Acta Cryst. (1983). B**39**, 34–39

Order of Titanium Atoms and Vacancies in Polytypic $Ti_{1+x}S_2$ ($x \simeq 0{\cdot}25$–$0{\cdot}33$)

BY MITSUKO ONODA AND MASANOBU SAEKI

National Institute for Research in Inorganic Materials, 1-1 *Namiki, Sakura-mura, Niihari-gun, Ibaraki* 305, *Japan*

(*Received* 25 *May* 1982; *accepted* 8 *July* 1982)

Abstract

Polytypic $Ti_{1+x}S_2$ ($x \simeq 0{\cdot}25$–$0{\cdot}33$) with ordered Ti atoms and vacancies has been studied by means of electron and X-ray diffractometry. Superstructures resulting from intra- and interlayer order have been found near $Ti_{1{\cdot}33}S_2$, and they are designated $12R$-$TC\sqrt{3}a\sqrt{3}ac$ and $6R$-$M\sqrt{3}a\sqrt{3}b2c$ according to the modified Gard notation system. Their ordered arrangements have been analyzed and described by comparison with those of $4H$-$M\sqrt{3}a\sqrt{3}b2c$, $4H$-$M\sqrt{3}b\sqrt{3}a3c$ and $2H$-$M2b2a2c$ previously reported. Two kinds of short-range-order states have been found in the $Ti_{1{\cdot}23}S_2$-$12R$ specimens quenched from 873 and 723 K respectively.

Introduction

The structures of titanium sulfide in the range TiS–TiS_2 were found to be based on close packing of S (Wiegers & Jellinek, 1970). Polytypism was observed (Tronc & Huber, 1973; Legendre, Moret, Tronc & Huber, 1975), and the structures with different periodicities along the *c* axis are designated by using the Ramsdell notation. The specimen prepared most readily in the composition range $Ti_{1{\cdot}4}S_2$–$Ti_{1{\cdot}2}S_2$ is the $4H$ type. The metastable structure of the $12R$ type also exists (Saeki & Onoda, 1982*a*,*c*). Two new structure types of $Ti_{1+x}S_2$ ($x \simeq 0{\cdot}3$) were recently synthesized by reducing TiS_2 in H_2S/H_2 atmospheres and are referred to as the $6R$ type and the $2H$ type, respectively (Onoda & Saeki, 1980; Saeki, Onoda, Kawada & Nakahira, 1981). In all structures found in the range $Ti_{1{\cdot}5}S_2$–TiS_2, Ti atoms occupy the octahedral holes fully and partially in alternating Ti layers as shown in Fig. 1.

The superstructure of $Ti_{1{\cdot}33}S_2$-$4H$ was first found by Bartram (1958). Two kinds of superstructures of $Ti_{1+x}S_2$-$4H$ ($x \simeq 0{\cdot}33$) were found and analyzed by means of X-ray diffractometry and high-resolution electron microscopy (Onoda, Saeki & Kawada, 1979; Bando, Saeki, Sekikawa, Matsui, Horiuchi & Nakahira, 1979; Bando, Saeki, Onoda, Kawada & Nakahira, 1979), and they have been designated $(4H)_2$ and $(4H)_3$. Structure refinement of $(4H)_3$ was performed and the Ti–Ti interactions and lattice distortions were discussed (Tronc & Moret, 1981). Recently the existence of the superstructure of the $4H$ type has been confirmed in the phase diagram by using the equilibrium sulfur pressure–composition isotherm method (Saeki & Onoda, 1982*b*). A superstructure of $Ti_{1{\cdot}23}S_2$-$2H$ was found (Bando, Saeki, Onoda, Kawada & Nakahira, 1980) and it has been designated $(2H)_2$. Each superstructure [$(4H)_2$, $(4H)_3$ or $(2H)_2$] arises from ordering of Ti vacancies in the partially occupied Ti layers.

