On the Origin of the Magnetic Anisotropy Energy of Ferrites

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(Received November 1, 1956)

Possible sources of the anisotropy energy are investigated for ferromagnetic ferrites, i.e., Ni-, Co-, Fe- and Mn-ferrites. The cubic anisotropy energy which arises from the anisotropy of the crystalline field acting on magnetic ions and is described by the function of the spin operator of one ion identically vanishes for ions with spin less than 2, so that this kind of anisotropy energy vanishes for Ni^{2+} and Co^{2+} ions. The anisotropy energy arising from the magnetic dipole-dipole interaction which appears for cubic crystals in its second order perturbation was calculated for Mn- and Ni-ferrites and that arising from the anisotropic exchange interaction calculated for Ni-ferrite but they were found to be too small to account for the experimental values. Therefore, *it is concluded that the major part of the anisotropy energy for Ni-ferrite arises from the anisotropy energy of Fe^{3+} ions, for magnetite from the anisotropy energy of Fe^{2+} and Fe^{3+} ions, and for Mn-ferrite from the anisotropy energy of Fe^{3+} and Mn^{2+} ions.* Especially it is shown that the experimental anisotropy energy of magnetite extrapolated to the absolute zero of temperature is in good agreement with the sum of the experimental anisotropy energy of Ni-ferrite and the calculated value of the anisotropy energy of Fe^{2+} ions. For Co-ferrite, its large anisotropy energy seems to come from the pseudo-quadrupole and anisotropic exchange interactions among Co and Fe ions, but the situation is too complex to carry out the calculation of the anisotropy energy in this case.

Finally, the temperature dependence of the cubic anisotropy energy is calculated for Mn-ferrite, and is shown to decrease as $(T_c - T)^2$ near the Curie temperature. Further, the sum of the coefficient, a of the cubic anisotropy Hamiltonian for Mn^{2+} and Fe^{3+} ions of the octahedral sites and that for Fe^{3+} ion of the tetrahedral sites have been determined for Mn-ferrite by adjusting the calculated anisotropy energy *vs.* temperature curve so as to fit the experimental one, and it is found, neglecting the small a-value of Mn^{2+} ions, that the a-value of Fe^{3+} ions on octahedral sites has five times as large an absolute value as that of Fe^{3+} ions on tetrahedral sites and that the former has the opposite sign to the latter.

§ 1.   Introduction

Numerous experimental investigations have been done on the magnetic anisotroqy energy of ferromagnetic ferrites with the static torque method, magnetization curvemethod and microwave resonance method.[1-19] Experimental data are summarized in the table of the paper by Bozorth, Tilden and Williams.[13] As seen from this table, Co-ferrite has much larger anisotropy energy compared with other ferromagnetic ferrites, namely Ni, Fe- and Mn-ferrites, and further the anisotropy constant K_1 for the latter ferrites is negative and their easy axis of magnetization lies in [111] direction, except for magnetite at low temperatures, whereas K_1 of Co-ferrite is positive and its easy axis is in the [100] direction. The anisotropy energy of ferrites is quite significantly influenced by a small added puantity of Co ions. Especially, Bickford, Pappis and Stull[10] showed that a small quantity

of cobalt ions mixed in magnetite can shift the temperature at which the easy axis of magnetization changes from [111] to [100] to a markedly high temperature. Bozorth, Beatrice, Cetlin, Galt, Merritt and Yager[19] have reported that, for Ni-ferrite with Fe^{2+} ions as impurities, the microwave method and the static method of measuring anisotropy energy give somewhat different values. Therefore, in order to know the intrinsic value of the anisotropy energy, experimental data for pure substances are needed.

The anisotropy energy of cubic crystal is in general small compared with that of crystal with low symmetry and, at the same time, its temperature dependence is very intense. Thus, the room temperature value can be very different from that at the absolute zero of temperature, especially in Mn-ferrite and Mn-Zn ferrite which have a comparatively low Curie temperature.

The following table shows the anisotropy constant K_1 of ferromagnetic ferrites at low temperature. The anisotropy constant of magnetite in this table is the value at the

Table I

Substance	K_1 erg/cc	K_1 cm^{-1}/molecule.	Reference
$NiFe_2O_4$	-1.18×10^5	-4.3×10^{-2}	(18)
$CoFe_2O_4$	$4.4 \sim 17.5 \times 10^6$	$1.6 \sim 6.4$	(13)
Fe_3O_4	-2.0×10^5	-7.4×10^{-2}	(11)
$MnFe_2O_4$	-2.2×10^5	-8.5×10^{-2}	(2)

absolute zero of temperature obtained by extrapolating the values at temperatures higher than the temperature at which the anisotropy constant changes its sign. The purpose of this paper is to investigate the sources of the anisotropy energy of ferrites and to clarify its nature.

The magnetic ions in ferrites are Fe^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}. Fe^{3+} and Mn^{2+} ions have no orbital moment, while Fe^{2+}, Co^{2+} and Ni^{2+} have non zero orbital moment in their free states. The latter divalent ions occupy the octahedral sites. The crystalline field acting on the octahedral site arises from the surrounding oxygen ions and metal ions. The part from the surrounding oxygen ions has a cubic symmetry neglecting a slight shift of the position of the oxygen ions, whereas the part from the metal ions has a trigonal symmetry whose axis lies in either of the four {111} directions, so far as we do not distinguish the difference between Fe^{3+} and divalent ions. If we discriminate this difference, this part has a lower symmetry and differs from ion to ion. Therefore, we can consider that the orbital moment of these divalent ions is quenched, namely the ground orbital state is not degenerate, so that the treatment of the anisotropy energy becomes considerably simple though the crystals under consideration have cubic symmetry. This fact has been proved by that g-values near 2 were found by the microwave resonance absorption.

The sources of the anisotropy energy of ferrites are the following interactions: the magnetic dipole-dipole interaction, the effective anisotropy Hamiltonian of each spin in

the crystalline field, and the anisotropic exchange interaction which is produced by the combined action of the $L \cdot S$ coupling and the exchange interaction. These were pointed out by Keffer[20] and Moriya and Yosida[21] in the case of antiferromagnetism. In the case of cubic crystals like ferrites, the magnetic dipole-dipole interaction does not give any cubic anisotropy energy in the classical treatment, but its higher order effect contributes to the cubic anisotropy as shown by Van Vleck.[22] For the anisotropy energy arising from the other sources, the situations are the same and higher order calculations are needed, so that the treatment becomes somewhat troublesome compared with the case of lower symmetry. We shall begin with the consideration of the simplest part of the anisotropy energy, namely the anisotropy energy coming from the anisotropy of the crystalline field.

§ 2. Anisotropy spin Hamiltonian for ions under the action of the crystalline field

The cubic spin Hamiltonian of ions whose orbital moment is quenched by the crystalline field is represented by

$$\frac{a}{6}(S_x^4 + S_y^4 + S_z^4), \qquad (2\cdot1)$$

where S_x, S_y and S_z are the x-, y- and z-components of the spin angular momentum S (x, y and z are the cubic principal axes). The constant a may be calculated by the perturbation method starting from the states which are split by the crystalline field and taking the spin-orbit coupling and intra spin-spin interaction as perturbations[23],[24]. We shall here deal with the calculation of the average value of $(2\cdot1)$ in the case in which the Weiss molecular field is acting in a certain direction, ζ, whose direction cosines referred to the cubic axes will be denoted by (n_1, n_2 and n_3).

If we take ξ- and η-axes perpendicular to the ζ-axis and also to each other and denote their direction cosines referred to the cubic axes by (l_1, l_2, l_3) and (m_1, m_2, m_3), respectively, S_x, S_y and S_z can be expressed in terms of S_ξ, S_η and S_ζ by the following relations:

$$S_x = l_1 S_\xi + m_1 S_\eta + n_1 S_\zeta$$
$$S_y = l_2 S_\xi + m_2 S_\eta + n_2 S_\zeta \qquad (2\cdot2)$$
$$S_z = l_3 S_\xi + m_3 S_\eta + n_3 S_\zeta.$$

With the use of $(2\cdot2)$ the average value of S_x^4 can be expressed as

$$\langle S_x^4 \rangle = (l_1^4 + m_1^4) \langle S_\xi^4 \rangle + n_1^4 \langle S_\zeta^4 \rangle$$
$$+ l_1^2 m_1^2 \{ \langle \{S_\xi S_\eta\}^2 \rangle + \langle \{S_\xi^2 S_\eta^2\} \rangle \}$$
$$+ (l_1^2 + m_1^2) n_1^2 \{ \langle \{S_\xi S_\zeta\}^2 \rangle + \langle \{S_\xi^2 S_\eta^2\} \rangle \}, \qquad (2\cdot3)$$

where $\{AB\}$ is the abbreviation of $AB+BA$ and we have taken into account that the averages of the terms including odd powers of S_ξ and S_η vanish and that $\langle S_\xi^4 \rangle$ and

$\langle S_\zeta^2 S_\zeta^2 \rangle$, etc., are respectively equal to $\langle S_\eta^4 \rangle$ and $\langle S_\eta^2 S_\zeta^2 \rangle$, etc.   Adding to $(2\cdot3)$ the corresponding expressions for $\langle S_y^4 \rangle$ and $\langle S_z^4 \rangle$, we obtain

$$\langle S_x^4 + S_y^4 + S_z^4 \rangle = \langle S_\xi^4 \rangle + \langle \{S_\xi S_\zeta\}^2 \rangle + \langle \{S_\xi^2 S_\zeta^2\} \rangle$$
$$+ (l_1^2 m_1^2 + l_2^2 m_2^2 + l_3^2 m_3^2) \{\langle \{S_\xi S_\eta\}^2 \rangle + \langle \{S_\xi^2 S_\eta^2\} \rangle - 2\langle S_\xi^4 \rangle \}$$
$$+ (n_1^4 + n_2^4 + n_3^4) \{\langle S_\zeta^4 \rangle + \langle S_\xi^4 \rangle - \langle \{S_\xi S_\zeta\}^2 \rangle - \langle \{S_\xi^2 S_\zeta^2\} \rangle \}. \qquad (2\cdot4)$$

If we use the relations

$$\langle \{S_\xi S_\eta\}^2 \rangle = 2\langle \{S_\xi^2 S_\eta^2\} \rangle + 5\langle S_\zeta^2 \rangle - 2S(S+1),$$
$$\langle \{S_\xi S_\zeta\}^2 \rangle = 2\langle \{S_\xi^2 S_\zeta^2\} \rangle - (5/2)\langle S_\zeta^2 \rangle + (1/2)S(S+1),$$

in $(2\cdot4)$, we obtain

$$\langle S_x^4 + S_y^4 + S_z^4 \rangle = \langle S_\xi^4 \rangle + 3\langle \{S_\xi^2 S_\zeta^2\} \rangle + (1/2)S(S+1) - (5/2)\langle S_\zeta^2 \rangle$$
$$+ (l_1^2 m_1^2 + l_2^2 m_2^2 + l_3^2 m_3^2) \{3\langle \{S_\xi^2 S_\eta^2\} \rangle - 2S(S+1) + 5\langle S_\zeta^2 \rangle - 2\langle S_\xi^4 \rangle \}$$
$$+ (n_1^4 + n_2^4 + n_3^4) \{\langle S_\zeta^4 \rangle + \langle S_\xi^4 \rangle - 3\langle \{S_\xi^2 S_\zeta^2\} \rangle - (1/2)S(S+1) + (5/2)\langle S_\zeta^2 \rangle \}, \qquad (2\cdot5)$$

Here we will express $\langle \{S_\xi^2 S_\eta^2\} \rangle$, $\langle \{S_\xi^2 S_\zeta^2\} \rangle$ and $\langle S_\xi^4 \rangle$ in terms of $\langle S_\zeta^4 \rangle$ and $\langle S_\zeta^2 \rangle$. There are following two relations between these three quantities, namely

$$2\langle S_\xi^4 \rangle + \langle S_\zeta^4 \rangle + 2\langle \{S_\xi^2 S_\zeta^2\} \rangle + \langle \{S_\xi^2 S_\eta^2\} \rangle = S^2(S+1)^2, \qquad (2\cdot6)$$

$$2\langle S_\xi^4 \rangle + \langle \{S_\xi^2 S_\eta^2\} \rangle + \langle \{S_\xi^2 S_\zeta^2\} \rangle = S^2(S+1)^2 - S(S+1)\langle S_\zeta^2 \rangle. \qquad (2\cdot7)$$

