

Title	Cation Distribution and Some Properties of Brownmillerite Phase $\text{Ca}_{1-x}\text{Fe}_x[\text{X}]\text{Mn}[\text{X}]\text{M}[\text{X}]\text{O}$ (M=Mg, Ni, Zn) (Commemoration Issue Dedicated to Professor Tsunenobu Shigematsu on the Occasion of his Retirement)
Author(s)	Akiyama, Toshihiko; Bando, Yoshichika; Takada, Toshio
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1980), 58(2): 252-259
Issue Date	1980-08-10
URL	http://hdl.handle.net/2433/76873
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

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

Toshihiko AKIYAMA,* Yoshichika BANDO,** and Toshio TAKADA***

Received March 11, 1980

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 $\text{Ca}_2\text{Fe}_{1.8}\text{Mn}_{0.1}\text{M}_{0.1}\text{O}_5$ ($\text{M}=\text{Mg}, \text{Ni}, \text{Zn}$) 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 $\text{Ca}_2[\text{Fe}_{0.8}^{3+}\text{Mn}_{0.1}^{4+}]_o[\text{Fe}_{0.5}^{3+}\text{Zn}_{0.5}^{2+}]_t\text{O}_5$. 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 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 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: $a_o=5.64\text{\AA}$, $b_o=14.68\text{\AA}$, $c_o=5.39\text{\AA}$.¹⁾ The crystals of $\text{Ca}_2\text{Fe}_2\text{O}_5$ have equal numbers of Fe^{3+} ions in octahedral and tetrahedral coordination. The trivalent ions, such as Al^{3+} , Ga^{3+} and Sc^{3+} , were substituted for iron ions on the two lattice sites to a certain degree.²⁾

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.³⁾ 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.⁴⁾ 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.⁵⁾

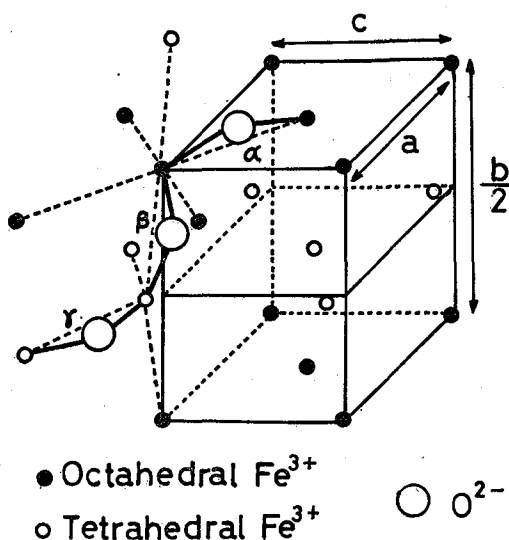
The lattice parameters and Néel temperatures of $\text{Ca}_2\text{Fe}_{2-2x}\text{M}_{2x}\text{O}_5$ ($\text{M}=\text{Al}, \text{Sc}, \text{Cr}, \text{Co}$,

* 秋山敏彦: Department of Materials Science, Himeji Institute of Technology, Shosha, Himeji-shi.

** 坂東尚周: Facility for Inorganic Synthesis, Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611.

*** 高田利夫: Laboratory of Solid State Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611.

Cation Distribution and Some Properties of Brownmillerite Phase



$\text{Fe}(\text{O})-\text{O}-\text{Fe}(\text{O})$	3.92_9 \AA	$\alpha = 165^\circ$
$\text{Fe}(\text{T})-\text{O}-\text{Fe}(\text{T})$	3.83_6 \AA	$\beta = 140^\circ$
$\text{Fe}(\text{O})-\text{O}-\text{Fe}(\text{T})$	3.95_5 \AA	$r = 126^\circ$

Fig. 1. Distance Fe-O-Fe and angle in $\text{Ca}_2\text{Fe}_2\text{O}_5$ lattice.

