The Effect of Hydrostatic Pressure on the Magnetic Anisotropy of Ferrous and Ferric Ions in Ferrites with Spinel Structure

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The first order magnetic anisotropy constant $K_1$ of eight ferrites with inverse-type spinel structure and two ferrites with normal-type has been measured under hydrostatic pressure by the use of a torque method. The pressure dependence of $K_1$, $K_1'(dK_1/dp)$, in Li$_{0.2}$Fe$_{2.5}$O$_4$ is $+4.1 \times 10^{-6}$ bar$^{-1}$, in NiFe$_{2.5}$O$_4$ is $+3.3 \times 10^{-6}$ bar$^{-1}$, in Li$_{0.5}$Fe$_{2.5}$O$_4$ is $-18.0 \times 10^{-6}$ bar$^{-1}$, in Fe$_2$O$_3$ is $-13.5 \times 10^{-6}$ bar$^{-1}$, in Fe$_{2.9}$Ti$_{0.1}$O$_4$ is $-9.4 \times 10^{-6}$ bar$^{-1}$, in Fe$_{2.9}$Ti$_{0.1}$O$_4$ is $-13.5 \times 10^{-6}$ bar$^{-1}$, in Fe$_{2.9}$Ti$_{0.1}$O$_4$ is $-14.0 \times 10^{-6}$ bar$^{-1}$, in Fe$_{2.9}$Ti$_{0.1}$O$_4$ is $+3.0 \times 10^{-6}$ bar$^{-1}$, in MnFe$_2$O$_4$ is $+7.0 \times 10^{-6}$ bar$^{-1}$, in Mn$_{0.9}$Zn$_{0.1}$Fe$_3$O$_4$ is $+6.0 \times 10^{-6}$ bar$^{-1}$ at room temperature. The results are discussed with regard to a single-ion model. In spinel, the contribution of ferrous ion to anisotropy constant $K_1$ increases, and that of ferric ion decreases, with decreasing lattice constant under hydrostatic pressure.

§ 1. Introduction

The crystal structure of ferrites having spinel structure is well known. Although many experimental and theoretical investigations of magnetocrystalline anisotropy of ferrites have been carried out, the origin of the anisotropy is not yet adequately explained. It is an especially interesting phenomenon that the contribution of ferrous ions in octahedral sites in spinel structure gives positive or negative value to the first order magnetic anisotropy constant $K_1$ in the solid solution Fe$_3$O$_4$-MeFe$_2$O$_4$, where Me is Mn$^{2+}$, Mg$^{2+}$ or Ni$^{2+}$. It is the purpose of this investigation to clarify the origin of magnetic anisotropy of ferrous (Fe$^{2+}$) and ferric (Fe$^{3+}$) ions in spinels through observations of anisotropy under hydrostatic pressure. It appears, from several experimental results of magnetic anisotropy of cubic ferrites, that the anisotropy of the crystals is the summation of the anisotropy of the individual magnetic ions rather than anisotropic coupling between magnetic neighbours. Thus a single-ion model can be used for analysis of the phenomenon. For our purpose it is necessary to note only the crystalline environments of the two kinds of cation sites. A tetrahedral or A-site is surrounded by a regular tetrahedron of oxygens. An octahedral or B-site is surrounded by an octahedron of oxygens. The single-ion model considers an electronic structure of relevant magnetic ions deformed by the crystalline field due to the surrounding ions. Iron group ions have an electronic structure consisting of a closed shell and an unfilled 3$d$ shell. In crystals of cubic symmetry, the 3$d$ orbits split into two groups, namely $d_{e}$ and $d_{t}$. For a cation in a B-site the $d_{t}$ state has a higher energy than the $d_{e}$ state. Furthermore, the local symmetry about a B-site is not completely cubic, but trigonal (see Fig. 1) due to the surrounding cations. The oxygen positions are displaced slightly from those of regular octahedrons and the deviation, which is described by a $U$-parameter, contributes also to the trigonal field. A further splitting of the lower-energy $d_{e}$ state at the B-site into a singlet and a doublet is caused by the trigonal field component $E_t$. $E_t$ is related to the origin of the magnetic anisotropy of the ferrous ion at the B-site in spinel structure, as will be
described in the following section.