The first relation is obtained by squaring the relation $S_\xi^2 + S_\eta^2 + S_\zeta^2 = S(S+1)$ and the second by adding two expressions which are obtained by multiplying this relation with S_ξ^2 from the right and from the left. $\langle S_\xi^4 \rangle$ can directly be calculated as

$$\langle S_\xi^4 \rangle = (3/8)\langle S_\zeta^4 \rangle - (3/4)S(S+1)\langle S_\zeta^2 \rangle + (3/8)S^2(S+1)^2$$
$$- (1/4)S(S+1) + (5/8)\langle S_\zeta^2 \rangle. \qquad (2\cdot8)$$

From $(2\cdot6)$, $(2\cdot7)$ and $(2\cdot8)$ we see that the coefficient of $(l_1^2 m_1^2 + l_2^2 m_2^2 + l_3^2 m_3^2)$ in $(2\cdot5)$ vanishes and $(2\cdot5)$ can be expressed completely in terms of $\langle S_\zeta^4 \rangle$ and $\langle S_\zeta^2 \rangle$ as

$$\langle S_x^4 + S_y^4 + S_z^4 \rangle = -(21/8)\langle S_\zeta^4 \rangle + (9/4)S(S+1)\langle S_\zeta^2 \rangle + (3/8)S^2(S+1)^2$$
$$- (15/8)\langle S_\zeta^2 \rangle + (1/4)S(S+1)$$
$$+ (n_1^4 + n_2^4 + n_3^4)[(35/8)\{\langle S_\zeta^4 \rangle - (1/5)[S^2(S+1)^2 - (1/3)S(S+1)]\}$$
$$- (15/4)\{\langle S_\zeta^2 \rangle - (1/3)S(S+1)\}\{S(S+1) - 5/6\}]. \qquad (2\cdot9)$$

This result can also be obtained by a more elegant method, namely by adding three Keffer's expressions[25]

$$\langle r_{ij}^{-4}(\mathbf{S}_i \cdot \mathbf{r}_{ij})^4 \rangle = cP_0(\theta_{ij}) + dP_2(\theta_{ij}) + eP_4(\theta_{ij})$$

with $\cos \theta_{ij} = n_1$, n_2 and n_3.

Above the Curie temperature $\langle S_\zeta^4 \rangle = (1/5)\{S^2(S+1)^2 - (1/3)S(S+1)\}$ and $\langle S_\zeta^2 \rangle = (1/3)S(S+1)$ so that the part including $(n_1^4 + n_2^4 + n_3^4)$ in (2·9) vanishes. On the other hand, at the absolute zero of temperature $\langle S_\zeta^4 \rangle = S^4$ and $\langle S_\zeta^2 \rangle = S^2$ so that the anisotropic part becomes

$$S(S-\tfrac{1}{2})(S-1)(S-\tfrac{3}{2})(n_1^4 + n_2^4 + n_3^4). \tag{2·10}$$

This result shows that for this kind of the anisotropy energy the quantum effect is significant and it makes the anisotropy energy identically vanish for S less than 2 in the whole temperature range. This was remarked by Van Vleck[22] as early as 1937. Thus, the anisotropy energy of cubic symmetry arising from the anisotropy of the crystalline field vanishes for Ni^{2+} and Co^{2+} ions. For Fe^{2+}, with $S=2$, the quantum effect reduces the anisotropy constant to one tenth of the classical value.

§ 3. Anisotropy energy in Mn- and Ni-ferrites arising from the dipole-dipole interaction

As mentioned in the preceding section, the anisotropy energy arising from the crystalline field in ferrites remains only for Fe^{3+}, Mn^{2+} and Fe^{2+} ions. Besides this anisotropy energy we can consider those arising from the magnetic dipole-dipole interaction and the anisotropic exchange interaction.

The cubic anisotropy energy arising from the magnetic dipole-dipole interaction at the absolute zero of temperature can be calculated by the perturbation method, taking the magnetic dipole-dipole interaction as the perturbing Hamiltonian. The dipole-dipole interaction between two spins can be divided into the following four parts, as done by Bloembergen, Purcell and Pound[26] :

$$V_{ij} = g^2 \mu_B^2 r_{ij}^{-3}(A+B+C+E), \tag{3·1}$$

$$A = S_{\zeta i} S_{\zeta j}(1 - 3\cos^2\theta_{ij}),$$

$$B = -(1/4)\left[(S_{\xi i} - iS_{\eta i})(S_{\xi j} + iS_{\eta j}) + (S_{\xi i} + iS_{\eta i})(S_{\xi j} - iS_{\eta j})\right](1 - 3\cos^2\theta_{ij}), \tag{3·2}$$

$$C = -(3/2)\left[(S_{\xi i} + iS_{\eta i})S_{\zeta j} + (S_{\xi j} + iS_{\eta j})S_{\zeta i}\right]\sin\theta_{ij}\cos\theta_{ij}e^{-i\varphi_{ij}} + \text{conj. comp.},$$

$$E = -(3/4)(S_{\xi i} + iS_{\eta i})(S_{\xi j} + iS_{\eta j})\sin^2\theta_{ij}e^{-2i\varphi_{ij}} + \text{conj. comp.},$$

where the ζ-axis is taken in the direction of the spontaneous magnetization. The part A has only a diagonal element in the representation which diagonalizes the spin component S_ζ of each ion, and it gives rise to the ordinary classical dipole-dipole anisotropy energy, which evidently vanishes in cubic crystals as shown by Kaplan.[27] The part B has off-diagonal elements between the ground state with absolute saturation magnetization and those excited states in which one spin of octahedral sites and one spin of tetrahedral sites are reversed. The matrix element between the ground state and the excited state in which the ζ-component of the i-th spin of the octahedral site is $S_B - 1$ and that of the j-th spin of the tetrahedral site is $-S_A + 1$ is given by

$$- (g^2\mu_B{}^2/2) \cdot \sqrt{S_B}\,\sqrt{S_A}\,r_{ij}^{-3}(1-3\cos^2\theta_{ij}), \qquad (3\cdot3)$$

where S_B and S_A are, respectively, the magnitudes of the spins of octahedral and tetrahedral sites. Therefore, the second order perturbed energy per one octahedral ion becomes

$$-\frac{g^4\mu_B{}^4 S_B S_A}{4\,(\varDelta E_B+\varDelta E_A)}\sum_{BAj}\left(\frac{r_{ij}^2-3\zeta_{ij}^2}{r_{ij}^5}\right)^2, \qquad (3\cdot4)$$

where $\varDelta E_B$ is an increase of energy due to the change of the ζ-component of an octahedral spin by one and $\varDelta E_A$ is the corresponding quantity for a tetrahedral spin, and $\sum\limits_{BAj}$ means the summation over the tetrahedral j-sites surrounding the octahedral i-site.

If we here transform the coordinate system from ξ, η and ζ to x, y and z of the cubic axes by

$$\xi = l_1 x + l_2 y + l_3 z,$$
$$\eta = m_1 x + m_2 y + m_3 z, \qquad (3\cdot5)$$
$$\zeta = n_1 x + n_2 y + n_3 z,$$

the summand in $(3\cdot4)$ becomes

$$
\begin{aligned}
\left(\frac{r_{ij}^2-3\zeta_{ij}^2}{r_{ij}^5}\right)^2 = \frac{1}{r_{ij}^6}&-6\left\{n_1{}^2\frac{x_{ij}^2}{r_{ij}^8}+n_2{}^2\frac{y_{ij}^2}{r_{ij}^8}+n_3{}^2\frac{z_{ij}^2}{r_{ij}^8}+2n_1n_3\frac{x_{ij}y_{ij}}{r_{ij}^8}\right.\\
&+2n_2n_3\frac{y_{ij}z_{ij}}{r_{ij}^8}+2n_3n_1\frac{z_{ij}x_{ij}}{r_{ij}^8}\biggr\}+9\left\{n_1{}^4\frac{x_{ij}^4}{r_{ij}^{10}}+n_2{}^4\frac{y_{ij}^4}{r_{ij}^{10}}\right.\\
&+n_3{}^4\frac{z_{ij}^4}{r_{ij}^{10}}+6n_1{}^2n_2{}^2\frac{x_{ij}^2y_{ij}^2}{r_{ij}^{10}}+6n_2{}^2n_3{}^2\frac{y_{ij}^2z_{ij}^2}{r_{ij}^{10}}+6n_3{}^2n_1{}^2\frac{z_{ij}^2x_{ij}^2}{r_{ij}^{10}}\\
&+4n_1{}^3n_2\frac{x_{ij}^3y_{ij}}{r_{ij}^{10}}+4n_1n_2{}^3\frac{x_{ij}y_{ij}^3}{r_{ij}^{10}}+4n_2{}^3n_3\frac{y_{ij}^3z_{ij}}{r_{ij}^{10}}+4n_2n_3{}^3\frac{y_{ij}z_{ij}^3}{r_{ij}^{10}}\\
&+4n_3{}^3n_1\frac{z_{ij}^3x_{ij}}{r_{ij}^{10}}+4n_3n_1{}^3\frac{z_{ij}x_{ij}^3}{r_{ij}^{10}}+12n_2{}^2n_3n_1\frac{y_{ij}^2z_{ij}x_{ij}}{r_{ij}^{10}}\\
&+12n_3{}^2n_1n_2\frac{z_{ij}^2x_{ij}y_{ij}}{r_{ij}^{10}}+12n_1{}^2n_2n_3\frac{x_{ij}^2y_{ij}z_{ij}}{r_{ij}^{10}}\biggr\}. \qquad (3\cdot6)
\end{aligned}
$$

We concentrate our attention to an octahedral site whose trigonal axis of symmetry lies in the [111] direction. Then, the summation, $\sum x_{ij}^2/r_{ij}^8$, $\sum x_{ij}y_{ij}/r_{ij}^8$, $\sum x_{ij}^4/r_{ij}^{10}$, $\sum x_{ij}^2y_{ij}^2/r_{ij}^{10}$, $\sum x_{ij}^3y_{ij}/r_{ij}^{10}$ and $\sum x_{ij}^2y_{ij}z_{ij}/r_{ij}^{10}$ are unchanged by cyclic changes among x, y and z. The corresponding expressions for the other three kinds of octahedral sites can be obtained by changing the signs of two of n_1, n_2 and n_3. Thus, apart from the parts independent of the direction cosines, the average of the sum of $(3\cdot6)$ over the four kinds of octahedral sites becomes

$$9\,(n_1{}^4+n_2{}^4+n_3{}^4)\sum_{BAj}x_{ij}^4/r_{ij}^{10}+54\,(n_1{}^2n_2{}^2+n_2{}^2n_3{}^2+n_3{}^2n_1{}^2)\sum_{BAj}x_{ij}^2y_{ij}^2/r_{ij}^{10}. \qquad (3\cdot7)$$

With the use of $(3 \cdot 4)$ and $(3 \cdot 7)$, we obtain the anisotropy constant per molecule arising from the B interaction as

$$9 \frac{g^4 \mu_B{}^4 S_B S_A}{(\Delta E_B + \Delta E_A)} \sum_{BAj} \left\{ \frac{x_{ij}^4 - 3x_{ij}^2 y_{ij}^2}{r_{ij}^{10}} \right\}. \qquad (3 \cdot 8)$$

The part E in $(3 \cdot 2)$ has off-diagonal elements between the ground state and those excited states in which two octahedral spins or two tetrahedral spins are reversed. Using similar notation to that used in the case of the B interaction, the matrix element between the ground state and the excited state in which the ζ-components of the i-th and j-th spins of the octahedral sites are equal to $S_B - 1$, is given by

$$- (3/2) S_B g^2 \mu_B{}^2 r_{ij}^{-3} \sin^2 \theta_{ij} e^{2i\varphi_{ij}}. \qquad (3 \cdot 9)$$

Therefore, the second order energy per two octahedral spins becomes

$$- \frac{9}{4} \frac{g^4 \mu_B{}^4 S_B{}^2}{2\Delta E_B} \sum_{BBj} \left(\frac{\xi_{ij}^2 + \eta_{ij}^2}{r_{ij}^5} \right)^2. \qquad (3 \cdot 10)$$

Expressing the summand here in terms of x, y and z, taking average over four kinds of octahedral spins, and picking out the terms including $(n_1{}^2 n_2{}^2 + n_2{}^2 n_3{}^2 + n_3{}^2 n_1{}^2)$, we obtain the anisotropy constant per molecule as

$$\frac{9}{4} \frac{g^4 \mu_B{}^4 S_B{}^2}{\Delta E_B} \sum_{BBj} \left\{ \frac{x_{ij}^4 - 3x_{ij}^2 y_{ij}^2}{r_{ij}^{10}} \right\}. \qquad (3 \cdot 11)$$

