

## Cation Distribution and Some Properties of Brownmillerite Phase $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{M}_x\text{O}_5$ (M=Mg, Ni, Zn)

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The lattice parameters and Néel temperature of  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_{2x}\text{O}_5$  are compared with those of  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{M}_x\text{O}_5$ . Cation distribution in  $\text{Ca}_2\text{Fe}_{1.8}\text{Mn}_{0.1}\text{M}_{0.1}\text{O}_5$  (M=Mg, Ni, Zn) were given from Mössbauer spectra to be  $\text{Ca}_2[\text{Fe}_{0.8}^{3+}\text{Mn}_{0.1}^{4+}\text{Mg}_{0.1}^{2+}]_o[\text{Fe}^{3+}]_t\text{O}_5$ ,  $\text{Ca}_2[\text{Fe}_{0.8}^{3+}\text{Mn}_{0.1}^{4+}\text{Ni}_{0.1}^{2+}]_o[\text{Fe}^{3+}]_t\text{O}_5$  and  $\text{Ca}_2[\text{Fe}_{0.8}^{3+}\text{Mn}_{0.1}^{4+}]_o[\text{Fe}_{0.8}^{3+}\text{Zn}_{0.1}^{2+}]_t\text{O}_5$ . The abnormality of lattice parameters in  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_{2x}\text{O}_5$  phase which meant the expansion of lattice along b axis was explained by the Jahn-Teller effect of  $\text{Mn}^{3+}$  ions. The lattice of  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{M}_x\text{O}_5$  uniformly changed with x in the same way as that of the brownmillerite substituted by the other trivalent ions. The variation of the Néel temperature of the brownmillerite phase with substitution of  $\text{Mn}^{3+}$  ion was discussed on the basis of the distance between the octahedral and tetrahedral sites along b axis which was associated with magnetic exchange interaction.

KEY WORDS : Brownmillerite phase / Jahn-Teller effect /  
Cation distribution / Néel temperature /

### INTRODUCTION

Dicalcium ferrite  $\text{Ca}_2\text{Fe}_2\text{O}_5$  (brownmillerite phase) has the orthorhombic structure, belonging to the space group  $Pcmm$  with lattice parameters:  $a_o=5.64\text{\AA}$ ,  $b_o=14.68\text{\AA}$ ,  $c_o=5.39\text{\AA}$ .<sup>1)</sup> The crystals of  $\text{Ca}_2\text{Fe}_2\text{O}_5$  have equal numbers of  $\text{Fe}^{3+}$  ions in octahedral and tetrahedral coordination. The trivalent ions, such as  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$  and  $\text{Sc}^{3+}$ , were substituted for iron ions on the two lattice sites to a certain degree.<sup>2)</sup>

In the system  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_{2x}\text{O}_{5+\delta}$ , the brownmillerite and perovskite phase exist in the ranges of  $0 \leq x \leq 0.25$  and  $0.5 \leq x \leq 1$ , respectively.<sup>3)</sup> The oxygen concentration in the brownmillerite phase is deviated from  $\text{Ca}_2\text{Fe}_{2-2x}\text{M}_{2x}\text{O}_5$ , where portion of manganese ions is tetravalent. We found that the lattice parameters and Néel temperature in the brownmillerite phase varied with heat treatment of the specimens.<sup>4)</sup> Furthermore, we reported that manganese and zinc ions in equal numbers could be substituted for iron in  $\text{Ca}_2\text{Fe}_2\text{O}_5$ , although only the zinc ions could not be substituted.<sup>5)</sup>

