The Modulated Structure of Synthetic Co-Åkermanite, Ca₂CoSi₂O₇

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Abstract

Diffraction patterns of synthetic Co-åkermanite, $Ca_2CoSi_2O_7$, reveal distinct satellite reflections at room temperature. An incommensurate modulation in this material has been determined by five-dimensional refinement of the structure. The basic structure is tetragonal $P\bar{4}2_1m$, unit-cell dimensions $a = 7.8417$ (6), $c = 5.0249$ (3) Å, $V = 308.99$ Å³, $Z = 2$, $M_r = 307.26$, $D_m = 3.307$ (4) g cm⁻³ at 293 K, $D_x = 3.302$ g cm⁻³, Mo $K\alpha$ with graphite monochromator, $\mu = 47.7$ cm⁻¹, $F(000) = 302$, $R = 0.049$ for 734 unique reflections. The modulated structure is also tetragonal $P^{P\bar{4}2_1m}_{p4mg}$, $k_1 = 0.2913 \times (a^* + b^*)$, $k_2 = 0.2913 \times (-a^* + b^*)$ where k_1, k_2 are wavevectors and a^*, b^* are reciprocal-lattice vectors of the basic structure; $R = 0.098$ for 3915 unique reflections. The modulation is caused by the shifts of the constituent atoms and no evidence of occupancy anomaly was found at metal sites. The transition temperature from the incommensurate to the normal phase was determined to be 489 (5) K by *in situ* observation of the satellite reflections at high temperature.

Introduction

Melilite forms a pseudo-binary solid solution between the end-members åkermanite, $Ca_2MgSi_2O_7$, and gehlenite, $Ca_2Al_2SiO_7$. The structure was first determined on a natural melilite of intermediate composition by Warren (1930) and on a synthetic gehlenite by Raaz (1930).

An anomaly in the heat capacity of synthetic åkermanite $Ca_2MgSi_2O_7$ was found by Hemingway, Evans, Nord, Haselton, Robie & McGee (1986). They observed also that each Bragg reflection in single-crystal X-ray and electron diffraction patterns of the material taken at room temperature is accompanied by a set of weak satellite reflections. These satellites indicate that the modulation in the material is incommensurate. The same phenomena in electron diffraction were found independently by Seifert, Czank, Simons & Schmahl (1987) during

their studies of synthetic iron-bearing åkermanites. In the structural studies of åkermanite at various temperatures, Kimata & Saito (1987) ascertained that some of the specimens indicate irrational super-structure reflections at room temperature. These groups also reported that the satellite reflections decrease in intensity at elevated temperatures and disappear finally at high temperature. Recently, Iishi, Fujimoto & Fujino (1989) grew single crystals of åkermanite solid-solution $Ca_2Mg_{1-x}Co_xSi_2O_7$ by a floating-zone method and also found satellite reflections in electron diffraction patterns throughout the series.

The structure of Co-åkermanite was examined by Kimata (1983) but he did not describe satellite reflections. Hemingway *et al.* (1986) and Seifert *et al.* (1987) considered that distortion of the structure should be the origin of the satellites in åkermanite. Seifert *et al.* (1987) also found from Mössbauer spectroscopy that two distinguishable tetrahedral sites containing Fe^{2+} exist in the structure. Similar phenomena were also found on Si sites from the interpretation of ²⁹Si MAS NMR (magic-angle spinning nuclear magnetic resonance) spectroscopy (Merwin, Sebald & Seifert, 1989). These phenomena have not yet been interpreted on the basis of the crystal structure. Present investigations have therefore been carried out to determine the modulated structure of Co-åkermanite based on the five-dimensional description (de Wolff, 1974; Janner & Janssen, 1977; Yamamoto, 1982) and to throw light, from the structural viewpoint, on the anomaly of tetrahedral sites found by spectroscopic studies.

Experimental

The specimen of Co-åkermanite used for the present studies was synthesized by Iishi *et al.* (1989) using a floating-zone method. A spherically shaped crystal [$r = 0.080$ (5) mm] was prepared to determine crystal and intensity data. A larger fragment of the material was selected to survey a possible Laue class, and