Similarly, we obtain the anisotropy constant per molecule arising from the excited states in which two i and j spins of the tetrahedral sites have the ζ-components equal to $-S_A + 1$ as follows:

$$\frac{9}{8} \frac{g^4 \mu_B{}^4 S_A{}^2}{\Delta E_A} \sum_{AAj} \left\{ \frac{x_{ij}^4 - 3x_{ij}^2 y_{ij}^2}{r_{ij}^{10}} \right\}. \qquad (3 \cdot 12)$$

The C term in $(3 \cdot 2)$ has off-diagonal elements between the ground state and those excited states in which one spin of the octahedral sites has ζ-component equal to $S_B - 1$ or one spin of the tetrahedral sites has ζ-component equal to $-S_A + 1$. The corresponding matrix elements are, respectively,

$$- \frac{3}{2} \sqrt{2S_B} g^2 \mu_B{}^2 \left\{ S_B \sum_{BBj} r_{ij}^{-5} \zeta_{ij} (\xi_{ij} + i\eta_{ij}) - S_A \sum_{BAj} r_{ij}^{-5} \zeta_{ij} (\xi_{ij} + i\eta_{ij}) \right\} \qquad (3 \cdot 13a)$$

and

$$- \frac{3}{2} \sqrt{2S_A} g^2 \mu_B{}^2 \left\{ -S_A \sum_{AAj} r_{ij}^{-5} \zeta_{ij} (\xi_{ij} - i\eta_{ij}) + S_B \sum_{ABj} r_{ij}^{-5} \zeta_{ij} (\xi_{ij} - i\eta_{ij}) \right\}. \qquad (3 \cdot 13b)$$

The summation in $(3 \cdot 13a)$ for an octahedral spin whose trigonal axis is in the direction [111] can be written as

$$\left(S_B \sum_{BBj} \frac{\zeta_{ij} (\xi_{ij} + i\eta_{ij})}{r_{ij}^5} - S_A \sum_{BAj} \frac{\zeta_{ij} (\xi_{ij} + i\eta_{ij})}{r_{ij}^5} \right)$$

$$= (l_1 n_2 + l_2 n_1 + l_2 n_3 + l_3 n_2 + l_3 n_1 + l_1 n_3) \left(S_B \sum_{BB_j} \frac{x_{ij} y_{ij}}{r_{ij}^5} - S_A \sum_{BA_j} \frac{x_{ij} y_{ij}}{r_{ij}^5} \right)$$

$$+ i(m_1 n_2 + m_2 n_1 + m_2 n_3 + m_3 n_2 + m_3 n_1 + m_1 n_3) \left(S_B \sum_{BB_j} \frac{x_{ij} y_{ij}}{r_{ij}^5} - S_A \sum_{BA_j} \frac{x_{ij} y_{ij}}{r_{ij}^5} \right).$$

$$(3 \cdot 14)$$

Using $(3 \cdot 14)$ in the calculation of the second order energy to be obtained from $(3 \cdot 13a)$ and averaging the obtained expression with respect to the four kinds of spins, we have the following value of the anisotropy constant per two octahedral spins:

$$36 \frac{g^4 \mu_B^4 S_B}{\Delta E_B} \left\{ S_B \sum_{BB_j} \frac{x_{ij} y_{ij}}{r_{ij}^5} - S_A \sum_{BA_j} \frac{x_{ij} y_{ij}}{r_{ij}^5} \right\}^2. \qquad (3 \cdot 15)$$

Similarly, we get the anisotropy constant per molecule from $(3 \cdot 13b)$,

$$18 \frac{g^4 \mu_B^4 S_A}{\Delta E_A} \left\{ S_B \sum_{AB_j} \frac{x_{ij} y_{ij}}{r_{ij}^5} - S_A \sum_{AA_j} \frac{x_{ij} y_{ij}}{r_{ij}^5} \right\}^2, \qquad (3 \cdot 16)$$

where, however, both summations are found to vanish because of the symmetry of the crystal structure.

The values of the latter sums appearing in $(3 \cdot 8)$, $(3 \cdot 11)$, $(3 \cdot 12)$ and $(3 \cdot 15)$ are calculated numerically by the direct sum method up to eighth neighbors. In units of $a/8$, a being the lattice parameter, they are as follows:

$$\sum_{BA_j} (x_{ij}^4 - 3x_{ij}^2 y_{ij}^2)/r_{ij}^{10} = 0.000350, \quad \sum_{BB_j} (x_{ij}^4 - 3x_{ij}^2 y_{ij}^2)/r_{ij}^{10} = -0.00104$$

$$\sum_{AA_j} (x_{ij}^4 - 3x_{ij}^2 y_{ij}^2)/r_{ij}^{10} = -0.000533, \quad \sum_{BB_j} x_{ij} y_{ij}/r_{ij}^5 = 0.038,$$

$$\sum_{BA_j} x_{ij} y_{ij}/r_{ij}^5 = -0.017. \qquad (3 \cdot 17)$$

The excitation energy ΔE_B and ΔE_A can be expressed, using Néel's[28] notatins, as

$$\Delta E_B = g\mu_B H_B = g\mu_B n(\beta\mu M_B + \lambda M_A), \quad \Delta E_A = g\mu_B H_A = g\mu_B n(\alpha\lambda M_A + \mu M_B), \quad (3 \cdot 18)$$

where H_B and H_A are the molecular fields acting on the octahedral and tetrahedral sites and are expressible as linear combinations of the magnetizations of the A and B sites, M_A and M_B, per N ions, N being the Avogadro number.

In the case of Mn-ferrite, the constants n, α and β in $(3 \cdot 18)$ are estimated from the experimental magnetization vs. temperature curve in Sec. 6. Using the values of $(6 \cdot 13)$ and $(6 \cdot 14)$, $S_B = S_A = 5/2$ and $\lambda = 1/3$ and $\mu = 2/3$, the excitation energies become

$$\Delta E_B = 251 \text{ cm}^{-1}, \quad \Delta E_A = 471 \text{ cm}^{-1}. \qquad (3 \cdot 19)$$

Inserting $(3 \cdot 19)$ and $(3 \cdot 17)$ in $(3 \cdot 8)$, $(3 \cdot 11)$, $(3 \cdot 12)$ and $(3 \cdot 15)$, we obtain for Mn-ferrite the following values of the anisotropy constants per molecule coming from the B, E and C parts:

$$K_B = 5.48 \times 10^{-5} \, \text{cm}^{-1},$$

$$K_E = -1.17 \times 10^{-4} \, \text{cm}^{-1} - 1.60 \times 10^{-5} \, \text{cm}^{-1},$$

$$K_C = 1.3 \times 10^{-2} \, \text{cm}^{-1}, \quad \text{(Mn-ferrite)} \tag{3$\cdot$20}$$

where the value of $a = 8.55 \, \overset{\circ}{\text{A}}$ is used. This result shows that the anisotropy constant from the dipole-dipole interaction has the opposite sign to that observed and that it amounts to about 15 per cent of the latter.

In the case of Ni-ferrite, we use the values determined by Néel[29] for n, α and β, namely

$$n = 720, \quad \alpha = -0.21 \quad \text{and} \quad \beta = -0.15. \tag{3$\cdot$21}$$

Then, we have the following values of ΔE_B and ΔE_A:

$$\Delta E_B = 503 \, \text{cm}^{-1}, \quad \Delta E_A = 745 \, \text{cm}^{-1}. \tag{3$\cdot$22}$$

Using (3$\cdot$21) and (3$\cdot$17), $a = 8.36 \, \overset{\circ}{\text{A}}$, and the mean value of 5/2 and 1 (i.e. 7/4) for S_B, we obtain the following value of the anisotropy constant for Ni-ferrite:

$$K_B = 2.56 \times 10^{-5} \, \text{cm}^{-1},$$

$$K_E = -3.33 \times 10^{-5} \, \text{cm}^{-1} - 1.16 \times 10^{-5} \, \text{cm}^{-1},$$

$$K_C = 3.41 \times 10^{-3} \, \text{cm}^{-1}. \quad \text{(Ni-ferrite)} \tag{3$\cdot$23}$$

This result shows that also in Ni-ferrite the anisotropy constant from this source is about ten per cent of the observed value.

We would better use the spin wave theory for a more accurate calculation, as Keffer[25] and Tessman[30] did in discussing the anisotropy energy of metallic ferromagnets. However, in order to know the order of magnitude, the present method would suffice, though there are some ambiguities in determining the values of ΔE_A and ΔE_B, especially for Ni-ferrite.

§4. Anisotropy energy arising from the anisotropic exchange interaction in Ni-ferrite

Another source of the anisotropy energy in Ni-ferrite is the anisotropic exchange interaction. We shall calculate this anisotropy energy. The orbital degeneracy of Ni^{2+} ion in its free state is lifted partially by the cubic crystalline field, which is the main part of the crystalline field acting on the octahedral sites, the ground state being singlet in this case. We shall here neglect the effect of a small trigonal part of the crystalline field. Like the case of the magnetic dipole-dipole interaction we shall deal with the exchange interaction, together with the crystalline field energy, as the unperturbed energies. The perturbing Hamiltonian in this case is the spin-orbit interaction of one Ni^{2+} ion. We shall calculate the perturbed energy of the ground state for completely aligned spins.

The orbital states of Ni^{2+} ions subjected to an octahedral cubic crystalline field are split into the following three groups:

$$\Gamma_2 \qquad\qquad\qquad \Gamma_5 \qquad\qquad\qquad \Gamma_4$$

$$\varphi_1 = (1/\sqrt{2})(\psi_2 + \psi_{-2}), \qquad \varphi_4 = \psi_0,$$

$$\varphi_0 = (1/\sqrt{2})(\psi_2 - \psi_{-2}), \quad \varphi_2 = \sqrt{5/8}\,\psi_1 - \sqrt{3/8}\,\psi_{-3}, \qquad \varphi_5 = \sqrt{3/8}\,\psi_1 + \sqrt{5/8}\,\psi_{-3},$$

$$\varphi_3 = \sqrt{5/8}\,\psi_{-1} - \sqrt{3/8}\,\psi_3, \qquad \varphi_6 = \sqrt{3/8}\,\psi_{-1} + \sqrt{5/8}\,\psi_3,$$

$$E = 0, \qquad\qquad\qquad E = \Delta E_1, \qquad\qquad\qquad E = \Delta E_2,$$

$$(4\cdot1)$$

where ψ_m means the wave function of the state in which the z-component of the orbital angular momentum is m. As mentioned before, we shall neglect the effect of the trigonal field and further we shall put the effect of ^3P state out of our consideration. The matrix elements of $(L \cdot S)$ with respect to $(4\cdot1)$ are calculated as

