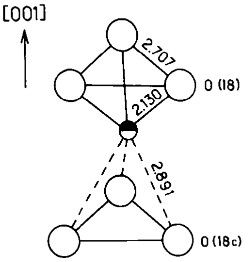

Fig. 5. The anionic environment of Ta(6) (distances are given in Å).

$K_6Ta_{6\cdot5}F_{9\cdot5}O_{14\cdot5}$ and $K_{12}Ta_{15\cdot5}F_{18\cdot5}O_{35\cdot5}$ have practically identical infinite tunnels in their frameworks (tunnel *B*) filled with six K^+ ions and a similar sublattice $[Ta_{0\cdot5}X_3]_n$. This sublattice, to within experimental error, is identical in both cases, except that in the present work no rotational disorder around *z* was observed for the trigonal prism. This may be explained by the formation of strong bonds with three of the six K^+ ions in the tunnel $[K(1)–X(18) = 2\cdot679$ Å].

A study is in progress to determine the homogeneity range in both the $K_6Ta_{6\cdot5}F_{9\cdot5}O_{14\cdot5}$ and $K_{12}Ta_{15\cdot5}F_{18\cdot5}O_{35\cdot5}$ phases due to the partial occupation of the 2(*i*) site by Ta atoms.

References

AWADALLA, A. A. & GATEHOUSE, B. M. (1978). *J. Solid State Chem.* **24**, 349–355.

BOUKHARI, A., CHAMINADE, J. P., VLASSE, M. & POUCHARD, M. (1979). *Acta Cryst.* B**35**, 1983–1986.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

CHAMINADE, J. P., VLASSE, M., POUCHARD, M. & HAGENMULLER, P. (1974). *Bull. Soc. Chim. Fr.* (9–10), 1791–1794.

DAUBEN, C. H. & TEMPLETON, D. H. (1962). *International Tables for X-ray Crystallography*, Vol. III, p. 214. Birmingham: Kynoch Press.

MCMASTER, W. H., KERR DEL GRANDE, N., MALLET, J. H. & HUBBEL, J. H. (1969). *Compilation of X-ray Cross Sections*, UCRL-50174, Sect. II, Rev. I. Washington: National Bureau of Standards.

PERRON-SIMON, A., VON DER MÜHLL, R., RAVEZ, J. & HAGENMULLER, P. (1977). *Mater. Res. Bull.* **12**, 543–547.

POUCHARD, M. & HAGENMULLER, P. (1978). *Solid Electrolytes*, edited by P. HAGENMULLER & W. VAN GOOL. New York: Academic Press.

VLASSE, M., BOUKHARI, A., CHAMINADE, J. P. & POUCHARD, M. (1979). *Mater. Res. Bull.* **14**, 101–108.

VLASSE, M., CHAMINADE, J. P., MASSIES, J. C. & POUCHARD, M. (1975). *J. Solid State Chem.* **12**, 102–109.

VLASSE, M., CHAMINADE, J. P. & POUCHARD, M. (1973). *Mater. Res. Bull.* **8**, 117–126.

VLASSE, M., CHAMINADE, J. P. & POUCHARD, M. (1976). *Bull. Soc. Fr. Minéral. Cristallogr.* **99**, 3–7.

VLASSE, M., CHAMINADE, J. P., SAUX, M. & POUCHARD, M. (1977). *Rev. Chim. Minér.* **14**, 429–434.

Acta Cryst. (1979). B35, 2522–2525

$(4H)_3$-6*C*-Type Superstructure of $TiS_{1\cdot51}$ as Revealed by High-Resolution Electron Microscopy

BY Y. BANDO, M. SAEKI, M. ONODA AND I. KAWADA

National Institute for Researches in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 300-31, *Japan*

AND M. NAKAHIRA

Okayama College of Science, Laboratory of Solid State Chemistry, Ridai-cho, Okayama 700, *Japan*

(*Received* 4 *April* 1979; *accepted* 29 *June* 1979)

Abstract

The $(4H)_3$-6*C*-type superstructure of $TiS_{1\cdot51}$ is examined by 100 kV high-resolution electron microscopy. The crystal has monoclinic symmetry (pseudohexagonal) with lattice parameters $a = 10\cdot3$, $b = 5\cdot92$, $c = 34\cdot9$ Å and $\beta = 90°$. The space group is *Cc*. The metal vacancies are confined to every second metal layer and ordered within the layers, resulting in the formation of a superstructure. They are arranged in a stacking sequence of the 6*C* type along the *c* axis, while S atoms have a 4*H*-type arrangement. It is shown that faults in the stacking of the metal-vacancy layers are present.

