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# Interlayer Short-Range Order of Titanium Vacancies in $\mathrm{Ti}_{1\cdot43}\mathrm{S}_2$-4*H*

By Mitsuko Onoda, Masanobu Saeki and Isao Kawada

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

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## Abstract

Diffuse streaks were observed on an electron diffraction pattern of $\mathrm{Ti}_{1\cdot43}\mathrm{S}_2$-4*H*. A model of an interlayer short-range order of Ti vacancies was proposed and examined by application of the matrix method for the one-dimensional disorder. The calculated diffuse intensity distribution explains the broad maxima observed.

## Introduction

Polytypism was observed for titanium sulfide (Tronc & Huber, 1973; Legendre, Moret, Tronc & Huber, 1975), and $\mathrm{Ti}_{1+x}\mathrm{S}_2$ ($x = 0\cdot2-0\cdot4$) crystallizes most easily in the 4*H*-type structure. The superstructure of $\mathrm{Ti}_{1\cdot33}\mathrm{S}_2$-4*H* was first found by Bartram (1958). Samples of the composition near $\mathrm{Ti}_{1\cdot33}\mathrm{S}_2$ ($=\mathrm{TiS}_{1\cdot50}$) have been examined by powder X-ray diffractometry (Onoda, Saeki & Kawada, 1979): $\mathrm{Ti}_{1\cdot37}\mathrm{S}_2$-4*H* ($=\mathrm{TiS}_{1\cdot46}$-4*H*) annealed at 773 or 973 K and $\mathrm{Ti}_{1\cdot32}\mathrm{S}_2$-4*H* ($=\mathrm{TiS}_{1\cdot51}$-4*H*) annealed at 773, 973 or 1173 K exhibited supercell reflections which were assigned to the order of Ti vacancies, while no supercell reflection was observed in the powder pattern of $\mathrm{Ti}_{1\cdot43}\mathrm{S}_2$-4*H* ($=\mathrm{TiS}_{1\cdot41}$-4*H*).

In the present paper, the appearance of diffuse streaks on an electron diffraction pattern of $\mathrm{Ti}_{1\cdot43}\mathrm{S}_2$-4*H* is reported. An interlayer short-range-order model is proposed and examined by application of the matrix method which has been used for one-dimensional disorder (Kakinoki & Komura, 1965; Kakinoki, 1967; Onoda & Kawada, 1980).

## Experimental

The powder samples of $\mathrm{Ti}_{1\cdot43}\mathrm{S}_2$-4*H* were synthesized as reported previously (Onoda *et al.*, 1979) and annealed at 873, 1073 or 1273 K for one week and then immersed in cold water with their sealing silica tubes. The crystal fragments were obtained by crushing and electron diffraction patterns were taken using a 100 kV electron microscope (Hitachi-500 type). Since the electron diffraction patterns thus obtained are found to be similar, the patterns of the sample annealed at 1073 K are used for discussion.

## Results and discussion

The diffraction patterns are fundamentally of the 4*H* type ($a = 3\cdot438$, $c = 11\cdot432$ Å). In the pattern with the incident beam perpendicular to the *c* axis, diffuse streaks appear as shown in Fig. 1. A section of the diffuse streaks indicates the hexagonal cell with $A = \sqrt{3}a$, and this hexagonal cell arises from an intralayer order of Ti vacancies. When the hexagonal supercell of $\sqrt{3}a$ is regarded as a unit cell, reciprocal coordinates of the diffuse streaks are expressed by $HK\zeta$ ($H-K \neq 3n$), *e.g.* $H=1$ and $K=0$. Then the diffuse intensity distributions may be examined on the basis of the stacking disorder model.

