

## Mössbauer Effect of $\text{ZnMn}_x\text{Fe}_{2-x}\text{O}_4$

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The antiferromagnetic normal spinel  $\text{ZnMn}_x\text{Fe}_{2-x}\text{O}_4$  is investigated from the viewpoint of the symmetry of crystalline field which causes quadrupole splittings.

The calculation of trigonal and tetragonal fields is carried out to analyze the experimental spectra, and its result agrees with them fairly well.

### §1. Introduction

$\text{ZnMn}_2\text{O}_4$  has a normal spinel structure, tetragonally distorted by the Jahn-Teller effect of  $\text{Mn}^{3+}$  ions, and is known to be antiferromagnetic at low temperature. The magnetic susceptibility is reported to have a broad maximum around 150 K, just like that of a one-dimensional antiferromagnet.<sup>1)</sup> It is also reported that its specific heat has an anomalous peak associated with Néel point at rather high temperature, about 250 K.

Through the study on the Mössbauer effect of  $\text{Fe}^{57}$  which is substituted in place of 1%  $\text{Mn}^{3+}$  of  $\text{ZnMn}_2\text{O}_4$ , some information about the behavior of  $\text{Fe}^{3+}$  as impurities and about the exchange interaction between  $\text{Mn}^{3+}$  ions and  $\text{Fe}^{3+}$  ions is given.

The Mössbauer spectra were measured for  $\text{Fe}^{57}$  in the system  $\text{ZnMn}_x\text{Fe}_{2-x}\text{O}_4$ . Among these system the material with  $x > 0.80$  have tetragonal spinel structures at the room temperature.

We shall report the results of the calculation of electric quadrupole splittings on the assumption that ions are point charges. The contribution of oxygen dipoles is not considered in this calculation, but the comparison with the experimental data shows a satisfactory agreement.

### §2. Experimental Results

#### 1) Sample

Polycrystalline samples with  $x=2.0, 1.98, 1.0, 0.82$  and  $0.6$  of  $\text{ZnMn}_x\text{Fe}_{2-x}\text{O}_4$  system were prepared from  $\text{ZnO}$ ,  $\text{MnO}_2$  and  $\text{Fe}_2\text{O}_3$  powder by ceramic method. After sintering at  $1000^\circ\text{C}$  for 3 hours in air, the samples were maintained at  $800^\circ\text{C}$  for 20 hours and were cooled slowly about  $70^\circ\text{C}/\text{hour}$ .

The  $x=2.0$  sample was prepared also from Zn metal and Mn metal which were solved into nitric acid, dried at  $400^{\circ}\text{C}$  and fired in the same way above mentioned.

The spectra of X-ray diffraction show higher resolution for the sample started with metal than that with oxide powder.

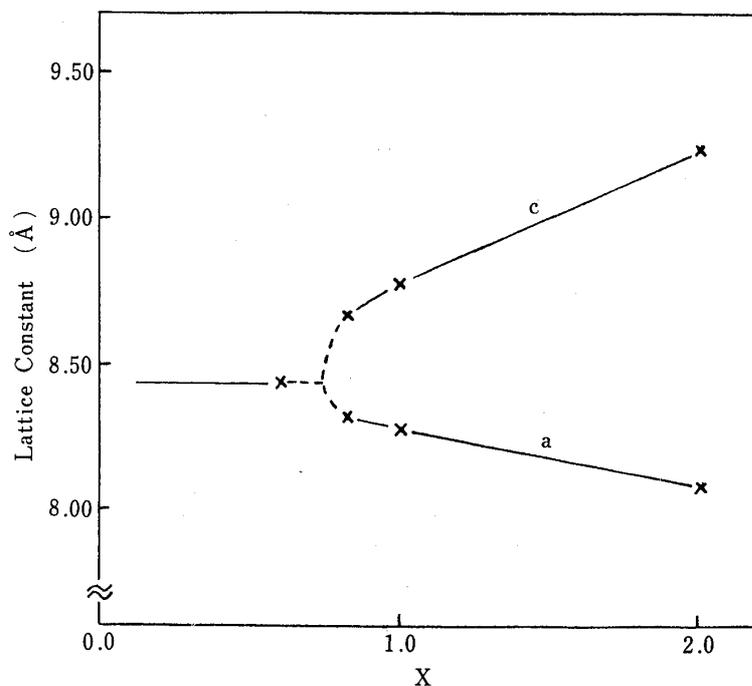


Fig. 1. Lattice constants of  $\text{ZnMn}_x\text{Fe}_{2-x}\text{O}_4$  at 295 K.

