

## Refinement of the Crystal Structure of Nonstoichiometric $Ti_{2+x}S_4$ \*

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Single crystals of the nonstoichiometric compound  $Ti_{2+x}S_4$  have been prepared in a vapor transport reaction. X-ray diffraction data were collected with an automatic single crystal diffractometer. The crystal structure proposed by Wadsley [*Acta Cryst.* 10, 715 (1957)] has been confirmed and refined to a crystallographic reliability index of 2.6%. The compositional parameter  $x$  has been determined to be  $0.455 \pm 9$ . One of the two crystallographically independent sites for Ti is only partially occupied in a random fashion. The Ti atoms are octahedrally coordinated by S with an additional Ti rather close. One of the S atoms is coordinated to a trigonal prism and the other one to an octahedron of Ti atoms. Accurate interatomic distances have been derived. There are no S-S bonds and probably no Ti-Ti bonds either. The lattice parameters of the hexagonal unit cell have been determined to be  $a = 3.4198 \pm 4 \text{ \AA}$  and  $c = 11.444 \pm 2 \text{ \AA}$ .

### Introduction

The titanium-sulphur binary system has received much attention over a period of about thirty years. Studies in the composition range between mono- and disulphide have been undertaken, to the best of our knowledge, by Blitz, Ehrlich and Meisel (1), Hahn and Harder (2), Wadsley (3), Bartram (4), Jeannin (5, 6), Jacquin and Jeannin (7), Jellinek (8), Flink, Wieggers and Jellinek (9) and Wieggers and Jellinek (10). The nonstoichiometric compound treated in this paper has been observed and studied by several of the above-mentioned authors. It has been assigned different formulas, for example,  $Ti_2S_3$ ,  $Ti_3S_4$ , and  $Ti_{2+x}S_4$ . The last alternative has been adopted in this paper because it is believed to be the most suggestive one, indicating the nonstoichiometric feature of the compound. No attempts have been made in this study to clarify the full and very complex range of composition mentioned above.

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### Experimental

#### Preparative Work

A single crystal sample of  $Ti_{2+x}S_4$  was successfully prepared in a vapor transport reaction. The starting material was titanium monosulphide and ammonium chloride. The latter was added in an amount of about  $6 \text{ mg/cm}^3$  to the inner volume of the fused silica preparation tube to provide the chloride species for vapor transport. The solid starting materials were sealed in a Vycor tube that was evacuated to a residual pressure of  $10^{-2}$  torr. The tube was kept in a temperature gradient of  $900^\circ \rightarrow 700^\circ\text{C}$  for 24 hr, the material being transported from the hotter to the cooler end.

A sulphide-rich condensed phase formed beautiful single crystals with a metallic brownish bulk color. The individual crystals were strongly reflecting with a dark brass-like color. The single crystal selected for the X-ray diffraction experiment was shaped as a hexagonal prism 0.131-mm long with an almost perfect hexagonal cross section 0.060 mm in diameter. The titanium monosulphide used as

starting material had been prepared in a previous step by heating mixtures of titanium fillings and sulphur in a similarly evacuated Vycor tube at 500°C for nine days. The 99.93% titanium metal was obtained from the Chicago Development Corporation, and the 99.999% sulphur from the Galland Schlesinger Chemical Manufacturing Corporation.

### Density Measurements

The density of the sample was determined both pycnometrically and by weighing in benzene to an average value of  $3.5 \pm 1$  g/cm<sup>3</sup>.

### X-Ray Work

The identification of the compound was principally made with use of a X-ray photograph obtained in a focusing Guinier-Hägg camera. The powder sample for this was obtained by grinding single crystals in a agate mortar. The accurate lattice dimension determination was also based on such a powder photograph (see Table I). The Guinier film

did not give evidence of axis multiplication or any form of superstructure, facts which were later used in the non-stoichiometric characterization of the compound (see below).

Single crystal X-ray diffraction data were collected with a Siemens Automatic Diffractometer. The symmetry of the reciprocal lattice was assumed to conform with the reflection conditions indicated in previous work on this compound [see (2) and (3)] MoK $\alpha$  radiation was used, the  $\beta$ -radiation being reduced with a Nb filter. All independent reflections within a reciprocal lattice sphere of radius  $\sin \theta/\lambda = 1.15 \text{ \AA}^{-1}$  except the 220 reflection, which was accidentally omitted, were measured in a double peak scan ("5-point measurement"). The 002 reflection, which has a Bragg angle of  $2\theta = 7.10^\circ$ , could not be measured accurately since the low-angle side of the peak was too close to the incident beam. The rest of the data, 297 reflections, were corrected for absorption, Lorentz factor and polarization. The linear absorption coefficient was calculated to  $58 \text{ cm}^{-1}$ . The size of the single crystal was measured visually in a microscope. Least-squares (L.S.) refinement of the lattice dimensions and the corrections applied to the diffractometer data were performed on an IBM 1800 computer.