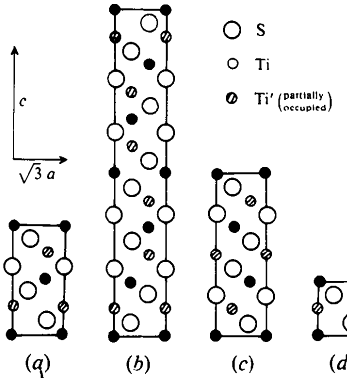


Fig. 1. The $(11\bar{0})$ section of polytypic $Ti_{1+x}S_2$ ($x \simeq 0{\cdot}25$–$0{\cdot}33$): (*a*) $4H$, (*b*) $12R$, (*c*) $6R$, (*d*) $2H$.

The superstructure of $12R$ or $6R$ has not yet been reported. We attempted to prepare specimens of $12R$ and $6R$ with ordering of Ti vacancies. In this paper, the experimental and analytical results are described.

Notation

Systematic notations of the polytypes and the superstructures are required. The notation described below is employed by reference to the modified Gard notation system recommended by the International Mineralogical Association–International Union of Crystallography Joint Committee on Nomenclature (Bailey *et al.*, 1977). The $4H$-type structure is represented by $Ti_{1+x}S_2$-$4H$. An additional suffix representing the symmetry and the periodicities of the superstructure is added following a hyphen. Thus, $(4H)_2$, $(4H)_3$ and $(2H)_2$ are written as $Ti_{1+x}S_2$-$4H$-$M\sqrt{3}a$-$\sqrt{3}b2c$, $Ti_{1+x}S_2$-$4H$-$M\sqrt{3}b\sqrt{3}a3c$ and $Ti_{1+x}S_2$-$2H$-$M2b2a2c$, respectively. The periodicities of the superstructure are represented on the basis of those of

0567-7408/83/010034-06$01.50

Table 1. *Experimental conditions*

Run number	Method	Starting material	Temperature	Period	Annealing condition after preparation
1	Chemical transport	$Ti_{1\cdot28}S_2$-$2H$ prepared at 773 K	923 K for starting material and 1163 K for product	6 days	*
2	Chemical transport	$Ti_{1\cdot21}S_2$-$2H$ prepared at 773 K	773 K for starting material and 873 K for product	17 days	*
3	Chemical transport	$Ti_{1\cdot21}S_2$-$2H$ prepared at 773 K	773 K for starting material and 873 K for product	6 days	723 K, 3 days
4	Reduction of TiS_2 in H_2S/H_2 flow	TiS_2-$2H$	873 K	6 hours	*

* The specimen was quenched for several seconds from the preparation temperature and no annealing process was performed.

the respective substructure such as $Ti_{1+x}S_2$-$4H$. Sometimes a suffix alone, *e.g.* $4H\text{-}M\sqrt{3}a\sqrt{3}b2c$, is employed for simplicity.

Experimental

The preparation procedures for $Ti_{1+x}S_2$-$12R$ ($x \simeq 0\cdot3$) and $Ti_{1+x}S_2$-$6R$ ($x \simeq 0\cdot3$) were reported previously (Saeki & Onoda, 1982*a*; Onoda & Saeki, 1980). The details of the preparation conditions are shown in Table 1 with run numbers. The composition of the product was determined by weight-loss measurements after it was oxidized to TiO_2 at 1073 K in air. An estimated error is $x = \pm0\cdot004$ in $Ti_{1+x}S_2$. The powder X-ray diffraction patterns were taken by the counter-diffractometer method using Ni-filtered Cu $K\alpha$ radiation. The crystal fragments were obtained by crushing, and electron diffraction patterns were taken by a 100 kV electron microscope.

Results

The analyzed compositions, substructures and periodicities of the detected superstructures are listed in Table 2 with run numbers which are common to Table 1. The previously reported data of the superstructures are also listed in Table 2. The superstructures are designated by use of the notation described above. The structure which contains short-range order is tentatively designated by the use of a suffix (SRO) instead of the periodicity. The details of diffraction patterns and the ordered arrangement models are described below.

$Ti_{1.33}S_2$-$12R\text{-}TC\sqrt{3}a\sqrt{3}ac$

The product of run 1 was revealed to be a mixture of the 12*R* type and the 4*H* type by X-ray and electron diffractometry. The product consists of both plate-like and needle-like crystals. When a plate-like crystal was crushed and examined under an electron microscope, the diffraction pattern was the 12*R* type with superspots as shown in Fig. 2. If the dimensions of a supercell and the symmetry elements which are required from the systematic absence of diffraction spots are taken into account, it is concluded that the model shown in Fig. 3 is the most probable among possible models of order of Ti vacancies. This was confirmed by comparison of the calculated structure factors with the observed intensities of diffraction spots. The model contains only centers of symmetry and the space group is $P\bar{1}$. The reduced triclinic unit cell is shown by broken lines in Fig. 3. Crystal data and atomic parameters are listed in Table 3.

