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On variety of the Ca coordination in the incommensurate structure of synthetic iron-bearing åkermanite, $Ca_2(Mg_{0.55},Fe_{0.45})Si_2O_7$.

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Abstract

The incommensurate modulation in a synthetic iron-bearing åkermanite, $Ca_2(Mg,Fe)Si_2O_7$, has been determined at room temperature by the five-dimensional refinements of the structure. The basic structure is tetragonal $P\bar{4}2_1m$ with unit-cell dimensions a =7.8679(3), c =5.0144(2)Å, V=310.41(2)Å^3, Z=2, M=286.69, D_x =3.067Mg · m^{-3}, Mo$K\alpha$ with graphite monochromator, μ =3.199mm^{-1}, $F(000)$=284.49, Mg/(Mg+Fe)=0.554(6), R=0.065 for 770 unique reflections. The modulated structure is also tetragonal $P^{P\bar{4}2_1m}_{p4mg}$, $\boldsymbol{k}_1 = 0.295(2)\times(\boldsymbol{a}^*+\boldsymbol{b}^*)$, $\boldsymbol{k}_2$=0.295(2)×$(-\boldsymbol{a}^*+\boldsymbol{b}^*)$, where $\boldsymbol{k}_1$, $\boldsymbol{k}_2$ are the wave vectors and $\boldsymbol{a}^*$, $\boldsymbol{b}^*$ the reciprocal lattice vectors of the basic structure. R=0.136 for 3965 unique reflections. The modulation is caused mainly by the shifts of Ca and O atoms, and substitutional modulation at (Mg, Fe) sites was not detected in the present studies. Six-coordinated Ca forming a distorted oxygen octahedra exists in the modulated structure and most of them form clusters together with the flattened $(Mg,Fe)O_4$ tetrahedra. The number of the clusters in the present material is less than that in Co-åkermanite. The reason may be attributed to the disorder of the modulation amplitudes and wavelength.

Introduction

A set of weak satellite reflections around each Bragg reflection has been discovered by Hemingway *et al.* (1986) at room temperature in single-crystal X-ray and electron diffraction patterns of synthetic åkermanite, $Ca_2MgSi_2O_7$. These satellites indicate that the modulation of the structure is incommensurate and a reversible phase transition to the normal phase (with no modulation) occurs at 358K. The same phenomena in electron diffraction were found independently by Seifert *et al.* (1987) during their synthetic studies on the system $Ca_2MgSi_2O_7$–$Ca_2FeSi_2O_7$. They showed that the all satellite peaks are sharp at Fe/(Fe+Mg) =0.0, but an increase of Fe content causes an increase of the intensity of diffuse streaks between the neighboring satellites and diffuse rings surrounding main reflections (circular diffuse scattering) are observed in the diffraction patterns. An interpretation of the circular diffuse scattering was proposed by Iishi *et al.* (1994). A rise of temperature also induces an increase of the diffuseness of the satellites. The incommensurate modulation was found also in the diffraction patterns of the Mg–Co solid solution (Iishi *et al.*, 1989).

Seifert *et al.* (1987) deduced that a misfit between the size of the interlayer cation and that of the space formed by the tetrahedral sheets would cause the occurrence of the incommensurate modulation in åkermanite. A microdomain model was proposed by Van Heurck *et al.* (1992) through HRTEM observation for the modulated structure of $Ca_2ZnGe_2O_7$ in which the framework consisting of the tetrahedra was deformed by correlation rotations and tilts of the corner-sharing GeO_4 and ZnO_4 tetrahedra. However, determination of the modulated structure was indispensable to realize how the shifts of the constituent atoms or the rotations and tilts of the tetrahedra were combined in the real structure to form the modulation. The modulated structure of Co-åkermanite was determined by Hagiya *et al.* (1993) based on the five-dimensional description (de Wolff, 1974; Janner and Janssen, 1977; Yamamoto, 1982). The modulation is caused mainly by the shifts of Ca and O atoms and the coordination number of Ca varies from six to eight. No evidence of anomaly of the occupancy was found at the Co sites. They clarified also that some of the Co–O and Si–O distances vary remarkably in the modulated structure.

Since the modulation is found also in the solid solution $Ca_2(Mg,Fe)Si_2O_7$, the present studies have been undertaken to analyse the modulated structure in the solid solution and to examine how the replacement between Mg and Fe affects the mode of the modulation. Careful investigations on the features of the determined structure and comparisons of the structure of the present material to that of the Co-analogue have been also undertaken from the crystal-chemical view points.