Table 1. *Crystal data of* $Ca_2CoSi_2O_7$ *and conditions of measurement*

Formula	$Ca_2CoSi_2O_7$
Unit cell	Tetragonal
	$a = 7.8417 (6)$ Å
	$c = 5.0249 (3)$ Å
	$V = 308.99$ Å^3
	$Z = 2$
Formula weight	307.26
Density (measured)†	3.307 (4) g cm^{-3} at 293 K
Density (calculated)	3.302 g cm^{-3}
Reflection condition for the basic structure	$h00$ (h even)
Wavevectors of the modulation	$k_1 = 0.2913 (1) \times (a^* + b^*)$
	$k_2 = 0.2913 (1) \times (-a^* + b^*)$
Wavelength of the modulation	19.04 (1) Å
Reflection conditions for the modulated structure	$h00m\bar{m}$ (h even); $hhlm0$ (m even)
Radiation	Mo $K\alpha$
Maximum value of (sin θ)/λ	1.0 Å^{-1}
Linear absorption coefficient	47.7 cm^{-1}
Maximum correction	1.75
Minimum correction	1.69
Range of h, k, l	$h = 0-11, k = 0-15, l = 0-10$ ($h \leq k$)
Standard reflections and their intensity variation	$13\bar{2}, \bar{5}34, 04\bar{7}, 0.012$

† Measured using an AccuPyc 1330 gas pycnometer (Shimadzu Co., Ltd, Kyoto, Japan).

extinction rules of the main reflections and of the satellites on precession photographs. The cell parameters, the components of the modulation wave and the intensities of the main and satellite reflections were determined on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation monochromatized by graphite.

The 25 main reflections with $23.2 \leq 2\theta \leq 64.0°$ were measured to determine the cell parameters of the basic structure. Faint spots were observed on the precession photographs at the points corresponding to 100 and some of its equivalent reflections. These were, however, excluded for the determination of the space group, because no spots were observed at the other $h00$ reflections with h odd. The Laue class $4/mmm$ and the extinction symbol $P\_2_1\_$ suggest $P42_12$ and $P\bar{4}2_1m$ as possible space groups of the basic structure.

The satellites indicate that the modulation is two-dimensional with wavevectors $k_1 = \alpha(a^* + b^*)$ and $k_2 = \alpha(-a^* + b^*)$. All reflections could thus be written in terms of five integers $hklmn$ and five vectors in the five-dimensional expression (de Wolff, 1974)

$$h = ha^* + kb^* + lc^* + mk_1 + nk_2, \qquad (1)$$

where a^*, b^* and c^* are the unit vectors of the reciprocal lattice for the basic structure. The higher-order satellites ($|m|,|n| \geq 2$) observed in the electron diffraction patterns (Iishi *et al.*, 1989) failed to appear in our experiments. The variable α, equal to 0.2913 (1), was determined from the coordinate of the middle point between the half-maxima in the profile of the satellite 34001, recorded along the

reciprocal row between the two main reflections, 34000 and 25000. The Laue class of the satellite reflections is $4/mmm$, and the reflection conditions are $h00m\bar{m}$ (h even) and $hhlm0$ (m even).

Intensities of 5553 reflections [(sinθ)/$\lambda \leq 1.0$ Å^{-1}] including 771 main reflections were collected. The intensities were corrected by Lorentz, polarization and absorption factors. Crystal data of $Ca_2CoSi_2O_7$ and measurement conditions are listed in Table 1.

Temperature dependence of the satellite intensities was examined *in situ* to determine the transition temperature between the incommensurate and normal phases. Synchrotron radiation was employed as an X-ray source since the intensities of the satellites are weak and diminishment of them must be detected. A fragment of the sample was mounted in a small electric furnace attached on the four-circle diffractometer at BL-10A in the Photon Factory, National Laboratory for High Energy Physics, Japan, and profiles of the satellites were measured at selected temperatures. The satellite 12111 was selected for the experiments because it is one of the strongest satellites on reciprocal rows parallel to b^* of the reciprocal basic lattice. Profiles of $1k100$ were recorded stepwise from $k = 1.80$ to 3.20 at intervals $\Delta k = 0.01$. The intensity at each point was measured for 1 s. The temperature of the sample was varied from room temperature to 573 K at arbitrary intervals. With a calibration curve determined before the experiments, the temperature of the sample was estimated from that measured by a thermocouple to regulate the furnace.

Structure determination

Basic structure

The space group $P\bar{4}2_1m$ was assumed in the present investigation because $P42_12$ does not fit the known framework of the structure of åkermanite. The basic structure was first studied carefully to find the anomaly caused by the modulation. A least-squares refinement on F was carried out with main reflections, the positional parameters given by Kimata (1983) and isotropic temperature factors. In the process of the refinement with isotropic temperature factors, an anomaly indicating an anisotropic thermal ellipsoid was detected at the Ca site in difference syntheses (Hagiya, Ohmasa & Iishi, 1990). Additional cycles of refinement by varying anisotropic temperature factors reduced R to 0.049 for 734 reflections [$|F_o| \geq 3\sigma(|F_o|)$]. Individual weights $w = 1/\sigma(|F_o|)^2$ were used for the refinement of the parameters. A full-matrix least-squares program in the *MOLEN* system (Fair, 1990) was employed during the refinement process. The effect of extinction was corrected in the final process (Table 2). The

Table 2. *Results of the refinement of the basic structure*

Space group of the basic structure	$P\bar{4}2_1m$
Number of main reflections measured	771
Value of R_{int}	0.012
Number of unobserved main reflections	37
Number of reflections used for refinement	734
Number of parameters refined	35
R	0.049
wR	0.043
S	3.70
Shift/e.s.d.	0.00
Value of secondary-extinction parameter g*	$1.51 (6) \times 10^{-5}$

* $|F_c^{corr}| = |F_c|/(1 + gI_c)$, a modified formula given by Stout & Jensen (1989).

