributed by the cobalt ion. The model was perfected by Tachiki [7], who supplemented the Hamiltonian (1) by adding a contribution V' from the crystalline field of lower symmetry due to the difference in charge of the ions Co^{2+} and Fe^{2+} at octahedral sites. Tachiki derived the following formula for the anisotropic part of the free energy related with the cobalt ion:

$$F_{an} = -\tfrac{1}{4}NkT \sum_{i=1}^{4} \ln \sum_{M=1/2}^{3/2} \cosh (M2\mu_B H_e/kT) \times$$
$$\times \cosh [(M\alpha\lambda \cos Q_i)^2 + a^* a]^{1/2}/kT, \tag{2}$$

where N is the number of cobalt atoms per 1 cm^3 of the sample, kT Boltzmann's factor, $\mu_B H_e$ — the product of Bohr's magneton and the internal field, α — a reduction factor of orbital angular momentum [8] amounting approximately to 3/2, λ a factor defining spin-orbit coupling given by the formula $W_{LS} = \lambda \vec{L} \cdot \vec{S}$, Q_i the angles subtended by the $\langle 111 \rangle$ crystallographical directions and the magnetization vector of the sample, and a a factor describing the crystalline field of lower symmetry. Slonczewski and Tachiki's theory was subjected to a verification only for low cobalt concentrations, in the papers by Slonczewski [5] and Miyamoto, Tanaka and Iida [9]. The proof of its validity for high concentrations of cobalt suggested by Tachiki [7] involves some rather unobvious assumptions on the constant a. In order to obtain agreement with experiment, an infinite value ($a_B = \infty$) is sometimes assigned to the a-constant of various configurations of the cobalt ion. Also, the experimental values used by Tachiki [1, 2, 3] stem from various authors employing different samples and, hence, are not necessarily concordant. Elbinger [10], performing measurements on very carefully prepared samples of CoNi-ferrite of high cobalt content, obtained a linear shape of the anisotropy constant K_1 *vs* the cobalt content. It will be shown further on that a linear dependence of K_1 on x points to undistinguishable configurations of the cobalt ions.

Commonly, the anisotropy energy is expressed in terms of the cosines α_1, α_2 and α_3 of the angles between the magnetization and the crystallographical axes:

$$E_{an} = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2\alpha_1^2\alpha_2^2\alpha_3^2. \tag{3}$$

The cosines do not occur directly in (2), and the anisotropy constants K_1 and K_2 cannot be obtained by a direct comparison of the appropriate expression from Eqs (2) and (3). Formulas for the crystal anisotropy constants K_1 and K_2 were derived according to Slonczewski [5], expressing K_1 and K_2 in terms of the free energies $E_{[100]}$, $E_{[110]}$ and $E_{[111]}$ required for magnetizing the sample in the crystallographical directions [100], [110] and [111], respectively:

$$K_1 = 4(E_{[110]} - E_{[100]}), \tag{4}$$

$$K_2 = 27E_{[111]} - 36E_{[110]} + 9E_{[100]}. \tag{5}$$

TABLE I

cos Q_i values for the angles Q_i between various crystallographical axes ⟨111⟩ and directions [hkl]

Directions [hkl]	Axes ⟨111⟩			
	[111]	$[1\bar{1}\bar{1}]$	$[\bar{1}1\bar{1}]$	$[\bar{1}\bar{1}1]$
[100]	$\sqrt{1/3}$	$\sqrt{1/3}$	$-\sqrt{1/3}$	$-\sqrt{1/3}$
[110]	$\sqrt{2/3}$	0	0	$-\sqrt{2/3}$
[111]	1	−1/3	−1/3	−1/3

The energy $E_{[hkl]}$ for the cases of Eqs (4) and (5) was calculated by us from Eq. (2) by inserting for the argument of cos Q_i the angles subtended by the various crystallographical axes ⟨111⟩ and the direction [hkl] (Table I). The following formulas for K_1 and K_2 were obtained:

$$K_1 = -2NkT\left\{\ln\left[\cosh\frac{A}{kT}\cosh\frac{\sqrt{(2/3)B^2+a^2}}{kT}+\cosh\frac{3A}{kT}\cosh\frac{\sqrt{9(2/3)B^2+a^2}}{kT}\right]+\right.$$

$$+\ln\left[\cosh\frac{A}{kT}\cosh\frac{a}{kT}+\cosh\frac{3A}{kT}\cosh\frac{a}{kT}\right]+$$