The consideration of the contribution to the magnetic anisotropy from the ions whose ground state is not degenerated was first made by Yosida and Tachiki \(^{18}\) and extended by Wolf. \(^{14}\) For such ions the most general spin Hamiltonian for a spin \(S \leq 5/2\) is \(^{14}\)

\[
\mathbf{H} = \beta \mathbf{H} \cdot \mathbf{S} + \frac{a}{6} (S_x^4 + S_y^4 + S_z^4) + D S_x^2 + f S_x^2 + \cdots ,
\]

where \(\alpha\) denotes the direction of the axial distortion. The first term represents the super-exchange energy where \(g\) is the gyromagnetic ratio. The second term represents the fourth-order perturbation of the spin-orbit coupling. If \(S<2\) as for \(\text{Ni}^{2+}\), the constant "\(a\)" vanishes identically, so that we may consider that only \(\text{Fe}^{2+}, \text{Mn}^{2+}\) and \(\text{Fe}^{3+}\) ions can contribute to the anisotropy from the second term in eq. (1). The third and fourth terms represent uniaxial crystalline fields existing locally in the crystal. Yosida and Tachiki \(^{18}\) took only the first two terms and successfully explained the temperature dependence of the first order magnetic anisotropy constant \(K_1\) of \(\text{MnFe}_2\text{O}_4\). They also estimated the contribution of ferrous ions in \(\text{Fe}_2\text{O}_4\). The third term in eq. (1) was neglected in their discussion. However, Wolf pointed out \(^{14}\) that the second-order perturbation of the \(D\) term can contribute to the cubic anisotropy and yields a positive \(K_1\) irrespective of the sign of \(D\). When \(\text{Fe}_2\text{O}_4\) is mixed with \(\text{MeFe}_2\text{O}_4\) where \(\text{Me} = \text{Mn}, \text{Mg},\) or \(\text{Ni},\) the anisotropy constant \(K_1\) of \(\text{Fe}^{2+}\) ions in the ferrites is positive near the composition \(\text{MeFe}_2\text{O}_4\). Slonczewski \(^{16}\) has theoretically suggested that Wolf's mechanism is responsible for the positive \(K_1\).

The present authors observed the change of \(K_1\) in eight kinds of ferrite single crystals with the inverse-type spinel structure, and two kinds with the normal-type, under hydrostatic pressure. An attempt has been made to explain the pressure effect of \(K_1\) using the single-ion model.

§ 2. Experimental Procedure

In order to measure the magnetic anisotropy of ferrite single crystals under hydrostatic pressure, the present authors have constructed a very simple apparatus which consists of a small non-magnetic high pressure vessel and a torque magnetometer. The high pressure vessel is made of a hardened Cu-1.82\% Be alloy. Construction details are shown in Fig. 2. This vessel is a modification of a vessel which was first made by Itskevich. \(^{17}\)

Pressure was produced in the sample chamber of the vessel by driving a piston \(C\) by a hydraulic press. After the desired pressure was attained, the piston \(C\) was locked tightly to the cylinder \(D\) with an attached screw nut \(B\). The pressure fluid was a 1:1 mixture of kerosene and electric transformer oil. The pressure is measured by the use of a manganin gauge which was calibrated using the phase transition of ammonium fluoride (\(\text{NH}_4\text{F}\)) at 3704 Kg/cm\(^2\) at 25°C. \(^{18}\) A relation of displacement of the piston, or change of electric resistance of manganin wire, with the load force on the piston are shown in Fig. 3(a), (b), respectively. The relations show the existence of hysteresis which is caused by friction of packing materials around the piston. The vessel containing the sample is connected directly to an air-bearing torque magnetometer having an unbounded strain gauge detector. A complete description may be
Pressure Effect on Anisotropy of Ferrites