Ga) have been measured as a function of x .^{6,7,8)} 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 $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_{2x}\text{O}_5$, the b axis enlarged and the a and c axes contracted with increase of x .

The $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_{2x}\text{O}_5$ phases were characterized by three different exchange interactions between the neighboring Fe^{3+} 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).⁹⁾ The evolution of the Néel temperature was explained by the cation distribution.⁷⁾ 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^{3+} , Ga^{3+} and Sc^{3+} .⁴⁾ The extraordinary behavior in the lattice parameters and magnetic properties of $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_{2x}\text{O}_{5+\delta}$ phase seems to be due to the deviation (δ) of oxygen concentration and characteristics of Mn^{3+} ions. The purpose of the present investigation is to clarify the characteristics of Mn^{3+} ions by comparing the structural and magnetic properties of $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_{2x}\text{O}_5$ with those of $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{M}_x\text{O}_5$.

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^2 , 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 α 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 α -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:

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

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

Cation Distribution and Some Properties of Brownmillerite Phase

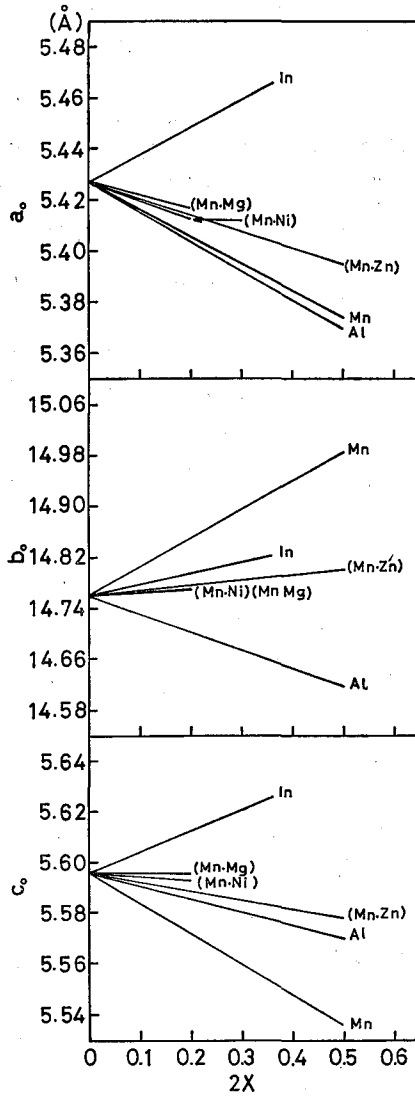


Fig. 2. Variation of lattice parameters with x in $\text{Ca}_2\text{Fe}_{2-2x}\text{M}_{2x}\text{O}_5$ and $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{M}_x\text{O}_5$.

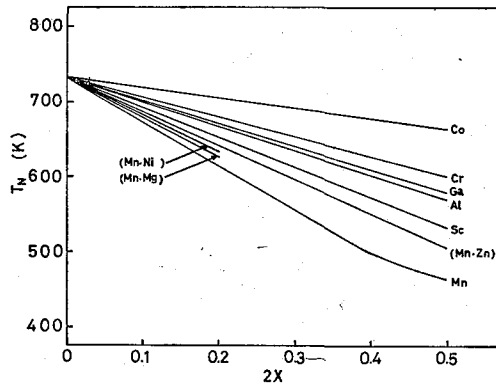


Fig. 3. Néel temperatures as a function of x in $\text{Ca}_2\text{Fe}_{2-2x}\text{M}_{2x}\text{O}_5$ and $\text{Ca}_2\text{Fe}_{2-2x}\text{Mn}_x\text{M}_x\text{O}_5$.