$$\left.-2\ln\left[\cosh\frac{A}{kT}\cosh\frac{\sqrt{(1/3)B^2+a^2}}{kT}+\cosh\frac{3A}{kT}\cosh\frac{\sqrt{9(1/3)B^2+a^2}}{kT}\right]\right\}. \qquad (6)$$

$$K_2 = -\tfrac{1}{4}NkT\left\{27\ln\left[\cosh\frac{A}{kT}\cosh\frac{\sqrt{B^2+a^2}}{kT}+\cosh\frac{3A}{kT}\cosh\frac{\sqrt{9B^2+a^2}}{kT}\right]+\right.$$

$$+81\ln\left[\cosh\frac{A}{kT}\cosh\frac{\sqrt{(1/9)B^2+a^2}}{kT}+\cosh\frac{3A}{kT}\cosh\frac{\sqrt{9(1/9)B^2+a^2}}{kT}\right]+$$

$$-72\ln\left[\cosh\frac{A}{kT}\cosh\frac{\sqrt{(2/3)B^2+a^2}}{kT}+\cosh\frac{3A}{kT}\cosh\frac{\sqrt{9(2/3)B^2+a^2}}{kT}\right]+$$

$$-72\ln\left[\cosh\frac{A}{kT}\cosh\frac{a}{kT}+\cosh\frac{3A}{kT}\cosh\frac{a}{kT}\right]+$$

$$\left.+36\ln\left[\cosh\frac{A}{kT}\cosh\frac{\sqrt{(1/3)B^2+a^2}}{kT}+\cosh\frac{3A}{kT}\cosh\frac{\sqrt{9(1/3)B^2+a^2}}{kT}\right]\right\}. \qquad (7)$$

$$A = \mu_B H_e, \qquad B = \tfrac{1}{2}\alpha\lambda.$$

The tacit assumption made here is that the individual cobalt ions are the sole source of magnetic anisotropy. There exist, however, contributions from other ions, as well as

other types of anisotropy. From assessments by Yosida and Tachiki [11], these are by at least two orders of magnitude smaller than the anisotropy due to the cobalt ions, and consequently can be neglected.

This paper is aimed at an experimental verification of Tachiki's theory for high concentrations of cobalt, and at a numerical determination of the constants occurring in Eq. (1), namely of the product $\alpha\lambda$ and the constant a.

2. *Measurements, and processing of the results*

The measurements were performed on the CoNi-ferrite samples, of composition $Co_xNi_{x-1}Fe_2O_{4\pm\gamma}$ at $x = 0.075$; 0.3; 0.5; 0.7; 0.9; 1.0, on which Elbinger [10] had measured the anisotropy of magnetization and on which, subsequently, measurements of the magnetization had been carried out [12]. The samples were X-ray oriented by Laue's back reflection method.

The measurements of the crystal anisotropy were performed with a torque anisometer [13], in which a light beam reflected from a mirror rigidly attached to the mobile parts was incident on a pair of photoelements of an autocompensating system, producing an electric signal proportional to the deviation of the light spot. The electric signal was recorded automatically. A rotating electromagnet was set in motion by an electric motor. The amplitude of the torque curves varied by several orders of magnitudes. By adjusting the suspension, the sensitivity of the anisometer was chosen so that the deviations of the mobile parts amounted to several degrees of the arc and the amplitude of the curve recorded varied between several and about 20 cm. The accuracy of amplitude measurement ranged from 5 per cent for the smallest amplitudes recorded to fractions of 1 per cent for the curves having amplitudes of the order of 20 cm. The driving moments of the various suspensions were determined from the period of torsional oscillations of a solid of known moment of inertia attached to the suspension.

For all the samples, magnetic torque curves were determined from room to Néel temperature in the crystallographical plane (110); we shall be denoting these curves by $L_{(110)}$. For the samples with $x = 0.7$ and $x = 1.0$, measurements were performed moreover at liquid nitrogen temperature in the plane (110). For the one with $x = 0.5$, supplementary measurements were performed in the plane (100), yielding the curves $L_{(100)}$.