Fig. 3(a). A relation of displacement of a piston with the load force on the piston.

found elsewhere.15,20

Preparation methods, shape and size of the single crystals of \(\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4\), \(\text{NiFe}_2\text{O}_4\), and \(\text{Fe}_3\text{O}_4\) are shown in Table I. The single crystals of the solid solution in \(\text{Fe}_3\text{O}_4\)-\(\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4\) and \(\text{Fe}_3\text{O}_4\)-\(\text{Fe}_2\text{TiO}_4\) were prepared using the Bridgman method, and were provided by Y. Syono. Results of chemical analysis, shape and size of the single crystals are summarized in Table II. The single crystals of

\[
E_a = K_0 + K_1(a_1a_2^2 + a_2a_3^2 + a_3a_1^2) + K_2(a_1^2a_2^2a_3^2) + \cdots,
\]

where \(a_1, a_2, a_3\) are the direction cosines of the magnetization vector relative to the crystallo-

\[\text{MnFe}_2\text{O}_4\] and \((\text{Mn}, \text{Zn})\text{Fe}_2\text{O}_4\) were prepared using the flame fusion method, and were provided by S. Kikuchi of SONY corporation. Results of chemical analysis, shape and size of the single crystal are summarized in Table III. Li\(^{2+}\) and Fe\(^{3+}\) ions on B-site in \(\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4\) have long range order below 755°C and disorder above that temperature. The single crystal used in this experiment was quenched from 850°C to room temperature in air. The other nine kinds of the crystals were well annealed at 600–800°C before torque measurements.

Table I. Preparation methods, shape and size of lithium, nickel and iron ferrites.

<table>
<thead>
<tr>
<th>compounds</th>
<th>preparation method</th>
<th>shape and size of sample</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Li}<em>{0.5}\text{Fe}</em>{2.5}\text{O}_4)</td>
<td>flux method</td>
<td>disc whose plane is</td>
<td>K. Shiratori</td>
</tr>
<tr>
<td></td>
<td></td>
<td>parallel to (100)</td>
<td>Osaka Univ.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3.45) mm diameter</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.50) mm thickness</td>
<td></td>
</tr>
<tr>
<td>(\text{NiFe}_2\text{O}_4)</td>
<td>flame fusion method</td>
<td>disc whose plane is</td>
<td>S. Kikuchi</td>
</tr>
<tr>
<td></td>
<td></td>
<td>parallel to (100)</td>
<td>SONY Corp.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(4.46) mm diameter</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.50) mm thickness</td>
<td></td>
</tr>
<tr>
<td>(\text{Fe}_3\text{O}_4)</td>
<td>Bridgman method</td>
<td>disc whose plane is</td>
<td>T. Yamada</td>
</tr>
<tr>
<td></td>
<td></td>
<td>parallel to (110)</td>
<td>Tokyo Univ.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(4.0) mm diameter</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.0) mm thickness</td>
<td></td>
</tr>
</tbody>
</table>

Table II. Chemical composition and size of solid solution system.

<table>
<thead>
<tr>
<th>run No.</th>
<th>compounds</th>
<th>nominal comp.</th>
<th>chemical comp.</th>
<th>diameter mm (sphere)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L8</td>
<td>(x\text{Li}<em>{0.5}\text{Fe}</em>{2.5}\text{O}_4)</td>
<td>0.10</td>
<td>0.10</td>
<td>2.89</td>
</tr>
<tr>
<td>T9</td>
<td>(x\text{Fe}_2\text{TiO}_4)</td>
<td>0.05</td>
<td>0.04</td>
<td>3.55</td>
</tr>
<tr>
<td>T6</td>
<td>(x\text{Fe}_2\text{TiO}_4)</td>
<td>0.10</td>
<td>0.10</td>
<td>2.18</td>
</tr>
<tr>
<td>T14</td>
<td>(x\text{Fe}_2\text{TiO}_4)</td>
<td>0.20</td>
<td>0.18</td>
<td>2.92</td>
</tr>
<tr>
<td>T22</td>
<td>(x\text{Fe}_2\text{TiO}_4)</td>
<td>0.30</td>
<td>0.31</td>
<td>2.61</td>
</tr>
</tbody>
</table>