	φ_0	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
φ_0	0	$2S_z$	$\sqrt{2}\,S^-$	$-\sqrt{2}\,S^+$	0	0	0
φ_1	$2S_z$	0	$\dfrac{1}{2\sqrt{2}}S^-$	$\dfrac{1}{2\sqrt{2}}S^+$	0	$\dfrac{\sqrt{15}}{2\sqrt{2}}S^-$	$\dfrac{\sqrt{15}}{2\sqrt{2}}S^+$
φ_2	$\sqrt{2}\,S^+$	$\dfrac{1}{2\sqrt{2}}S^+$	$-\dfrac{1}{2}S_z$	0	$\dfrac{\sqrt{15}}{2\sqrt{2}}S^-$	$\dfrac{\sqrt{15}}{2}S_z$	0
φ_3	$-\sqrt{2}\,S^-$	$\dfrac{1}{2\sqrt{2}}S^-$	0	$\dfrac{1}{2}S_z$	$\dfrac{\sqrt{15}}{2\sqrt{2}}S^+$	0	$-\dfrac{\sqrt{15}}{2}S_z$
φ_4	0	0	$\dfrac{\sqrt{15}}{2\sqrt{2}}S^+$	$\dfrac{\sqrt{15}}{2\sqrt{2}}S^-$			
φ_5	0	$\dfrac{\sqrt{15}}{2\sqrt{2}}S^+$	$\dfrac{\sqrt{15}}{2}S_z$	0			
φ_6	0	$\dfrac{\sqrt{15}}{2\sqrt{2}}S^-$	0	$-\dfrac{\sqrt{15}}{2}S_z$			

$$(4\cdot2)$$

Now we suppose that in the ground state each ion is in Γ_2 state and its spin points to a direction with direction cosines (n_1, n_2, n_3) referred to the cubic axes. Taking the spin orbit coupling as the perturbation, the anisotropy energy is given by the perturbed energy which includes the biquadratic form of the direction cosines $(n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2)$. Taking the ξ- and η-axes perpendicular to the ζ-axis and to each other and denoting their direction cosines by (l_1, l_2, l_3) and (m_1, m_2, m_3), there are following relations between the spin components $S^\pm = S_x \pm iS_y$ and S_z and those referred to the ξ-, η- and ζ-axes, $S'^\pm$ and S_ζ':

$$S^+ = (1/2)\{(l_1 - im_1) + i(l_2 - im_2)\}S'^+ + (1/2)\{(l_1 + im_1) + i(l_2 + im_2)\}S'^-$$
$$+ (n_1 + in_2)S_\zeta',$$

$$S^- = (1/2)\{(l_1 - im_1) - i(l_2 - im_2)\}S'^+ + (1/2)\{(l_1 + im_1) - i(l_2 + im_2)\}S'^-$$
$$+ (n_1 - in_2)S_\zeta', \qquad\qquad (4\cdot3)$$

$$S_z = (1/2)(l_3 - im_3)S'^+ + (1/2)(l_3 + im_3)S'^- + n_3 S_\zeta'.$$

As seen from this expression, the fourth order terms with respect to n_1, n_2 and n_3 come from the fourth order perturbation of $\lambda(\boldsymbol{L} \cdot \boldsymbol{S})$. In the case in which the diagonal element of the perturbing Hamiltonian vanishes in the ground state, the fourth order perturbed energy can be expressed by

$$\Delta E_4 = \sum_{n \neq g} \frac{(g|V|n)(n|V|g)}{\Delta E_n^2} \sum_{n'} \frac{(g|V|n')(n'|V|g)}{\Delta E_{n'}}$$
$$- \sum_{n,n',n'' \neq g} \frac{(g|V|n)(n|V|n')(n'|V|n'')(n''|V|g)}{\Delta E_n \Delta E_{n'} \Delta E_{n''}}, \tag{4.4}$$

where g and n, n', n'' mean the ground and excited states. The first term of this expression does not give any anisotropy because each factor of it is of the second order with respect to the direction cosines and so it is reduced to a mere constant in cubic case.

The perturbation processes which contribute to the second term in (4.4) can be divided into the following two groups as seen from (4.2):

1) Those which include only $\varGamma_5$ states as the excited states.

1. $(0-1-2-1-0)$		7. $(0-1-2-2-0)$
2. $(0-1-3-1-0)$		8. $(0-1-3-3-0)$
3. $(0-2-1-2-0)$		9. $(0-2-2-1-0)$
4. $(0-2-1-3-0)$		10. $(0-3-3-1-0)$
5. $(0-3-1-3-0)$		11. $(0-2-2-2-0)$
6. $(0-3-1-2-0)$		12. $(0-3-3-3-0)$

$$\tag{4.5}$$

2) Those which include both $\varGamma_5$ and $\varGamma_4$ states.

1. $(0-1-5-1-0)$		7. $(0-2-4-3-0)$
2. $(0-1-6-1-0)$		8. $(0-2-5-2-0)$
3. $(0-1-5-2-0)$		9. $(0-3-4-2-0)$
4. $(0-1-6-3-0)$		10. $(0-3-6-1-0)$
5. $(0-2-4-2-0)$		11. $(0-3-4-3-0)$
6. $(0-2-5-1-0)$		12. $(0-3-6-3-0)$

$$\tag{4.6}$$

The perturbed energy denominator for the first group is ΔE_1^3, while that for the second group is $\Delta E_1^2 \Delta E_2$ provided we do not take account of the change of the exchange energy. The numerator is given by the product of λ^4 and four matrix elements of $(\boldsymbol{L} \cdot \boldsymbol{S})$ corresponding to each process. The matrix elements of the numerators for the cases of (4.5) and (4.6) can be written with the use of (4.2) as

1) 1. $(1/2)S_zS^-S^+S_z$ 7. $-(1/2)S_zS^-S_zS^+$

    2. $(1/2)S_zS^+S^-S_z$ 8. $-(1/2)S_zS^+S_zS^-$

    3. $(1/4)S^-S^+S^-S^+$ 9. $-(1/2)S^-S_zS^+S_z$

    4. $-(1/4)S^-S^+S^+S^-$ 10. $-(1/2)S^+S_zS^-S_z$ (4·7)

    5. $(1/4)S^+S^-S^+S^-$ 11. $(1/2)S^-S_zS_zS^+$

    6. $-(1/4)S^+S^-S^-S^+$ 12. $(1/2)S^+S_zS_zS^-$,

2) 1. $(15/2)S_zS^-S^+S_z$ 7. $-(15/4)S^-S^-S^-S^-$

    2. $(15/2)S_zS^+S^-S_z$ 8. $(15/2)S^-S_zS_zS^+$

    3. $(15/2)S_zS^-S_zS^+$ 9. $-(15/4)S^+S^+S^+S^+$

    4. $(15/2)S_zS^+S_zS^-$ 10. $(15/2)S^+S_zS^-S_z$ (4·8)

    5. $(15/4)S^-S^-S^+S^+$ 11. $(15/4)S^+S^+S^-S^-$

    6. $(15/2)S^-S_zS^+S_z$ 12. $(15/2)S^+S_zS_zS^-$.

In the ground state the spin component of Ni^{2+} ion along the ζ-axis is S, and possible processes of the change of the spin component in the fourth order perturbation and spin operators producing those processes are limited to the following six cases:

A. $(S)-(S)-(S)-(S)-(S)$: $S_\zeta'S_\zeta'S_\zeta'S_\zeta'$

B_1. $(S)-(S)-(S)-(S-1)-(S)$: $S_\zeta'S_\zeta'S'^-S'^+$

B_2. $(S)-(S)-(S-1)-(S)-(S)$: $S_\zeta'S'^-S'^+S_\zeta'$

B_3. $(S)-(S-1)-(S)-(S)-(S)$: $S'^-S'^+S_\zeta'S_\zeta'$ (4·9)

C $(S)-(S-1)-(S)-(S-1)-(S)$: $S'^-S'^+S'^-S'^+$

D. $(S)-(S-1)-(S-2)-(S-1)-(S)$: $S'^-S'^-S'^+S'^+$

where the quantities in the parentheses represent the ζ-component of the spin.   Other processes have zero matrix elements in the case of spin one.

Now we shall turn to the calculation of the fourth order perturbed energy.   First we express the products of four S's in (4·7) and (4·8) in terms of those of four primed S''s with the use of (4·3) and add them over twelve terms of (4·7) and (4·8). Then we find that all the coefficients of the products of four primed S''s corresponding to processes described by (4·9) for the group (1) vanish.   Thus, the anisotropy energy appears from the group (2) alone.   The calculated anisotropy energy arising from the second group for each of the six processes of (4·9) is as follows:

A. $-\dfrac{60 S^4 \lambda^4}{\Delta E_1^2 \Delta E_2} (n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2)$,

B_1. $\dfrac{30 S^3 \lambda^4}{\Delta E_1 \Delta E_2 (\Delta E_1 + \Delta E_x)} (n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2)$,

$$B_2. \quad -\frac{15\,\lambda^4 S^3}{\Delta E_1{}^2(\Delta E_2+\Delta E_x)}\left\{1-2\,(n_1{}^2 n_2{}^2+n_2{}^2 n_3{}^2+n_3{}^2 n_1{}^2)\right\}, \qquad (4\cdot10)$$

$$B_3. \quad \frac{30\,\lambda^4 S^3}{(\Delta E_1+\Delta E_x)\,\Delta E_1\,\Delta E_2}\,(n_1{}^2 n_2{}^2+n_2{}^2 n_3{}^2+n_3{}^2 n_1{}^2),$$

$$C. \quad -\frac{15\,\lambda^4 S^2}{(\Delta E_1+\Delta E_x)^2\Delta E_2}\,(n_1{}^2 n_2{}^2+n_2{}^2 n_3{}^2+n_3{}^2 n_1{}^2),$$

$$D. \quad -\frac{30\,\lambda^4 S(S-(1/2))}{(\Delta E_1+\Delta E_x)^2(\Delta E_2+2\Delta E_x)}\left\{1+(n_1{}^2 n_2{}^2+n_2{}^2 n_3{}^2+n_3{}^2 n_1{}^2)\right\},$$

where ΔE_x means the change of the exchange energy of the ion due to the change of its spin component by one in the Weiss molecular field produced by the neighboring spins. Summing up the above six terms of $(4\cdot10)$ and putting $S=1$, we obtain the coefficient of $(n_1{}^2 n_2{}^2+n_2{}^2 n_3{}^2+n_3{}^2 n_1{}^2)$, namely the anisotropy constant per molecule, as

$$K_1=-15\,\lambda^4\left\{\frac{4}{\Delta E_1{}^2\Delta E_2}-\frac{2}{\Delta E_1\,\Delta E_2(\Delta E_1+\Delta E_x)}-\frac{2}{\Delta E_1{}^2(\Delta E_2+\Delta E_x)}\right.$$
$$-\frac{2}{(\Delta E_1+\Delta E_x)\,\Delta E_1\,\Delta E_2}+\frac{1}{(\Delta E_1+\Delta E_x)^2\Delta E_2}$$
$$\left.+\frac{1}{(\Delta E_1+\Delta E_x)^2(\Delta E_2+2\Delta E_x)}\right\}. \qquad (4\cdot11)$$

If we expand $(4\cdot11)$ with respect to $\Delta E_x/\Delta E_{1,2}$, we obtain

$$K_1=-30\,\frac{\lambda^4}{\Delta E_1{}^2\Delta E_2}\left(\frac{\Delta E_x}{\Delta E_1}+\frac{\Delta E_x}{\Delta E_2}\right)^2. \qquad (4\cdot12)$$

This anisotropy energy tends the spin to point to the $\{111\}$ direction. It is inversely proportional to the fifth power of the energy separation ΔE in the cubic field so that it depends sensitively upon the strength of the cubic field. If we treat the exchange interaction as the perturbation together with the $L\cdot S$ coupling, we obtain the same result in its sixth order perturbation. The above calculation is concerned only with the excitation of one Ni ion, but it can be easily shown that processes which include the excitation of two Ni ions give only an isotropic energy up to the fourth order with respect to $\lambda(L\cdot S)$.

The g-factor of a Ni ion becomes

$$g-2=-(8\lambda/\Delta E_1). \qquad (4\cdot13)$$

For the energy separation due to the cubic field the ratio of ΔE_1 to ΔE_2 is equal to $5/9$. If we use this relation, $(4\cdot12)$ becomes

$$K_1=-40.3\cdot(\lambda^4/\Delta E_1{}^3)\cdot(\Delta E_x/\Delta E_1)^2. \qquad (4\cdot14)$$

Considering exchange interactions only between octahedral ions and tetrahedral ions, the change of the exchange energy ΔE_x at absolute zero using the molecular field approximation can be put as

$$\varDelta E_x = 2Jz S_{Fe}, \tag{4.15}$$

where J is the exchange integral and z the number of tetrahedral sites neighboring an octahedral ion and S_{Fe} means the spin of an Fe^{3+} ion, namely 5/2. $2Jz$ can be estimated from the Curie temperature of Ni-ferrite in the same approximation as

$$T_c = (2Jz/3k)\left[\left\{S_{Fe}(S_{Fe}+1)+S_{Ni}(S_{Ni}+1)\right\}S_{Fe}(S_{Fe}+1)\right]^{1/2}. \tag{4.16}$$

Using $T_c = 860°K$ and $S_{Ni} = 1$, we obtain

$$\varDelta E_x = 465 \text{ cm}^{-1}, \quad 2Jz = 186 \text{ cm}^{-1}. \tag{4.17}$$

This value of $\varDelta E_x$ is less than $\varDelta E_B$ of (3.22) by ten per cent. Inserting $\varDelta E_x$ of (4.17) into (4.14) and taking the value of λ equal to -335 cm^{-1} in (4.14) and (4.13), we obtain the following table :

<div align="center">Table II</div>

$\varDelta E_1$ cm^{-1}	5000	7000	10000	15000
$-K_1$ cm^{-1}/mole.	3.5×10^{-2}	6.6×10^{-3}	1.1×10^{-2}	1.5×10^{-4}
g	2.54	2.38	2.27	2.18

Considering the experimental g-value equal to about 2.2, it would be reasonable to assume $\varDelta E_1 = 1 \sim 1.5 \times 10^4 \text{ cm}^{-1}$. Then, we might conclude that the anisotropy constant arising from the anisotropic exchange interaction is less than 10^{-3} cm^{-1} per molecule.