With the aim of calculating the anisotropy constants K_1 and K_2, the torque curves were processed by Fourier analysis [14, 15]. The amplitudes of the first six components of the Fourier series:

$$L = \tfrac{1}{2}a_0 + \sum_{n=1}^{\infty} (A_n \sin nQ_i + B_n \cos nQ_i) \tag{8}$$

were calculated from the formulas:

$$A_n = \frac{2}{k}\sum_{i=1}^{k} L(Q_i) \sin nQ_i, \qquad B_n = \frac{2}{k}\sum_{i=1}^{k} L(Q_i) \cos nQ_i. \tag{9}$$

For computing the components of the Fourier distribution, amplitudes $L(Q_i)$ were taken for 24 equidistant angles Q_i *i.e.* every 7.5° at a period of the function amounting to 180°, by means of an "Odra" electronic computer. In the plane (100), with the angle Q counted from the direction [001], the torque is given by the formula:

$$L_{(100)} = -K_u \sin 2Q - \tfrac{1}{2}K_1 \sin 4Q. \tag{10}$$

In the crystallographic plane (110), with the angles measured similarly from the direction [001], the magnetic torque is given as:

$$L_{(110)} = -(K_u + \tfrac{1}{4}K_1 + \tfrac{1}{64}K_2)\sin 2Q +$$

$$-(\tfrac{3}{8}K_1 + \tfrac{1}{16}K_2)\sin 4Q + \tfrac{3}{64}K_2 \sin 6Q. \tag{11}$$

The constant K_u, which in either case intervenes in the amplitude of the second harmonic, expresses the anisotropy of low order due to deviations of the sample from perfect sphericity, inhomogeneities of the measuring field, magnetostriction, and so forth. By Eqs (10) and (11), all amplitudes B_n and odd amplitudes A_n should vanish or not exceed the error of measurements. In very many cases, the amplitude A_6 in the plane (110) also was very small, not permitting the direct calculation of K_2. In the plane (100), relatively large amplitudes A_2 were obtained pointing to a large value of K_u. In some cases, the values of even amplitudes B_n for both $L_{(100)}$ and $L_{(110)}$ curves exceeded experimental error. This was assumed as being due to an incorrect position of the zero point on the axis of angles of the magnetic torque curve. The resulting error in angle was calculated from the ratio of amplitudes A_n/B_n as amounting to several degrees of the arc. In the plane (110), with regard to the low value of A_6, it proved impossible to determine separately the influence of the constant K_u on the results obtained when calculating K_1 and K_2.

For a comparison of the results obtained when using different methods of calculating the anisotropy constants, the constant K_1 for the sample with $x = 0.5$ was calculated by three distinct procedures: from the amplitudes of the $L_{(110)}$ curves as done in Ref. [10]; by Fourier analysis of the $L_{(100)}$ curves; and by Fourier analysis of the $L_{(110)}$ curves. In each case, different values were obtained for K_1. Whereas Fourier analysis of the $L_{(100)}$ and $L_{(110)}$ curves yielded similar results, those calculated from the amplitudes of the $L_{(100)}$ curve were on the average by 19 per cent larger than those obtained by Fourier analysis. The anisotropy constants from Fourier analysis at room temperature coincided with those obtained by Elbinger [10] on elimination of the influence of the anisotropy of magnetization. A slightly larger discrepancy occurred for the sample with $x = 1.0$ only.

In this paper, the influence of magnetization anisotropy is not taken into account; according to Elbinger, it should be of the order of 5 per cent. This seemed hardly worth taking into consideration, since an error of the same order of magnitude is incurred by neglecting the influence of anisotropy of lower order and, moreover, in the crystallographical plane (110), it had not proved feasible to determine separately the effect of magnetization anisotropy on K_2.

Fig. 1a shows the constant K_1 *vs* the temperature. In all samples, K_1 decreases steeply with the temperature, though the process cannot be approximated by the exponential function. At constant temperature, K_1 increases linearly with the cobalt content (Fig. 1b) in agreement with measurements by Elbinger [10] at room temperature. The anisotropy