§ 3. Experimental Results

Torque measurements of \(\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4\) and \(\text{Fe}_3\text{O}_4\) were carried out in the planes (110) and for the other eight specimens in the (100) plane. In general, in a crystal having cubic symmetry the anisotropy energy \(E_a\) can be expressed by the following equation:

\[
E_a = K_0 + K_1(a_1a_2^2 + a_2a_3^2 + a_3a_1^2) + K_2(a_1^2a_2^2a_3^2) + \cdots,
\]

Fig. 3(b). A relation of change of electric resistance of manganin wire with the load force on the piston.

\[
E_a = K_0 + K_1(a_1a_2^2 + a_2a_3^2 + a_3a_1^2) + K_2(a_1^2a_2^2a_3^2) + \cdots,
\]
Table III. Preparation methods, shape and size of manganese, manganese-zinc ferrites.

<table>
<thead>
<tr>
<th>compounds</th>
<th>preparation method</th>
<th>shape and size of sample</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$<em>{0.95}$Fe$</em>{2.05}$O$_4$</td>
<td>flame fusion method</td>
<td>disc whose plane is parallel to (100)</td>
<td>S. Kikuchi of SONY Corp.</td>
</tr>
<tr>
<td>Mn$<em>{0.8}$Zn$</em>{0.2}$Fe$_2$O$_4$</td>
<td></td>
<td>disc whose plane is parallel to (100)</td>
<td></td>
</tr>
</tbody>
</table>

graphic axes. The torque $L$ is given by the derivative $E_\alpha$ with respect to an angle $\theta$ of rotation in an infinitely strong magnetic field:

$$L = -\frac{dE_\alpha}{d\theta}.$$  \hspace{1cm} (3)

The torques effective in the planes (100) and (110) are given by the following equations:

$$L_{100} = -\frac{K_1}{2} \sin 4\theta,$$  \hspace{1cm} (4)

$$L_{110} = -\frac{K_1}{8} (2 \sin 2\theta + 3 \sin 4\theta) + \frac{K_2}{64} (\sin 2\theta - 4 \sin 4\theta - 3 \sin 6\theta),$$  \hspace{1cm} (5)

where the basal direction of $\theta$ is $<001>$ for $L_{100}$ and $<110>$ for $L_{110}$. $K_1$ under hydrostatic pressure was estimated by the use of the above equations. In this experiment, however, errors of about $\pm 1^\circ$ occur in cutting and setting the crystals. This misorientation from the (100) or (110) plane during the measurements can cause slight deviations of the curve from that expected from the above equation. The value of $K_1$ was, therefore, determined by averaging the measured torque curve.

Fig. 4. Torque curves of a single crystal of Fe$_2$O$_4$ in the (110) plane taken at room temperature with an applied magnetic field of 9600 Oe. The open and closed circles show values observed under atmospheric pressure and 9240 bar, respectively.

Fig. 5. Torque curves of a single crystal of NiFe$_2$O$_4$ in the (100) plane taken at room temperature with an applied magnetic field of 8600 Oe. The open and closed circles show values observed under atmospheric pressure and 8500 bar, respectively.

Fig. 6. Change of first order magnetic anisotropy constant $K_1$ of some ferrites at room temperature under high pressure. □-Li$_{0.3}$Fe$_{2.3}$O$_4$, △-NiFe$_2$O$_4$, and ○-Fe$_3$O$_4$.  
Fig. 7. Change of first order magnetic anisotropy constant $K_1$ of several ferrites at room temperature under high pressure.