The lattice constants versus  $x$ , shown in Fig. 1, agree well with the reported values.<sup>2)</sup> The magnetic susceptibility of  $\text{ZnMn}_2\text{O}_4$  is almost constant below 150 K down to liquid nitrogen temperature. As the sample  $x=1.98$  shows the similar  $\chi-T$  curve with  $x=2.0$ , there is scarcely any effect of substituting small amount of  $\text{Mn}^{3+}$  for  $\text{Fe}^{3+}$  on magnetism over this temperature range.

## 2) Mössbauer Effect

The spectrum of  $\text{ZnMn}_{1.98}\text{Fe}_{0.02}^{57}\text{O}_4$  at 4.2 K shows the hyperfine splittings caused by magnetic and quadrupole interactions. It shows only a doublet at 77 K. Namely,  $\text{Fe}^{3+}$  ion does not feel any magnetic field, because of the weak B-B exchange interaction of  $\text{Mn}^{3+}$  with  $\text{Fe}^{3+}$ .

All spectra of the prepared samples above liquid nitrogen temperature show only quadrupole splittings. The magnitude of these splittings are given in Table 1 with the values of  $c/a$ . The quadrupole interaction for a ferric ion reflects the symmetry of crystalline field around it, so that  $e^2qQ$  does not vanish in any composition of the present samples. The splittings apparently depend on  $c/a$  of the crystal as shown in Table 1.

Table 1. Experimental results at room temperature.

$x$	$c/a$	$\Delta E$ (mm/sec)
1.98	1.14	1.46
1.00	1.06	0.67
0.82	1.04	0.51
0.60	1.00	0.41

A quantitative analysis was made by the use of the OKIMINITAC 7000 of the Ochanomizu University.

### § 3. Computation of Quadrupole Splittings

As the valence electrons in  $\text{Fe}^{3+}$  ion have spherically symmetric distribution, so only the ions in crystal are considered to be the origin of the electric field gradient (EFG).

$$q = \frac{V_{zz}}{e} (1 - r_\infty) \sqrt{1 + \frac{\eta^2}{3}} \quad (1)$$

where  $V_{zz}$  is the largest component of a diagonalized EFG tensor,  $r_\infty$  is an antishielding factor of  $\text{Fe}^{3+}$  and  $\eta$  is an asymmetry parameter.

Each component of the EFG tensor at  $\text{Fe}^{3+}$  ion in the B-site of spinel is written as follows,

$$V_{pq} = \frac{e}{a^3} \left\{ \frac{\partial}{\partial p} \frac{\partial}{\partial q} \left( \sum_{j=1}^{14} E_j \sum_s \frac{1}{|r-s-\rho_j|} \right) \right\}_{r=0} \quad (2)$$

Here,  $p, q$  are  $x, y, z$ , and  $eE_j$  is the electric charge of each ion in a unit cell, i.e.  $eE_1 = \dots = eE_4 = 3$  for B-site,  $eE_5 = eE_6 = 2$  for A-site and  $eE_7 = \dots = eE_{14} = -2$  for anion site. The detailed treatment of this calculation is given in Appendix. The parameters used in this calculation are anion parameter,  $u$ , and tetragonality,  $c/a$ . When the lattice distorts tetragonally the volume is assumed not to change.

The calculated EFG tensor is diagonalized to obtain the quadrupole splittings,

$$\Delta E = \frac{1}{2} e^2 q Q, \quad (3)$$

and  $\eta = |(V_{xx} - V_{yy})/V_{zz}|$ .

Computed values of  $q$  as the function of  $c/a$  and  $u$  are plotted in Fig. 2 and 3. These calculations give only absolute values of  $q$ , because of the mathematical treatment.

As long as the crystal keeps a cubic structure, the major axis of EFG tensor at B-site coincides to the axis of three-fold symmetry, [111]. When it distorts tetragonally, the major axis does not remain in the [111] direction, but turns toward the  $c$ -axis of the crystal.