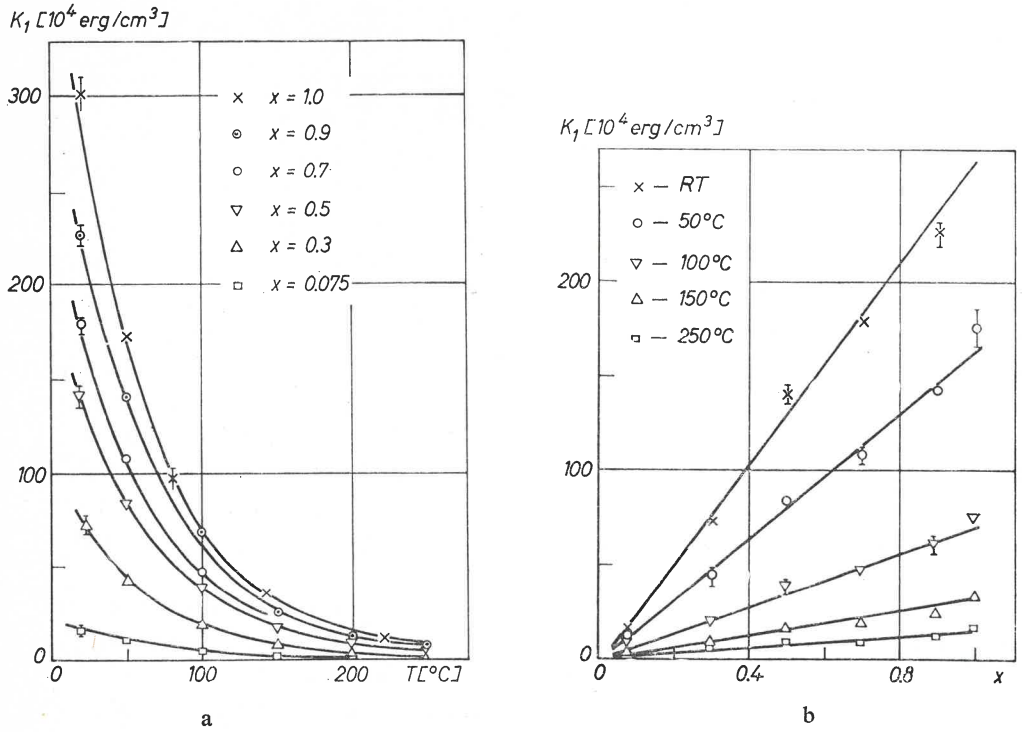

Fig. 1. Anisotropy constant K_1 of $Co_xNi_{1-x}Fe_2O_{4\pm\gamma}$ ferrite *vs* the temperature at constant x (curve a) and *vs.* x at constant T (curve b). Standard deviations are noted

constant K_2 is negative; its absolute value decreases with the temperature like K_1 (Fig. 2a). At constant temperature, it also increases linearly with x, the cobalt content (Fig. 2b). In all the graphs, standard deviations of the anisotropy constants are noted for some values of x; they are relatively small for K_1 but are very large in the case of K_2. In cases when it was possible to determine K_2 from the amplitude of the 6-th harmonic, error in K_2 was twice smaller.

The values of K_1 obtained by us in the present investigation are in greement with the values of others [1, 2, 3, 16]. Elbinger [10] too, and recently Pakhamova *et al.* [17] (for small x) have reported a linear dependence of K_1 on the cobalt content x. The results of Pakhamova the linearity of $K_1(x)$ to the region of very low cobalt concentrations ($x < 0.14$), where the effect of the anisotropy contributed by the Fe ions is no longer negligible.