The 4*H*-type substructure and the superstructure analyzed for $\mathrm{Ti}_{1\cdot37}\mathrm{S}_2$-4*H* (Onoda *et al.*, 1979) are shown in Fig. 2. The equidistant-layer approximation is employed for simplicity. Based on the hexagonal cell with $A = \sqrt{3}a$, the structure of the 4*H* type with an intralayer order of Ti vacancies can be described in terms of the stacking sequence of the layer units whose sizes are expressed by using $\mathbf{A}_1$, $\mathbf{A}_2$ and $\mathbf{C}$ shown in Fig. 2. Only the contribution of partially occupied Ti layers is necessary to consider the short-

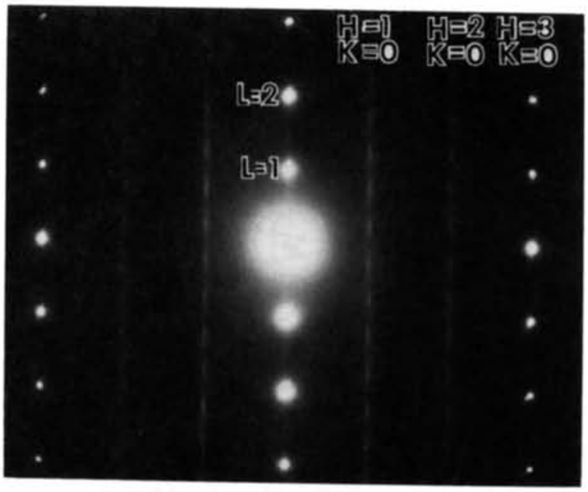

Fig. 1. Electron diffraction patterns from $\mathrm{Ti}_{1\cdot43}\mathrm{S}_2$-4*H*. The incident beam is parallel to the $[\bar{1}10]$ direction of the 4*H* type (hexagonal unit cell: *a*, *c*). Indices (*H*, *K* and *L*) are based on the hexagonal cell with $A = \sqrt{3}a$ and $C = c/2$.

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Table 1. *Probability table based on the layers illustrated in Fig.* 3

| $l-1$ | $l$ | Q1 Q2 Q3<br>P1 | P1 P2 P3<br>Q1 | Q2 Q3 Q1<br>P2 | P2 P3 P1<br>Q2 | Q3 Q1 Q2<br>P3 | P3 P1 P2<br>Q3 |
|---|---|---|---|---|---|---|---|
| Q1 | P1 |  | 0·0 |  | 0·5 |  | 0·5 |
| Q2 |  |  | 0·5 |  | 0·0 |  | 0·5 |
| Q3 |  |  | 0·5 |  | 0·5 |  | 0·0 |
| P1 | Q1 | 0·0 |  | 0·5 |  | 0·5 |  |
| P2 |  | 0·5 |  | 0·0 |  | 0·5 |  |
| P3 |  | 0·5 |  | 0·5 |  | 0·0 |  |
| Q2 | P2 |  | 0·5 |  | 0·0 |  | 0·5 |
| Q3 |  |  | 0·5 |  | 0·5 |  | 0·0 |
| Q1 |  |  | 0·0 |  | 0·5 |  | 0·5 |
| P2 | Q2 | 0·5 |  | 0·0 |  | 0·5 |  |
| P3 |  | 0·5 |  | 0·5 |  | 0·0 |  |
| P1 |  | 0·0 |  | 0·5 |  | 0·5 |  |
| Q3 | P3 |  | 0·5 |  | 0·5 |  | 0·0 |
| Q1 |  |  | 0·0 |  | 0·5 |  | 0·5 |
| Q2 |  |  | 0·5 |  | 0·0 |  | 0·5 |
| P3 | Q3 | 0·5 |  | 0·5 |  | 0·0 |  |
| P1 |  | 0·0 |  | 0·5 |  | 0·5 |  |
| P2 |  | 0·5 |  | 0·0 |  | 0·5 |  |

range order of Ti and vacancies. All six possible configurations of these layers are shown in Fig. 3. The six layers for stacking are divided into two groups, *P* and *Q*, with respect to the positions of the layers. Each group is divided into three types such as *P*1, *P*2 and *P*3 with respect to the Ti sites in a partially occupied Ti layer. In order to maintain the structure in the 4*H* type, a *P*-type layer (*P*1, *P*2 or *P*3) must be followed only by a *Q*-type layer (*Q*1, *Q*2 or *Q*3) and *vice versa.* Since the composition is richer in Ti than $Ti_{1.33}S_2$, excess Ti atoms are assumed to occupy the vacancy sites. Therefore, layer form factors of *P*1 and *Q*1 for the calculation of the diffuse intensity distribution are given by