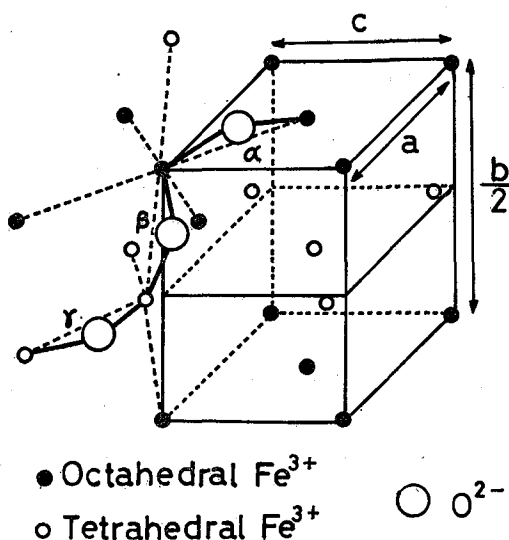
The lattice parameters and Néel temperatures of  $\text{Ca}_2\text{Fe}_{2-2x}\text{M}_{2x}\text{O}_5$  (M=Al, Sc, Cr, Co,

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Fe(O)-O-Fe(O)	3.92 <sub>9</sub> Å	$\alpha = 165^\circ$
Fe(T)-O-Fe(T)	3.83 <sub>6</sub> Å	$\beta = 140^\circ$
Fe(O)-O-Fe(T)	3.95 <sub>5</sub> Å	$r = 126^\circ$

Fig. 1. Distance Fe-O-Fe and angle in Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> lattice.

Ga) have been measured as a function of  $x$ .<sup>6,7,8)</sup> According to the literature, the lattice parameters  $a_0$ ,  $b_0$  and  $c_0$  vary uniformly with  $x$ , corresponding to radii of substituted ions. However, in Ca<sub>2</sub>Fe<sub>2-2x</sub>Mn<sub>2x</sub>O<sub>5</sub>, the  $b$  axis enlarged and the  $a$  and  $c$  axes contracted with increase of  $x$ .

The Ca<sub>2</sub>Fe<sub>2-2x</sub>Mn<sub>2x</sub>O<sub>5</sub> phases were characterized by three different exchange interactions between the neighboring Fe<sup>3+</sup> ions: interaction  $J_{aa}$  between the octahedral sites,  $J_{cc}$  between the tetrahedral sites,  $J_{ac}$  between the octahedral and the tetrahedral sites, where  $J_{cc}$  was the strongest (see Fig. 1).<sup>9)</sup> The evolution of the Néel temperature was explained by the cation distribution.<sup>7)</sup> The Néel temperature of the brownmillerite phase substituted by Mn was considerably lower than that of the phase substituted by diamagnetic ions such as Al<sup>3+</sup>, Ga<sup>3+</sup> and Sc<sup>3+</sup>.<sup>4)</sup> The extraordinary behavior in the lattice parameters and magnetic properties of Ca<sub>2</sub>Fe<sub>2-2x</sub>Mn<sub>2x</sub>O<sub>5+δ</sub> phase seems to be due to the deviation ( $\delta$ ) of oxygen concentration and characteristics of Mn<sup>3+</sup> ions. The purpose of the present investigation is to clarify the characteristics of Mn<sup>3+</sup> ions by comparing the structural and magnetic properties of Ca<sub>2</sub>Fe<sub>2-2x</sub>Mn<sub>2x</sub>O<sub>5</sub> with those of Ca<sub>2</sub>Fe<sub>2-2x</sub>Mn<sub>x</sub>M<sub>x</sub>O<sub>5</sub>.

### EXPERIMENTALS

Preparation of sample: The components were thoroughly mixed by ball mill. Mixtures were heated in air at 1000°C for 2 hr and then the specimens were pulverized. The powder were pressed at 2 ton/cm<sup>2</sup>, fired at 1350°C in air for 25 hr and quenched. The sintered samples were ground to fine powder for X-ray analysis, magnetic and Mössbauer effect measurements.

X-ray diffractometry: X-ray powder diffractometry using Fe-K $\alpha$  radiation was used for the assignment of the structure as well as for the measurement of the lattice parameters of the samples.