Experimental

The specimens of iron-bearing åkermanite were synthesized by a floating-zone method. The ratio Mg/(Mg+Fe) of the starting charge of the syntheses was controlled approximately to 0.55. A spherical crystal was prepared for measurements of diffraction data. The Laue classes and the reflection conditions of the main and satellite reflections were determined from the diffraction patterns recorded on precession photographs. An Enraf-Nonius CAD-4 diffractometer with Mo$K\alpha$ radiation monochromatized by graphite was used for the collections of the intensity data. The cell parameters of the basic structure were determined by a least-squares refinement of the angular data of 25 main reflections.

The diffraction patterns of the specimen indicate that the modulation is two dimensional one with the two wave vectors $\boldsymbol{k}_1=\alpha\times(\boldsymbol{a}^*+\boldsymbol{b}^*)$ and $\boldsymbol{k}_2=\alpha\times(-\boldsymbol{a}^*+\boldsymbol{b}^*)$. All reflections including satellite reflections can be indexed with five integers and five base vectors that are related to the three crystallographic axes and the two wave vectors ($\boldsymbol{h}=h\boldsymbol{a}^*+k\boldsymbol{b}^*+l\boldsymbol{c}^*+m\boldsymbol{k}_1+n\boldsymbol{k}_2$; $\boldsymbol{a}^*$, $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$ are the base vectors of the reciprocal lattice of the basic structure, and m and n are integers). Thus the whole reflections can be described in the five-dimensional reciprocal

TABLE 1. Crystal data and measurement conditions of $Ca_2(Mg,Fe)Si_2O_7$

Chemical formula	$Ca_2Mg_{0.55}Fe_{0.45}Si_2O_7$
Formula weight	286.69
Crystal system	Tetragonal
Unit-cell lengths of the basic structure	a=7.8679(3)Å c=5.0144(2)Å
Unit-cell volume	V=310.41(2)Å^3
Number of formulae per unit cell (Z)	2
Modulation wave vectors	$\boldsymbol{k}_1=0.295(2)\times(\boldsymbol{a}^*+\boldsymbol{b}^*)$ $\boldsymbol{k}_2=0.295(2)\times(-\boldsymbol{a}^*+\boldsymbol{b}^*)$
Wavelength of modulation	18.87(1)Å
Measurement temperature	297K
Number of reflections used to measure unit cell	25 ($20.05\leq 2\theta \leq 29.35$)
Radius of specimen (spherical)	0.107mm
Density calculated from unit cell and contents	3.067Mg · m^{-3}
F(000)	284.49
Linear absorption coefficient	3.199mm^{-1}
Minimum transmission factor from corrections	0.641
Maximum transmission factor from corrections	0.654
Reflection conditions	
the basic structure	$h00$(h:even)
the modulated structure	$h00m\bar{m}$ (h:even) $hhlm0$ (m:even)
Radiation type	Mo$K\alpha$
Radiation wavelength	0.71073Å
Diffractometer maker and type	Enraf-Nonius CAD–4
Total number of reflections measured (main reflections)	7352 (816)
Range of h,k,l	$0\leq h\leq 11$, $0\leq k\leq 15$, $0\leq l\leq 9$, ($h\leq k$)
Maximum sinθ/λ	1.0Å^{-1}
Standard reflections	223, $\bar{2}2\bar{3}$
Intensity variation	none

space (de Wolff, 1974). Higher-order satellites were not detected in the diffraction patterns. To determine α, the peak profiles of the eleven satellite reflections (05010, $1500\bar{1}$, 34010, 26101, $250\bar{1}0$, $232\bar{1}0$, $1900\bar{1}$, $133\bar{1}0$, $1320\bar{1}$, $131\bar{1}0$ and $071\bar{1}0$ were measured along the zones parallel to <110>* and connecting two neighboring main reflections. The fitting of the eleven profiles to a Gaussian function $y=a\exp\{-b(x-\alpha)^2\}$ gave an average value 0.295(2) to α. The intensities of the main and satellite reflections were measured in the range $\sin\theta/\lambda\leq 1.0$Å^{-1}. The data were corrected for the Lorentz, polarization and absorption factors. The crystal data and the conditions of the measurements are given in Table 1. Weak diffuse streaks connecting neighboring satellites (the satellites with the indices $m\times n=0$ and those with $m\times n=\pm 1$) and surrounding main reflections were observed in the precession photographs (the circular diffuse scattering).

Structure Determination

Basic structure

Since the Laue class and reflection conditions of the main reflections are the same as

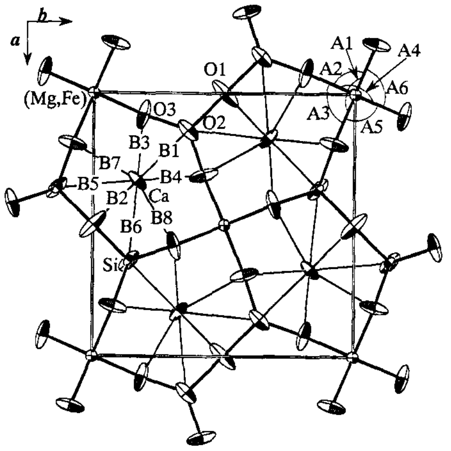

FIG. 1. Projection of the basic structure on (001) plane. Eight Ca–O distances and six O–T–O angles are denoted with B1~B8 and A1~A6 respectively.