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 $\text{M}=\text{Mg}$, Ni , and Zn , respectively. These ratios lead to the following cation distributions:

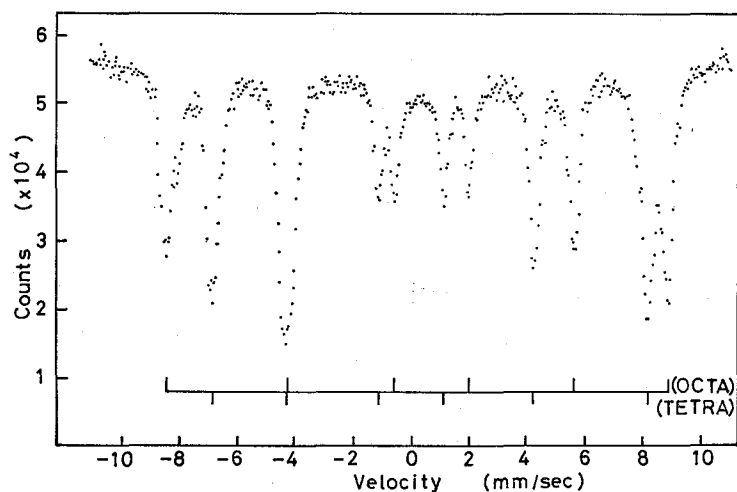
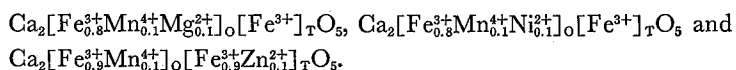


Fig. 4. Mössbauer spectrum of $\text{Ca}_2\text{Fe}_{1.8}\text{Mn}_{0.1}\text{Mg}_{0.1}\text{O}_5$ at liquid nitrogen temperature.

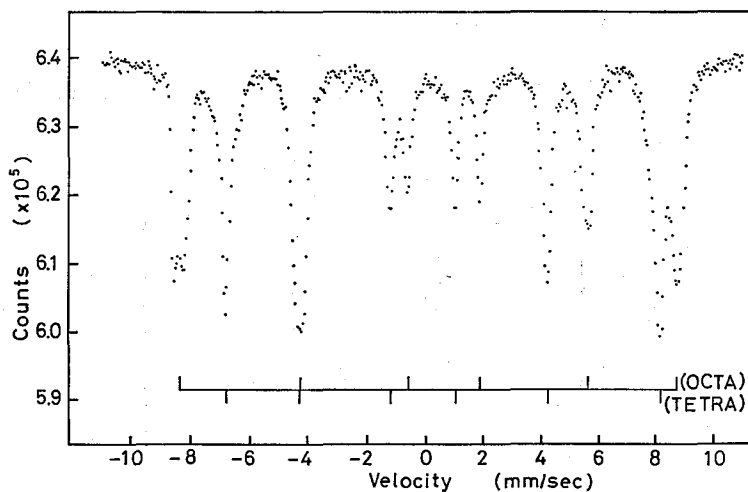


Fig. 5. Mössbauer spectrum of $\text{Ca}_2\text{Fe}_{1.8}\text{Mn}_{0.1}\text{Ni}_{0.1}\text{O}_5$ at liquid nitrogen temperature.