$Ti_{1\cdot23}S_2$-$12R$-(SRO)(SRO)(SRO)

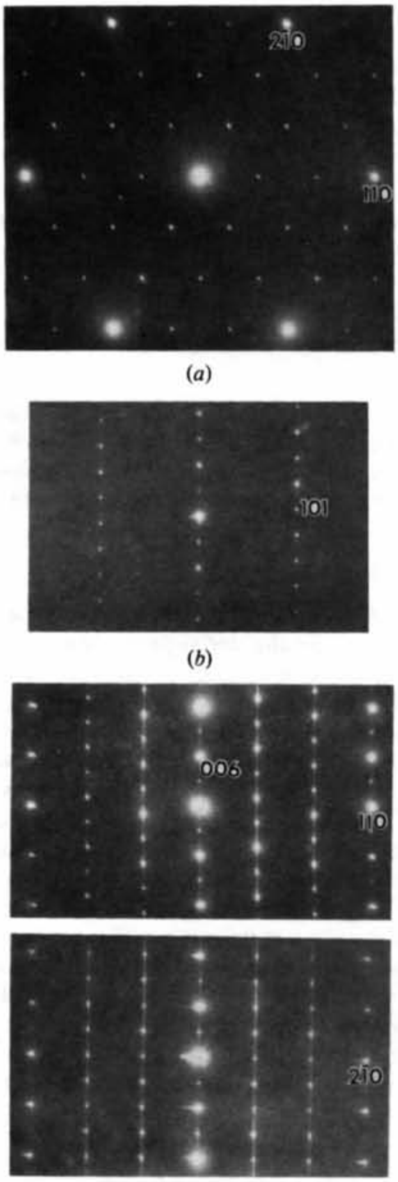
A homogeneous specimen was obtained as a product of run 2; it was the 12*R* type. In the electron diffraction

Table 2. *Comparison of the experimental results*

Run number	Composition	Substructure	Periodicities of supercell (hexagonal cell) *A* (Å)	*C* (Å)	Designation of superstructure
1	$Ti_{1\cdot33}S_2$	$12R(+4H)$	$3\cdot43 \times \sqrt{3}$	$34\cdot3 \times 1$	$12R\text{-}TC\sqrt{3}a\sqrt{3}ac$
2	$Ti_{1\cdot23}S_2$	$12R$	*	*	$12R$-(SRO)(SRO)(SRO)
3	$Ti_{1\cdot23}S_2$	$12R$	$3\cdot42 \times 2$	*	$12R\text{-}H2a2a$(SRO)
4	$Ti_{1\cdot34}S_2$	$6R$	$3\cdot44 \times \sqrt{3}$	$17\cdot1 \times 2$	$6R\text{-}M\sqrt{3}a\sqrt{3}b2c$
(*a*)	$Ti_{1\cdot37}S_2$	$4H$	$3\cdot43 \times \sqrt{3}$	$11\cdot4 \times 2$	$4H\text{-}M\sqrt{3}a\sqrt{3}b2c$
(*a*)	$Ti_{1\cdot32}S_2$	$4H$	$3\cdot43 \times \sqrt{3}$	$11\cdot4 \times 3$	$4H\text{-}M\sqrt{3}b\sqrt{3}a3c$
(*b*)	$Ti_{1\cdot23}S_2$	$2H$	$3\cdot43 \times 2$	$5\cdot75 \times 2$	$2H\text{-}M2b2a2c$

Notes: (*a*) Onoda *et al.* (1979); (*b*) Bando *et al.* (1980).

* Diffuse scattering is observed.