TABLE 2. Results of the refinements

(a) Basic structure	
Space group	$P\bar{4}2_1m$
Number of main reflections used in refinements	770
Structure factors used in refinements	$\|F_o\|>3\sigma(\|F_o\|)$
Weight type	Unit weight (w=1)
Number of parameters refined	35
R	0.065
R_w	0.064
(b) Modulated structure	
Five dimensional space group	$P^{P\bar{4}2_1m}_{p4mg}$
Number of reflections used in refinements	3965
Structure factors used in refinements	$\|F_o\|>3\sigma(\|F_o\|)$
Weight type	Unit weight (w=1)
Number of parameters refined	103
R (for all reflections)	0.136
Rw	0.098
R_0 (for 770 main reflections)	0.063
R_{0w}	0.061
R_1 (for 1993 satellites with $m \times n$=0)	0.210
R_{1w}	0.240
R_2 (for 1202 satellites with $m \times n$=±1)	0.275
R_{2w}	0.343

those of the Co-analogue, the space group of the material is assigned to $P\bar{4}2_1m$. The coordinates and atomic displacement parameters of the basic structure were refined by a least-squares method using the program *LSFM* in the system *MOLEN* (Fair, 1990). The positional parameters of the Co-analogue were used as the starting parameters in the refinements. The final refinement of the parameters including anisotropic atomic displacement parameters reduced R and R_w for 770 observed main reflections to 0.065 and 0.064 respectively. Unit weights w=1 were used for the above refinements. The occupancy Mg/(Mg+Fe) at (Mg, Fe) site (the notation T-site or T-atom is used hereafter) was determined to be 0.554(6) by the refinement of the occupancy of Mg at the site.

The basic structure determined is illustrated in Fig. 1. Similar tendencies to the anisotropy of the displacement ellipsoids found in the Co-analogue were found also in the present material and this fact strongly suggests that the modulation of the structure should mainly be caused by shifts of the Ca and O atoms. The results of the refinements and the final parameters are listed in Table 2(a) and 3 respectively.

Modulated structure

Since the Laue class and the reflection conditions of the main and satellite reflections are the same as those of Co-åkermanite, the same five-dimensional space group $P^{P\bar{4}2_1m}_{p4mg}$ (with the notation proposed by Janner *et al.*, 1983) and the same symmetry generators, (S_4^+ | 0,0,0,0,0) and (σ_{db}|1/2,1/2,0, 1/2,1/2), were assumed to be the correct

TABLE. 3. Positional parameters, occupancy and anisotropic atomic displacement parameters of the basic structure with estimated standard deviations in parentheses.

Positional parameters and occupancy

Atom	x	y	z	B_{eq}(Å^2)*	Occupancy
(Mg,Fe)		0	0	0	1.00(1) 0.554(6)**
Ca	0.3307(1)	1/2–x	0.5061(3)	1.914(8)	
Si	0.1384(1)	1/2–x	0.9383(3)	0.88(1)	
O1	0	1/2	0.825(1)	3.51(6)	
O2	0.1390(5)	1/2–x	0.2570(8)	2.25(4)	
O3	0.0795(7)	0.1898(5)	0.7891(7)	2.97(7)	

* $B_{eq}=4/3(\beta_{11}a^2+\beta_{22}b^2+\beta_{33}c^2)$
** Mg/(Mg+Fe)

Anisotropic atomic displacement parameters

Atom	β_{11}	β_{22}	β_{33}	β_{23}	β_{31}	β_{12}
(Mg,Fe)	0.00404(9)	β_{11}	0.0099(4)	0	0	0
Ca	0.00980(8)	β_{11}	0.0088(2)	–0.0016(3)	$-\beta_{23}$	0.0130(2)
Si	0.00395(8)	β_{11}	0.0067(3)	–0.0019(3)	$-\beta_{23}$	0.0018(3)
O1	0.0202(7)	β_{11}	0.005(1)	0	0	0.032(2)
O2	0.0125(4)	β_{11}	0.0055(8)	0.0005(9)	$-\beta_{23}$	0.016(1)
O3	0.0243(9)	0.0058(4)	0.0143(9)	–0.005(1)	0.018(2)	–0.011(1)

The form of the anisotropic atomic displacement parameters is $\exp\{-(\beta_{11}\times h^2+\beta_{22}\times k^2+\beta_{33}\times l^2+\beta_{12}\times hk+\beta_{13}\times hl+\beta_{23}\times kl)\}$.

ones, where

$$S_4^+ = \begin{pmatrix} 0 & -1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix} \quad \text{and} \quad \sigma_{db} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & -1 \end{pmatrix}.$$

(i) *Model of the modulated structure*

The basic structure determined implies that the modulation should be caused principally by the shifts of Ca and O atoms. Since Mg at the T-site is partially replaced by Fe, the components of the displacive modulation for all sites together with that of the substitutional modulation for T-site were investigated at the first step of the refinements.