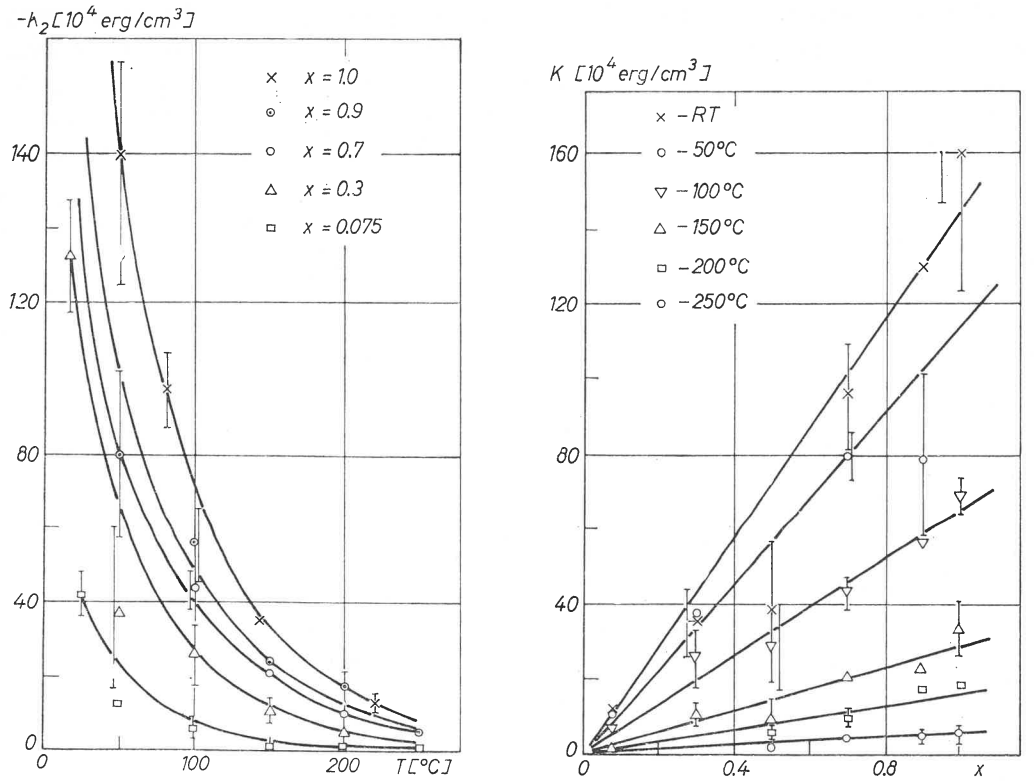

Fig. 2. Anisotropy constant K_2 of $Co_xNi_{1-x}Fe_2O_{4\pm\gamma}$ ferrite *vs* the temperature at constant x (curve a) and *vs* x at constant T (curve b). Standard deviations are noted

3. *Interpretation of the results*

The crystal anisotropy constants K_1 and K_2 of CoNi-ferrite were assumed as being given by the formulas (6) and (7), resulting from the theory of Tachiki. When deriving those formulas, no distinction had been made between the two possible configurations of cobalt ions. Similarly, no such distinction was made by Miamoto *et al.* [9]. The assignment of different a-values to different configurations of the Co^{2+} ions leads to a nonlinear dependence of K_1 and K_2 on the cobalt content. Now, we found a well-defined linearity of $K_1(x)$ (Fig. 1b), and in spite of rather large experimental error $K_2(x)$ too is satisfactorily approximated by a straight line (Fig. 2b). With regard to the fact that Eqs (6) and (7) express a linear proportionality to N (the number of cobalt ions), agreement with Tachiki's theory is in this respect complete.

When quantitatively adjusting the parameters of Eqs (6) and (7) to the experimental curves, it was necessary to take into account the temperature-dependence of the effective field H_e. The product $\mu_B H_e$ was assumed to vary with temperature in the same way as the magnetization. The previously studied [12] temperature-dependence of the magnetiza-

tion of the samples from room up to Curie temperature was extrapolated to $T = 0°K$ on the assumption (in conformity with the results of Refs [18, 19]) that from 0°K to room temperature the magnetization of the samples decreases by about 10 per cent. The value of $\mu_B H_e$ at 0°K was assumed to be given by the relation $g\mu_B H_e = kT_N$, where $g = 2$ is Landé's factor and T_k the Néel temperature. The results of evaluations of $\mu_B H_e$ are shown in Fig. 3.

Henceforth we chose the values of $\alpha\lambda$ and a so that Eq. (6) shall describe the experimentally determined dependence of K_1 for the selected value $x = 0.7$. With regard to the linearity in N, agreement between the theory and experiment for $x = 0.7$ will automatically

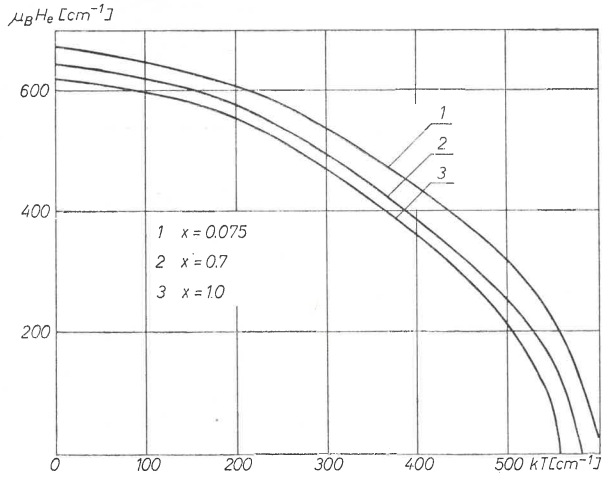

Fig. 3. Product of Bohr's magneton and the internal field *vs* temperature, evaluated from measurements of the magnetic moments *vs* temperature [12]