TABLE I

GUINIER POWDER PATTERN OF  $Ti_{2+x}S_4$

(CuK $\alpha_1$  radiation,  $\lambda = 1.54050 \text{ \AA}$ . KCl added as an internal standard  $a_{KCl} = 6.29194 \pm 9 \text{ \AA}$ , 20°C.)

Intensity <sup>a</sup>	<i>h k l</i>	$\text{Sin}^2 \theta_{\text{obsd}} 10^5$	$\text{Sin}^2 \theta_{\text{calcd}} 10^5$
<i>st</i>	0 0 2	1810	1812
<i>vw</i>	1 0 0	6766	6763
<i>mst</i>	1 0 1	7213	7217
<i>st</i>	1 0 2	8576	8576
<i>mst</i>	1 0 3	10829	10841
<i>m</i>	1 0 4	14010	14012
<i>exw</i>	0 0 6	16321	16309
<i>vw</i>	1 0 5	18087	18089
<i>est</i>	1 1 0	20300	20291
<i>m</i>	1 1 2	22090	22104
<i>w</i>	1 0 6	23074	23073
<i>w</i>	2 0 1	27517	27508
	(1 1 4		27540)
<i>m</i>	2 0 2	28868	28868
<i>m</i>	0 0 8	29022	28994
<i>mst</i>	2 0 3	31146	31133
<i>vw</i>	2 0 4	34281	34304
<i>vw</i>	1 1 6	36598	36601
<i>mst</i>	2 0 5	38411	38381
<i>w</i>	1 0 9	43431	43459

$$a = 3.4198 \pm 4 \text{ \AA}, \quad c = 11.444 \pm 1 \text{ \AA}$$

<sup>a</sup> Intensity notation in falling magnitude: *est*, *st*, *mst*, *m*, *w*, *vw*, *exw*

### Crystal Structure Refinement

Least-squares refinement was started utilizing the full matrix program LALS on an IBM 360/75 computer. One scale factor and four individual isotropic temperature factor coefficients were refined. The atomic scattering factors used for Ti and S were obtained from Cromer (11).

At first, the two slightly different structure models suggested by Hahn and Harder (2) were tried. Their first alternative converged to a crystallographic reliability index *R*, defined by

$$R = \frac{\sum |F_{\text{obsd}} - |F_{\text{calcd}}||}{\sum F_{\text{obsd}}} \cdot 100.$$

of 22%, and their second to 42%. Then the structure model proposed by Wadsley (3), which is similar to those first tried, but with a different, acentric space group, was tried. An *R* value of 6% was obtained, although no atomic positional parameters were refined. Clearly, the data collected in this investigation fitted very well with Wadsley's model, and all subsequent refinements were based on that structure.

The five strongest structure factors observed were much smaller than the calculated ones. This was considered to be due to extinction. No extinction correction was applied, but these five reflections were

TABLE II  
WEIGHT ANALYSES AFTER LAST CYCLE OF LEAST-SQUARES REFINEMENT  
(The  $w\Delta^2$  quantities are average values normalized to 1.00.)

$F_{\text{obsd}}$ -Interval	$w\Delta^2$	Number of Reflections	Sin $\theta$ -Interval	$w\Delta^2$	Number of Reflections
0.0-2.5	0.70	29	0.00-0.38	1.96	37
2.5-3.8	1.22	29	0.38-0.48	0.98	28
3.8-4.6	1.45	29	0.48-0.55	1.45	33
4.6-5.8	0.96	29	0.55-0.60	0.86	29
5.8-6.8	0.38	30	0.60-0.65	0.81	32
6.8-8.4	1.06	29	0.65-0.69	0.59	27
8.4-10.3	1.18	29	0.69-0.73	0.75	27
10.3-13.2	1.58	29	0.73-0.76	0.93	30
13.2-17.9	0.61	29	0.76-0.79	0.64	25
17.9-35.1	0.88	30	0.79-0.82	0.58	24

instead excluded in the further refinements. The observed and calculated structure factors for these are included, however, in Table V and marked with asterisks. All weak reflections were used in the refinement, even when the relative error in intensity,  $\sigma(I_{\text{obsd}})/I_{\text{obsd}}$ , was about unity. A refinement with anisotropic thermal parameters was also carried out but without significant effect. Also the anomalous dispersion corrections, according to Cromer (12), were tried without significant effect, even when the signs of the imaginary terms were reversed.