Mössbauer effect measurement: Mössbauer spectra were taken using a spectrometer equipped with Erlon's driving unit and Nothern Scientific Co's 1000 channel pulse height analyzer. Calibration of velocity scale was made using  $\alpha$ -Fe $_2$ O $_3$  as standard absorbers. All the measurements were carried out at liquid nitrogen temperature.

## RESULTS

### Lattice Parameter

X-ray diffraction indicated to be only the brownmillerite phase for all the samples of Ca $_2$ Fe $_{2-2x}$ Mn $_{2x}$ O $_5$  ( $x \leq 0.25$ ) and Ca $_2$ Fe $_{2-2x}$ Mn $_x$ M $_x$ O $_5$  ( $x \leq 0.25$ ) quenched from 1100°C. The variations of lattice parameters  $a_o$ ,  $b_o$  and  $c_o$  with  $x$  in Ca $_2$ Fe $_{2-2x}$ M $_{2x}$ O $_5$  ( $M = \text{Mn, Al, In}$ ) and Ca $_2$ Fe $_{2-2x}$ Mn $_x$ M $_x$ O $_5$  ( $M = \text{Mg, Ni, Zn}$ ) are shown in Fig. 2. The ionic radii are as follows:

$$\begin{aligned} R_{\text{Fe}^{3+}} &= 0.64\text{\AA}, R_{\text{Mn}^{3+}} = 0.66\text{\AA}, R_{\text{Mn}^{4+}} = 0.54\text{\AA}, R_{\text{Ni}^{2+}} = 0.70\text{\AA}, \\ R_{\text{Mg}^{2+}} &= 0.72\text{\AA}, R_{\text{Zn}^{2+}}(\text{tetra}) = 0.6\text{\AA}, R_{\text{Al}^{3+}} = 0.51\text{\AA}, R_{\text{In}^{3+}} = 0.81\text{\AA}. \end{aligned}$$

The lattice parameters  $a_o$ ,  $b_o$  and  $c_o$  of Ca $_2$ Fe $_{2-2x}$ Al $_{2x}$ O $_5$  decreased and those of Ca $_2$ Fe $_{2-2x}$ In $_{2x}$ O $_5$  increased with increase of  $x$ , corresponding to the ratio of respective ionic radius to ferric ion radius. The similar tendency have been observed for the Ca $_2$ Fe $_{2-2x}$ M $_{2x}$ O $_5$  ( $M = \text{Co, Cr, Sc, Ge}$ ). On the other hand, in the Ca $_2$ Fe $_{2-2x}$ Mn $_{2x}$ O $_5$ , the lattice parameters  $a_o$  and  $c_o$  decreased and  $b_o$  increased with increase of  $x$ . The ratios represented by  $2b_o/\sqrt{a_o^2+c_o^2}$  and  $c_o/a_o$  are presented in Table I. The ratios  $c_o/a_o$  are the same for all the specimens listed, but only the ratio  $2b_o/\sqrt{a_o^2+c_o^2}$  in Ca $_2$ Fe $_{1.5}$ Mn $_{0.5}$ O $_5$  is larger than the ratios in others. The lattice in the brownmillerite phase containing Mn $^{3+}$  ions clearly expands along  $b$  axis compared with that in the phase substituted by other ions.

### Néel Temperature

The Néel temperatures as a function of  $x$  were shown in Fig. 3. The decrease in the Néel temperature of Ca $_2$ Fe $_{2-2x}$ M $_{2x}$ O $_5$  substituted by magnetic ions such as Cr $^{3+}$  and Co $^{3+}$  is smaller than by diamagnetic ions such as Al $^{3+}$ , Ga $^{3+}$  and Sc $^{3+}$ . However, the Néel temperature of the Ca $_2$ Fe $_{2-2x}$ M $_{2x}$ O $_5$  in the case of  $M = \text{Mn}^{3+}$  which is a magnetic ion is considerably lower than that in the case of  $M = \text{diamagnetic ions}$ . The Néel temperature

Table I. Ratios of the Lattice Parameters in the Ca $_2$ Fe $_{1.5}$ M $_{0.5}$ O $_5$  Phase