extend to the other values of x. Since Eq. (6) is rather involved, it was not possible to achieve an adjustment of the parameters $\alpha\lambda$ and a in a simple manner. We thus wrote seven functions of the type:

$$F_i(K_1) = K_{1i} - f_i(\alpha\lambda, a), \tag{12}$$

where K_{1i} is the experimental value of K_1 at a given temperature T_i and $f_i(\alpha\lambda, a)$ stands for Eq. (6) at temperature T_i. The "Odra" computer was then used for finding those values of $\alpha\lambda$ and a which made the sum:

$$\sum_{i=1}^{7} [F_i(K_1)]^2 = \sum_{i=1}^{7} \beta_i^2 [K_{1i} - f_i(\alpha\lambda, a)]^2 \tag{13}$$

a minimum. The coefficients ($\beta_i = 1$, for $i = 1, \ldots, 7$) were omitted in the first calculations. The function (13) was found to present a unique minimum in the points $\alpha\lambda = 84.5$ and $a = 20\ \text{cm}^{-1}$; however, the values of the various functions (12) in the minimum were comparable with those of K_{1i}. In further work, various values were assumed for the β's or values of the parameters were determined separately for various pairs of experimental points. In this way values of $\alpha\lambda$ ranging from 56 to 88.4 cm^{-1} and a-values ranging widely

from 0 to 90 cm^{-1} were obtained. The temperature-dependence of the K_1's calculated from Eq. (5) for arbitrary values of $\alpha\lambda$ and a from the interval determined in the previous calculations was found to decrease more slowly than the experimental curve (Fig. 4), and the deviations of the various experimental points from the theoretical curve were very large. This led us to the conclusion that on assuming the parameters $\alpha\lambda$ and a as

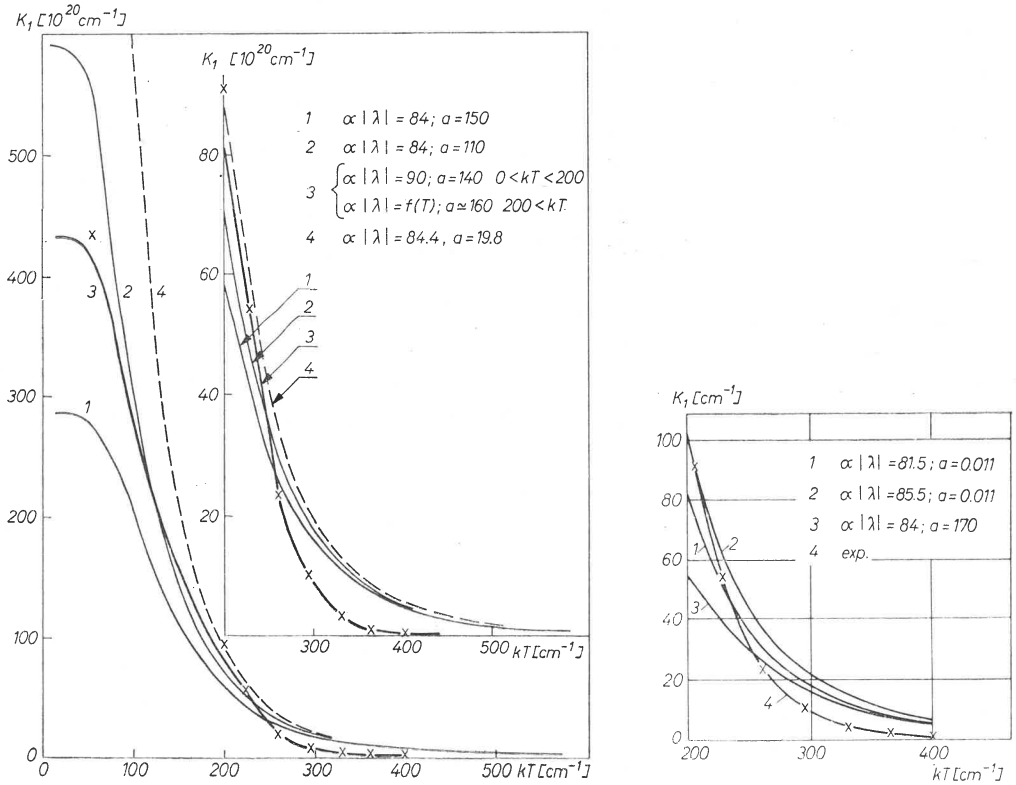

Fig. 4. Temperature-dependence of K_1 calculated from Eq. (6) for various values of the parameters $\alpha\lambda$ and a, and experimental curves for $Co_xNi_{1-x}Fe_2O_{4\pm\gamma}$ ferrite at $x = 0.7$ (curve a comprises the entire temperature range; curve b — only the range above room temperature)