- Li$_{0.8}$Fe$_{2.98}$O$_4$, $\square$ -Fe$_{2.96}$Ti$_{0.04}$O$_4$, $\triangle$ -Fe$_{2.96}$Ti$_{0.10}$O$_4$,
- Fe$_{2.82}$Ti$_{0.16}$O$_4$, and $\blacktriangle$ -Fe$_{2.69}$Ti$_{0.31}$O$_4$.

Fig. 8. Change of first order magnetic anisotropy constant $K_1$ of some ferrites at room temperature under high pressure.

- MnFe$_2$O$_4$, and $\blacktriangle$ -Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$.

Torque curves are obtained with an applied magnetic field of 9600 Oe for Fe$_3$O$_4$ and 8600 Oe for the other nine crystals. Figure 4 and Fig. 5 show some typical torque curves of Fe$_3$O$_4$ and NiFe$_2$O$_4$ single crystals at room temperature under high pressure, respectively. The change of $K_1$ of these ferrites, $dK_1/K_1$, at room temperature is shown in Figs. 6-8. The pressure dependence of $K_1$, $K_1^{-1}(dK_1/dP)$, which was obtained from the above results, was transformed into the volume dependence, $(V/K_1)(dK_1/dV)$, using the compressibility of Fe$_3$O$_4$ and NiFe$_2$O$_4$.

The values obtained are in Table IV.

<table>
<thead>
<tr>
<th>compound</th>
<th>lattice constant (Å)</th>
<th>$U$-parameter</th>
<th>$-\frac{1}{dK_1} \frac{dP}{dV}$ bar$^{-1}$</th>
<th>$\frac{1}{V} \frac{dV}{dP}$</th>
<th>$V \frac{dK_1}{K_1} dV$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{0.8}$Fe$</em>{2.98}$O$_4$</td>
<td>8.332</td>
<td>0.382</td>
<td>+ $4.1 \times 10^{-6}$</td>
<td>+ $5.4 \times 10^{-6}$</td>
<td>$-0.54 \times 10^{-6}$</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>8.339</td>
<td>0.381</td>
<td>+ $3.3 \times 10^{-6}$</td>
<td>+ $0.51 \times 10^{-6}$</td>
<td>+ 32</td>
</tr>
<tr>
<td>Li$<em>{0.8}$Fe$</em>{2.98}$O$_4$</td>
<td>8.388</td>
<td>0.379</td>
<td>$-18.0 \times 10^{-6}$</td>
<td>+ $0.51 \times 10^{-6}$</td>
<td>+ 32</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>8.397</td>
<td>0.397</td>
<td>$-13.5 \times 10^{-6}$</td>
<td>+ $0.51 \times 10^{-6}$</td>
<td>+ 25</td>
</tr>
<tr>
<td>Fe$<em>{2.96}$Ti$</em>{0.04}$O$_4$</td>
<td>8.398</td>
<td>0.389</td>
<td>$-9.4 \times 10^{-6}$</td>
<td>+ $0.51 \times 10^{-6}$</td>
<td>+ 17</td>
</tr>
<tr>
<td>Fe$<em>{2.96}$Ti$</em>{0.10}$O$_4$</td>
<td>8.401</td>
<td></td>
<td>$-6.5 \times 10^{-6}$</td>
<td>+ $0.51 \times 10^{-6}$</td>
<td>+ 12</td>
</tr>
<tr>
<td>Fe$<em>{2.82}$Ti$</em>{0.16}$O$_4$</td>
<td>8.417</td>
<td>0.379</td>
<td>$-1.4 \times 10^{-6}$</td>
<td>+ $0.51 \times 10^{-6}$</td>
<td>+ 2.6</td>
</tr>
<tr>
<td>Fe$<em>{2.69}$Ti$</em>{0.31}$O$_4$</td>
<td>8.433</td>
<td>0.385</td>
<td>+ $3.0 \times 10^{-6}$</td>
<td>+ $0.51 \times 10^{-6}$</td>
<td>$-0.51 \times 10^{-6}$</td>
</tr>
<tr>
<td>Mn$<em>{0.8}$Fe$</em>{2.98}$O$_4$</td>
<td>8.503</td>
<td>0.385</td>
<td>+ $7.0 \times 10^{-6}$</td>
<td>+ $0.51 \times 10^{-6}$</td>
<td>+ 12</td>
</tr>
<tr>
<td>Mn$<em>{0.8}$Zn$</em>{0.2}$Fe$_2$O$_4$</td>
<td>8.493</td>
<td></td>
<td>+ $6.0 \times 10^{-6}$</td>
<td>+ $0.51 \times 10^{-6}$</td>
<td>+ 2.6</td>
</tr>
</tbody>
</table>