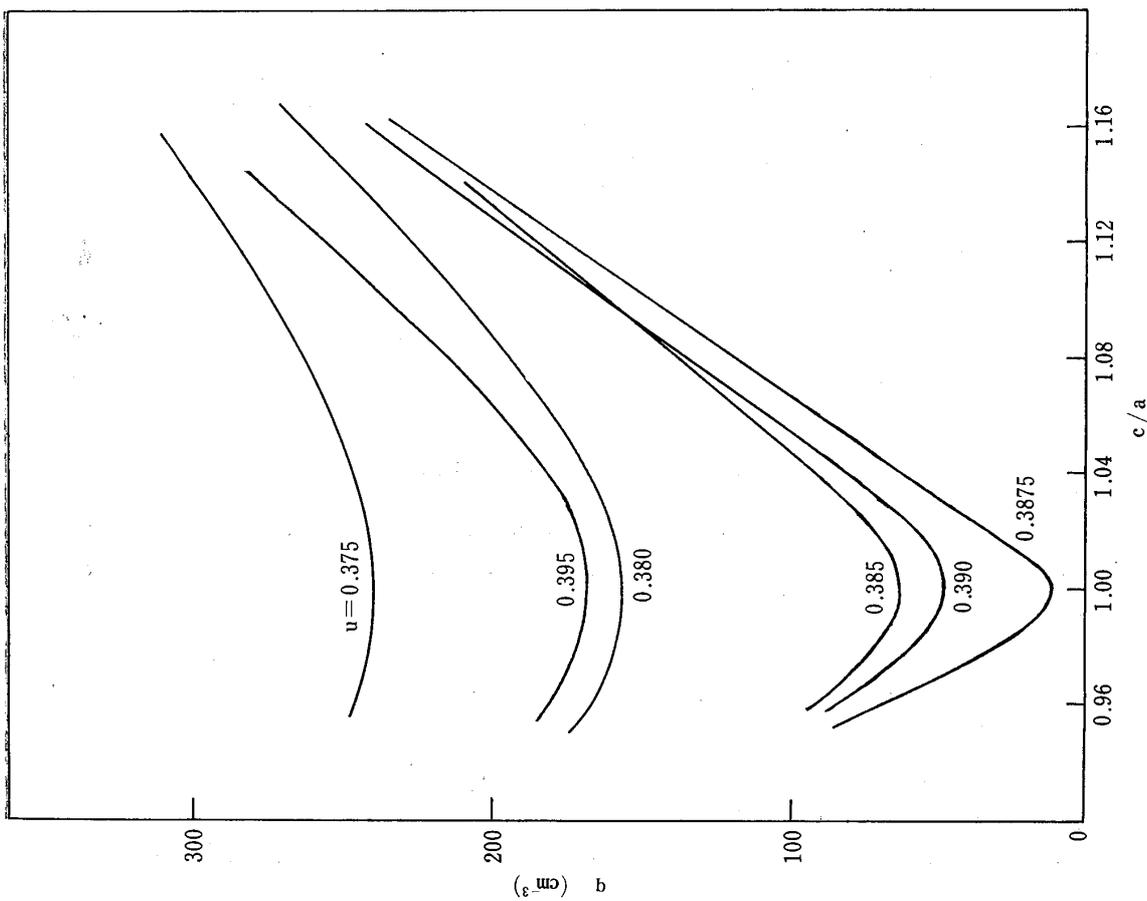


Fig. 3.  $c/a$  dependence of  $q = V_{zz} \sqrt{1 + \frac{\eta^2}{3}}$ .