The atomic position vector $\boldsymbol{x}$ in the three dimensional space is written as

$$\boldsymbol{x} = \boldsymbol{n} + \bar{\boldsymbol{x}} + \boldsymbol{u}$$

where $\boldsymbol{n}$ is a lattice vector, $\bar{\boldsymbol{x}}$ a position vector of an atom in the unit cell of the basic structure and $\boldsymbol{u}$ a displacement vector of the atom. In a two-dimensionally modulated structure, displacements of atoms from the sites in the basic structure are expressed by plane waves with the wave vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$. We may neglect terms of the higher order harmonics in the present case, because no higher-order satellites were detected. Then the modulation function for the x, y and z components of a displacement $\boldsymbol{u}$ is expressed as

$$\begin{aligned} u_{ij} = {} & A_{ij1}+A_{ij2}\cos(2\pi s)+A_{ij3}\cos\{2\pi(s+t)\}+A_{ij4}\cos(2\pi t)+A_{ij5}\cos\{2\pi(-s+t)\} \\ & +A_{ij6}\sin(2\pi s)+A_{ij7}\sin\{2\pi(s+t)\}+A_{ij8}\sin(2\pi t)+A_{ij9}\sin\{2\pi(-s+t)\}, \end{aligned}$$

where i=1, 2, 3 : x, y, z components of the $\boldsymbol{u}$ of the jth atom. A_{ijk}'s are Fourier amplitudes of the modulation wave and s, t are phases of the modulation at the atomic position $\boldsymbol{n}+\bar{\boldsymbol{x}}$. $s=\boldsymbol{k}_1\cdot(\boldsymbol{n}+\bar{\boldsymbol{x}})$ and $t=\boldsymbol{k}_2\cdot(\boldsymbol{n}+\bar{\boldsymbol{x}})$.

The occupation probability P for Mg partially replaced by Fe is written as

$$P=\bar{P}+P'$$

where $\bar{P}$ is the occupation probability of Mg in the basic structure and P' is its variation in the modulated structure. P' is then expanded to a Fourier series:

$$\begin{aligned}P'=&P_1+P_2\cos(2\pi s)+P_3\cos\{2\pi(s+t)\}+P_4\cos(2\pi t)+P_5\cos\{2\pi(-s+t)\}\\&+P_6\sin(2\pi s)+P_7\sin\{2\pi(s+t)\}+P_8\sin(2\pi t)+P_9\sin\{2\pi(-s+t)\},\end{aligned}$$

where P_k's are the Fourier amplitudes of the modulation.

(ii) Refinements

Since the Fourier amplitudes of the displacive modulation of the 5 (Ca, T, Si, O1, O2) of the 6 atoms and the substitutional modulation of the T-atom are constrained by the site symmetry of the special positions, the number of the independent parameters to be refined is 105 (78 displacive parameters, 23 anisotropic atomic displacement parameters, 3 occupation probability parameters and one parameter for the scale factor). The modulated structure was then refined by the full-matrix least-squares program *REMOS* (Yamamoto, 1984). The Fourier amplitudes of the modulation determined for the Co-analogue (Hagiya *et al.*, 1993) were used as the initial parameters of the refinements, because the modulation wave length and the distribution of satellite intensities of the present material are similar to those of Co-åkermanite. The refinement of all 105 parameters with the weights w=1 reduced R to 0.136 and R_w to 0.098 for all 3965 reflections. The modulation function for the occupation probability of Mg determined by the refinement is

$$P'=-0.016(8)-0.011(6)\{\cos(2\pi s)+\cos(2\pi t)\}+0.003(7)[\cos\{2\pi(s+t)\}+\cos\{2\pi(-s+t)\}].$$

The magnitudes of the Fourier amplitudes of the occupation probability are not significantly larger than their *e.s.d.*'s and this fact strongly suggests that the substitution of Mg by Fe must be random in the whole structure. Thus we assumed that the structure would be only displacively modulated. The refinement of 103 parameters reduced R to 0.136 and R_w to 0.098 for 3965 reflections. Since no change of R and R_w factors was found in the results of the refinements, we concluded that no substitutional modulation exists in the material used for the present studies. The results and the final parameters of the refinement without substitutional modulation are listed in Table 2(b) and 4 respectively.