Table 3. *Positional parameters of the basic structure with estimated standard deviations in parentheses*

	x	y	z	B_{eq} (Å²)*
Ca	0.3310 (1)	$\frac{1}{2} - x$	0.5059 (2)	1.93 (1)
Co	0	0	0	0.94 (1)
Si	0.1390 (1)	$\frac{1}{2} - x$	0.9386 (2)	0.88 (1)
O(1)	0	$\frac{1}{2}$	0.8229 (10)	2.99 (5)
O(2)	0.1411 (3)	$\frac{1}{2} - x$	0.2548 (7)	1.93 (3)
O(3)	0.0800 (4)	0.1894 (3)	0.7854 (5)	2.97 (6)

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

Table 4. *Root-mean-square displacement of atoms in $Ca_2CoSi_2O_7$*

Atom	Axes of ellipsoid	Angle (°) between ellipsoid axis and crystal axis			Displacement (Å)
		a	b	c	
Ca	1	128	52	61	0.09
	2	110	70	151	0.12
	3	45	45	90	0.22
Co	1	90	90	0	0.10
	2	90	0	90	0.11
	3	0	90	90	0.11
Si	1	121	59	46	0.08
	2	119	61	136	0.11
	3	45	45	90	0.12
O(1)	1	90	90	0	0.09
	2	45	135	90	0.12
	3	45	45	90	0.30
O(2)	1	83	97	10	0.09
	2	46	134	100	0.12
	3	45	45	90	0.22
O(3)	1	69	29	109	0.11
	2	84	113	157	0.11
	3	22	107	77	0.30

sitional parameters thus determined are listed in Table 3. The maximum and minimum values of anomalies in the difference syntheses evaluated from these parameters were 1.39 and $-1.50 \, e \, Å^{-3}$ respectively. No evidence has been detected in favour of substitutional modulation. This fact together with the strong anisotropy of the thermal ellipsoids indicated in Table 4 suggest that the modulation is caused by atomic displacements only. *UMBADTEA* (Finger, 1968) was used to calculate the mean-square displacement of the atoms.

Modulated structure

All elements of the space-group symmetry of the basic structure $P\bar{4}2_1m$ are generated by the set of $(S_4^+|0,0,0)$ and $(\sigma_{db}|\frac{1}{2},\frac{1}{2},0)$ or the set of $(S_4^+|0,0,0)$ and $(C_{2x}|\frac{1}{2},\frac{1}{2},0)$. (3 + 2)-reducible rotation matrices of the space-group generators in five-dimensional space are derived from the rotation matrices of the above generators according to the following process. The first 3×3 parts of the (3 + 2)-reducible matrices are the same as the rotation matrices of the space group of the basic structure and the remaining 2×2 parts of them are determined from the 3×3 parts under the conditions: S_4^+ transforms k_1, k_2 into k_2, $-k_1$ and σ_{db} transforms them into k_1, $-k_2$, respectively. Thus the matrices derived are

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

The same symbols S_4^+ and σ_{db} as those in three-dimensional space are used for convenience. In the same way as the derivation of the three-dimensional symmetry, all symmetry elements of the five-dimensional space group are generated by the set of $(S_4^+|0,0,0,\tau_a,\tau_b)$ and $(\sigma_{db}|\frac{1}{2},\frac{1}{2},0,\tau_c,\tau_d)$ or the set of $(S_4^+|0,0,0,\tau_a,\tau_b)$ and $(C_{2x}|\frac{1}{2},\frac{1}{2},0,\tau_a + \tau_c, -\tau_b + \tau_d)$, which is generated by the former set. The nonprimitive translations τ_a, τ_b, τ_c and τ_d were determined from the extinction rules of the satellites. The rule for possible reflections $hhlm0$ (m even) and $(\sigma_{db}|\frac{1}{2},\frac{1}{2},0,\tau_c,\tau_d)$ determine the condition $\tau_c = \frac{1}{2}$; the rule $h00m\bar{m}$ (h even) and $(C_{2x}|\frac{1}{2},\frac{1}{2},0,\tau_a + \tau_c, -\tau_b + \tau_d)$ determine the condition $\tau_a + \tau_c = -\tau_b + \tau_d$. From these two conditions and the condition $\tau_a = \tau_b = 0$ for assignment of the origin, $(S_4^+|0,0,0,0,0)$ and $(\sigma_{db}|\frac{1}{2},\frac{1}{2},0,\frac{1}{2},\frac{1}{2})$ are derived for the symmetry generators in the five-dimensional space. The five-dimensional space group of the material is consequently determined to be $P^{P\bar{4}2_1m}_{p4mg}$ [in the notation proposed by Janner, Janssen & de Wolff (1983)].