§ 4. Discussion

Lithium ferrite has a cation distribution such as (Fe$^{3+}$)[Li$_{0.8}$Fe$_{2.98}$]$O_4$, where ( ) and [ ] denote A and B-sites, respectively. Since the contribution of the second term $\alpha/6(S^4_x+S^4_y+S^4_z)$ to the magnetic anisotropy from the ions whose group state is not degenerated, can be expected, a positive value of $K_1^{-1}(dK_1/dP)$ of this compound means that the sum of the cubic crystal field splitting parameter "a" of ferric ions at the A and the B-sites increases with decreasing lattice constant.

Nickel ferrite has a cation distribution such as (Fe$^{3+}$)[Ni$_{2+}$Fe$^{3+}$]$O_4$. Yosida and Tachiki showed that the magnetic anisotropy of Ni$^{2+}$ at the B-site in NiFe$_2$O$_4$ arises from the mechanism of exchange anisotropy and is negligibly small compared to the...
anisotropy of the Fe\(^{3+}\) ion. Therefore, the magnetic anisotropy of NiFe\(_2\)O\(_4\) arises mainly from a term due to the Fe\(^{3+}\) ion. A positive value of \(K_1=\frac{1}{a_0}(dK_1/dP)\) of this compound also means that the sum of "a" term for the A and the B-sites increases with decreasing lattice constant. The difference of \(K_1\) at 0\(^\circ\)K of Li\(_{0.2}\)Fe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\) at the same lattice constant means a contribution of Fe\(^{3+}\) of 0.5 ions at the B-site. The \(K_1\) value of Fe\(^{3+}\) calculated from the above relation is \(-0.98\times10^{-2}\) cm\(^{-1}\) per ion at the A-site and \(-3.35\times10^{-2}\) cm\(^{-1}\) per ion at the B-site. Thus the ratio \([(K_1)_{\text{at the B-site}}]/[(K_1)_{\text{at the A-site}}]\) is 3.4. This value is consistent with the value of ratio \(['a' at the B-site]/['a' at the A-site]\) of 3.1, which was obtained using the results of paramagnetic resonance absorption of Fe\(^{3+}\) ions in MgAl\(_2\)O\(_4\) and ZnAl\(_2\)O\(_4\) by Sugiiura.\(^{23}\)

Magnetite has a cation distribution such as \((\text{Fe}^{3+}+\text{Fe}^{2+})\) [Fe\(^{2+}\)+Fe\(^{3+}\)]\(_4\). \(K_1\) for this compound is negative at room temperature. It increases in absolute magnitude with decreasing temperature and decreases sharply from 200\(^\circ\)K, becoming positive below 114\(^\circ\)K. At 119\(^\circ\)K, the well-known transition\(^{24}\) that is ascribed to the ordering of Fe\(^{3+}\) and Fe\(^{2+}\) at the B-site takes place. Solid solutions Li\(_{0.2}\)Fe\(_2\)O\(_3\), Fe\(_{2.95}\)Ti\(_{0.05}\)O\(_4\), Fe\(_{2.95}\)Ti\(_{0.10}\)O\(_4\), Fe\(_{2.75}\)Ti\(_{0.25}\)O\(_4\) and Fe\(_{2.65}\)Ti\(_{0.35}\)O\(_4\) show the same tendency of the relation between temperature and \(K_1\). \(K_1\) of these six ferrites at 0\(^\circ\)K is treated in the discussion, and the values are an extrapolation of data above 250\(^\circ\)K to that temperature.