The R factors obtained in the basic and modulated structure refinements are 0.065 and 0.136 respectively and the values are larger than those obtained in the studies on Co-analogue (0.049 and 0.098; Hagiya *et al.*, 1993). Since the circular diffuse streaks were also observed in the precession photographs of the present material as described in the preceding section, the high R values for the modulated structure can be ascribed to the occurrence of the diffuse streaks. Moreover, the peak profiles of the satellite reflections with the indices $m\times n=\pm1$ are more diffuse than those of the main and satellite reflections with $m\times n=0$. Such phenomena may

TABLE 4. Fourier amplitudes of the modulation functions ($\times 10^4$) and anisotropic atomic displacement parameters ($\times 10^4$) with estimated standard deviations in parentheses.

Fourier amplitudes

		A_{ij1}	A_{ij2}	A_{ij3}	A_{ij4}	A_{ij5}	A_{ij6}	A_{ij7}	A_{ij8}	A_{ij9}
(Mg,Fe)	u_{1j}	0	0	0	0	0	−39(1)	23(2)	75(1)	−24(2)
	u_{2j}	0	0	0	0	0	$-A_{1j8}$	$-A_{1j9}$	A_{1j6}	A_{1j7}
	u_{3j}	0	25(3)	12(3)	$-A_{3j2}$	$-A_{3j3}$	0	0	0	0
Ca	u_{1j}	−2(0)	70(1)	1(1)	116(1)	−23(1)	4(1)	71(1)	23(1)	−65(1)
	u_{2j}	$-A_{1j1}$	A_{1j2}	$-A_{1j5}$	A_{1j4}	$-A_{1j3}$	$-A_{1j6}$	$-A_{1j9}$	A_{1j8}	$-A_{1j7}$
	u_{3j}	6(1)	0	7(2)	0	A_{3j3}	95(3)	−44(2)	0	A_{3j7}
Si	u_{1j}	0(0)	65(1)	−21(2)	10(1)	25(1)	61(1)	2(2)	1(1)	−1(2)
	u_{2j}	$-A_{1j1}$	A_{1j2}	$-A_{1j5}$	A_{1j4}	$-A_{1j3}$	$-A_{1j6}$	$-A_{1j9}$	A_{1j8}	$-A_{1j7}$
	u_{3j}	0(1)	0	38(3)	0	A_{3j3}	89(3)	−10(2)	0	A_{3j7}
O1	u_{1j}	0	0	0	0	0	78(7)	−39(13)	−179(12)	71(12)
	u_{2j}	0	0	0	0	0	$-A_{1j6}$	$-A_{1j9}$	A_{1j8}	$-A_{1j7}$
	u_{3j}	−1(8)	0	32(15)	0	A_{3j3}	0	0	0	0
O2	u_{1j}	0(3)	99(7)	−26(8)	51(7)	28(7)	9(5)	15(8)	11(7)	−34(7)
	u_{2j}	$-A_{1j1}$	A_{1j2}	$-A_{1j5}$	A_{1j4}	$-A_{1j3}$	$-A_{1j6}$	$-A_{1j9}$	A_{1j8}	$-A_{1j7}$
	u_{3j}	0(5)	0	28(9)	0	A_{3j3}	85(11)	−13(8)	0	A_{3j7}
O3	u_{1j}	21(4)	151(7)	56(9)	170(7)	90(8)	28(7)	110(8)	156(7)	−59(8)
	u_{2j}	−4(3)	3(5)	−47(6)	−48(5)	2(6)	−74(5)	−15(6)	−57(5)	23(6)
	u_{3j}	14(4)	115(9)	41(11)	75(9)	91(10)	99(9)	47(10)	30(9)	−15(11)

Anisotropic atomic displacement parameters

	β_{11}	β_{22}	β_{33}	β_{23}	β_{31}	β_{12}
(Mg,Fe)	31(0)	β_{11}	95(2)	0	0	0
Ca	64(0)	β_{11}	70(1)	−8(0)	$-\beta_{23}$	33(0)
Si	27(0)	β_{11}	49(2)	−2(0)	$-\beta_{23}$	7(0)
O1	133(8)	β_{11}	50(9)	0	0	104(9)
O2	98(3)	β_{11}	41(6)	5(3)	$-\beta_{23}$	53(5)
O3	122(5)	38(2)	99(6)	−8(3)	33(5)	−29(3)

The form of the anisotropic atomic displacement parameters is
$\exp\{-(\beta_{11}\times h^2 + \beta_{22}\times k^2 + \beta_{33}\times l^2 + 2\times\beta_{12}\times hk + 2\times\beta_{13}\times hl + 2\times\beta_{23}\times kl)\}$.

cause the higher partial R factor for the satellites with $m\times n=\pm 1$ and also higher R for the total reflections than those of the main and the satellite reflections with the indices $m\times n=0$ (Table 2).