REMOS, a least-squares program developed by Yamamoto (1984), was employed to refine the modulated structure on F according to the multi-dimensional treatment (higher than three dimensions). The modulation is ascribed mainly to the shift of one Ca atom and three O atoms from the results of the refinement of the basic structure. Therefore, an atomic position vector x in the crystal is expressed

Table 5. *Fourier amplitudes of the modulation functions* ($\times 10^4$) *and isotropic thermal parameters* ($\times 10^2$) *with estimated standard deviations in parentheses*

		A_{ij1}	A_{ij2}	A_{ij3}	A_{ij4}	A_{ij5}	A_{ij6}	A_{ij7}	A_{ij8}	A_{ij9}
Ca	u_{1j}	-4 (0)	97 (1)	13 (1)	160 (1)	-46 (1)	2 (0)	105 (1)	27 (1)	-96 (1)
	u_{2j}	$-A_{1j1}$	A_{1j2}	$-A_{1j5}$	A_{1j4}	$-A_{1j3}$	$-A_{1j6}$	$-A_{1j9}$	A_{1j8}	$-A_{1j7}$
	u_{3j}	10 (1)	0	3 (2)	0	A_{3j3}	108 (3)	-77 (2)	0	A_{3j7}
	B	75 (1)								
Co	u_{1j}	0	0	0	0	0	-50 (4)	44 (1)	95 (0)	-45 (0)
	u_{2j}	0	0	0	0	0	$-A_{1j8}$	$-A_{1j9}$	A_{1j6}	A_{1j7}
	u_{3j}	0	43 (2)	17 (2)	$-A_{3j2}$	$-A_{3j3}$	0	0	0	0
	B	57 (1)								
Si	u_{1j}	-2 (0)	72 (1)	-39 (1)	11 (1)	44 (1)	72 (1)	1 (1)	-1 (1)	4 (1)
	u_{2j}	$-A_{1j1}$	A_{1j2}	$-A_{1j5}$	A_{1j4}	$-A_{1j3}$	$-A_{1j6}$	$-A_{1j9}$	A_{1j8}	$-A_{1j7}$
	u_{3j}	-4 (1)	0	61 (2)	0	A_{3j3}	104 (3)	-19 (3)	0	A_{3j7}
	B	45 (1)								
O(1)	u_{1j}	0	0	0	0	0	94 (5)	-116 (7)	-269 (6)	146 (6)
	u_{2j}	0	0	0	0	0	$-A_{1j6}$	$-A_{1j9}$	A_{1j8}	$-A_{1j7}$
	u_{3j}	16 (6)	0	52 (12)	0	A_{3j3}	0	0	0	0
	B	69 (6)								
O(2)	u_{1j}	0 (2)	157 (4)	-71 (5)	72 (4)	65 (4)	23 (3)	25 (5)	38 (4)	-45 (4)
	u_{2j}	$-A_{1j1}$	A_{1j2}	$-A_{1j5}$	A_{1j4}	$-A_{1j3}$	$-A_{1j6}$	$-A_{1j9}$	A_{1j8}	$-A_{1j7}$
	u_{3j}	6 (4)	0	56 (8)	0	A_{3j3}	88 (10)	-23 (8)	0	A_{3j7}
	B	92 (4)								
O(3)	u_{1j}	33 (2)	213 (4)	102 (5)	235 (4)	101 (4)	43 (4)	148 (5)	205 (4)	-118 (4)
	u_{2j}	-9 (2)	-10 (3)	-76 (4)	-72 (3)	14 (4)	-93 (3)	-24 (4)	-78 (3)	49 (4)
	u_{3j}	38 (3)	151 (7)	57 (9)	89 (7)	134 (7)	111 (7)	26 (8)	41 (7)	-14 (8)
	B	68 (3)								

as $x = n + \bar{x} + u$, where n is a lattice vector, $\bar{x}$ a position vector in a unit cell of the basic structure and u a displacement vector. Since the indices of the observed satellites were $|m|,|n| \leq 1$ in (1), the displacement u_{ij} ($i = 1, 2, 3$ for the x, y, z components of u) of atom j from the basic structure is given by

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

where the A_{ijk} are Fourier amplitudes of the modulation and s, t are phases of the modulation at the atomic position $n + \bar{x}$, namely, $s = k_1 \cdot (n + \bar{x})$, $t = k_2 \cdot (n + \bar{x})$.