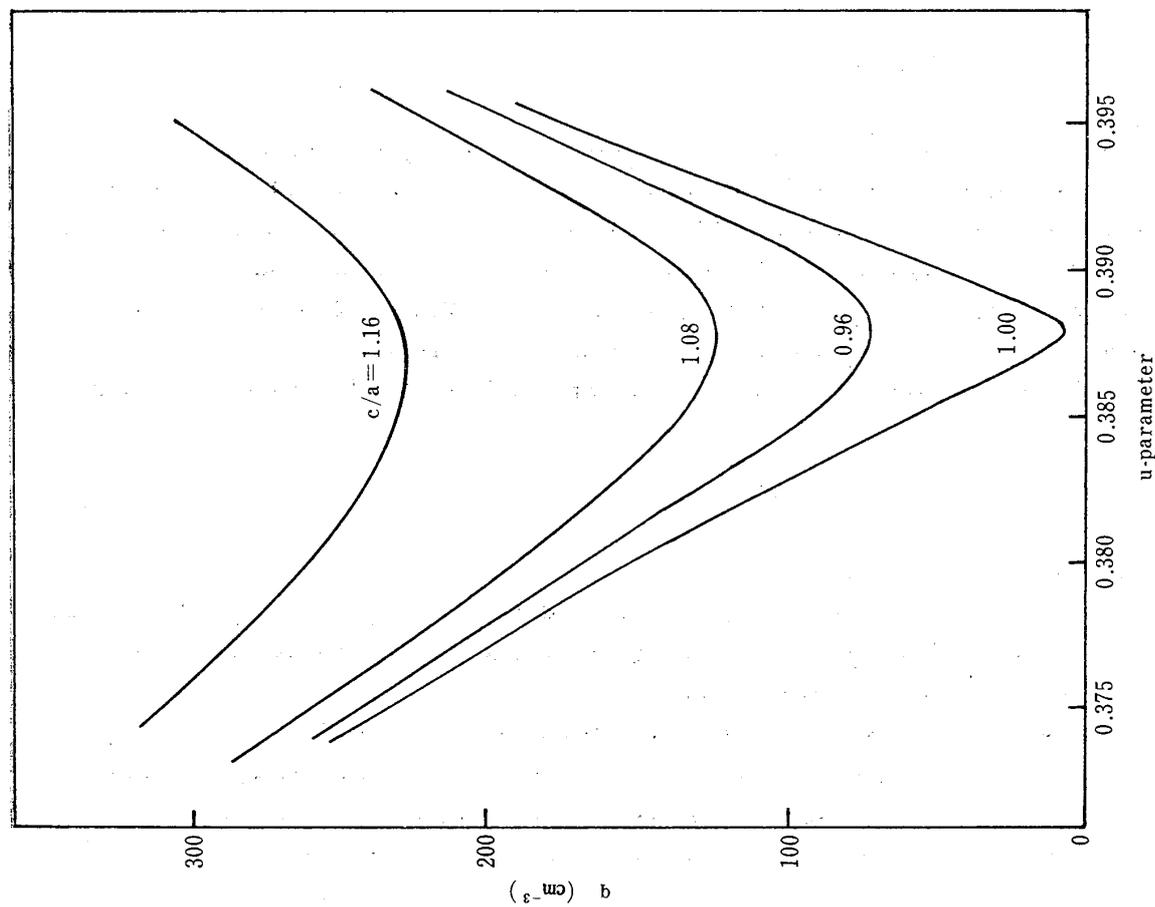


Fig. 2.  $u$ -parameter dependence of  $q = V_{zz} \sqrt{1 + \frac{\eta^2}{3}}$ .