Results and Discussions

The basic structure, corresponding to the projection of the modulated structure in the five-dimensional space onto the three-dimensional space, reveals characteristic forms of the displacement ellipsoids at each atom site (Fig. 1). The sizes of the ellipsoids of the T and Si atoms are much smaller than those of the Ca and O atoms and their forms are almost spherical. These features imply that those atoms are arranged periodically in the incommensurately modulated structure. The Ca atom is coordinated by the eight O atoms (B1 ~ B8). The

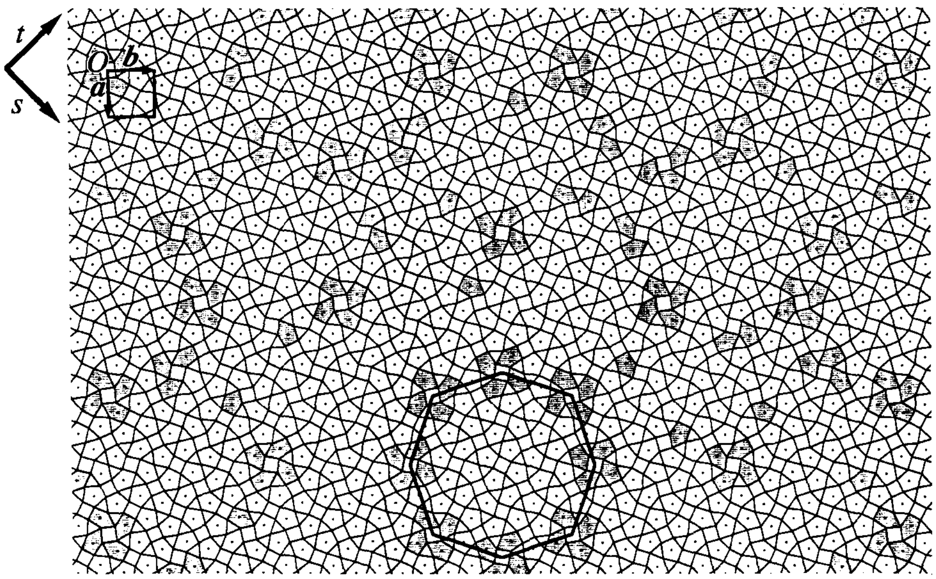

FIG. 2. A part of the modulated structure projected on (001) plane. The origin in the modulated structure and a unit cell of the basic structure are expressed by *O* and the square outlined with solid lines respectively. Triangles, squares and dots indicate SiO_4 tetrahedra, TO_4 tetrahedra and Ca atoms respectively. Shaded pentagons correspond to the six-coordinated Ca.

ellipsoids of the Ca and O atoms are strongly anisotropic and the features are caused by displacement of the atoms in the modulated structure, or the modulation can be explained with the distortion of the TSi_2O_7 framework from that of the basic structure through deformations and/or rotations of the tetrahedra around the T and Si sites. The same features were found in the structure of Co-åkermanite (Hagiya *et al.*, 1993).

A part of the modulated structure calculated with the refined parameters and projected on (001) plane is depicted in Fig. 2. The oxygen polyhedra around Ca atoms are identified as pentagons in the figure and two types of the pentagons can be distinguished, that is, the pentagons with a large distortion from the regular one (to be denoted as 'distorted') and those with a small distortion (to be denoted as 'regular'). The form of the latter is similar to the pentagon in the basic structure. Variations of the eight Ca–O distances (B1~B8) calculated from the modulation functions are indicated in Fig. 3. The Ca–O distances denoted as B5 and B7 are remarkably long at around t=0.0 and 1.0, whereas the distances B6 and B8 are very long at around t=0.5 [Fig. 3(a)]. Those long distances specify the coordination number of the Ca atoms to be six in those parts and to be seven or eight in the other parts. The forms of the oxygen polyhedra around the six-coordinated Ca are distorted octahedra and those around the eight-coordinated Ca are bicapped trigonal prisms (Fig. 4). The former corresponds to a 'distorted' pentagon and the latter a 'regular' one in the (001) projection (Fig. 2).