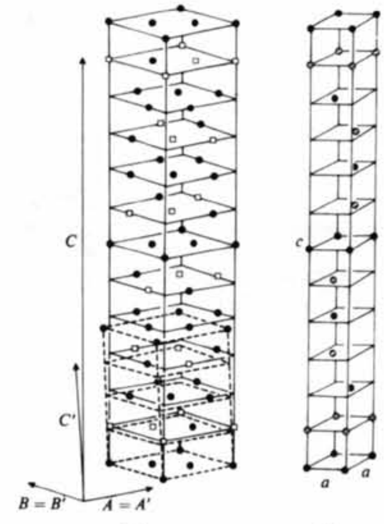


(a)

(b)

(c)

Fig. 2. Electron diffraction patterns from $Ti_{1\cdot33}S_2$-12*R*-*TC*$\sqrt{3}a\sqrt{3}ac$. The incident beam is parallel to the (*a*) [001], (*b*) [010], (*c*) [$\bar{1}$10] or [120] direction of the 12*R* type. Indices are of fundamental reflections of the 12*R* type.



(*a*) (*b*)

Fig. 3. Ti arrangements of (*a*) 12*R*-*TC*$\sqrt{3}a\sqrt{3}ac$ and (*b*) the 12*R* substructure. The cell indicated by ---- is the reduced triclinic unit cell. ● Ti atom; □ vacancy; ⊘ partially occupied Ti site.

Table 3. *Crystal data and atomic parameters of* $Ti_{1\cdot33}S_2$-12*R*-*TC*$\sqrt{3}a\sqrt{3}ac$

Crystal data [triclinic, space group $P\bar{1}$ (No. 2)]

Pseudohexagonal cell: $A = 5\cdot961$ (3), $C = 34\cdot24$ (2) Å, $V = 1054\cdot0$ (8) Å^3, $Z = 18$ (according to the formula $Ti_{1\cdot33}S_2$)

Reduced triclinic unit cell: $A' = B' = 5\cdot961$ (3), $C' = 11\cdot586$ (4) Å, $\alpha' = \beta' = 94\cdot92$ (3), $\gamma' = 120\cdot00$ (3)°, $V = 351\cdot3$ (2) Å^3, $Z = 6$ (according to the formula $Ti_{1\cdot33}S_2$)

Atomic parameters based on the pseudohexagonal cell

Coordinates of equivalent positions: (0,0,0; $\frac{2}{3},\frac{1}{3},\frac{1}{3}$; $\frac{1}{3},\frac{2}{3},\frac{2}{3}$) from the unit-cell relation; $+x,y,z$; $\bar{x},\bar{y},\bar{z}$ from the space group

	Weight	x	y	z*
Ti(1)	1·0	$\frac{2}{3}$	$\frac{1}{3}$	0·0886
Ti(2)	0·5	0	0	0·0
Ti(3)	1·0	$\frac{2}{3}$	$\frac{1}{3}$	0·0
Ti(4)	0·5	$\frac{1}{3}$	$\frac{1}{3}$	0·1667
Ti(5)	1·0	0	$\frac{2}{3}$	0·1667
S(1)	1·0	$\frac{1}{3}$	$\frac{1}{3}$	0·0419
S(2)	1·0	0	$\frac{2}{3}$	0·0419
S(3)	1·0	$\frac{2}{3}$	0	0·0419
S(4)	1·0	0	$\frac{1}{3}$	0·1248
S(5)	1·0	$\frac{2}{3}$	$\frac{2}{3}$	0·1248
S(6)	1·0	$\frac{1}{3}$	0	0·1248

* The z value obtained by the structure refinement study of 12*R* (Tronc, Moret, Legendre & Huber, 1975) is employed.

pattern, diffuse scattering is observed as shown in Fig. 4(*a*). This resembles the X-ray diffuse-scattering pattern observed by Moret, Huber & Comès (1976), and a short-range-order or microdomain model was proposed within a two-dimensional approximation (Moret, Tronc, Huber & Comès, 1978). In addition, a diffuse-scattering pattern is observed in the electron diffraction pattern with the incident beam perpendicular to the *c* axis as shown in Fig. 4(*b*). The scattering suggests occurrence of three-dimensional short-range order. Thus, the tentative notation with the suffix (SRO)(SRO)(SRO) is employed.