In the structure model given by Wadsley there are two crystallographically different titanium sites. Ti(1) is completely occupied, while Ti(2) is only partially so. When comparing the lattice dimensions and density obtained in this study with values given in previous works, the composition of the compound studied should be  $\approx \text{Ti}_{2.42}\text{S}_4$ . By means of the full matrix L.S. program LINUS, it was possible, however, to refine the occupancy parameter and the isotropic temperature factor coefficient of Ti(2) simultaneously. Of course, there is a large correlation between these two parameters, but the value of the correlation coefficient obtained, 0.79, is not larger than those generally obtained between scale factors and temperature factor coefficients. The occupancy parameter thus refined yields a compositional parameter  $x = 0.455 \pm 9$ . The unit cell then contains one unit of  $\text{Ti}_{2.455}\text{S}_4$ . The density calculated on the basis of this composition and the lattice dimensions given above is  $3.522 \pm 6 \text{ g/cm}^3$ , which compares well with the observed density (see above), i.e., the composition derived in the L.S. refinement is reasonable.

The quantity minimized in the L. S. refinement was

$$\sum w(F_{\text{obsd}} - |F_{\text{calcd}}|)^2,$$

and the weights applied were

$$w = 1/\sigma^2(F_{\text{obsd}}).$$

Assuming, as usual, the following relation,

$$F_{\text{obsd}} \propto [I_{\text{obsd}} \cdot Lp^{-1} \cdot A^*]^{1/2},$$

where  $Lp$  is the Lorentz-polarization factor and  $A^*$  the absorption factor,  $\sigma(F_{\text{obsd}})$  was derived as

$$\sigma(F_{\text{obsd}}) = \frac{F_{\text{obsd}}}{2} \cdot \left[ \left( \frac{\sigma(I_{\text{obsd}})}{I_{\text{obsd}}} \right)^2 + \left( \frac{\sigma(Lp^{-1})}{Lp^{-1}} \right)^2 + \left( \frac{\sigma(A^*)}{A^*} \right)^2 \right]^{1/2}.$$

The factor in brackets thus contains the sum of the squares of the relative errors of the observed intensity, the inverse of the  $Lp$  factor and the absorption factor, respectively. The first term was calculated (IBM 1800) for each reflection on the basis of the counter statistics. For all reflections the second term was found to be smaller than the first one by a factor of  $10^4$  or more and, hence, could be cancelled. The relative error in the absorption factor was assumed to be constant over all reflections and estimated to be 5%. The weights thus derived served well, as indicated by a value of 1.15 of the standard deviation of an observation of unit weight,  $[\sum w\Delta^2/(n-m)]^{1/2}$ , which is expected to be 1.00, as well as by reasonable weight analyses (see Table II). The  $R$  value, defined

TABLE III  
LEAST-SQUARES REFINED PARAMETERS OF THE  
CRYSTAL STRUCTURE OF  $Ti_{2+x}S_4$ <sup>a</sup>

Atom	Multiplier	<i>z</i>	B (in Å <sup>2</sup> )
Ti (1)	1	$\frac{2}{3}$	$0.631 \pm 7$
Ti (2)	$0.2273 \pm 43$	$0.01551 \pm 18$	$0.403 \pm 31$
S (1)	1	$0.37711 \pm 7$	$0.504 \pm 9$
S (2)	1	$0.12461 \pm 9$	$0.573 \pm 9$

<sup>a</sup> The three first atoms are in the point position 2 (*b*)  $\frac{1}{3}, \frac{2}{3}, z$  and the last atom is in 2 (*a*) 0, 0, *z* of the spacegroup  $P6_3mc$ .

above, finally obtained was 2.6%. The final structural parameters are contained in Table III.

### Description and Discussion of the Crystal Structure

Each titanium atom is located at the centre of a (slightly distorted) octahedron of sulphur atoms with an additional Ti neighbor at a distance of 3.04 Å. This distance is larger by 0.24 Å than the sum of the Slater atomic radii (13) for two Ti atoms. Following Slater, this fairly short Ti–Ti distance should correspond to, at most, very weak Ti–Ti interactions. The sulphur atoms are located at the

center of (slightly distorted) polyhedra of titanium, S(1), in a trigonal prism and S(2) in an octahedron. These two kinds of coordination polyhedra alternate in the *c* direction sharing triangular faces. There are no sulphur–sulphur bonds. See Table IV and Fig. 1.