The titanium–sulfur system has a variety of structures in the range between TiS and TiS_2 (Jeannin, 1962).

0567-7408/79/112522-04$01.00

Among them, the crystal structure of nonstoichiometric $Ti_{1+x}S_2$ ($0 \cdot 1 < x < 0 \cdot 5$) was first determined by Wadsley (1957) and later refined by Norrby & Franzen (1970). The crystal is hexagonal with lattice parameters $a = 3 \cdot 42$ and $c = 11 \cdot 4$ Å. The S atoms are arranged in hexagonal- and cubic-close-packing units, which are stacked alternately along the *c* axis. Their stacking sequence is referred to as a $4H$ type. The Ti atoms are placed in the octahedral holes between the S atoms and these sites in every second metal layer are only partly occupied. These authors considered that metal vacancies were distributed in a random fashion. Bando, Saeki, Sekikawa, Matsui, Horiuchi & Nakahira (1977, 1979) examined $TiS_{1 \cdot 46}$ crystals by high-resolution electron microscopy and found that the metal vacancies were ordered within the partly filled metal layers, resulting in the formation of the superstructure, which was called a $(4H)_2$-$4C$ type. The $(4H)_2$-$4C$-type superstructure has monoclinic symmetry with lattice parameters $a = 5 \cdot 92$, $b = 10 \cdot 3$, $c = 22 \cdot 8$ Å and $\beta = 90°$. Parallel to the studies of Bando *et al.* (1977, 1979), Onoda, Saeki & Kawada (1979) studied superstructures, referred to as the $4H$ type with compositions near Ti_2S_3, by X-ray powder diffraction. They found that slight differences in chemical composition resulted in two kinds of superstructures. $TiS_{1 \cdot 46}$ was a $(4H)_2$-type superstructure, while $TiS_{1 \cdot 51}$ was a $(4H)_3$ type. The accuracy of intensity measurements from $TiS_{1 \cdot 51}$ crystals was not high ($R = 0 \cdot 20$), because the crystals contained stacking faults. In order to confirm the superstructure model from the $TiS_{1 \cdot 51}$ crystal, structure images were taken by a 100 kV high-resolution electron microscope, in which the arrangements of metal vacancies were obtained directly.

The crystals of $TiS_{1 \cdot 51}$ prepared by Onoda *et al.* (1979) were crushed in an agate mortar to fragments of several microns in size. They were placed on a holey carbon supporting film and observed by the 100 kV electron microscope (Hitachi-500 type). The images, taken at underfocus of about 1000 Å, were interpreted intuitively.

Fig. 1 shows an electron diffraction pattern from the $TiS_{1 \cdot 51}$ crystals. Some of the reflexions are indexed on the basis of a NiAs subcell, although the subcell is not exactly of NiAs type in the present crystal. The incident electron beam was parallel to the $[\bar{1}10]$ direction of the subcell. Superstructure spots were situated at $h = m/3$, $k = n/3$ and $l = r/6$, where m, n and r are integers. The lattice relations between the supercell and the NiAs subcell are $a = 3A_2$, $b = 2A_1 + A_2$ and $c = 6C$, where a, b and c are lattice parameters of the supercell and A_1, A_2 and C those of the NiAs subcell. The symmetry of the superstructure was monoclinic with lattice parameters $a = 10 \cdot 3$, $b = 5 \cdot 92$, $c = 34 \cdot 9$ Å and $\beta = 90°$, which were in good agreement with those obtained by X-ray diffraction (Onoda *et al.*, 1979). The reduced cell is monoclinic with lattice parameters $a = 10 \cdot 3$, $b = 5 \cdot 98$, $c = 11 \cdot 9$ Å and $\beta = 107°$. The systematic absences were $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$. The rectangular monoclinic cell is adopted in this paper. The possible space groups are therefore *Cc* (noncentrosymmetric) or *C*2/*c* (centrosymmetric). Since the sublattice of S atoms has noncentro-