M	$2b_o/\sqrt{a_o^2+c_o^2}$	$c_o/a_o$
Fe	3.79	1.03
Mn	3.89	1.03
Al	3.79	1.04
Cr	3.80	1.03
Co	3.81	1.04
Mn-Zn	3.81	1.03

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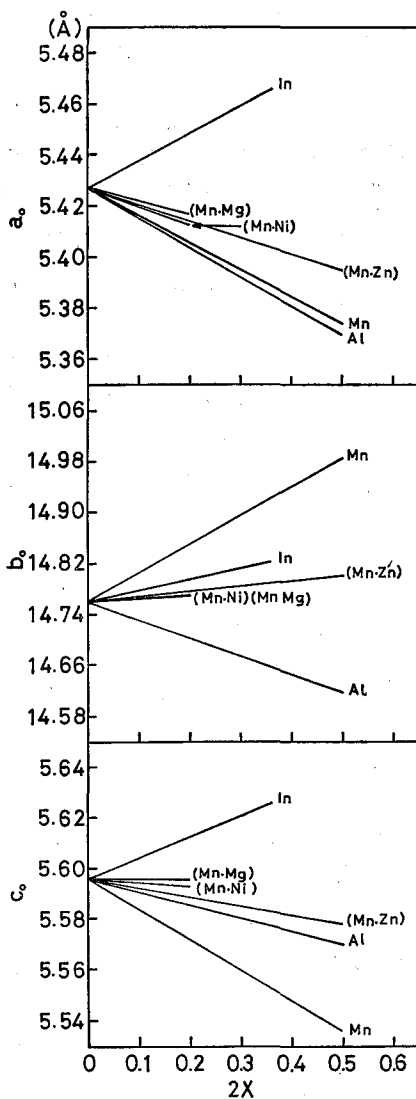


Fig. 2. Variation of lattice parameters with  $x$  in  $\text{Ca}_2\text{Fe}_{2-2x}\text{M}_{2x}\text{O}_5$  and  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{M}_x\text{O}_5$ .

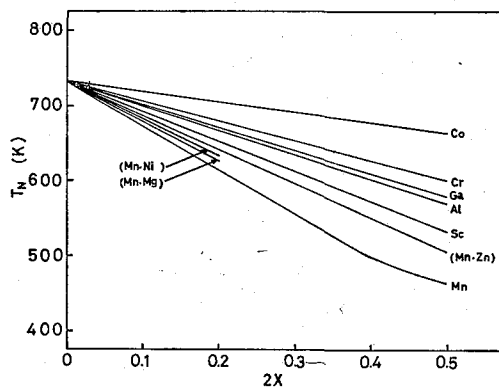


Fig. 3. Néel temperatures as a function of  $x$  in  $\text{Ca}_2\text{Fe}_{2-2x}\text{M}_{2x}\text{O}_5$  and  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{M}_x\text{O}_5$ .

of the brownmillerite phase containing Mn ions was increased by substitution of divalent ions as shown in Fig. 3.

### Cation Distribution

Mössbauer spectra were taken at liquid nitrogen temperature below the Néel temperature. As shown in Figs. 4, 5 and 6, the Mössbauer spectra are characteristic of trivalent iron ion octahedrally and tetrahedrally coordinated. The ratios between the line areas corresponding to each site are equal to 0.8, 0.8 and 1.0 for  $\text{Ca}_2\text{Fe}_{1.8}\text{Mn}_{0.1}\text{M}_{0.1}\text{O}_5$  of  $\text{M}=\text{Mg}$ ,  $\text{Ni}$ , and  $\text{Zn}$ , respectively. These ratios lead to the following cation distributions:

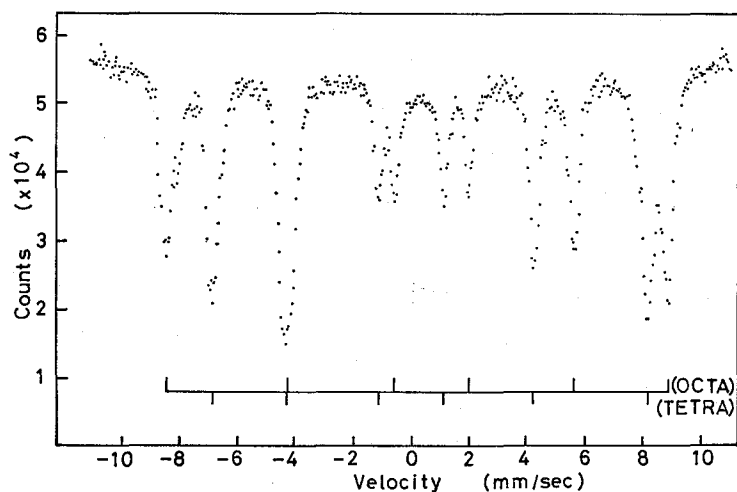
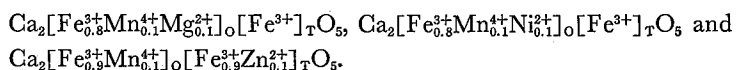


Fig. 4. Mössbauer spectrum of  $\text{Ca}_2\text{Fe}_{1.8}\text{Mn}_{0.1}\text{Mg}_{0.1}\text{O}_5$  at liquid nitrogen temperature.

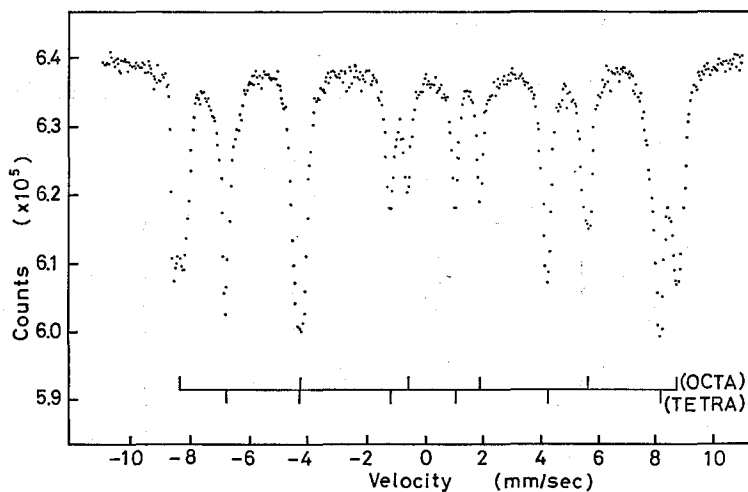


Fig. 5. Mössbauer spectrum of  $\text{Ca}_2\text{Fe}_{1.8}\text{Mn}_{0.1}\text{Ni}_{0.1}\text{O}_5$  at liquid nitrogen temperature.

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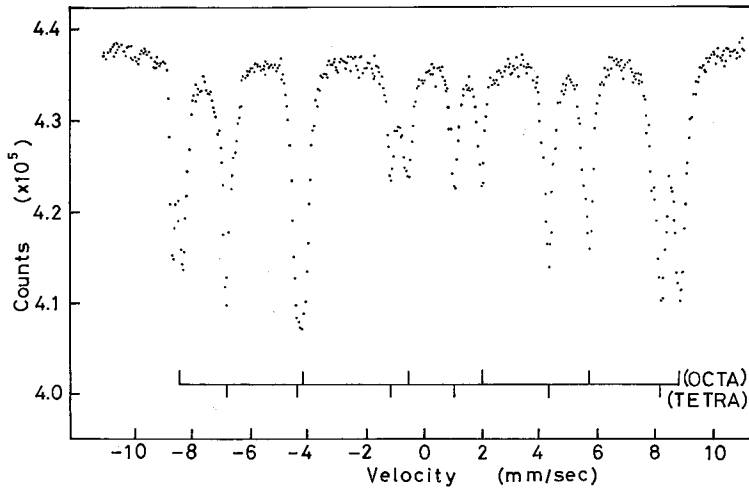


Fig. 6. Mössbauer spectrum of  $\text{Ca}_2\text{Fe}_{1.8}\text{Mn}_{0.1}\text{Zn}_{0.1}\text{O}_5$  at liquid nitrogen temperature.