As another source of the anisotropy energy we can consider the electric quadrupole-quadrupole interaction between two Ni ions. As seen from the above calculations, we must in this case also consider the perturbed energy quartic in $L \cdot S$ coupling because the quadrupole-quadrupole interaction does not include the direction cosines of the spins. Such energies would have an order of $(\lambda/\varDelta E)^4 H_Q$, where H_Q represents the quadrupole-quadrupole interaction in the free state of the ions. This part of anisotropy is estimated as 10^{-4} cm^{-1} if we put $H_Q = 10^2 \text{ cm}^{-1}$.

Thus, it becomes very probable that the anisotropy energy found experimentally in Ni-ferrite arises from Fe^{3+} ions which occupy the tetrahedral and octahedral sites. Using the value of the anisotropy constant of Ni-ferrite in Table I, we obtain the fine structure constant a of Fe^{3+} ion as

$$a_{Fe}^B + a_{Fe}^A = 1.87 \times 10^{-2} \text{ cm}^{-1}, \tag{4.18}$$

where A and B mean the tetrahedral and octahedral sites respectively.

§ 5. Anisotropy energy of Fe^{2+} ions in magnetite

In magnetite, anisotropy energy arising from Fe^{2+} ions exists besides that arising from Fe^{3+} ions. In this section, we shall estimate this part of the anisotropy energy. The orbital state of Fe^{2+} ion occupying an octahedral site is considered to be split by the

large cubic part of the crystalline field. The ground state is triply degenerate. If we assume, for simplicity, that the charges of Fe^{2+} and Fe^{3+} ions on the octahedral sites are replaced by their average, the low symmetry part of the crystalline field becomes trigonal and its axis lies in one of the four $\{111\}$ directions. Therefore, the Fe^{2+} ions are divided into four kinds of ions according as the direction of the axis of the field to which the ions are subjected.

We shall concentrate our attention to one Fe^{2+} ion whose trigonal axis coincides with the $[111]$ direction. If we denote the five degenerate orbital wave functions of Fe^{2+} ion in its free state by φ_0, $\varphi_{\pm 1}$ and $\varphi_{\pm 2}$, where suffixes represent the z-components of the orbital moment, the cubic field splits these states into doubly degenerate states Γ_3: φ_0, $(1/\sqrt{2})(\varphi_2 + \varphi_{-2}) = \varphi_{2+}$ and triply degenerate states Γ_5: $(1/\sqrt{2}\,i)(\varphi_2 - \varphi_{-2}) = \varphi_{xy}$, $-(1/\sqrt{2}\,i)(\varphi_1 + \varphi_{-1}) = \varphi_{yz}$, $-(1/\sqrt{2})(\varphi_1 - \varphi_{-1}) = \varphi_{zx}$. The energy separation between these two groups will be denoted by ΔE. These states are further split by the trigonal field, whose expressions are, following Abragam and Pryce,[31] represented by

$$V_T = T_2(yz + zx + xy) + T_4\{(x^3y + y^3z + z^3x + x^3z + y^3x + z^3y)$$
$$- 6(x^2yz + y^2zx + z^2xy)\} \cdots\cdots. \qquad (5\cdot1)$$

The matrix element of this trigonal field with respect to the five cubic wave functions can be calculated as follows:

$$(V_T) = \begin{array}{c} \\ \varphi_{yz} \\ \varphi_{zx} \\ \varphi_{xy} \\ \varphi_{2+} \\ \varphi_0 \end{array} \begin{array}{ccccc} \varphi_{yz} & \varphi_{zx} & \varphi_{xy} & \varphi_{2+} & \varphi_0 \\ \left[\begin{array}{ccccc} 0 & a & a & -\sqrt{3}\,b & b \\ a & 0 & a & \sqrt{3}\,b & b \\ a & a & 0 & 0 & -2b \\ -\sqrt{3}\,b & \sqrt{3}\,b & 0 & 0 & 0 \\ b & b & -2b & 0 & 0 \end{array} \right], \end{array} \qquad (5\cdot2)$$

where

$$a = \frac{1}{7}\langle r^2 \rangle_{\text{av.}}\,T_2 - \frac{4}{21}\langle r^4 \rangle_{\text{av.}}\,T_4,$$

$$b = \frac{1}{7\sqrt{3}}\langle r^2 \rangle_{\text{av.}}\,T_2 + \frac{1}{7\sqrt{3}}\langle r^4 \rangle_{\text{av.}}\,T_4. \qquad (5\cdot3)$$

The matrix $(5\cdot2)$ including the cubic part can be brought into the diagonal form by the following unitary transformation S:

$$S = \left| \begin{array}{ccccc} \dfrac{1}{\sqrt{3}}, & \dfrac{1}{\sqrt{3}}, & \dfrac{1}{\sqrt{3}}, & 0, & 0 \\[2mm] -\dfrac{1}{\sqrt{6}}\sin\theta, & -\dfrac{1}{\sqrt{6}}\sin\theta, & -\dfrac{2}{\sqrt{6}}\sin\vartheta, & 0, & \cos\theta \\[2mm] \dfrac{1}{\sqrt{6}}\cos\theta, & \dfrac{1}{\sqrt{6}}\cos\theta, & -\dfrac{2}{\sqrt{6}}\cos\theta, & 0, & \sin\theta \end{array} \right| \qquad (5\cdot4)$$

$$
\left|
\begin{array}{ccccc}
\dfrac{1}{\sqrt{2}}\sin\theta, & -\dfrac{1}{\sqrt{2}}\sin\theta, & 0, & \cos\theta, & 0 \\[3mm]
-\dfrac{1}{\sqrt{2}}\cos\theta, & \dfrac{1}{\sqrt{2}}\cos\theta, & 0, & \sin\theta, & 0
\end{array}
\right|
$$

where

$$
\tan 2\theta = -\frac{2\sqrt{6}\,b}{(a+\varDelta E)}. \tag{5.5}
$$

The eigenfunctions and their eigenvalues are

$$
S\varphi =
\begin{bmatrix}
\varphi_0 \\[2mm]
\varphi_1 \\[2mm]
\varphi_2 \\[2mm]
\varphi_3 \\[2mm]
\varphi_4
\end{bmatrix}
=
\begin{bmatrix}
\dfrac{1}{\sqrt{3}}\,(\varphi_{yz}+\varphi_{zx}+\varphi_{xy}) \\[3mm]
\dfrac{1}{\sqrt{6}}\sin\theta\,(2\varphi_{xy}-\varphi_{yz}-\varphi_{zx})+\cos\theta\cdot\varphi_0 \\[3mm]
-\dfrac{1}{\sqrt{6}}\cos\theta\,(2\varphi_{xy}-\varphi_{yz}-\varphi_{zx})+\sin\theta\cdot\varphi_0 \\[3mm]
\dfrac{1}{\sqrt{2}}\sin\theta\,(\varphi_{yz}-\varphi_{zx})+\cos\theta\cdot\varphi_{2+} \\[3mm]
-\dfrac{1}{\sqrt{2}}\cos\theta\,(\varphi_{yz}-\varphi_{zx})+\sin\theta\cdot\varphi_{2+}
\end{bmatrix}
\tag{5.6}
$$

and

$$
SVS^{-1} =
\begin{bmatrix}
2a & 0 & 0 & 0 & 0 \\
0 & E_1 & 0 & 0 & 0 \\
0 & 0 & E_2 & 0 & 0 \\
0 & 0 & 0 & E_1 & 0 \\
0 & 0 & 0 & 0 & E_2
\end{bmatrix},
\tag{5.7}
$$

where

$$
E_1 = \varDelta E\cos^2\theta - a\sin^2\theta - 2\sqrt{6}\,b\sin\theta\cos\theta ,
$$
$$
E_2 = -a\cos^2\theta + \varDelta E\sin^2\theta + 2\sqrt{6}\,b\sin\theta\cos\theta .
\tag{5.8}
$$

As shown by these results, the trigonal field splits the energy levels into one singlet and two doublets. From the distribution of Fe ions around the considering Fe^{2+} ion, it may be reasonable to assign the ground state to a singlet. This fact is consistent with the g-value near two obtained by ferromagnetic resonance absorption. Otherwise, the enormously large anisotropy would come out, because of the surviving orbital moment in the doublet states. The actual crystalline field acting on an individual Fe^{2+} ion has a lower symmetry than trigonal and is different from ion to ion so that the trigonal field assumed here must be interpreted as the average representation.

The matrix elements of the $L \cdot S$ coupling with respect to the basic functions of (5.6) omitting a factor λ are obtained as

$$(\boldsymbol{L}\cdot\boldsymbol{S})=\begin{pmatrix}
0 & \begin{array}{c}i(S_x-S_y)\\ \times\left(\frac{1}{\sqrt{2}}\sin\theta-\cos\theta\right)\end{array} & \begin{array}{c}-i(S_x-S_y)\\ \times\left(\frac{1}{\sqrt{2}}\cos\theta+\sin\theta\right)\end{array} & \begin{array}{c}\frac{i}{\sqrt{3}}(S_x+S_y-2S_z)\\ \times\left(\frac{1}{\sqrt{2}}\sin\theta-\cos\theta\right)\end{array} & \begin{array}{c}-\frac{i}{\sqrt{3}}(S_x+S_y-2S_z)\\ \times\left(\frac{1}{\sqrt{2}}\cos\theta+\sin\theta\right)\end{array} \\
 & 0 & \frac{i}{\sqrt{2}}(S_x-S_y) & \begin{array}{c}\frac{i}{\sqrt{3}}(S_x+S_y+S_z)\\ \times(\sin^2\theta\\ +2\sqrt{2}\sin\theta\cos\theta)\end{array} & \begin{array}{c}-\frac{i}{\sqrt{3}}(S_x+S_y+S_z)\\ \times(\sin\theta\cos\theta\\ -2\sqrt{2}\sin^2\theta)\\ -\frac{3i}{\sqrt{6}}(S_x+S_y)\end{array} \\
\text{conjugate complex} & & 0 & \begin{array}{c}-\frac{i}{\sqrt{3}}(S_x+S_y+S_z)\\ \times(\sin\theta\cos\theta\\ +2\sqrt{2}\cos^2\theta)\\ +\frac{3i}{\sqrt{6}}(S_x+S_y)\end{array} & \begin{array}{c}\frac{i}{\sqrt{3}}(S_x+S_y+S_z)\\ \times(\cos^2\theta\\ -2\sqrt{2}\cos\theta\sin\theta)\end{array} \\
 & & & 0 & -\frac{i}{\sqrt{2}}(S_x-S_y) \\
 & & & & 0
\end{pmatrix}$$

$$(5\cdot9)$$

With the use of (5·7) and (5·9) we can calculate the g-value of Fe^{2+} ion, namely

$$g=2(1-\lambda\varLambda),$$

$$\varLambda_{\mu\nu}=\sum_{n}(0\,|\,L_{\mu}\,|\,n)\,(n\,|\,L_{\nu}\,|\,0)/\varDelta E_{n} \qquad (5\cdot10)$$

where λ is the coefficient of the $\boldsymbol{L}\cdot\boldsymbol{S}$ coupling, and

$$\varLambda_{xx}=\varLambda_{yy}=\varLambda_{zz}=\frac{4}{3}\cdot\frac{1}{\varDelta E_{1}}\left(\frac{1}{\sqrt{2}}\sin\theta-\cos\theta\right)^{2}+\frac{4}{3}\cdot\frac{1}{\varDelta E_{2}}\left(\frac{1}{\sqrt{2}}\cos\theta+\sin\theta\right)^{2},$$

$$\varLambda_{xy}=\varLambda_{yz}=\varLambda_{zx}=-\frac{2}{3}\cdot\frac{1}{\varDelta E_{1}}\left(\frac{1}{\sqrt{2}}\sin\theta-\cos\theta\right)^{2}-\frac{2}{3}\cdot\frac{1}{\varDelta E_{2}}\left(\frac{1}{\sqrt{2}}\cos\theta+\sin\theta\right)^{2},$$

$$(5\cdot11)$$

where $\varDelta E_{1}=E_{1}-2a$ and $\varDelta E_{2}=E_{2}-2a$. Thus, the g-value has a trigonal symmetry. The g-values of the other three kinds of ions for which the trigonal axes are in $[\bar{1}1\bar{1}]$, $[1\bar{1}\bar{1}]$ and $[\bar{1}\bar{1}1]$ directions respectively can be derived by changing the signs of (xy), (yz) and (zx). Averaging (5·11) over these four values, the off-diagonal part vanishes and we obtain the following result:

$$g-2=-\frac{8}{3}\frac{\lambda}{\varDelta E_{1}}\left(\frac{1}{\sqrt{2}}\sin\theta-\cos\theta\right)^{2}-\frac{8}{3}\frac{\lambda}{\varDelta E_{2}}\left(\frac{1}{\sqrt{2}}\cos\theta+\sin\theta\right)^{2}. \quad (5\cdot12)$$

Compared with the calculation of the g-value, the calculation of the cubic anisotropy constant fo Fe^{2+} ions is considerably complicated. The perturbation in this case consists

of two parts, one is the $L \cdot S$ coupling and the other is the intra spin-spin interaction which has been expressed as

$$-\rho[(L \cdot S)^2 + (1/2)(L \cdot S) - (1/3)L(L+1)S(S+1)] \qquad (5 \cdot 13)$$

by Pryce and Abragam[23,24] who also have estimated ρ to be 0.95 cm^{-1} for Fe^{2+} ion. The latter interaction is very small in its magnitude, but it contains $(L \cdot S)^2$ so that the cubic anisotropy possibly arises from the lower order perturbation than the $L \cdot S$ coupling alone which needs the fourth order calculation to produce the cubic anisotropy, because it has a quartic form of the spin operator S.