$Ti_{1\cdot23}S_2$-12*R*-*H*2*a*2*a*(SRO)

The product of run 3 gives the electron diffraction patterns shown in Fig. 5, and they are fundamentally of the 12*R* type. The superspots corresponding to a hexagonal axis 2*a* seem to be present in Fig. 5(*a*).

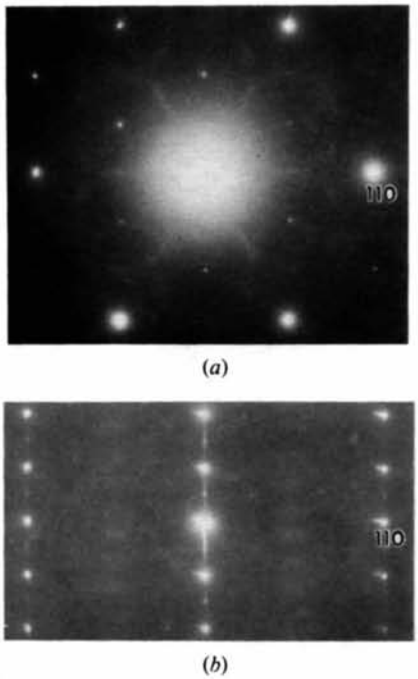


Fig. 4. Electron diffraction patterns from $Ti_{1\cdot23}S_2$-12*R*-(SRO)(SRO)(SRO). The incident beam is nearly parallel to the (*a*) [001] or (*b*) [$\bar{1}$10] direction of the 12*R* type.

Table 4. *Crystal data and atomic parameters of* $Ti_{1\cdot34}S_2$-6*R*-*M*$\sqrt{3}a\sqrt{3}b2c$

Crystal data [monoclinic, space group *C*2/*c* (No. 15)]

Rectangular monoclinic unit cell: $A = 5\cdot951$ (2), $B = 10\cdot313$ (3), $C = 34\cdot169$ (5) Å, $\beta = 90\cdot00$ (2)°, $V = 2096\cdot9$ (5) Å³, $Z = 36$ (according to the formula $Ti_{1\cdot34}S_2$)

Reduced monoclinic unit cell: $A' = 5\cdot951$ (2), $B' = 10\cdot313$ (3), $C' = 11\cdot560$ (2) Å, $\beta' = 99\cdot82$ (3)°, $V = 699\cdot1$ (2) Å³, $Z = 12$ (according to the formula $Ti_{1\cdot34}S_2$)

Atomic parameters based on the rectangular monoclinic unit cell

Coordinates of equivalent positions: $(0,0,0; \frac{2}{3},0,\frac{1}{3}, \frac{1}{3},0,\frac{2}{3})$ from the unit-cell relations; $+(0,0,0; \frac{1}{2},\frac{1}{2},0)$ and $+x,y,z; \bar{x},\bar{y},\bar{z}; \bar{x}, y, \frac{1}{2}-z; x,\bar{y},\frac{1}{2}+z$ from the space group.

	Weight	x	y	z*
Ti(1)	0·5	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{12}$
Ti(2)	0·5	0	0	0
Ti(3)	1·0	0	$\frac{1}{3}$	0
S(1)	1·0	$\frac{1}{3}$	0	$\frac{1}{24}$
S(2)	1·0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{24}$
S(3)	1·0	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{24}$

* The z value of the equidistant-layer model is employed.