Each of the six atoms in the basic structure has 27 parameters (A_{ijk}) but the total number of parameters to be refined is 78 instead of 162 ($= 27 \times 6$) because the five atoms Ca, Co, Si, O(1) and O(2) are at special positions of the basic cell. To get rapid convergence of the varied parameters, it was necessary at the beginning of the refinement to reduce the number of parameters and the number of possible combinations of parameters. As a first approximation, Co and Si atoms, which were assumed not to be modulated, were excluded in the process of the refinement, because their thermal ellipsoids are almost spherical. Moreover, directions of the shifts of the remaining atoms were considered to be parallel to the longest axes of their ellipsoids (Table 4). The number of the parameters was thereby reduced to 20. Eleven of the 20 A_{ijk} are coefficients of the

trigonometric terms with s or t as arguments and the rest are those with $s + t$ or $-s + t$ as arguments. The former were refined first. Since initial values and their signs must be given to the 11 A_{ijk}, all A_{ijk} were assigned initial values of 0.01, equal to one hundredth of the period of the basic cell. Combinations of the signs for 11 A_{ijk} were derived by the following considerations. An SiO_4 tetrahedron neighbouring a Ca atom was assumed to be rigid and tightly bound to the Ca atom because the bonds between Ca and O(2) or O(3) of the tetrahedron should be strong since they are short. Then movement of the tetrahedron should correlate to that of the Ca atom and the signs of the parameters of the three O atoms can be assigned when those of the Ca atom are given. Finally, the number of combinations of the signs for the 11 A_{ijk} was found to be four because the number of independent combinations of the signs for the Ca atom is four. The four combinations of the 11 A_{ijk} with individual signs were refined separately with fixed isotropic temperature factors (0.5 for Ca, Co and Si atoms and 0.7 for O atoms) and with penalty functions by which interatomic distances were constrained not to exceed reasonable ranges. The reflections with $m \times n = 0$ and with $|F_o| \geq 30\sigma(|F_o|)$ were used for the calculations. Two of the four sets gave lower residual factors and were used in the following step.

Combinations of the nine remaining A_{ijk} were then derived by a process similar to that described above and four independent sets were also obtained. Eight sets of the parameters, being the combinations of the first two sets and next four sets, were then refined with the same temperature factors and penalty func-

tions. The satellite reflections with $m \times n = \pm 1$ were also used in this process. Since one of them converged and gave a low residual factor, all reflections with $|F_o| \geq 3\sigma(|F_o|)$ were used thereafter and the shifts of Co and Si atoms were also refined. The constraint, which kept the directions of the shifts of all atoms parallel to the longest axes of their ellipsoids, was relaxed and the penalty functions were not used in the final process. The refinement of 85 parameters, including six isotropic temperature factors and one scale factor, with individual weights $w = 1/\sigma(|F_o|)^2$, reduced R to 0.098 and wR to 0.065 for all 3915 reflections. $R_0 = 0.047$, $wR_0 = 0.046$ for 734 main reflections, $R_1 = 0.113$, $wR_1 = 0.095$ for 1787 satellites with $m \times n = 0$ and $R_2 = 0.188$, $wR_2 = 0.163$ for 1394 satellites with $m \times n = \pm 1$. The final refined parameters are listed in Table 5.*

Results and discussion

The positional and thermal parameters of the basic structure are in agreement with those given by Kimata (1983). The structure is depicted in Fig. 1. The Co—O distance 1.940 (3) Å agrees well with that in Co_3O_4, 1.94 (3) Å (Knop, Reid, Sutarno & Nakagawa, 1968). The average Si—O distance, 1.618 (3) Å, agrees with that in Mg-åkermanite, 1.619 (2) Å (Kimata & Ii, 1981). The mean Ca—O distance obtained agrees with those in Mg- and Co-åkermanite as reported by Kimata (1983).