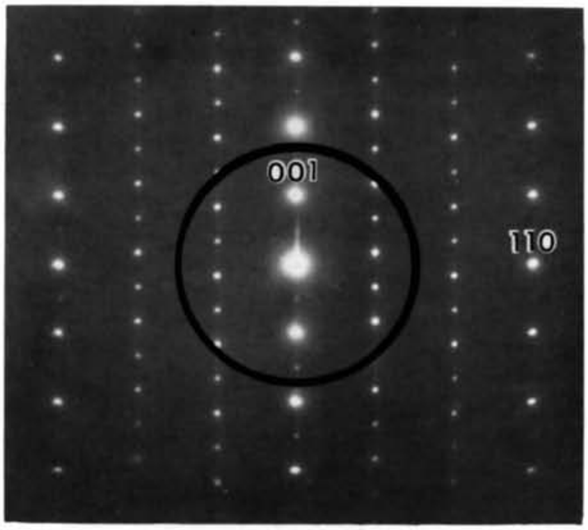

Fig. 1. An electron diffraction pattern from $TiS_{1 \cdot 51}$ crystal fragments. The incident electron beam is parallel to the $[\bar{1}10]$ direction of the subcell. The indexed spots are of fundamental reflexions of the NiAs subcell.

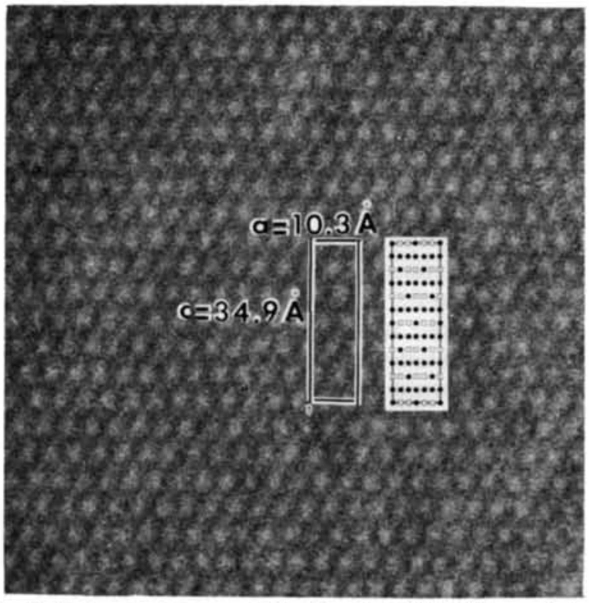

Fig. 2. A structural image obtained by the 100 kV high-resolution electron microscope. The corresponding diffraction pattern is shown in Fig. 1, in which the position and the size of the objective aperture are outlined. The structure model is inserted into the figure, in which open squares indicate the sites of metal vacancies and dark circles those of Ti atoms. The unit cell is outlined: $a = 10 \cdot 3$, $b = 5 \cdot 92$, $c = 34 \cdot 9$ Å and $\beta = 90°$.

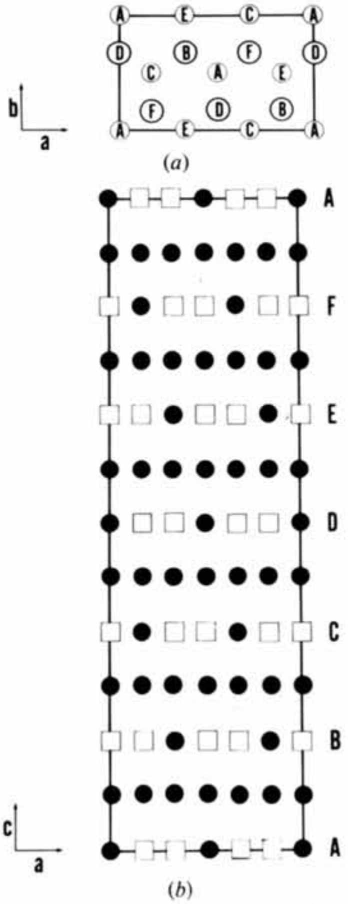

Fig. 3. The $(4H)_3$-6C-type superstructure of $\mathrm{TiS}_{1\cdot51}$. (a) A set of possible sites of Ti atoms within the partly filled metal layers. Light circles A, C and E, and heavy circles B, D and F indicate sites within the same layer. (b) A superstructure projected on to the (010) plane. Open squares indicate sites of metal vacancies and dark circles those of Ti atoms. The S atoms are abbreviated for simplicity. The unit cell is outlined: $a = 10\cdot3$, $b = 5\cdot92$, $c = 34\cdot9$ Å and $\beta = 90°$.

symmetric symmetry, the space group of the present crystal must be *Cc*.