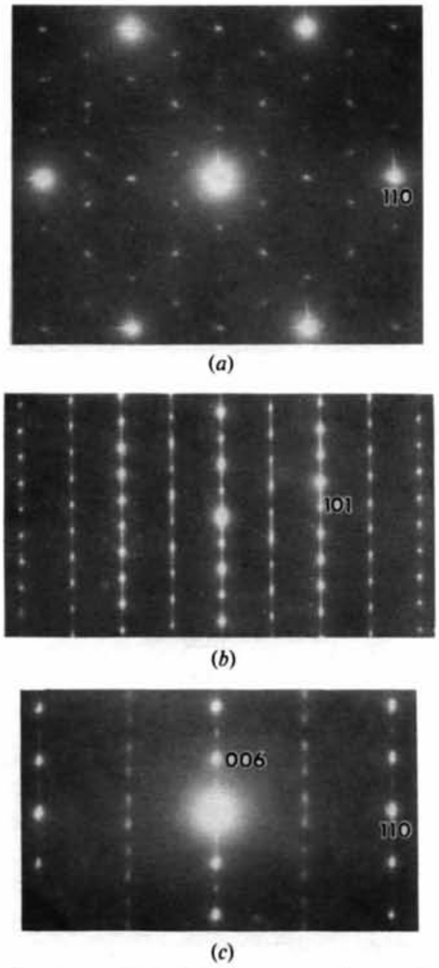


Fig. 5. Electron diffraction patterns from $Ti_{1\cdot23}S_2$-12*R*-*H*$\sqrt{3}a\sqrt{3}a$(SRO). The incident beam is parallel to the (*a*) [001], (*b*) [010], or (*c*) [$\bar{1}$10] direction of the 12*R* type. Indices are of fundamental reflections of the 12*R* type.

However, they are intercepts of the diffuse streaks as shown in Fig. 5(*b*) and (*c*). The streaks suggest that the intralayer ordered vacancies are in short-range order along the *c* axis. Thus the notation used in the heading is adopted, where (SRO) indicates one-dimensional short-range order.

$Ti_{1\cdot34}S_2$-6*R*-*M*$\sqrt{3}a\sqrt{3}b2c$

The product of run 4 was revealed to be the 6*R* type from the powder X-ray diffraction pattern. In the electron diffraction pattern of the crushed specimen, the superspots are observed as shown in Fig. 6. From the supercell dimensions, the systematic absence of superspots and structural features of the 6*R* type, only one ordered arrangement is probable. The arrangement shown in Fig. 7 is supported by comparison of the calculated structure factors with the intensities of the observed patterns. The space group of the arrangement is *C*2/*c* and the reduced monoclinic unit cell is shown by broken lines in Fig. 7. Crystal data and atomic parameters are listed in Table 4.

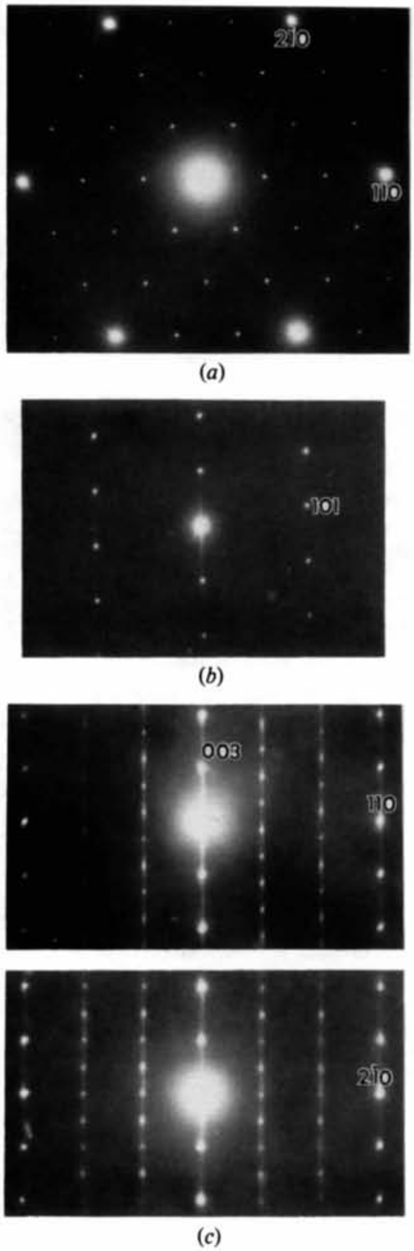


Fig. 6. Electron diffraction patterns from $Ti_{1.34}S_2$-$6R$-$M\sqrt{3}a\sqrt{3}b2c$. The incident beam is parallel to the (a) [001], (b) [010], or (c) [$\bar{1}$10] or [120] direction of the $6R$ type. Indices are of fundamental reflections of the $6R$ type.

Discussion

It has been found that the superstructures resulting from the intra- and interlayer ordering of Ti atoms and vacancies exist in both polytypes ($12R$ and $6R$) of $Ti_{1+x}S_2$ ($x \simeq 0.33$). In addition, the existence of superstructures was previously found in the $4H$ and $2H$ polytypes as shown in Table 2.