constant it is not possible to adjust the theoretical curve to the experimental one in the entire range of temperatures. It was thus decided to chose separately values of these parameters for each experimental point including the one corresponding to the temperature of liquefied nitrogen. The results of this adjustment are listed in Table II, where the squared deviation of the experimental point from the theoretical value is also given. Compared to the values of the K_1's, the deviations are very small. The results of Table II are plotted in Fig. 5; they suggest the necessity of assuming the constants $\alpha\lambda$ and a as varying according to the temperature. The constant $\alpha\lambda$ can be taken to be proportional to the internal field, $\alpha\lambda = \gamma\mu_B H_e(T)$, with a proportionality factor of $\gamma = 0.143$. It is not possible to express

TABLE II

Results of simultaneous adjustment of the parameters $\alpha\lambda$ and a to the experimental points for sample $x = 0.7$ (temperature in °C, other quantities in cm^{-1})

i	τ	kT	$\mu_B H_e$	K_{1i}	Adjusted values			$\alpha\lambda = 0.143\mu_B H_e$
					a	$\alpha\lambda$	$[K_{1i} - f_i(\alpha\lambda, a)]^2$	
1	−195.8	54	630	$430 \cdot 10^{20}$	141.	91.4	$1.0 \cdot 10^{39}$	90
2	18	202.2	580	$90 \cdot 10^{20}$	111.5	91.4	$1.3 \cdot 10^{36}$	83
3	50	224.6	560	$54.1 \cdot 10^{20}$	60.0	84.0	$1.12 \cdot 10^{37}$	80
4	100	260.1	526	$23.1 \cdot 10^{20}$	152.5	81.6	$2.72 \cdot 10^{35}$	76
5	150	294.3	496	$10.2 \cdot 10^{20}$	153.5	74.0	$1.3 \cdot 10^{37}$	71
6	200	330	462	$3.3 \cdot 10^{20}$	166.6	63.0	$1.3 \cdot 10^{31}$	66
7	250	365	426	$1.3 \cdot 10^{20}$	171.0	53.8	$3.8 \cdot 10^{36}$	61
8	300	400	384	$4.3 \cdot 10^{19}$	161.5	46.2	$2.5 \cdot 10^{32}$	55

the temperature-dependence of the constant a so simply; from Fig. 4, a is seen to have a very strong influence on the value of K_1 (as well as on that of K_2) at low temperature. At high ones (above 100°C), the shape of the dependence is defined by the constant $\alpha\lambda$ (Fig. 4b). No considerable error is thus incurred by neglecting the rising portion of a at $kT > 240\ cm^{-1}$.

To prove that the quantity $\alpha\lambda$ cannot take a constant value, we give in Table III the results obtained when adjusting a at $\alpha\lambda = 84\ cm^{-1}$. No univocal interpretation of the

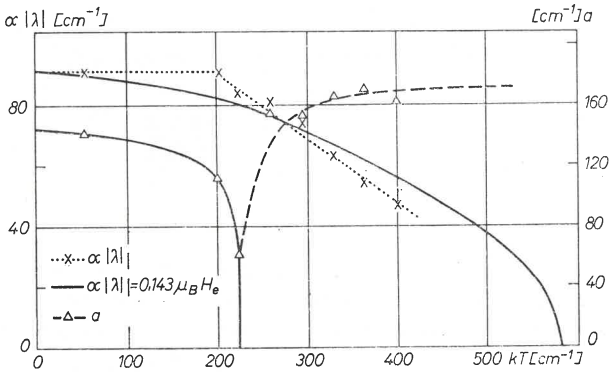

Fig. 5. Temperature-dependence of the product $\alpha\lambda$ and constant a from the data of Table II (points in the graph), and their shape assumed when interpreting the results (continuous line)

constant a is then possible; the deviations of the theoretically adjusted points from experiment are comparable with the anisotropy constants and, at higher temperatures, exceed the constant K_1 many times.