Cation Distribution and Some Properties of Brownmillerite Phase

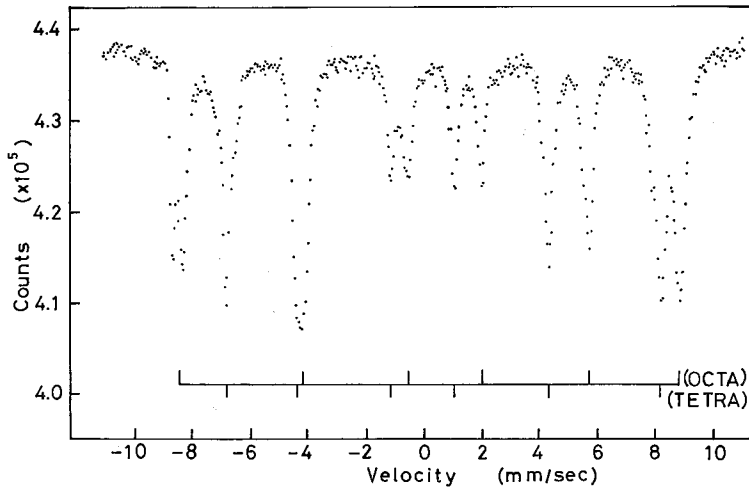


Fig. 6. Mössbauer spectrum of $\text{Ca}_2\text{Fe}_{1.8}\text{Mn}_{0.1}\text{Zn}_{0.1}\text{O}_5$ at liquid nitrogen temperature.

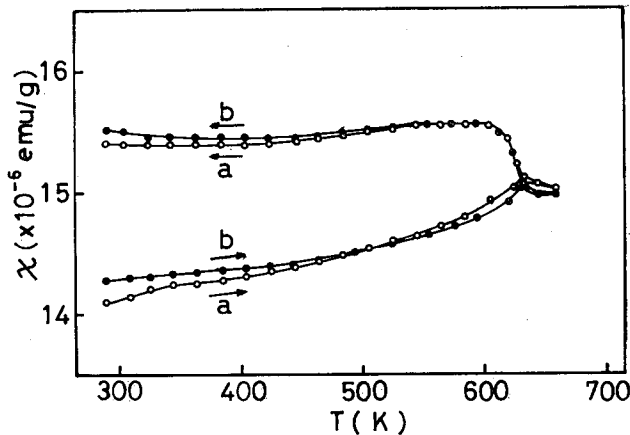


Fig. 7. Temperature dependence of magnetic susceptibilities of $\text{Ca}_2\text{Fe}_{1.8}\text{Mn}_{0.1}\text{N}_{0.1}\text{O}_5$. (a) quenched from 1300°C , (b) heated at 300°C in air

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°C and heated at 300°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.⁴⁾ 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 Mn^{2+} for Fe^{3+} in the brownmillerite phase expanded the lattice

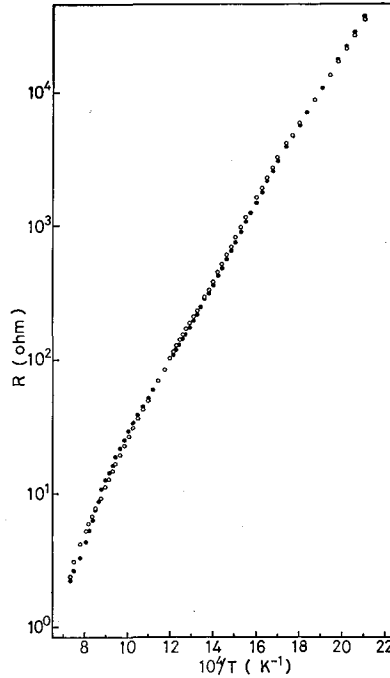


Fig. 8. Temperature dependence of electrical resistance for $\text{Ca}_2\text{Fe}_{1.5}\text{Mn}_{0.1}\text{Zn}_{0.1}\text{O}_5$.
 ○ quenched from 1300°C, ● heated at 300°C in air

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 ₉	3.84 ₉	3.88 ₄	3.91 ₁
Fe(T)-O-Fe(T)	3.83 ₆	—	—	—
Fe(O)-O-Fe(T)	3.95 ₅	3.90	3.98 ₆	3.96 ₃

along b axis. The b axis in the brownmillerite lattice corresponds to z axis in the octahedron. As Mn^{3+} ion is a Jahn-Teller ion, the lattice of the brownmillerite containing Mn^{3+} ions is expected to expand along b axis by the Jahn-Teller effect. As 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 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}

Cation Distribution and Some Properties of Brownmillerite Phase

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

ACKNOWLEDGMENTS

The authors wish to thank Drs. M. Takano and T. Shinjo for Mössbauer effect measurements and helpful discussions.

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).