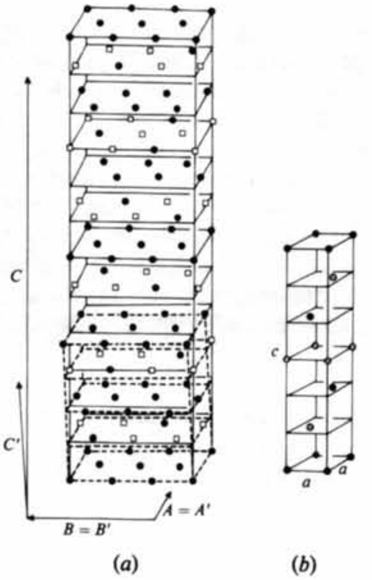


Fig. 7. Ti arrangements of (a) $6R$-$M\sqrt{3}a\sqrt{3}b2c$ and (b) the $6R$ substructure. The unit cells shown in (a) are as follows: ---- the reduced monoclinic unit cell; —— the rectangular monoclinic unit cell; ● Ti atom; □ vacancy; ⊘ partially occupied Ti site.

The atomic arrangements within the partially occupied Ti layers are the same for $12R$-$TC\sqrt{3}a\sqrt{3}ac$, $6R$-$M\sqrt{3}a\sqrt{3}b2c$, $4H$-$M\sqrt{3}a\sqrt{3}b2c$ and $4H$-$M\sqrt{3}b\sqrt{3}a3c$. The arrangement, in which one of three sites is occupied by a Ti atom and two are regularly vacant, corresponds well to the compositions determined for the specimens of these four superstructures, *i.e.* close to $Ti_{1.33}S_2$. On the other hand, the stacking sequences of such ordered layers are different between the superstructures. The stacking sequences are shown in Fig. 8 by use of projections along the c axis of the Ti

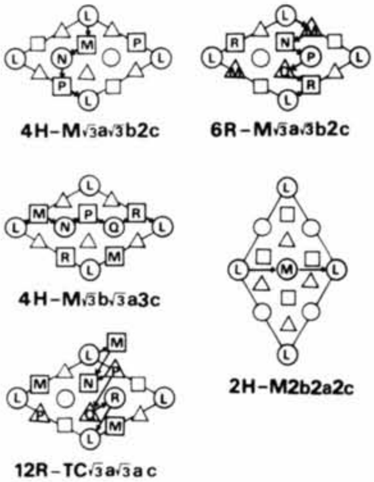


Fig. 8. Projections of the Ti-atom positions in the partially occupied Ti layer along the c axis. The primitive hexagonal cell is adopted for convenience of comparison.

atom positions in the ordered layers together with that of the superstructure of the $2H$ type. In the first ordered layer, the positions indicated by circles with the letter L are occupied by Ti atoms and the sites indicated by other circles are vacant. The second ordered layer consists of the positions indicated by squares for $12R\text{-}TC\sqrt{3}a\sqrt{3}ac$, $4H\text{-}M\sqrt{3}a\sqrt{3}b2c$ and $4H\text{-}M\sqrt{3}b\sqrt{3}a3c$ and by triangles for $6R\text{-}M\sqrt{3}a\sqrt{3}b2c$, and the sites with the letter M are occupied by Ti atoms. In this manner, the stacking sequences are represented by $LMNPLMNP\cdots$ for $4H\text{-}M\sqrt{3}a\sqrt{3}b2c$ and $LMNPQRLMNPQR\cdots$ for $12R\text{-}TC\sqrt{3}a\sqrt{3}ac$, $6R\text{-}M\sqrt{3}a\sqrt{3}b2c$ and $4H\text{-}M\sqrt{3}b\sqrt{3}a3c$, respectively.

It has been revealed that short-range order exists in a crystal of $12R$ near $Ti_{1.25}S_2$. The crystal as grown at 873 K by a chemical-transport process has three-dimensional short-range order, *i.e.* $12R$-(SRO)(SRO)(SRO). A crystal annealed at 723 K has two-dimensional long-range order and one-dimensional short-range order, *i.e.* $12R\text{-}H2a2a$(SRO). The supercell dimension suggests that the arrangement model in an ordered layer of $12R\text{-}H2a2a$(SRO) is as follows: one quarter of the sites are occupied by Ti atoms and three quarters are regularly vacant. This arrangement has been known as an ordered layer in $2H\text{-}M2b2a2c$ (Bando *et al.*, 1980), the composition of which is very similar to that of $12R\text{-}H2a2a$(SRO).