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* Lists of anisotropic thermal parameters, bond lengths and bond angles of the basic structure, and a list of modulated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55505 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0589]

Fig. 2 indicates a part of the modulated structure calculated with the modulation functions. The change of coordination around the Ca atom with the deformation is clearly represented in Fig. 2 and also by the Ca—O distances calculated from the modulation functions. Figs. 3(a) and 3(b) indicate variations of Ca—O distances *versus* t at $s = 0.0$ and 0.5, respectively. In Fig. 3(a), two Ca—O distances, denoted as B5 and B7, change sinusoidally with phases
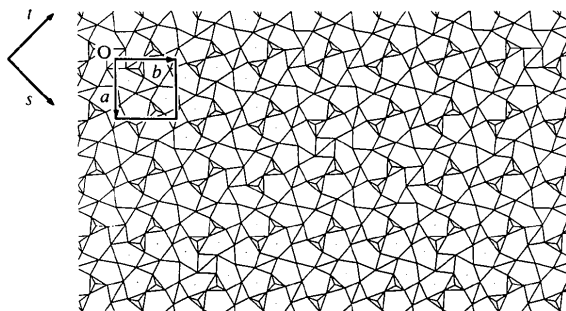

Fig. 2. A part of modulated structure viewed along the c axis. The figure is calculated from the modulation functions. The origin of the modulated structure is indicated by O, together with the outline of the unit cell of the basic structure. The directions of the internal coordinates s and t are also given. Triangles represent Si tetrahedra, squares with a diagonal represent Co tetrahedra and dots represent the positions of Ca atoms.

Fig. 1. Drawing of the structure. Eight Ca—O distances and four Co—O distances are indicated by the symbols B1 to B8 and e to h, respectively.
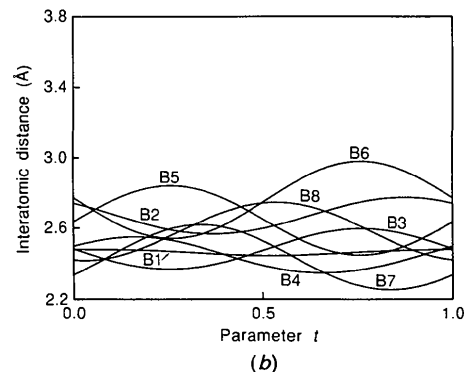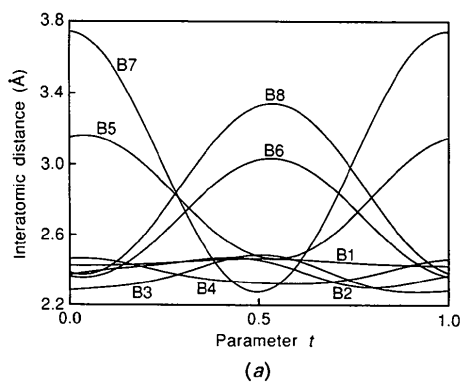

Fig. 3. The variation of eight Ca—O distances as functions of t (a) at $s = 0.0$; (b) at $s = 0.5$. The symbols on the curves correspond to the Ca—O bonds indicated in Fig. 1.

almost equal to each other, while $B6$ and $B8$ have phases equal but opposite to those of $B5$ and $B7$. Coordination of O atoms around a Ca atom is 6, or $4 + 4$ when the distances longer than 3 Å are excluded. The Ca—O distances $B5$ and $B7$ are much longer but $B6$ and $B8$ are normal in the region $s = 0$ and $t = 0$, while $B6$ and $B8$ are longer than the rest when $s = 0$ and $t = 0.5$. However, deviations of Ca—O distances are not so large when $s = 0.5$, as indicated in Fig. 3(b), and the coordination number of Ca in this case is assumed to be 8.

When the Ca—O distances change as above, it is to be concluded that the SiO$_4$ tetrahedron does not

(a)

(b)

Fig. 4. The variation of four Si—O distances as functions of t
(a) at $s = 0.0$; (b) at $s = 0.5$.

Fig. 5. The variation of the O(1)—Si—O(3) angle as a function of t. Curves are drawn at intervals $\Delta s = 0.2$.

behave as a rigid body. Figs. 4 and 5 indicate changes of Si—O distances and those of the O(1)—Si—O(3) angle along t. The Si—O(2) distance is almost constant, while the rest vary markedly. Deviation of the O(1)—Si—O(3) angle from the ideal tetrahedral angle (109.5°) is also remarkable. These facts demonstrate that the distortion of Si—O tetrahedral bonds is variable throughout the crystal. Merwin et $al.$ (1989) studied ^{29}Si MAS NMR spectra of Ca$_2$MgSi$_2$O$_7$ and found that peaks of the spectra split into three or more subpeaks. They interpreted this phenomenon with the aid of the 'multitude of Si sites' model. The variety of Si—O bonds found in the present study will probably present a reasonable interpretation of the spectra observed by them.