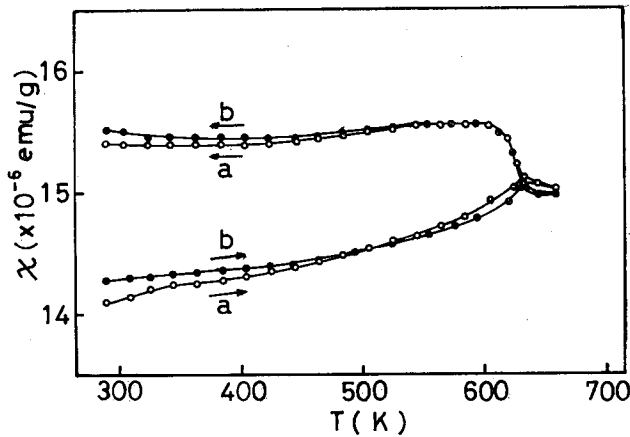


Fig. 7. Temperature dependence of magnetic susceptibilities of  $\text{Ca}_2\text{Fe}_{1.8}\text{Mn}_{0.1}\text{N}_{0.1}\text{O}_5$ . (a) quenched from  $1300^\circ\text{C}$ , (b) heated at  $300^\circ\text{C}$  in air

Valency of Mn Ions

Stability of Mn ions in  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{M}_x\text{O}_5$  was investigated by magnetic and electrical measurements. The temperature dependence of magnetic susceptibility of the samples which are quenched from  $1300^\circ\text{C}$  and heated at  $300^\circ\text{C}$  in air, is shown in Fig. 7. The temperature dependence of magnetic susceptibility of  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{O}_5$  had been reported to vary with heat treatment.<sup>4)</sup> On the other hand, magnetic and electrical properties of  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{M}_x\text{O}_5$  were but little affected by heat treatment as shown in Figs. 7 and 8. These facts indicated that manganese ions in  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{M}_x\text{O}_5$  were stabilized as tetra-valency.

DISCUSSION

The substitution of  $\text{Mn}^{2+}$  for  $\text{Fe}^{3+}$  in the brownmillerite phase expanded the lattice

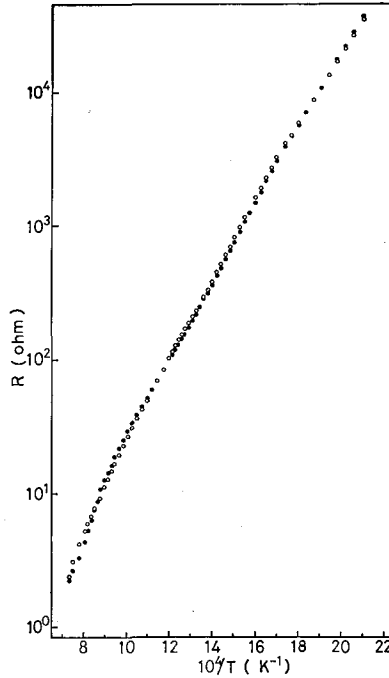


Fig. 8. Temperature dependence of electrical resistance for  $\text{Ca}_2\text{Fe}_{1.5}\text{Mn}_{0.1}\text{Zn}_{0.1}\text{O}_5$ .  
 ○ quenched from 1300°C, ● heated at 300°C in air