We will omit the detailed description of this perturbation calculation, but its gist is as follows. We select the part including the fourth order of the spin S from each order of perturbed energy, because the second order term with respect to S vanishes when it is averaged over the four kinds of ions. Such parts appear in the second order perturbation quadratic only in the intra spin-spin coupling $(5 \cdot 13)$, the third order perturbation linear in the intra spin-spin coupling and quadratic in the $L \cdot S$ coupling and the fourth order perturbation quartic only in the $L \cdot S$ coupling. In these calculations, we can ignore the non-commutability between the components of S because surplus terms produced by the commutation have a lower order of S. The calculated result for the coefficient of $(S_x^2 S_y^2 + S_y^2 S_z^2 + S_z^2 S_x^2)$ is as follows:

$$-\frac{16}{9}\lambda^4\left\{\frac{1}{\Delta E_1^2}\left(\frac{1}{\sqrt{2}}\sin\theta - \cos\theta\right)^2 + \frac{1}{\Delta E_2^2}\left(\frac{1}{\sqrt{2}}\cos\theta + \sin\theta\right)^2\right\}$$

$$\times\left\{\frac{3}{2}\frac{\rho}{\lambda^2} + \frac{1}{\Delta E_1}\left(\frac{1}{\sqrt{2}}\sin\theta - \cos\theta\right)^2 + \frac{1}{\Delta E_2}\left(\frac{1}{\sqrt{2}}\cos\theta + \sin\theta\right)^2\right\}$$

$$+\frac{8}{9}\lambda^4\left(\frac{1}{\Delta E_1^3} + \frac{3\rho}{\lambda^2}\frac{1}{\Delta E_1^2} + \frac{\rho^2}{\lambda^4}\frac{1}{\Delta E_1}\right)$$

$$\times\left(\frac{1}{\sqrt{2}}\sin\theta - \cos\theta\right)^2(\sin^2\theta + 2\sqrt{2}\sin\theta\cos\theta)^2$$

$$+\frac{8}{9}\lambda^4\left(\frac{1}{\Delta E_2^3} + \frac{3\rho}{\lambda^2}\frac{1}{\Delta E_2^2} + \frac{\rho^2}{\lambda^4}\frac{1}{\Delta E_2}\right)$$

$$\times\left(\frac{1}{\sqrt{2}}\cos\theta + \sin\theta\right)^2(\cos^2\theta - 2\sqrt{2}\cos\theta\sin\theta)^2$$

$$+\lambda^4\left\{\frac{1}{\Delta E_1^2 \Delta E_2} + \frac{\rho}{\lambda^2}\left(\frac{1}{\Delta E_1^2} + \frac{2}{\Delta E_1 \Delta E_2}\right) + \frac{\rho^2}{\lambda^4}\frac{1}{\Delta E_2}\right\}$$

$$\times\left\{\frac{8}{9}(\sin\theta\cos\theta - 2\sqrt{2}\sin^2\theta)^2 + \frac{56\sqrt{2}}{9}(\sin\theta\cos\theta - 2\sqrt{2}\sin^2\theta) + \frac{88}{9}\right\}$$

$$\times\left(\frac{1}{\sqrt{2}}\sin\theta - \cos\theta\right)^2$$

$$+\lambda^4\left\{\frac{1}{\Delta E_1^2\,\Delta E_2}+\frac{\rho}{\lambda^2}\left(\frac{1}{\Delta E_1^2}+\frac{2}{\Delta E_1\,\Delta E_2}\right)+\frac{\rho^2}{\lambda^4}\,\frac{1}{\Delta E_1}\right\}$$

$$\times\left\{\frac{16}{9}(\sin\theta\cos\theta-2\sqrt{2}\sin^2\theta)-\frac{8\sqrt{2}}{3}\right\}(\sin^2\theta+2\sqrt{2}\sin\theta\cos\theta)$$

$$\times\left(\frac{1}{\sqrt{2}}\sin\theta-\cos\theta\right)\left(\frac{1}{\sqrt{2}}\cos\theta+\sin\theta\right)$$

$$+\lambda^4\left\{\frac{1}{\Delta E_1\,\Delta E_2^2}+\frac{\rho}{\lambda^2}\left(\frac{1}{\Delta E_2^2}+\frac{2}{\Delta E_1\,\Delta E_2}\right)+\frac{\rho^2}{\lambda^4}\,\frac{1}{\Delta E_1}\right\}$$

$$\times\left\{\frac{8}{9}(\sin\theta\cos\theta+2\sqrt{2}\cos^2\theta)^2-\frac{56\sqrt{2}}{9}(\sin\theta\cos\theta+2\sqrt{2}\cos^2\theta)+\frac{88}{9}\right\}$$

$$\times\left(\frac{1}{\sqrt{2}}\cos\theta+\sin\theta\right)^2$$

$$+\lambda^4\left\{\frac{1}{\Delta E_1\,\Delta E_2^2}+\frac{\rho}{\lambda^2}\left(\frac{1}{\Delta E_2^2}+\frac{2}{\Delta E_1\,\Delta E_2}\right)+\frac{\rho^2}{\lambda^4}\,\frac{1}{\Delta E_2}\right\}$$

$$\times\left\{\frac{16}{9}(\sin\theta\cos\theta+2\sqrt{2}\cos^2\theta)+\frac{8}{3}\sqrt{2}\right\}(\cos^2\theta-2\sqrt{2}\cos\theta\sin\theta)$$

$$\times\left(\frac{1}{\sqrt{2}}\cos\theta+\sin\theta\right)\left(\frac{1}{\sqrt{2}}\sin\theta-\cos\theta\right).$$

$$(5\cdot14)$$

In order to evaluate the above derived anisotropy constant, it is necessary to know the magnitudes of the cubic separation ΔE and the strength of the trigonal field a and b. From the point charge approximation, ΔE and the trigonal separation are expected to be about 10^4 cm^{-1} and 10^3 cm^{-1}, respectively, and in $(5\cdot3)$ the first term is considerably larger than the second term so that a is approximately $\sqrt{3}$ times as large as b. Putting

$$-(2\sqrt{6}/\Delta E)b=\beta,\quad -a/\Delta E=\alpha,\qquad(5\cdot15)$$

and using $\lambda=-100$ cm^{-1} and $\rho=0.95$ cm^{-1}, we obtain the following table which shows the g-value calculated from $(5\cdot12)$ for several combinative sets of α and β:

Table III

E	α	β	$g-2$
10^4 cm^{-1}	0.05	0.15	0.13
,,	0.08	0.24	0.10
,,	0.10	0.30	0.09
,,	0.10	0.50	0.11

The experimental g-value obtained by Bickford at high temperature range from 2.1 to 2.00. Thus, the values of $\alpha=0.08$ and $\beta=0.24$ would be considered appropriate. We

calculated the anisotropy constant with the use of these two values and obtain the following value :

$$K_1 = -3.56 \times 10^{-2} \text{ cm}^{-1} \text{ per Fe}^{2+} \text{ ion.} \qquad (5 \cdot 16)$$

The anisotropy energy arising from the anisotropic exchange interaction might be considered to come from the higher order perturbation with respect to $\Delta E_x / \Delta E$, where ΔE_x is the change of the exchange energy from the view-point of the molecular field treatment mentioned in Sec. 4, in which the exchange energy is treated as an unperturbed energy. Therefore, this contribution would be less than $(5 \cdot 16)$. Thus, the anisotropy constant is concluded to consist of $(5 \cdot 16)$ and the anisotropy constant from Fe^{3+} ions. As seen from Table I, the sum of $(5 \cdot 16)$ and the anisotropy constant of Ni-ferrite is nearly equal to the experimental value of magnetite.

In deriving $(5 \cdot 16)$ we assumed the uniform charge distribution of Fe^{2+} and Fe^{3+} ions of octahedral sites. At low temperature where the short range order in the arrangement of those two kinds of ions develops, this assumption will not be allowed any longer even as an approximation. The reason of the drastic change of the anisotropy constant in its magnitude and even in its sign might be due partly to the effect of the short range order on the crystalline field.

§ 6. Temperature dependence of the anisotropy energy of Mn-ferrite

From the considerations made in the preceding sections, we arrive at the conclusion that the experimental anisotropy energies of Ni-, Fe- and Mn-ferrites can be accounted for by the fine structure coupling of Fe^{3+}, Mn^{2+} and Fe^{2+} ions with the surrounding crystalline field. For such anisotropy energies, the temperature variation can be described by $(2 \cdot 9)$. In this section we shall calculate the temperature dependence of the anisotropy energy of Mn-ferrite and determine the fine structure constant a for Fe^{3+} and Mn^{2+} of octahedral and tetrahedral sites. The reason why we choose Mn-ferrite is that all the magnetic ions in this substance have spin of $5/2$ and the Curie temperature is relatively low so that we may neglect the effect of thermal expansion.

We shall begin with the determination of the exchange couplings between magnetic ions. Since there has not been any experimental data of the susceptibility above the Curie temperature, we shall utilize the spontaneous magnetization *vs.* temperature curve obtained by Guillaud and Greveaux[32] for the determination of parameters. The total magnetizations of N ions situated in the tetrahedral and octahedral positions, $\mathfrak{M}_A$ and $\mathfrak{M}_B$, can, respectively, be expressed by

$$\mathfrak{M}_A = -Ng\mu_B \langle S_\zeta \rangle_A, \quad \mathfrak{M}_B = -Ng\mu_B \langle S_\zeta \rangle_B \qquad (6 \cdot 1)$$

where g is the g-factor of ions of tetrahedral and octahedral sites, μ_B is the Bohr magneton and $\langle S_\zeta \rangle_A$ and $\langle S_\zeta \rangle_B$ represent the average values of the spin component along the ζ-axis. Here, we neglect the difference between Fe^{3+} and Mn^{2+} ions in the octahedral sites in order to diminish the number of parameters. Introducing λ and μ which express the

fractions of the numbers of tetrahedral and octahedral lattice points, we put the molecular fields acting on the tetrahedral and octahedral sites, after Néel,[28] as

$$H_A = q_{AA}\lambda \mathfrak{M}_A + q_{AB}\mu \mathfrak{M}_B,$$
$$H_B = q_{BA}\lambda \mathfrak{M}_A + q_{BB}\mu \mathfrak{M}_B, \qquad (6\cdot 2)$$
$$\lambda = 1/3, \quad \mu = 2/3.$$