Variations of Co—O distances show a feature different from those of Si—O distances, that is, all four Co—O distances change simultaneously and sinusoidally (Fig. 6). Seifert et $al.$ (1987) measured Mössbauer spectra of synthetic iron-bearing Ca$_2$MgSi$_2$O$_7$ at various temperatures and found that the spectra reveal two sets of doublets, inner and outer, corresponding to a 'compressed' site and a 'normal' site, respectively. The outer doublet shifts toward the inner one at high temperatures and overlaps it at the transition temperature. A histogram of the mean Co—O distances evaluated from the modu-
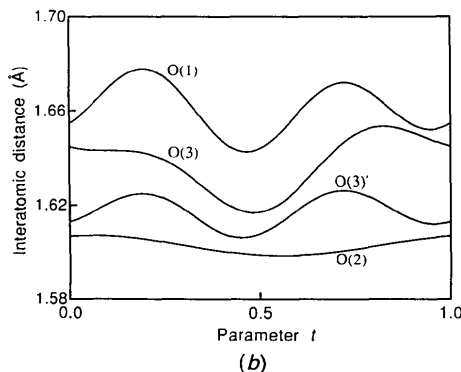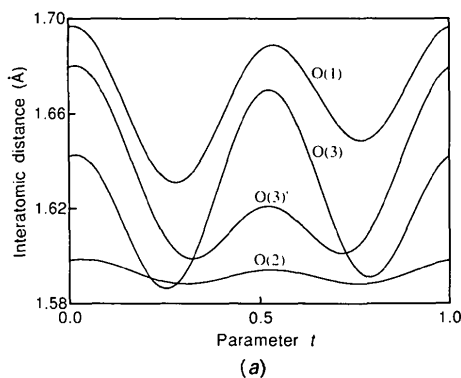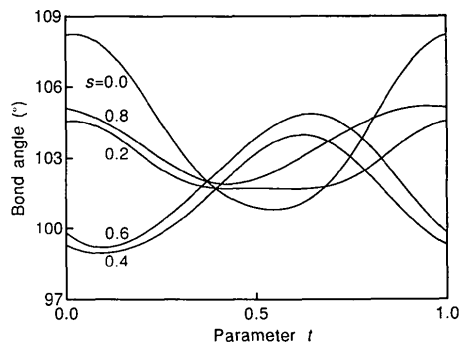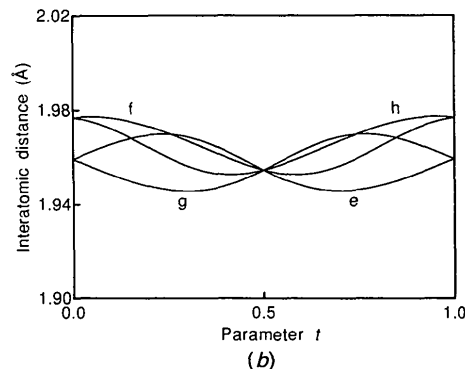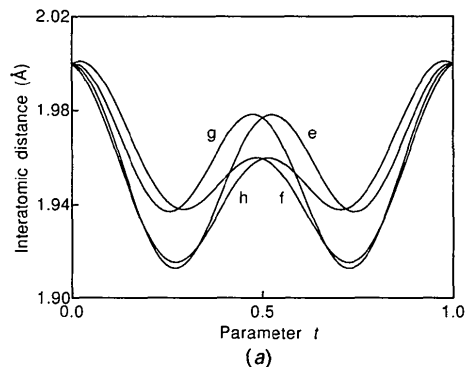

(a)

(b)

Fig. 6. The variation of four Co—O distances as functions of t
(a) at $s = 0.0$; (b) at $s = 0.5$. The symbols on the curves correspond to the Co—O bonds indicated in Fig. 1.

lation functions of Co—O distances at intervals Δs = 0.01 and Δt = 0.01 is shown in Fig. 7. There are two peaks in the diagram, in the ranges 1.928–1.930 and 1.956–1.958 Å. It is probable that these two peaks correspond to the compressed and normal sites proposed by Seifert et al. (1987), although the compositions of these materials are different.

Seifert et al. (1987) considered that the modulation is not sinusoidal but is more or less rectangular because of the presence of two discrete Fe sites. However, higher harmonics of satellites ($|m|,|n|$ > 1) that imply a rectangular modulation were not observed even in the diffraction patterns produced by the synchrotron radiation. This fact suggests that the rectangular component will in all probability be very weak in the modulation of Ca$_2$CoSi$_2$O$_7$. Many higher-order satellites have so far been recorded in the electron diffraction studies on Mg–Fe and Mg–Co series (Seifert et al., 1987; Iishi et al., 1989). If these are also observed in X-ray diffraction patterns, it must be noted that a systematic extinction rule by which even-order satellites are forbidden should be observed in the case when the modulation
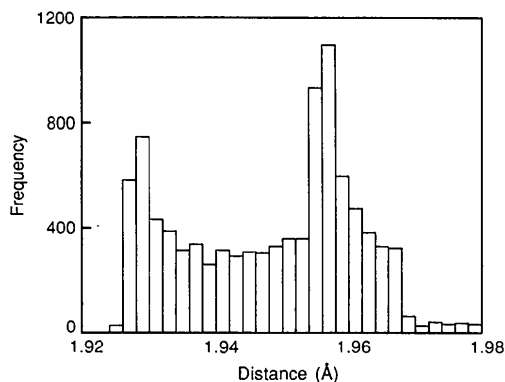
of those compounds have rectangular components only. Further studies with a stronger X-ray source are desirable to clarify the details of the mode of modulation.