The tetrahedra around T-atoms are drawn as squares in the (001) projection: some of

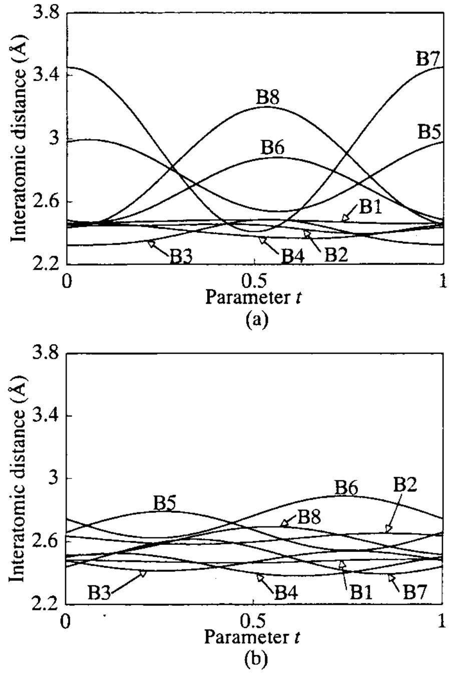

FIG. 3. Variations of eight Ca-O distances as functions of the parameter t (a) at s=0.0, (b) at s=0.5. The symbols of the curves correspond to the Ca-O bonds given in Fig. 1.

them are almost regular in the form and the others are distorted. Deformation of the tetrahedra is also one of the characteristic features in the modulated structure. The T–O distances vary in the structure just as the Co–O distances in the Co-analogue (Hagiya *et al.*, 1993). The O–T–O angles denoted as A1 and A4 (Fig. 1) change in phase with each other but in opposite phase with the rest (A2, A3, A5 and A6) as indicated in Fig. 5. The change of the distance between the two edges almost parallel to (001) is opposite to the change of the angles A1 and A4; that is, the distance between the two edges is shorter (e.g. at s=0.0 and t=0.0.) and the tetrahedron is a flat one (Fig. 6), in case the angles A1 and A4 are large. Besides the flattening, twist from the orientations in the basic structure are observed for TO_4 tetrahedra. The sizes and forms of the squares, being roughly classified into two types, change from place to place and have a correlation with the forms of the Ca-pentagons: the regular squares with the largest size (e.g. at s=0.0 and t=0.0) are surrounded by four 'distorted' pentagons and the rest of the squares are partially or fully surrounded by 'regular' pentagons.

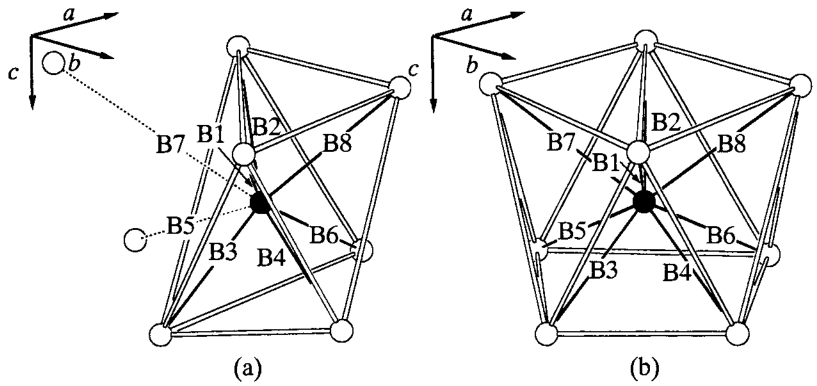

FIG. 4. Typical Ca-O polyhedra in the modulated structure. Shaded and open circles are Ca and O atoms, respectively. (a) The oxygen polyhedron around the six-coordinated Ca. Two extra O atoms are located at long distances from Ca atom. (b) The O–polyhedron around the eight-coordinated Ca.

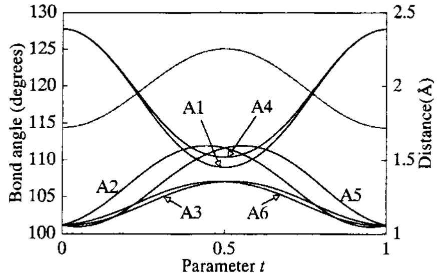

FIG. 5. Variations of the six O–T–O angles as functions of the parameter *t*. s=0.0. The symbols of the curves correspond to the O–T–O angles given in Fig. 1. Change of the distance between the two edges almost parallel to (001) is also indicated in the diagram.

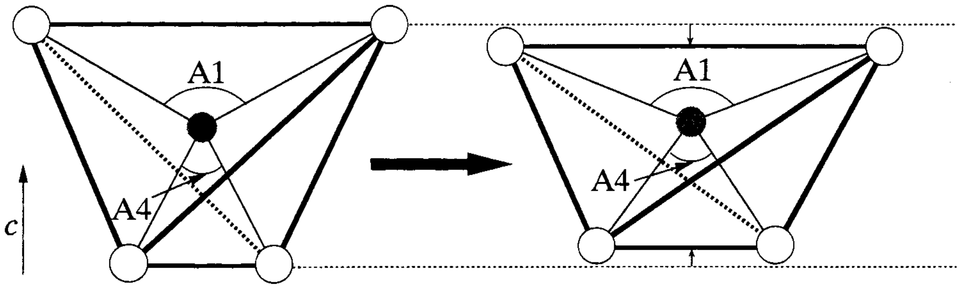

FIG. 6. The schematic view indicating flattening of a TO_4 tetrahedron in the modulated structure. Shaded and open circles indicate T and O3 atoms, respectively.