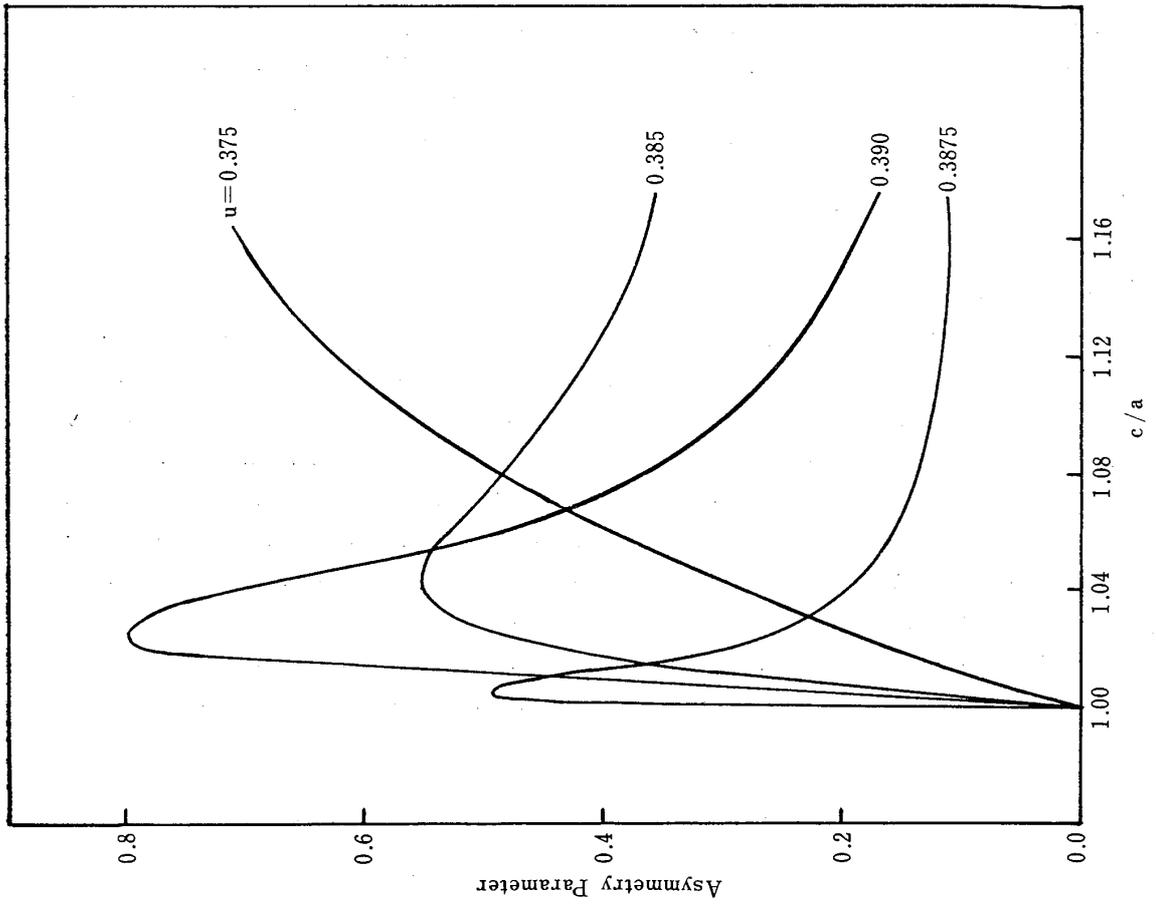


Fig. 5.  $c/a$  dependence of asymmetry parameter,  $\eta$ .

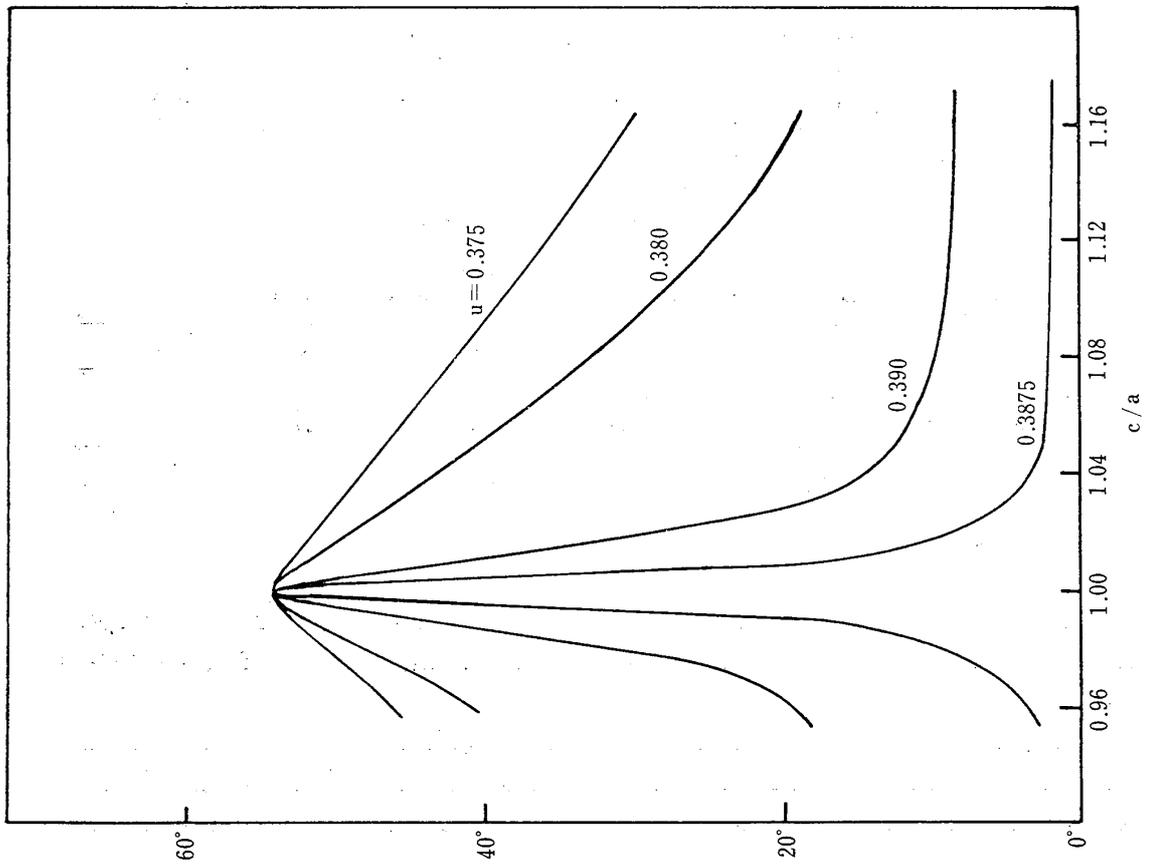


Fig. 4. Angle between  $c$ -axis of crystal and principal axis of EFG tensor.