$$V_{P1} = L^{1/2}(\xi, \eta) f_{\mathrm{Ti}}(1 + \delta\varepsilon^* + \delta\varepsilon)$$

and

$$V_{Q1} = L^{1/2}(\xi, \eta) f_{\mathrm{Ti}}(1 + \delta\varepsilon^* + \delta\varepsilon)\sigma,$$

where $L(\xi, \eta)$ is the Laue function involving $\mathbf{A}_1^*$ and $\mathbf{A}_2^*$, $f_{\mathrm{Ti}}$ is the atomic scattering amplitude for electrons of the Ti ion, $\delta$ is the occupancy factor of Ti in the vacancy sites, $\varepsilon = \exp[i2\pi(H-K)/3]$, $\sigma = \exp[i2\pi(H+K)/3]$ and $\varepsilon^* = \varepsilon^2$. Since only the relative intensity distribution is of interest, the essential terms of $V_{P1}$ and $V_{Q1}$ are $f_{\mathrm{Ti}}$ and $f_{\mathrm{Ti}}\sigma$ respectively. *P*2 and *P*3 are obtained from *P*1 by shifts of $\frac{1}{3}$ and $\frac{2}{3}$ in the $[\bar{1}10]$ direction of the hexagonal cell with $\sqrt{3}a$, and *Q*2 and *Q*3 are obtained from *Q*1 in the same manner. Then

$$V_{P2} = V_{P1}\varepsilon^*,\ V_{P3} = V_{P1}\varepsilon,\ V_{Q2} = V_{Q1}\varepsilon^*$$
$$\text{and} \quad V_{Q3} = V_{Q1}\varepsilon.$$

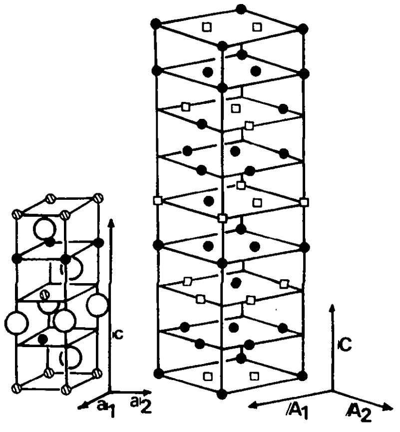

Fig. 2. The 4*H*-type substructure and the superstructure analyzed for $Ti_{1.37}S_2$. ○ S; ● Ti; ◍ partially occupied Ti site; □ vacancy. The primitive hexagonal cell is adopted and S atoms are eliminated for the superstructure, although the superstructure has a monoclinic unit cell ($4H - M\sqrt{3}a\sqrt{3}b2c$). Relations between the vectors shown above are expressed as $\mathbf{A}_1 = \mathbf{a}_1 - \mathbf{a}_2$, $\mathbf{A}_2 = \mathbf{a}_1 + 2\mathbf{a}_2$ and $\mathbf{C} = \mathbf{c}/2$.

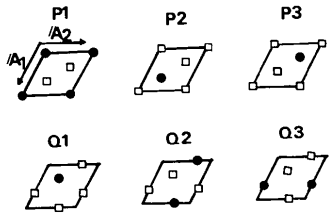

Fig. 3. Possible configurations of the partially occupied Ti layer with intralayer ordering. ● Ti; □ vacancy.

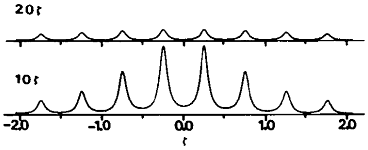

Fig. 4. Intensity distributions of scattering calculated for the model of Table 1. Diffuse intensity distributions corresponding to streaks are obtained for $H-K=1$ and $H-K=2$.