Table II. Fe-O-Fe distance in the Brownmillerite Lattice

	$\text{Ca}_2\text{Fe}_2\text{O}_5$	$\text{Ca}_2\text{Fe}_{1.5}\text{Al}_{0.5}\text{O}_5$	$\text{Ca}_2\text{Fe}_{1.5}\text{Mn}_{0.5}\text{O}_5$	$\text{Ca}_2\text{Fe}_{1.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{O}_5$
Fe(O)-O-Fe(O)	3.92 <sub>9</sub>	3.84 <sub>9</sub>	3.88 <sub>4</sub>	3.91 <sub>1</sub>
Fe(T)-O-Fe(T)	3.83 <sub>6</sub>	—	—	—
Fe(O)-O-Fe(T)	3.95 <sub>5</sub>	3.90	3.98 <sub>6</sub>	3.96 <sub>3</sub>

along b axis. The b axis in the brownmillerite lattice corresponds to z axis in the octahedron. As  $\text{Mn}^{3+}$  ion is a Jahn-Teller ion, the lattice of the brownmillerite containing  $\text{Mn}^{3+}$  ions is expected to expand along b axis by the Jahn-Teller effect. As  $\text{Mn}^{4+}$  ion is not a Jahn-Teller ion, the  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{O}_5$  lattice should not distort. The lattice distortion in the brownmillerite containing  $\text{Mn}^{3+}$  ions can be explained by the Jahn-Teller effect.

The large decrease of the Néel temperature in  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{O}_5$  may be associated with the distance between the octahedral and the tetrahedral sites (see Fig. 1). Assuming the Fe-O-Fe angles to be equal to those in the  $\text{Ca}_2\text{Fe}_2\text{O}_5$  lattice, the Fe(O)-O-Fe(O) and Fe(O)-O-Fe(T) distances were calculated, as shown in Table II. The Fe(O)-O-Fe(T) distance in the  $\text{Ca}_2\text{Fe}_{1.5}\text{Mn}_{0.5}\text{O}_5$  lattice may be actually longer than calculated one. The Fe(O)-O-Fe(T) distance in the  $\text{Ca}_2\text{Fe}_{1.5}\text{Mn}_{0.5}\text{O}_5$  lattice is long compared with that in the other brownmillerite lattice. The difference in the Fe(O)-O-Fe(O) distance between the  $\text{Ca}_2\text{Fe}_{1.5}\text{Mn}_{0.5}\text{O}_5$  and  $\text{Ca}_2\text{Fe}_{1.5}\text{Al}_{0.5}\text{O}_5$  is small. The exchange interaction  $J_{ac}$  in  $\text{Ca}_2\text{Fe}_{1.5}\text{Mn}_{0.5}\text{O}_5$  will be weak compared with that in  $\text{Ca}_2\text{Fe}_{1.5}\text{Al}_{0.5}\text{O}_5$  and  $\text{Ca}_2\text{Fe}_{1.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{O}_5$ , because of the long Fe(O)-O-Fe(T) distance. The decrease of interaction  $J_{ac}$

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may be responsible for the low Néel temperature in the  $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_{2x}\text{O}_5$  phase.

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### REFERENCES

- (1) E. F. Bertaut, P. Blum, and A. Sagnières, *Acta Cryst.*, **12**, 149 (1959).
- (2) R. W. Grant, H. Wiedersich, S. Geller, U. Gonser, and G. P. Espinosa, *J. Appl. Phys.*, **38**, 1455 (1967).
- (3) R. V. Goates and J. W. McMillan, *J. Appl. Chem.*, **14**, 346 (1964).
- (4) Y. Bando, T. Takada, and T. Akiyama, *Bull. Inst. Chem. Res., Kyoto Univ.*, **49**, 342 (1971).
- (5) Y. Bando, T. Kato, Y. Ikeda, and T. Takada, *Bull. Inst. Chem. Res., Kyoto Univ.*, **46**, 289 (1968).
- (6) M. Conkic, *Compt. Rend.*, **278B**, 1091 (1974).
- (7) J-C. Grenier, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.*, **13**, 92 (1975).
- (8) J-C. Grenier, M. Pouchard, and P. Hagenmuller, *Mat. Res. Bull.*, **11**, 721 (1976).