Using the eigen-vectors of diagonalization we can obtain the direction cosines of the major axis relative to the  $c$ -axis. The dependence of the angle between them on tetragonality is illustrated in Fig. 4.

#### § 4. Analysis

##### 1) Quadrupole Splittings

The anion parameters are 0.390 and 0.385 for  $\text{ZnMn}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  respectively. There are no other informations about the  $u$ -parameter for  $\text{ZnMn}_x\text{Fe}_{2-x}\text{O}_4$  system. According to the present computation, there appears the minimum of  $q$  in the region of 0.385~0.390 for  $u$ , so that  $q$  is not always sensitive to the deviation of  $u$  in the tetragonal case. So we assume that  $u$  varies linearly with  $x$ . Then the calculated values, using point charge approximation, can explain the tendency of experimental results. The deviation may be attributed to not only inaccuracy of approximation, but also experimental errors.

In Table 3, the present results of computation are compared with the Mössbauer experiments of  $\text{Fe}^{3+}$  in normal spinel B-site already reported.<sup>3,4)</sup>

Table 2. Comparison between calculation and experiment (1).

$c/a$	$u^*$	$q_{\text{cal}}^{**}$	$q_{\text{exp}}^{**}$	$u^{***}$
1.14	0.390	213	204.3	0.389
1.06	0.3875	93	93.9	0.3875
1.05	0.3870	70	71.0	0.3865
1.00	0.3865	30	57.1	0.3852

\*)  $u$  is supposed to vary linearly.

\*\*)  $q$  is reduced to lattice constant=1.

\*\*\*)  $u$  is determined from  $q_{\text{exp}}$  using computed curves.

Table 3. Comparison between calculation and experiment (2).

	$c/a$	$u$	$\Delta E^*$	$q_{\text{exp}}$	$q_{\text{cal}}$
$\text{ZnFe}_2\text{O}_4^{**}$	1.00	0.385	0.36	50.2	62
$\text{MnFe}_2\text{O}_4^{***}$	1.00	0.3846	0.57	81.2	71

\*)  $\Delta E$  is in mm/sec.

\*\*) Reference 3

\*\*\*) Reference 4

In calculation,  $Q=0.283 \times 10^{-24} \text{ cm}^2$  for the nuclear quadrupole moment, and  $r_{\infty}=-9.14$  for the antishielding factor of  $\text{Fe}^{3+}$  were used.<sup>5,6)</sup>

In general, it is known that the anion parameter depends on the difference of ionic radii between an A-site ion and a B-site ion. When B-site contains only trivalent metal ions,  $u$ -parameter will be around

0.385~0.390, so that  $q$  is not so sensitive to the change in  $u$ , but is almost determined by  $c/a$ .

## 2) Hyperfine Splittings

The direction of the principal axis of EFG tensor is determined as the function of  $u$  and  $c/a$ . The spin arrangement for  $\text{Fe}^{3+}$  in  $\text{ZnMn}_{1.98}\text{Fe}_{0.02}\text{O}_4$  can be obtained, using the hyperfine splitting at low temperature and the information above mentioned. According to the results given in Fig. 4, the principal axis of EFG tensor inclines about  $8^\circ$  from the  $c$ -axis of the crystal, where the values of  $u$ -parameter and  $c/a$  for  $\text{ZnMn}_2\text{O}_4$  are used as those for  $\text{ZnMn}_{1.98}\text{Fe}_{0.02}\text{O}_4$ . From the magnetic point of view, it is assumed that the easy axis is either perpendicular to  $c$ -axis,  $[110]$ , or parallel to it,  $[001]$ .