Once formed, polytypes such as $12R$ or $4H$ can exist over a large composition range (Saeki & Onoda, 1982*a*,*c*). As described in this paper, each polytype has a tendency to generate the superstructure according to the composition. The arrangement model in an ordered layer is dependent on the composition of the specimen, while the periodicity along the c axis arises from the definite stacking sequence of the ordered layers.

The authors thank Drs I. Kawada, M. Ishii and H. Nozaki for valuable discussions.

References

Bailey, S. W., Frank-Kamenetskii, V. A., Goldsztaub, S., Kato, A., Pabst, A., Schulz, H., Fleischer, M., Taylor H. F. W. & Wilson, A. J. C. (1977). *Acta Cryst.* A**33**, 681–684.

Bando, Y., Saeki, M., Onoda, M., Kawada, I. & Nakahira, M. (1979). *Acta Cryst.* B**35**, 2522–2525.

Bando, Y., Saeki, M., Onoda, M., Kawada, I. & Nakahira, M. (1980). *J. Solid State Chem.* **34**, 381–384.

Bando, Y., Saeki, M., Sekikawa, Y., Matsui, Y., Horiuchi, S. & Nakahira, M. (1979). *Acta Cryst.* A**35**, 564–569.

Bartram, S. F. (1958). PhD dissertation, Rutgers Univ., New Brunswick, New Jersey, USA.

Legendre, J.-J., Moret, R., Tronc, E. & Huber, M. (1975). *J. Appl. Cryst.* **8**, 603–608.

Moret, R., Huber, M. & Comès, R. (1976). *Phys. Status Solidi A*, **8**, 695–700.

Moret, R., Tronc, E., Huber, M. & Comès, R. (1978). *Philos. Mag.* B**38**, 105–119.

Onoda, M. & Saeki, M. (1980). *Chem. Lett.* pp. 665–666.

Onoda, M., Saeki, M. & Kawada, I. (1979). *Z. Anorg. Allg. Chem*, **457**, 62–74.

Saeki, M. & Onoda, M. (1982*a*). *Bull. Chem. Soc. Jpn*, **55**, 113–116.

Saeki, M. & Onoda, M. (1982*b*). *Bull. Chem. Soc. Jpn*, **55**, 3144–3146.

Saeki, M. & Onoda, M. (1982*c*). In preparation.

Saeki, M., Onoda, M., Kawada, I. & Nakahira, M. (1981). *J. Less Common Met.* **77**, 131–135.

Tronc, E. & Huber, M. (1973). *J. Phys. Chem. Solids*, **34**, 2045–2058.

Tront, E. & Moret, R. (1981). *J. Solid State Chem.* **36**, 97–106.

Tronc, E., Moret, R., Legendre, J.-J. & Huber, M. (1975). *Acta Cryst.* B**31**, 2800–2804.

Wiegers, G. A. & Jellinek, F. (1970). *J. Solid State Chem.* **1**, 519–525.

Acta Cryst. (1983). B**39**, 39–48

Tetrahedral AX_2 Structures

By A. F. Wells

Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, CT 06268, *USA*

(*Received* 8 *February* 1982; *accepted* 4 *August* 1982)

Abstract

Structures built from tetrahedral AX_4 groups sharing some or all of their X atoms may be classified according to the numbers of tetrahedra to which the X atoms belong. This survey is restricted to structures of composition AX_2 in which all AX_4 groups share their X atoms in the same way, and it is concerned with the topology rather than the geometry of the structures. If v_x is the number of X atoms of each AX_4 group common to x such groups (that is, x is the coordination number of X) then $\sum v_x = 4$ and $\sum v_x/x = 2$. A study is made of the types of structure, finite, one-, two-, or three-dimensional, which are possible in the three classes, I ($v_2 = 4$), II ($v_1 = 1$, $v_3 = 3$), and III ($v_1 = 1$, $v_2 = 1$, $v_4 = 2$).

0567-7408/83/010039-10$01.50