For each term in eq. (1) the temperature dependence of the contribution to the anisotropy energy may be calculated in the molecular field approximation from \(\langle S_{<j}^j \rangle\), which is proportional to the sublattice magnetization \(M_1\). Since the pressure dependence of saturation magnetization of those ferrites obtained in the preliminary experiments by the present authors is very small, \((1/M)(dM/dP)\) \(<10^{-6}\) bar\(^{-1}\) at room temperature, the assumption that the volume dependence of \(K_1\), \((V/K_1)(dK_1/dV)\), at 0\(^\circ\)K is nearly equal to that obtained at room temperature, would be reasonable. The authors tried, by using the volume dependence of \(K_1\) obtained at room temperature, to express \(K_1\) of those ferrites at 0\(^\circ\)K taking lattice constant as parameter. When a lattice constant is \((a_0+\Delta a)\),

\[
K_1(a_0+\Delta a)=K_1+\Delta K_1, \tag{6}
\]

where \(a_0\) and \(\Delta a\) are lattice constant under atmospheric pressure and the change of it, respectively. The change of \(K_1\), \(\Delta K_1\), under hydrostatic pressure is given by the following equation:

\[
\Delta K_1=\frac{3}{a_0}\left(\frac{V}{K_1}\frac{dK_1}{dV}\right)K_1 \tag{7}
\]

It can be considered that the difference of \(K_1\) at 0\(^\circ\)K of NiFe\(_2\)O\(_4\) and Fe\(_2\)O\(_3\) at the same lattice constant means a contribution of Fe\(^{3+}\) to \(K_1\) at the B-site in Fe\(_2\)O\(_3\). The \(K_1\) value of Fe\(^{3+}\) estimated by using eq. (6) is shown in Fig. 9. The \(K_1\) value of Fe\(^{2+}\)

\[
\text{Fig. 9. The first order magnetic anisotropy constant} \ \ K_1 \ \text{of NiFe}_2\text{O}_4 \ \text{and Fe}_2\text{O}_3 \ \text{at 0}\,^\circ\text{K, taking lattice constant as parameter.} \ a-K_1 \ \text{of NiFe}_2\text{O}_4 \ \text{per molecule,} \ b-K_1 \ \text{of Fe}_2\text{O}_3 \ \text{per molecule, and} \ c-K_1 \ \text{of Fe}^{2+}\ \text{per ion. Open and closed circles show} \ K_1 \ \text{obtained under atmospheric pressure.}
\]

is \(-3.7\times10^{-1}\) cm\(^{-1}\) per ion at \(a_0=8.397\) Å which is the lattice constant of Fe\(_2\)O\(_3\) under atmospheric pressure and decreases in absolute magnitude with decreasing lattice constant, changing sign at \(a_0=8.351\) Å. Fe\(^{2+}\) at the B-site in NiFe\(_2\)O\(_4\) whose lattice constant is 8.339 Å, has the value of \(K_1\) of \(+0.9\times10^{-1}\) cm\(^{-1}\) per ion. Both the \(K_1\) values which were observed in the solid solution system Ni\(_{3-x}\)Fe\(_{x}\)-\text{Fe}_2\text{O}_4 by Elbinger\(^{27}\) and estimated using the results of high pressure experiments are shown taking lattice constant as parameter in Fig. 10. As seen in the figure, the estimations obtained in this way are consistent in the trend of changes with the results on actual measurements of anisotropy in the solid solution system.