The angle,  $\theta$ , between the direction of spin easy axis and that of the major axis of EFG tensor should be  $8^\circ$  or  $82^\circ$ . The values of  $\theta$  and  $\lambda = e^2qQ/6g_1H$ , ( $g_1 = \mu_1/I$ ), are interpolated in the table of the calculated energy levels<sup>7)</sup> to search for the best fitted spectrum to the experimental results. An asymmetry parameter,  $\eta$ , is assumed to be zero in the Ref. 7. In case of  $\text{ZnMn}_{1.98}\text{Fe}_{0.02}\text{O}_4$ , Fig. 5 shows that  $\eta$  is less than 0.2, so this does not have so important effect upon the spectrum. The values of magnetic moments of Fe,  $\mu_0$  (ground state) and  $\mu_1$  (excited state), are adopted from the data for iron metal by R.S. Preston et al.<sup>8)</sup>

Then  $8^\circ$  for  $\theta$ , and 0.14 for  $\lambda$  are the most suitable values for the experimental spectrum. So  $\frac{1}{2} e^2qQ$  is evaluated to be 1.32 mm/sec and the magnitude of the internal field is 466 kOe.

In conclusion,  $\text{Fe}^{3+}$  in  $\text{ZnMn}_2\text{O}_4$  has the spin easy axis parallel to the  $c$ -axis, but  $\text{Mn}^{3+}$  does not necessarily behave in the same way.

## Acknowledgements

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## Appendix

### Detail of the Calculation of EFG Tensors

The electrostatic potential near the origin produced by charges at other sites, is expressed as follows.

$$V = \frac{e}{a} \sum_{j=1}^{14} E_j \sum_s' \frac{1}{|r-s-\rho_j|}, \quad (\text{A1})$$

where,  $a$  is a lattice constant. A lattice point in a face centered crystal is written as  $a\rho_j = (a\alpha_j, a\beta_j, a\gamma_j)$ . The face centered lattice is denoted as  $\mathbf{s}$ , one of which coincides with the origin of the coordinate. Summation over  $\mathbf{s}$  must be carried out except the position where  $\mathbf{s} + \rho_j = 0$ . Primitive vectors of a face centered lattice and a body centered lattice, which is its reciprocal lattice, are as follows.

$$e_1 = \left(0, \frac{1}{2}, \frac{1}{2}\right), \quad e_2 = \left(\frac{1}{2}, \frac{1}{2}, 0\right), \quad e_3 = \left(\frac{1}{2}, 0, \frac{1}{2}\right) \quad (\text{A2})$$

$$\mathbf{s} = m_1 e_1 + m_2 e_2 + m_3 e_3.$$

$$f_1 = (-1, 1, 1), \quad f_2 = (1, -1, 1), \quad f_3 = (1, 1, -1), \quad (\text{A3})$$

$$\mathbf{q} = n_1 f_1 + n_2 f_2 + n_3 f_3.$$

To calculate (A1), we use the integral expression

$$\frac{1}{x} = \frac{1}{\sqrt{\pi}} \int_0^\infty e^{-tx^2} \frac{dt}{\sqrt{t}}, \quad x > 0,$$

and get,

$$V = \frac{e}{a} \frac{1}{\sqrt{\pi}} \int_0^\infty \sum_j E_j \sum_s e^{-t(r-s-\rho_j)^2} \frac{dt}{\sqrt{t}}.$$

The integrand is modified by the Poisson formula of Fourier transform.

$$\sum_s \delta(x-s) = \frac{1}{[e_1 e_2 e_3]_q} \sum_q e^{2\pi i x q} = 4 \sum_q e^{2\pi i x q}. \quad (\text{A4})$$

After being multiplied by  $e^{-t(r-\rho-x)^2}$ , eq. (A4) is integrated with respect to  $x$  over all space.

$$\sum_s e^{-t(r-s-\rho)^2} = 4 \left(\frac{\pi}{t}\right)^{\frac{3}{2}} \sum_q e^{-\frac{\pi^2}{t} q^2 + 2\pi i q(r-\rho_j)}. \quad (\text{A5})$$

Finally, the potential is expressed by (A6) as well as (A7).

$$V = \frac{e}{a} \frac{1}{\sqrt{\pi}} \int_0^\infty \left\{ \sum_j E_j \sum_s e^{-t(r-s-\rho)^2} - E_1 e^{-tr^2} \right\} \frac{dt}{\sqrt{t}} \quad (\text{A6})$$

$$= \frac{e}{a} \frac{1}{\sqrt{\pi}} \int_0^\infty \left\{ 4 \left(\frac{\pi}{t}\right)^{\frac{3}{2}} \sum_j E_j \sum_q e^{-\frac{\pi^2}{t} q^2 + 2\pi i q(r-\rho_j)} - E_1 e^{-tr^2} \right\} \frac{dt}{\sqrt{t}}. \quad (\text{A7})$$