Putting $q_{AB} = q_{BA} = -n$, $q_{AA} = n\alpha$ and $q_{BB} = n\beta$ and denoting the absolute values of the magnetizations $\mathfrak{M}_A$ and $\mathfrak{M}_B$ by M_A and M_B, $(6\cdot 2)$ can be written as

$$H_A = -n(\alpha\lambda M_A + \mu M_B),$$
$$H_B = n(\lambda M_A + \beta\mu M_B), \qquad (6\cdot 3)$$

where we take the direction of $\mathfrak{M}_B$ as the positive direction. With the use of $(6\cdot 3)$, $(6\cdot 1)$ becomes

$$M_A = M_0 B_{5/2}[M_0 n(\alpha\lambda M_A + \mu M_B)/RT],$$
$$M_B = M_0 B_{5/2}[M_0 n(\beta\mu M_B + \lambda M_A)/RT], \qquad (6\cdot 4)$$

where $M_0 = Ng\mu_B S$ and $R = kN$, and B is the Brillouin function. $(6\cdot 4)$ is equivalent to the following set of equations:

$$M_A = M_0 B_{5/2}[u], \quad u = (M_0 n/RT) \cdot (\alpha\lambda M_A + \mu M_B),$$
$$M_B = M_0 B_{5/2}[v], \quad v = (M_0 n/RT) \cdot (\beta\mu M + \lambda M_A). \qquad (6\cdot 5)$$

We define φ and ψ by the relations:

$$M_A/M_B = B_{5/2}[u]/B_{5/2}[v] = \varphi, \quad u/v = (\alpha\lambda\varphi + \mu)/(\beta\mu + \lambda\varphi) = \psi. \qquad (6\cdot 6)$$

φ is related to the temperature by the equation of

$$RT/M_0^2 n = (\beta\mu + \lambda\varphi)(B_{5/2}[v]/v). \qquad (6\cdot 7)$$

Denoting the value of φ corresponding to the Curie temperature by φ_c, we obtain from $(6\cdot 7)$

$$\frac{T}{T_c} = \frac{15}{7} \cdot \frac{\beta\mu + \lambda\varphi}{\beta\mu + \lambda\varphi_c} \cdot \frac{B_{5/2}[v]}{v}. \qquad (6\cdot 8)$$

φ_c is determined by the following equation which is derived from $(6\cdot 6)$:

$$\lambda\varphi_c^2 + (\beta\mu - \lambda\alpha)\varphi_c - \mu = 0. \qquad (6\cdot 9)$$

Solving this equation, we obtain

$$\varphi_c = (1/2)\{-(2\beta - \alpha) + \sqrt{(2\beta - \alpha)^2 + 8}\}. \qquad (6\cdot 10)$$

The magnetization per mol is given by

$$M_S = 3(\mu M_B - \lambda M_A) = 3(\mu - \lambda\varphi)M_0 B_{5/2}[v]. \qquad (6\cdot 11)$$

If a value of v is determined for an arbitrary value of φ, the temperature and magnetization for that value of φ can be obtained by $(6\cdot 7)$ and $(6\cdot 11)$. The value of v is

obtained by solving the simultaneous equations (6·6). As has been shown by Néel,[28] it may be convenient to express them in the logarithmic equations :

$$\log B_{5/2}[u] - \log B_{5/2}[v] = \log \varphi ,$$

$$\log u - \log v = \log \psi ,$$

$$\psi = (\alpha\lambda\varphi + \mu)/(\beta\mu + \lambda\varphi). \qquad (6 \cdot 12)$$

The value of α and β must be taken from the hatched region in Fig. 1 in order to fit the calculated magnetization to the experimental one of Mn-ferrite. We move a point (α, β) in this region with the precision 0.01 and seek a point which fits best to the experimental magnetization curve obtained by Guillaud and Greveaux[32] in the temperature region of 25°K to 290°K. The values of α and β thus determined are

$$\alpha = -0.50 , \quad \beta = -0.10. \quad (6 \cdot 13)$$

The magnetization curve calculated with these values of α and β is shown in Fig. 2. The agreement with the experimental values is very good in the whole temperature range.
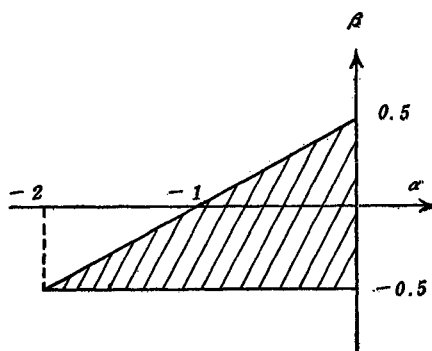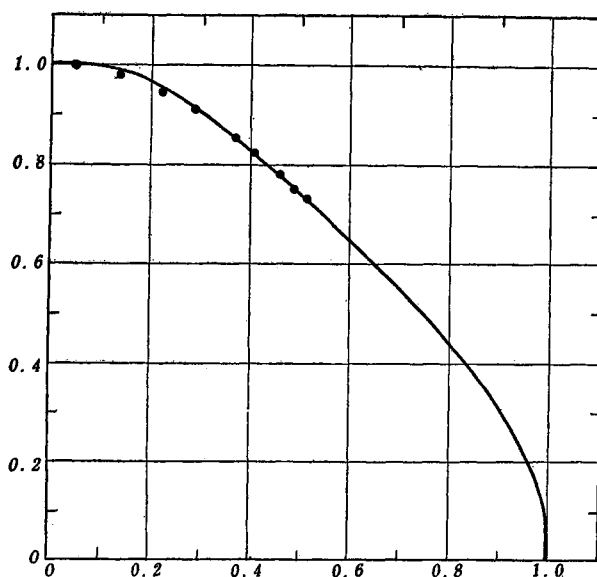

Fig. 1

Fig. 2. The calculated magnetization vs. temperature curve of Mn-ferrite. The points represent the experimental values by Guillaud and Greveaux.

Another parameter n can be determined from the Curie temperature. We obtain

$$n = 361 \, . \tag{6.14}$$

The interaction between the ions of tetrahedral sites and that between the ions of octahedral sites are represented by $n\alpha$ and $n\beta$. These are shown below together with those of magnetite which have been calculated by Néel.[28]

Table IV

	$n\alpha$	$n\beta$
Mn-ferrite	-181	-36.1
Fe-ferrite	-282	$+5.53$

Now we shall turn to the calculation of the temperature dependence of the anisotropy constant. As seen from (2.9), the anisotropy constant K_1 in Mn-ferrite is expressed by

$$K_1 = -\frac{N}{6} \left[(a_{Fe}^B + a_{Mn}^B) \left(\frac{35}{4} \langle S_\zeta^4 \rangle_B - \frac{15}{2} \left\{ S(S+1) - \frac{5}{6} \right\} \langle S_\zeta^2 \rangle_B \right.\right.$$

$$\left. + \frac{3}{4} S(S+1) \{ S(S+1) - 2 \} \right)$$

$$+ a_{Fe}^A \left(\frac{35}{4} \langle S_\zeta^4 \rangle_A - \frac{15}{2} \left\{ S(S+1) - \frac{5}{6} \right\} \langle S_\zeta^2 \rangle_A \right.$$

$$\left.\left. + \frac{3}{4} S(S+1) \{ S(S+1) - 2 \} \right) \right], \tag{6.15}$$

where A and B mean respectively the tetrahedral and octahedral sites. The average value of $\langle S_\zeta \rangle$ is obtained as

$$\langle S_\zeta \rangle = \frac{\sum S_\zeta \exp(-pS_\zeta)}{\sum \exp(-pS_\zeta)} = -\left\{ \left(S + \frac{1}{2} \right) \coth \left(S + \frac{1}{2} \right) p - \frac{1}{2} \coth \frac{p}{2} \right\},$$

$$p = \frac{g\mu_B H}{kT} \, . \tag{6.16}$$

It can be shown that $\langle S_\zeta^{n+1} \rangle$ satisfies the following recurrence formula:

$$\langle S_\zeta^{n+1} \rangle = (-\partial/\partial p + \langle S_\zeta \rangle) \langle S_\zeta^n \rangle \, . \tag{6.17}$$

Therefore, if we use the two relations

$$\frac{\partial}{\partial p} \langle S_\zeta \rangle = \langle S_\zeta \rangle^2 - \langle S_\zeta \rangle \coth \frac{p}{2} - S(S+1), \tag{6.18}$$

$$\frac{\partial}{\partial p} \coth \frac{p}{2} = \frac{1}{2} \left(1 - \coth^2 \frac{p}{2} \right), \tag{6.19}$$

together with the above recurrence formula, we can calculate $\langle S_\zeta^n \rangle$ for an arbitrary n value. Putting

$$\langle S_\zeta \rangle = x, \quad \coth p/2 = y \, ,$$

(6·17), (6·18) and (6·19) can be expressed in a more simplified form,

$$\langle S_\zeta^{n+1}\rangle = (-\partial/\partial p + x)^n x$$
$$\partial x/\partial p = x^2 - xy - S(S+1) \tag{6·20}$$
$$\partial y/\partial p = (1/2)(1-y^2).$$

$\langle S_\zeta^2\rangle$ and $\langle S_\zeta^4\rangle$ calculated with the use of (6·20) are as follows:

$$\langle S_\zeta^2\rangle = S(S+1) + xy, \tag{6·21}$$

$$\langle S_\zeta^4\rangle = 3xy^3 + 2S(S+1)y^2 + 2\{S(S+1)-1\}xy + S^2(S+1)^2 - S(S+1). \tag{6·22}$$

Using (6·21) and (6·22) we obtain

$$\left[\frac{35}{4}\langle S_\zeta^4\rangle - \frac{15}{2}\left\{S(S+1) - \frac{5}{6}\right\}\langle S_\zeta^2\rangle + \frac{3}{4}S(S+1)\{S(S+1)-2\}\right]$$

$$= \frac{1}{4}\left[105\,xy^3 + 70S(S+1)y^2 + \{40S(S+1)-45\}xy\right.$$

$$\left. + 8S^2(S+1)^2 - 16S(S+1)\right]. \tag{6·23}$$

If we put

$$z = Sp = g\mu_B SH/kT \tag{6·24}$$

we obtain

$$x = \langle S_\zeta\rangle = -SB_S[z], \tag{6·25}$$

and

$$y = \coth(p/2) = \coth(z/2S). \tag{6·26}$$

Inserting (6·25) and (6·26) into (6·23) and putting $S=5/2$, we get

$$\left[\frac{35}{4}\langle S_\zeta^4\rangle - \frac{15}{2}\left\{S(S+1) - \frac{5}{6}\right\}\langle S_\zeta^2\rangle + \frac{3}{4}S(S+1)\{S(S+1)-2\}\right]$$

$$= \frac{5}{8}\left[-105\,B_S[z]\left(\coth\frac{z}{2S}\right)^3 + 245\left(\coth\frac{z}{2S}\right)^2\right.$$

$$\left. - 305\,B_S[z]\coth\frac{z}{2S} + 189\right] = \frac{5}{8}[z] \tag{6·27}$$

Then, we can write (6·15) as

$$K_1 = -N\frac{5}{48}\{(a_{Fe}^B + a_{Mn}^B)[v] + a_{Fe}^A[u]\}, \tag{6·28}$$

or

$$\frac{K_1}{M_S} = -\frac{1}{24}\frac{1}{g\mu_B}\left\{(a_{Fe}^B + a_{Mn}^B)\frac{[v]}{m} + a_{Fe}^A\frac{[u]}{m}\right\}, \tag{6·29}$$

where

$$m = M_S / Ng\mu_B S,$$

$[u]$ and $[v]$ defined by (6·27) with $z=u$ and $z=v$ can be calculated with the use of the values of α, β and n determined by (6·13) and (6·14). Dillon, Geschwind and Jaccarino[2] have measured K_1/M_S of Mn-ferrite over the temperature range of $4°K$ to $300°K$. We shall select two points, $T=4.2°K$ and $T=300°K$, and determine the values of $(a_{Fe}^B + a_{Mn}^B)$ and a_{Fe}^A so that the calculated K_1/M_S may coincide with the experimental values at these two points. The determined values of $(a_{Fe}^B + a_{Mn}^B)$ and a_{Fe}^A are as follows:

$$a_{Fe}^B + a_{Mn}^B = 4.21 \times 10^{-2} \ cm^{-1},$$

$$a_{Fe}^A = -0.817 \times 10^{-2} \ cm^{-1}. \tag{6·30}$$

The anisotropy constant *vs.* temperature curve calculated with the use of (6·30) is shown in Fig. 3. The agreement with the experimental value is satisfactory. This curve is very sensitive for a slight change of the a-value.
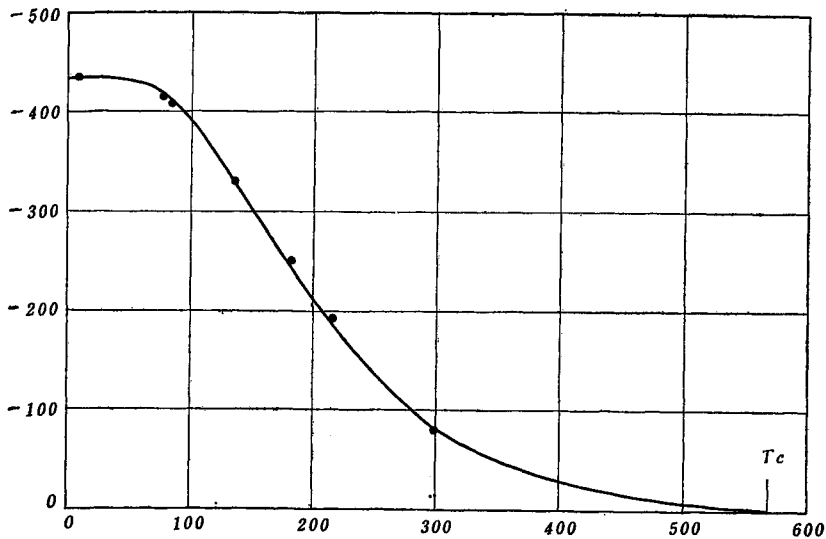

Fig. 3. The calculated temperature dependence of K_1/M_s of Mn-ferrite. The points represent the experimental values obtained by Dillon, Geschwind and Jaccarino.