The contribution of the \(D\) term in eq. (1) for the Fe\(^{2+}\) ion is important as pointed out by Wolf\(^{14}\) and Slonczewski.\(^{10}\) The \(D\) term for the Fe\(^{2+}\) ion depends on the trigonal field component \(E_t\), which is
due to the lack of cubic symmetry at the B-site. A splitting of the $d$ states into a singlet and a doublet at the B-site is caused by the trigonal field component $E_t$. The trigonal field potential $V_t$ is given by the following equation:

$$V_t = -Ce^2(xy+yz+zx)/a_0^8,$$

where $C$ and $a_0$ are the trigonal field potential constant and the lattice constant, respectively. The contributions to the constant $C$ are given by a summation of the electrostatic potential which consists of terms from (1) the neighbouring cations which have a trigonally symmetric arrangement, (2) the point charge effect of the oxygen ions, whose positions are described by the $U$-parameter and (3) the polarization effect of oxygen ions. Since calculations indicate that contribution of the neighbouring cations to the trigonal field component $E_t$ predominates in inverse spinels,\textsuperscript{6,16,25} the singlet has lower energy than the doublet.

For the $3d^6$ configuration of Fe$^{3+}$ at the B-site, the ground state is an orbital singlet which has no orbital momentum in first order and the first exited state is a doublet with energy $E_t$. We expect this ion contributes a significant anisotropy which arises from $D$ term, where $D$ is given as $x^2/E_t$.\textsuperscript{16} Therefore, the contribution of the $D$ for Fe$^{3+}$ at the B-site increases with decreasing $E_t$. It was reported by Smit et al.\textsuperscript{8,24} that the trigonal field potential at the B-site in ferrites having inverse-type spinel structure decreases with increasing $U$-parameter and change its sign at $U=0.380$. It can be expected by the use of rigid sphere approximation for ions of spinel structure that the $U$-parameter increases with decreasing lattice constant under hydrostatic pressure. Therefore, the contribution of the $D$ term of Fe$^{3+}$ ion at the B-site to a positive $K_1$ increases with decreasing lattice constant under hydrostatic pressure. It is known by X-ray and neutron diffraction measurements that the $U$-parameter of the ferrites having inverse-type spinel structure depends on the lattice constants. Since it is expected that the $U$-parameter in the system Ni$_2$Fe$_{2-x}$O$_4$ increases with increasing $x$, a positive value of $K_1$ for Fe$^{3+}$ in the range of $0.8<x<1$ means that contribution of the $D$ term to $K_1$ is dominant.

The values of pressure dependence of $K_1$, $K_1^{-1}(dK_1/dp)$, in the solid solution system Fe$_2$O$_3$-Li$_{1-x}$Fe$_x$O$_4$ and Fe$_2$O$_3$-Fe$_x$TiO$_4$ are changed continuously according to lattice constant, as seen in Table IV. The values can be explained by using the same idea described in the previous discussion. Detail discussions of the origin and the pressure dependence of the magnetic anisotropy of these ferrites will be carried out elsewhere.

It reported by Hasting and Corliss\textsuperscript{26} that MnFe$_2$O$_4$ is 80% normal-type spinel. Yosida and Tachiki\textsuperscript{18} have explained successfully the temperature dependence of $K_1$ of this compound, where the contribution of Mn$^{2+}$ to $K_1$ is negligibly small compared with that of Fe$^{3+}$. If $K_1$ of this compound arises mainly from Fe$^{3+}$ at the B-site, the positive value of pressure dependence of $K_1$ is consistent with the results of lithium ferrite and nickel ferrite. Recently Hira\textsuperscript{27} showed by the use of N.M.R. measurements that some of Mn$^{2+}$ exist at the B-site. The contribution of Mn$^{2+}$ at B-site to anisotropy is fairly large compare to Fe$^{3+}$. Therefore, the origin and pressure effect of the anisotropy of manganese ferrite and manganese zinc ferrite will be complex.

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