Since diffuse intensity distributions calculated for the models with $s = 1$, where $s$ is the number of layer units necessary to distinguish the stacking disorder, did not resemble the broad maxima observed in Fig. 1, the various models with $s = 2$ were calculated. The results for the model of Table 1 were in agreement with the observed diffuse maxima, as shown in Fig. 4.

In the model of Table 1, the sequences such as *Q*1-*P*1-*Q*1, in which the second-neighbor layers are the same, do not occur, and *Q*1-*P*1-*Q*2 and *Q*1-*P*1-*Q*3 occur with the same probability and so on. The distance between the ordered Ti sites which belong respectively to the second-neighbor layers are shorter for *Q*1-*P*1-*Q*1 than for *Q*1-*P*1-*Q*2 or *Q*1-*P*1-*Q*3 and so on. The calculated results excluded sequences such as *Q*1-*P*1-*Q*1, *Q*1-*P*2-*Q*1, *Q*1-*P*3-*Q*1, *Q*2-*P*1-*Q*2 *etc.* This fact is reasonable with respect to the Coulomb interaction between Ti atoms and vacancies.

The diffuse streaks have not yet been detected in X-ray photographs. The calculated intensities shown in Fig. 4 are the results of kinematical scattering theory. On the assumption that the geometry of the diffuse maxima is not affected by dynamical interactions, the model of Table 1 gives an explanation for the diffuse maxima observed. The designation $Ti_{1\cdot43}S_2$-4$H$-$H\sqrt{3}a\sqrt{3}a$(SRO) is adopted for the structure discussed above, according to the notation system for polytypes and superstructures described previously (Onoda & Saeki, 1983).

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# Concerning the Relative Numbers of Atomic Coordination Types in Tetrahedrally Close Packed Metal Structures

BY DAVID P. SHOEMAKER AND CLARA BRINK SHOEMAKER

*Department of Chemistry, Oregon State University, Corvallis, Oregon* 97331, *USA*

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## Abstract

Tetrahedrally close packed (t.c.p.) metal or alloy crystal structure types are those in which the interstices are exclusively tetrahedral and the coordination types are restricted to a particular set of four, which are here called *P*, *Q*, *R*, and *X*, with fully triangulated coordination polyhedra and coordination numbers (CN) respectively 16, 15, 14, and 12. At least 20 of these are known. Yarmolyuk & Kripyakevich [*Kristallografiya* (1974), **19**, 539-545; *Sov. Phys. Crystallogr.* **19**, 334-337] have shown empirically that the coordination formula of a t.c.p. structure, which may be represented in general as $P_pQ_qR_rX_x$, can be reformulated as $(PX_2)_i(Q_2R_2X_3)_j(R_3X)_k$ (where $i, j, k$ are integers or rational fractions) in the cases of all of the 16 t.c.p. structure types then known. This has also proved true for the four structure types discovered since. It is shown that the relationship results from the requirement that the structure average of the dihedral angles in the interstitial tetrahedra must closely match the appropriately weighted average of the up to four 'cluster' average dihedral angles, where a cluster is defined as an atom plus the 16, 15, 14, or 12 atoms of its coordination shell, and the associated 28, 26, 24, or 20 tetrahedra, respectively, coming together at the central atom. These cluster averages are themselves within about 0·1° of the dihedral angle in the regular tetrahedron, 70·529°. Given the integers $p$, $q$, and $r$ for a t.c.p. formula, with this model $x$ can be calculated correctly for all 20 known t.c.p. structures (although $x$ covers a wide range, up to 49), without any assumptions from Yarmolyuk & Kripyakevich being invoked. A related problem, concerning the close packing of atoms in amorphous metallic glasses, has been treated by some workers in relation to the {3, 3, 5} regular polytope in four-dimensional space. We conclude that while such treatments may provide useful insights for t.c.p. structures, they do not yet satisfactorily explain the Yarmolyuk & Kripyakevich observation.

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