In the vicinity of the Curie temperature, $\langle S_\zeta^n \rangle$ defined by (6·21) or (6·22) can be expanded in a power series of p or z, because the molecular field there is small, and we obtain

$$(5/8)[z] = 5p^4 + \cdots = (2^4/5^3)z^4 + \cdots . \tag{6·31}$$

On the other hand, u and v are proportional to $(T_c - T)^{1/2}$ in the neighborhood of the Curie temperature so that the anisotropy constant K_1 is proportional to $(T_c - T)^2$ near the Curie temperature. In the calculation of K_1/M_S in Fig. 3 this expansion formula

has been used in this region.

The fact that the sign of the a-value of the ions of octahedral sites is opposite to that of the ions of tetrahedral sites, as seen from $(6\cdot30)$, seems to be reasonable because the cubic crystalline field acting on the tetrahedral position is opposite in sign to that on the octahedral position. The a-value of Fe^{3+} ion in several alums is about -1.34 to -1.27×10^{-2} cm^{-1} and that of Mn^{2+} ion in Tutton salts and fluosilicates is $+0.10$ to $+0.03\times10^{-2}$ cm^{-1} [33]. The a-value of Mn^{2+} ion is less than one tenth of that of Fe^{3+} ion. Thus, a_{Fe}^{B} has a magnitude nearly three times as large as that of the Fe^{3+} ions in alums and has the opposite sign to the latter if we neglect the contribution of a_{Mn}^{B} in $(6\cdot30)$. Recently, Low[34] has measured the fine structure of the paramagnetic resonance absorption of Fe^{3+} ion in the single crystals of MgO and obtained a considerably large a-value of 1.83×10^{-2} cm^{-1}, though its sign has not been determined. Therefore, the a-value given by $(6\cdot30)$ does not seem to be unreasonable. For Ni-ferrite, the a-value of Fe^{3+} ion of the octahedral site is considered to be about 2.0×10^{-2} cm^{-1} and this is quite reasonable. Very recently Sugiura et al.[35] observed the paramagnetic resonance absorption of Fe^{3+} ion in the mixed ferrite of $ZnOAl_2O_3$ and $ZnOFe_2O_3$ and that of $MgOAl_2O_3$ and $MgOFe_2O_3$ and found that the resonance widths extrapolated to zero content of Fe^{3+} ion are, respectively, about 600 and 180 oersteds. The fact that the ratio is equal to 33 : 1 seems to be favourable for our result $(6\cdot30)$ because Fe^{3+} ions in the former mixed ferrite occupy the octahedral sites and those in the latter occupy the tetrahedral positions.*

§ 7. Conclusion

From the results of calculations made so far, we draw the conclusion that the anisotropy energies of Ni- and Mn-ferrites arise from the fine structure coupling of Fe^{3+} ions which occupy the octahedral and tetrahedral positions. For Mn-ferrite, we determined the a-values of Fe^{3+} ions of the octahedral and tetrahedral sites by analyzing the experimental anisotropy constant $vs.$ temperature curve obtained by Dillon, Geschwind and Jaccarino to be $a_{Fe}^{A}=-0.8\times10^{-2}$ cm^{-1} and $a_{Fe}^{B}=4.2\times10^{-2}$ cm^{-1}. This value of a_{Fe}^{B} seems to be somewhat larger than that expected from the a-value of Fe^{3+} ion in MgO. The magnitude of a_{Fe}^{B} in Ni-ferrite is expected from the anisotropy constant of this ferrite to be about 2×10^{-2} cm^{-1}. This value is quite reasonable. The reason for the large a-value of Fe^{3+} ion in Mn-ferrite is not clear at the present stage. However, the temperature dependence of the anisotropy constant of Mn-ferrite calculated with the use of these a-values shows a good agreement with the experiment.

For Co-ferrite, the situation is very complex. It has a very large anisotropy constant,

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* G. T. Rado and V. J. Folen have found that at room temperature the anisotropy constant for Fe^{3+} ion at the B site is negative and that for Fe^{3+} ion at the A site is positive and the ratio of these is about 3.1 by the magnetic measurements of single crystals of $(MgO)_{1-x}(FeO)_xFe_2O_3$. See G. T. Rado and V. J. Folen, Bull. Am. Phys. Soc. Ser. 2, 1 (1956), 132. We would like to thank to Dr. Rado for his private communication.

namely 2 cm^{-1} per molecule and also has a very large magnetostriction of $\lambda_{100} = 5.9 \times 10^{-4}$ and $\lambda_{111} = 1.1 \times 10^{-4}$. Thus, it might be supposed that in this substance the orbital moment is only partially quenched and the combined action of the electric quadrupole-quadrupole interaction, the exchange interaction between Co ions and the spin-orbit interaction would give rise to a large anisotropy energy.

For magnetite, it is considered that the anisotropy energies arising from Fe^{2+} and Fe^{3+} ions are leading terms in the high temperature range. The anisotropy energy below the transition temperature at 120°K is orthorhombic because of the orthorhombic super-structure of the arrangement of Fe^{2+} and Fe^{3+} ions in the octahedral sites. This anisotropy energy may be due to the Fe^{2+} and Fe^{3+} ions and the magnetic dipole-dipole interaction between these magnetic ions. In the temperature region above the transition, where the anisotropy constant decreases drastically and changes its sign from plus to minus, the effect of the short range order may play a certain role in determining the anisotropy energy. In order to account for the behavior of the anisotropy constant over this range, precise knowledge about the nature of the order-disorder transition would be needed.

In conclusion, the authors would like to express their sincere thanks to Professor T. Nagamiya and Mr. J. Kanamori for their valuable discussions.

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Note added in proof

A recent neutron diffraction experiment by J. M. Hastings and L. M. Corliss (Phys. Rev. **104** (1956), 328) on Mn-ferrite shows that the fraction of the tetrahedral sites occupied by manganese ions is 0.8 for three samples used. We, on the other hand, assumed that Mn-ferrite is of the inverse spinel type, i. e. the fraction is zero. To get out of this contradiction, the following three possibilities may be suggested.

1. The fraction of 0.8 is assumed to be valid also in the sample used by Dilllon[2] for measuring the anisotropy constant and in the sample used by Guillaud[32] for measuring the magnetization; Our analysis is based on these two measurements. Then the following values of $a_{F_e}^A$ and $a_{F_e}^B$ (neglecting the anisotropy constants arising from the manganese ions) can be shown to explain excellently the curve of K_1/M_s versus temperature of Dillon.

However, $a_{F_e}^A + a_{F_e}^B = -1.8 \times 10^{-2} \mathrm{cm}^{-1}$ in this case, which seems to be unacceptable since in Ni-ferrite the corresponding value is $+1.87 \times 10^{-2} \mathrm{cm}^{-1}$ (the opposite sign).

2. The fraction of 0.8 and the value of $a_{F_e}^A + a_{F_e}^B$ found for Ni-ferrite are assumed to be valid for Mn-ferrite, again neglecting the contribution of the manganese ions to the anisotropy constant. Taking the Dillon's[2] experimental value of K_1/M_s at $300°\mathrm{K}$–Dillon's and Tannenwald's[3] measurements give about the same value at $300°\mathrm{K}$–we obtain

$$a_{F_e}^B = 1.37 \times 10^{-2} \mathrm{cm}^{-1}, \qquad a_{F_e}^A = 0.50 \times 10^{-2} \mathrm{cm}^{-1}.$$

The ratio $a_{F_e}^B / a_{F_e}^A = 2.74$ is favourable for the experimental results due to Sugiura[35] and Rado (private communication) but the sign of $a_{F_e}^A$ is opposite to that found by Rado. The temperature dependence of K_1/M_s comes nearer to that observed by Tannenwald[3] (Fig. 4).

3. The sample used by Dillon[2] is assumed to have had a different fraction of the manganese ions on the tetrahedral sites. This fraction will be denoted by x. The following numerical values found by our analysis are assumed to be valid:

$$(1-x)\ a_{F_e}^A = -0.82 \times 10^{-2} \mathrm{cm}^{-1}, \qquad (1+x) a_{F_e}^B = 4.21 \times 10^{-2} \mathrm{cm}^{-1},$$

$$a_{F_e}^A + a_{F_e}^B = 1.87 \times 10^{-2} \mathrm{cm}^{-1} \quad \text{(for Ni-ferrite).}$$

Then we obtain

$$x = 0.347, \qquad a_{F_e}^A = -1.26 \times 10^{-2} \mathrm{cm}^{-1}, \qquad a_{F_e}^B = 3.13 \times 10^{-2} \mathrm{cm}^{-1},$$

The ratio $|a_{F_e}^B / a_{F_e}^A|$ is 2.48 and the sign of $a_{F_e}^A$ is in agreement with that found by Rado.

We note that the sublattice magnetizations per ion observed by neutron diffraction experiment and those found by our calculation (based on Guillaud's[32] measurements) are in good agreement:

neutron diffraction study :

$$\frac{(m_B)_{300°K}}{(m_B)_{4.2°K}}=0.822 \ ,$$

$$\frac{(m_A)_{300°K}}{(m_A)_{4.2°K}}=0.941 \ ,$$

our calculation :

$$\frac{(m_B)_{300°K}}{(m_B)_{4.2°K}}=0.815 \ ,$$
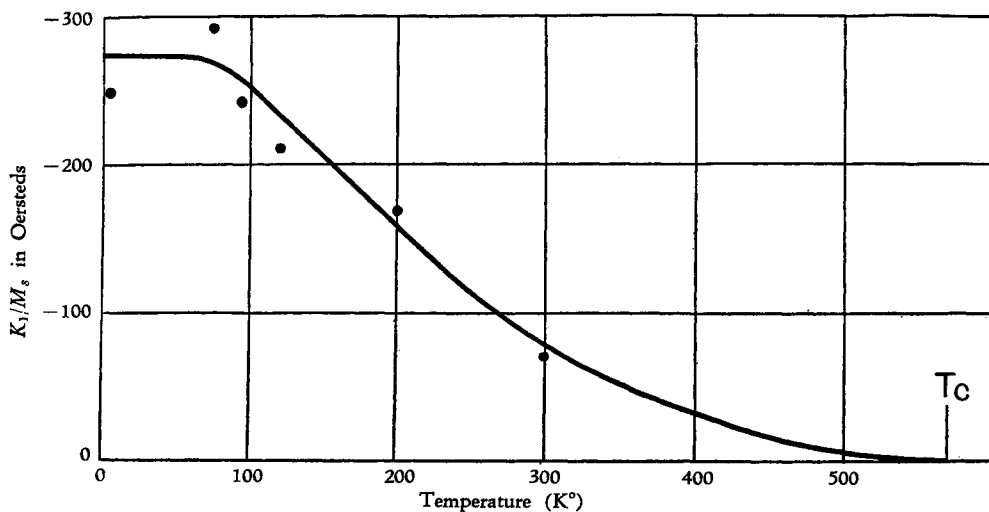
$$\frac{(m_A)_{300°K}}{(m_A)_{4.2°K}}=0.914 \ .$$

Fig. 4. The calculated temperature dependence of K_1/M_s of M_n-ferrite. The points represents the experimental values obtained by Tannenwald.