Values of K_2 were calculated for a given set of values of the constants $\alpha\lambda$ and a. In accordance with experiment, a negative sign of K_2 was obtained (thus opposite to that of K_1), but the numerical values were slightly lower than those of K_1. On the other hand,

TABLE III

Results of adjustment of the parameter a for sample $x = 0.7$ at $\alpha\lambda = 84\ \mathrm{cm}^{-1}$ (all quantities in cm^{-1})

i	kT	$\mu_B H_e$	K_{1i}	a	$[K_{1i} - f_i(\alpha\lambda, a)]^2$
1	54	630	$430 \cdot 10^{20}$	121	$225 \cdot 10^{40}$
2	202.2	580	$90 \cdot 10^{20}$	0	$87 \cdot 10^{40}$
3	224.6	560	$54.1 \cdot 10^{20}$	60	$0.01 \cdot 10^{40}$
4	260.1	526	$23.2 \cdot 10^{20}$	151	$7.3 \cdot 10^{40}$
5	294.3	496	$10.2 \cdot 10^{20}$	151	$44 \cdot 10^{40}$
6	330	462	$3.3 \cdot 10^{20}$	151	$55 \cdot 10^{40}$
7	365	426	$1.3 \cdot 10^{20}$	151	$40 \cdot 10^{40}$
8	400	384	$0.43 \cdot 10^{20}$	151	$18 \cdot 10^{40}$

experiment yields K_2-values larger than K_1. With regard to large experimental error on K_2, this discrepancy cannot be taken as justified.

The results of the foregoing analysis can be summed up as follows:

1. Assuming the internal field to decrease with temperature like the magnetization and the crystalline field of lower symmetry and spin-orbit coupling to remain constant, Tachiki's theory though yielding the correct sign of the anisotropy constants K_1 and K_2 and permitting their correct interpretation *vs* the cobalt content nevertheless fails to yield the correct temperature-dependence of K_1 and K_2.

2. The low temperature-dependence of K_1 and K_2 is essentially defined by the constant a *i.e.* by the lower symmetry field, stemming from the differences in charge of Co^{2+}, Ni^{2+} and Fe^{3+} ions occupying octahedral sites. Above 100°C, this field is practically irrelevant, and the shape of $K_1(T)$ is solely defined by the spin-orbit coupling given by the parameter $\alpha\lambda$.

3. Tachiki's theory can be brought to agree with the experimental temperature--dependence of the anisotropy constants only by assuming the spin-orbit coupling and lower symmetry field (besides the internal field) as temperature-dependent. $\alpha\lambda$ decreases with temperature in the same manner as the internal field; the constant a decreases similarly, but falls to zero already at a temperature approximately equal to 0.4 of the Néel temperature (Fig. 5). The rising portion of the $a(T)$-curve for temperatures upward of $0.4\,T_N$ can be neglected since in this region T almost completely ceases to affect the theoretical shape of $K_1(T)$ and $K_2(T)$.

It should be noted that the decrease in $\alpha\lambda$ with temperature is due to the decrease in λ, the coefficient defining spin-orbit coupling. This interpretation is confirmed by the very large magnetostriction of cobalt ferrite — at least 10 times more than that of other ferrites and metals [20].

The value of $\alpha\lambda$ extrapolated to 0°K is $91.5\ \mathrm{cm}^{-1}$ — much less than that of Slonczewski, who obtained $\alpha\lambda = 132\ \mathrm{cm}^{-1}$. Miyamoto, Tanaka and Iida [9] determined $\alpha\lambda$ by ferromagnetic resonance measurements on Co-doped magnetite, obtaining a value of $\alpha\lambda = 97\ \mathrm{cm}^{-1}$ very close to ours.

The value of a extrapolated to 0°K is $141\ \mathrm{cm}^{-1}$, in excellent agreement with Miyamoto, Tanaka and Iida [9], who obtained $146\ \mathrm{cm}^{-1}$ (Ref. [9] does not state this value directly;

it can be calculated from their factor r). Thus, the experimental values lie very close to the value $a = 146\ \mathrm{cm}^{-1}$ calculated by Tachiki [7] with Slater's 3d electron wave function.

The temperature-dependence of a, and in particular its vanishing already at the temperature of $0.4\ T_N$, still await clarification. This suggests an averaging of the charges of cations occupying octahedral sites despite the fact that the latter are occupied by the three ion species Co^{2+}, Ni^{2+} and Fe^{3+}.

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