Fig. 2 shows a structure image of a very thin part of the crystal obtained by the 100 kV electron microscope. The corresponding diffraction pattern is shown in Fig. 1, in which the position and the size of the objective aperture are outlined. The size of the objective aperture corresponds to about $0\cdot3$ Å^{-1} in reciprocal space. From the previous observation of $\mathrm{TiS}_{1\cdot46}$ crystals (Bando *et al.*, 1979), it is shown that metal vacancies appear as white spots. A structure model read from the real image is shown in the figure. It can be seen that two neighboring metal-vacancy sites are imaged as a single white spot.

The superstructure of $\mathrm{TiS}_{1\cdot51}$ projected on to the (001) and (010) planes are shown in Fig. 3(*a*) and (*b*), respectively. The sites of the Ti atoms and the vacancies are shown as dark circles and open squares, respectively, in Fig. 3(*b*). S atoms are abbreviated for simplicity. Circles A, C and E in Fig. 3(*a*) represent one set of possible sites of Ti atoms within the partly filled metal layers, and circles B, D and F represent the other set of possible sites of Ti atoms. Metal vacancies are confined to every second metal layer and they are ordered within the partly filled metal layers. Almost two thirds of the metal sites are vacant in such layers. The stacking sequence of metal layers is represented as $\ldots V_AGV_BGV_CGV_DGV_EGV_FGV_A\ldots$ along the c axis, where V_A, V_B, V_C, V_D, V_E and V_F are the defective layers and G the completely filled layers. The layers of S atoms are interleaved with the complete and defective metal layers and form the stacking sequence $\ldots S_1S_2S_1S_3S_1\ldots$ ($4H$ type). Thus, the superstructure of $\mathrm{TiS}_{1\cdot51}$ consists of twelve S layers, six defective metal layers and six completely filled metal layers, and is represented as $\ldots V_AS_1GS_2V_BS_1GS_3V_CS_1GS_2V_DS_1$-$GS_3V_ES_1GS_2V_FS_1GS_3V_A\ldots$ along the c axis. It is then called a $(4H)_3$-6C-type superstructure.

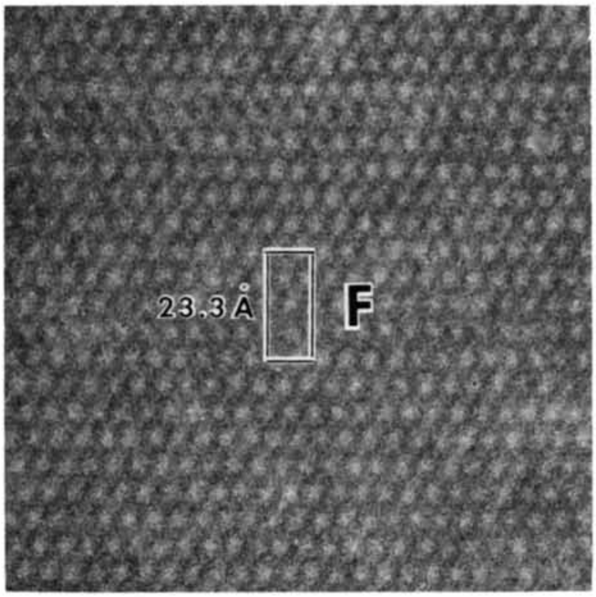

Fig. 4. A defect region observed in $\mathrm{TiS}_{1\cdot51}$. The stacking sequence of layers containing metal vacancies in the region marked as F is $\ldots V_AV_BV_EV_DV_A\ldots$.

In the region marked F in Fig. 4, the arrangement of metal vacancies was different from that in the matrix. The stacking sequence of metal-vacancy layers in the region was $\ldots V_AV_BV_EV_DV_A\ldots$ along the c axis. The stacking periodicity was $23\cdot3$ Å and the arrangement of metal-vacancy layers was identical to that of the $(4H)_2$-4C-type superstructure. The result suggests that the $(4H)_2$-4C-type superstructure may be formed if periodic stacking faults of metal-vacancy layers occur in the $(4H)_3$-6C-type superstructure. The superstructure spots accompanied by streaks in Fig. 1 originate in faults in the stacking of the metal-vacancy layers as shown in Fig. 4.