The integrand in (A6) diminishes when  $t \rightarrow \infty$ , while that in (A7) diminishes when  $t \rightarrow 0$ , so we use (A6) for the region  $(0, 2\pi)$  and (A7) for  $(2\pi, \infty)$ , to procure the rapid convergence.

$$V = \frac{e}{a} \frac{1}{\sqrt{\pi}} \int_{2\pi}^\infty \left\{ \sum_j E_j \sum_s e^{-t(r-s-\rho)^2} - E_1 e^{-tr^2} \right\} \frac{dt}{\sqrt{t}}$$

$$+ \frac{e}{a} \frac{1}{\sqrt{\pi}} \int_0^{2\pi} \left[ 4 \left( \frac{\pi}{t} \right)^{\frac{3}{2}} \sum_j E_j \sum_q' e^{-\frac{\pi^2}{t} q^2 + 2 \cdot i q (r - \rho_j)} - E_1 e^{-t^2} \right] \frac{dt}{\sqrt{t}}. \quad (\text{A8})$$

The components of EFG tensor are abbreviated as  $V_{xx}$ ,  $V_{yy}$ ,  $V_{zz}$ ,  $V_{xy}$ , and so on.

$$V_{xx} = \frac{1}{a^2} \left( \frac{\partial^2 V}{\partial^2 X} \right)_{r=0}, \quad V_{xy} = \frac{1}{a^2} \left( \frac{\partial^2 V}{\partial X \partial Y} \right)_{r=0}, \quad \text{etc.}$$

$$V_{xx} = \frac{e}{a^3} \left[ \frac{1}{\sqrt{\pi}} \int_{2\pi}^{\infty} \left\{ \sum_j E_j \sum_s (4t^2 (s_x + \alpha_j)^2 - 2t) e^{-t(s - \rho_j)^2} + E_1 \cdot 2t \right\} \frac{dt}{\sqrt{t}} \right. \\ \left. + \frac{1}{\sqrt{\pi}} \int_0^{2\pi} \left[ 4 \left( \frac{\pi}{t} \right)^{\frac{3}{2}} \sum_j E_j \sum_q' (2\pi i q_x)^2 e^{-\frac{\pi^2}{t} q^2 - 2 \cdot i q \rho_j} + 2E_1 t \right] \frac{dt}{\sqrt{t}} \right]. \quad (\text{A9})$$

Using the error function (A10), we carry out the definite integration.

$$\Phi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^x e^{-\frac{t^2}{x}} dt, \quad (\text{A10})$$

$$\frac{2}{\sqrt{\pi}} \int_{2\pi}^{\infty} t e^{-tA} \frac{dt}{\sqrt{t}} = \frac{\sqrt{2}}{t} e^{-2\pi A} + \frac{1}{A\sqrt{A}} \{1 - \Phi(\sqrt{4\pi A})\} = F_1(A), \quad (\text{A11})$$

$$\frac{4}{\sqrt{\pi}} \int_{2\pi}^{\infty} t^2 e^{-tA} \frac{dt}{\sqrt{t}} = e^{-2\pi A} \left( \frac{2\pi\sqrt{2}}{A} + \frac{3\sqrt{2}}{2A^2} \right) \\ + \frac{3}{2\sqrt{2} A^2} \{1 - \Phi(\sqrt{4\pi A})\} = F_2(A), \quad (\text{A12})$$

$$V_{xx} = \frac{e}{a^3} \left[ \sum_j E_j \left\{ \sum_s ((s_x + \alpha_j)^2 F_2(X) - F_1(X)) \right. \right. \\ \left. \left. - \sum_q' \left( \frac{q_x}{2} \right)^2 \cos(2\pi \rho_j q) G(Y) \right\} + \frac{8\sqrt{2}\pi}{3} E_1 \right], \quad (\text{A13})$$

where,  $G(Y) = 16\pi e^{-2\pi Y}/Y$ ,  $X = (\mathbf{s} + \boldsymbol{\rho}_j)^2$  and  $Y = (\mathbf{q}/2)^2$ .

In the summation over  $\mathbf{q}$ , only the real part is taken. The other components of the tensor are computed in the same way.

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