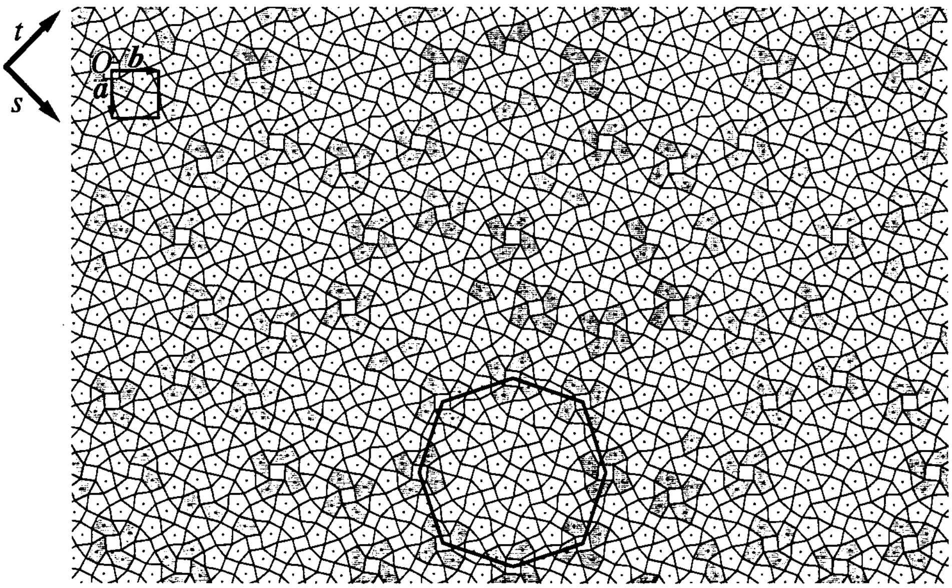

FIG. 7. A part of the modulated structure of Co-åkermanite projected on (001) plane. The origin in the modulated structure and a unit cell of the basic structure are expressed by *O* and the square outlined with solid lines respectively. Triangles, squares and dots indicate SiO_4 tetrahedra, CoO_4 tetrahedra and Ca atoms respectively. Shaded pentagons correspond to the six-coordinated Ca.

The other feature of the modulated structure is characterized by the distribution of the 'distorted' pentagons (the shaded ones, Fig. 2). Most of the 'distorted' pentagons (i.e. the six-coordinated Ca atoms) form clusters together with the large regular squares (i.e. the flattened T-tetrahedra) in the structure and the central TO_4 tetrahedra surrounded by the four six-coordinated Ca may be deformed in such a way that their O–O edges adapt to the polyhedra around the Ca atoms. No periodicity of the clusters is found, but octagonal distributions of the clusters can be seen in some parts of the structure as indicated in Fig. 2. The features postulated by Van Heurck *et al.* (1992) in their model are partly consistent with the above structural features. All the coordination polyhedra around the Ca atoms are eight-coordination in the normal phase, while many clusters of the six-coordinated Ca are formed in the incommensurate phase. If we assume that the six-coordination is more stable than the eight-coordination below the transition temperature, the formation of the six-coordination and the clusters would play an important role to minimize the free energy of the whole structure at the temperature.

A part of the modulated structures of Co-åkermanite is indicated in Fig. 7 to compare it with the modulated structure of the present material. The ratio of the six-coordinated Ca atoms (the shaded pentagons) to the whole Ca sites in the Co-analogue (28.5%) is larger than that in the present material (17.8%). This difference can be attributed to the disorder discussed below. The distribution of the Mg and Fe atoms is completely random as shown in the results of the refinement of the modulated structure. Since the ionic radii of the both metals are 0.49 and 0.63Å (Shannon and Prewitt, 1969) respectively and the difference is fairly large, partial disorder of the modulation amplitudes and the wave lengths should exist in the structure and such disorders would reduce the number of the clusters in the iron-bearing åkermanite. The disorder postulated above is consistent with the following phenomena obtained in the results of the present experiments and the refinements. One of them is the circular diffuse scattering observed in the diffraction patterns (cf. Iishi *et al.*, 1994) and the second is a large anisotropy of the atomic displacement parameters of the Ca and O atoms in the modulated structure.

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