The authors would like to express their deep gratitude to Dr S. Horiuchi and Mr Y. Matsui for valuable discussions. They thank Mr Y. Sekikawa for help with the electron microscopic observations.

References

Bando, Y., Saeki, M., Sekikawa, Y., Matsui, Y., Horiuchi, S. & Nakahira, M. (1977). Proc. 5th Int. Conf. High Voltage Electron Microscopy, pp. 305–308.

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

Jeannin, Y. (1962). *Ann. Chim. (Paris)*, **7**, 57.

Norrby, L. J. & Franzen, H. F. (1970). *J. Solid State Chem.* **2**, 36–41.

Onoda, M., Saeki, M. & Kawada, I. (1979). *Z. Anorg. Allg. Chem.* In the press.

Wadsley, A. D. (1957). *Acta Cryst.* **10**, 715–716.

Acta Cryst. (1979). B35, 2525–2528

Structure d'Hydrogénoorthophosphates de Thallium(I).
III. Structure du Monohydrogénoorthophosphate de Thallium(I)

Par Yves Oddon, Jean-René Vignalou et Aymond Tranquard

Laboratoire de Physico-Chimie Minérale III, *Université Claude Bernard Lyon* I,
43 *boulevard du* 11 *Novembre* 1918, 69621 *Villeurbanne, France*

et Gérard Pèpe

Centre des Mécanismes de la Croissance Cristalline, Faculté des Sciences de Saint Jérôme,
13397 *Marseille CEDEX* 4, *France*

(*Reçu le* 11 *décembre* 1978, *accepté le* 19 *juin* 1979)

Abstract

Crystals of Tl_2HPO_4 are monoclinic (Pc) with cell parameters: a = 5·215 (2), b = 6·412 (2), c = 16·100 (3) Å and β = 108·92 (3)°; d_m = 6·62 (5) Mg m^{-3}, Z = 4. Full-matrix least-squares refinement led to an R factor of 0·024 on 857 independently measured reflections. Comparison of this structure with the structures of $TlH_5(PO_4)_2$, TlH_2PO_4 and Tl_3PO_4 allows the proposal of a hypothesis to explain the particular properties of Tl^I compounds in relation to the lone pair of electrons on this atom, analogous alkaline phosphates having no such lone pair. The crystal hydrogen-bonding analysis leads to the location of one atom on only one site, while a second H atom is probably shared between two positions.

Introduction

La structure de Tl_2HPO_4 vient compléter la liste des déterminations de structure d'hydrogénoorthophosphates de Tl^I, en relation avec les études physico-chimiques effectuées sur les différents sels.

Une comparaison de la structure du composé présentement étudié avec celles de $TlH_5(PO_4)_2$ (Oddon, Pèpe, Vignalou & Tranquard, 1978), de TlH_2PO_4 (Oddon, Pèpe & Tranquard, 1979) et Tl_3PO_4 (Ganne & Tournoux, 1973) permet de comprendre la différence de propriétés chimiques qui existe entre ces phosphates et les phosphates alcalins du même type, à partir d'une hypothèse fondée sur l'existence du doublet solitaire sur Tl^+.

Le monohydrogénophosphate de Tl^I est préparé par action d'acide orthophosphorique sur du thallium très pur en présence d'eau oxygénée (Oddon, Porte, Coffy & Tranquard, 1975); les monocristaux de ce composé sont obtenus par évaporation lente d'une solution dont la composition est choisie à l'intérieur du domaine d'existence de ce sel. Ils se présentent sous forme de baguettes transparentes et incolores de 2 à 3 mm de long et de 0,5 mm de diamètre. La mise en évidence d'un effet piézoélectrique net indique que les cristaux appartiennent obligatoirement à une classe de symétrie dépourvue de centre de symétrie.

Données radiocristallographiques

Des études radiocristallographiques préliminaires, effectuées sur chambre de précession, semblent indiquer une maille cristalline orthorhombique ($Pna2_1$) avec les paramètres cristallins a = 6,39; b = 15,16 et c = 5,20 Å. L'impossibilite d'interpréter la structure dans ce

0567-7408/79/112525-04$01.00