In situ observation of the satellite 12111 by synchrotron radiation revealed that its intensity decreases at elevated temperatures and weakens to the background level at 489 (5) K. Thus the transition temperature from the incommensurate to the normal phase was determined to be 489 K. The transition was ascertained to be reversible. Fig. 8 shows temperature dependence of the intensities of the satellite 12111 and those of the main reflection, 12100. The intensity of the satellite decreases at higher temperatures, while that of the main reflection increases slightly. These phenomena can be explained as follows. Since the total scattered X-ray intensity remains constant, the intensities of the main reflections become stronger when the intensities of the satellites diminish. In this case, the intensities of thermal diffuse scattering are assumed to be negligible.

Fig. 7. Histogram of the mean Co—O distances in a modulation period evaluated from the modulation functions of Co—O distances at intervals Δs = 0.01 and Δt = 0.01.
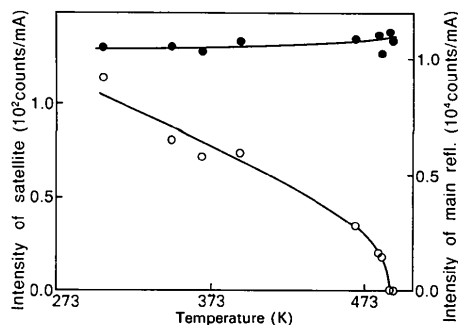

Fig. 8. The variation of intensities of the main reflection 12100 and the satellite 12111 with temperature. Intensities are normalized by the storage-ring current. Filled circles indicate intensities of the main reflection and open circles those of the satellite.

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The Experimental Electron Density in Monoclinic Cobalt Sulfate Hexahydrate, $CoSO_4.6D_2O$, at 25 K*

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Abstract

The electron density in $CoSO_4.6D_2O$ has been determined at 25 K by multipole refinement against single-crystal X-ray intensity data. Hydrogen positional and displacement parameters have been taken from a refinement using single-crystal neutron data. The influence of superposition on the total deformation density has been assessed by calculating the densities separately from the deformation functions of the individual constituents of the structure. The deformation density is significantly distorted from octahedral symmetry for the two crystallographically independent Co^{2+} ions, although the water O-atom arrangement around them is close to octahedral in both cases. The individual deformation densities for the six water molecules show clear polarization effects in the oxygen lone-pair region, which correspond to the respective coordination modes, ranging from trigonal planar to tetrahedral. The results are compared with those of similar studies on both tetragonal and monoclinic $NiSO_4.6(H,D)_2O$. Crystal

data: cobalt(II) sulfate hexahydrate ($-d_{12}$), $CoSO_4.6D_2O$, $M_r = 275.15$, monoclinic, $C2/c$, $a = 10.006 (5)$, $b = 7.252 (4)$, $c = 24.122 (12)$ Å, $\beta = 98.96 (4)°$, $V = 1729.0 (9)$ Å^3, $Z = 8$, $D_x = 2.03$ g cm^{-3}; $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 29.90$ cm^{-1}, $F(000) = 1080$, $T = 25$ K, $R(F) = 0.0186$ for 4676 observed unique reflections up to $[(\sin\theta)/\lambda]_{max} = 0.995$ Å^{-1} (X-ray); $R(F) = 0.0407$ for 3963 observed reflections up to $[(\sin\theta)/\lambda]_{max} = 0.910$ Å^{-1} (neutron).

1. Introduction

The d-electron distribution around first-row transition-metal ions has been the subject of a large number of experimental studies during the last decade. For some recent reviews, see Angermund, Claus, Goddard & Krüger (1985), Hall (1986) and Coppens (1989). Generally, such studies have to deal with many difficulties due to the higher absorption coefficients of materials containing heavier atoms and, because of the large inert cores, only a small fraction of the total scattering arises from the valence electrons. On the other hand, the contraction of the d-electron shell of the heavier elements of the first transition row gives somewhat stronger scattering at