The crystal structure can also be represented by layers of atoms stacked perpendicular to the hexagonal *c* axis with a spacing of  $\approx 1/8$ . Each layer contains only one kind of atoms. The stacking sequence is Ti(2), S(1), Ti(1), S(2), Ti(2). This can be represented by the array *ABCBABCBA...* or *chchch...*, i.e., alternating cubic and hexagonal close packing. It should be recognized that the *A* layers are only about 25% occupied. In their work on transition metal-rich chalcogen compounds, Franzen and coworkers found chalcogen coordination numbers between six and nine [see, for example, (14) and references therein]. They proposed, as an explanation for these high coordination numbers, that chalcogen *d* orbitals are used in the bonding to transition metals. Consideration of sulphur *d* orbitals also provides a rationalization for the non-stoichiometric structure reported here. Thus, the six-coordination of sulphur in  $Ti_{2+x}S_4$  suggests utilization of sulphur *d* orbitals. As was shown above, more than 3/4 of the Ti(2) atoms constituting the trigonal prism and octahedra of Ti around S are missing. The fact that the structure sustains such

TABLE IV  
INTERATOMIC DISTANCES IN  $Ti_{2+x}S_4$

Reference Atom	Neighbouring Atom	Number of Neighbouring Atoms	Distance (in Å)
Ti (1)	S (2)	3	$2.441 \pm 1$
	S (1)	3	$2.452 \pm 1$
	Ti (2)	1	$3.038 \pm 2$
	Ti (2)	3	$3.332 \pm 2$
	Ti (1)	6	$3.420 \pm 0$
Ti (2)	S (2)	3	$2.336 \pm 1$
	S (1)	3	$2.531 \pm 1$
	Ti (1)	1	$3.038 \pm 2$
	Ti (1)	3	$3.332 \pm 2$
	Ti (2)	6	$3.420 \pm 0$
S (1)	Ti (1)	3	$2.452 \pm 1$
	Ti (2)	3	$2.531 \pm 1$
	S (1)	6	$3.420 \pm 0$
	S (2)	3	$3.453 \pm 1$
	S (2)	Ti (2)	3
Ti (1)		3	$2.441 \pm 1$
S (2)		6	$3.420 \pm 0$
S (1)		3	$3.453 \pm 1$

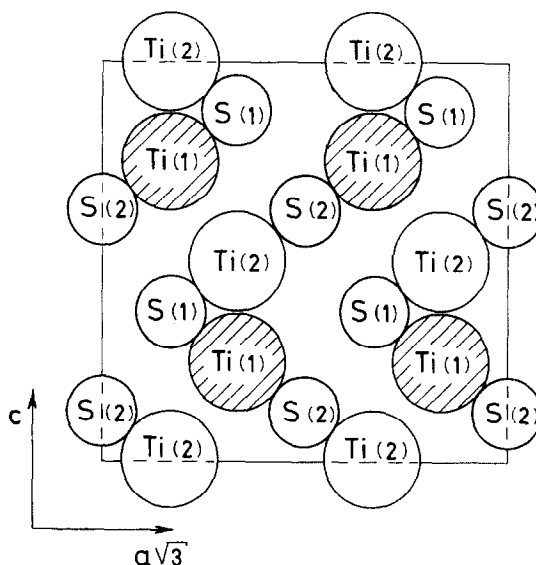


FIG. 1. The crystal structure of  $Ti_{2+x}S_4$  represented by a section of the hexagonal (110) plane. The atoms are drawn with radii according to Slater. Sulphur atoms—small circles ( $r_S = 1.00$  Å). Titanium atoms—large circles ( $r_{Ti} = 1.40$  Å). The completely filled Ti(1) sites are hatched, while the Ti(2) sites, which are occupied only to about 23% are open.

TABLE V  
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  $Ti_{2+x}S_4$

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
	(0, 0, L)		24	1.2	-1.3	8	13.8	13.6	21	5.1	-5.0	8	2.3	-2.4
			25	3.9	-3.9	10	3.4	-3.7	22	5.9	6.0	9	3.9	4.0
4	7.7	7.0				12	0.9	-1.4				10	8.6	8.7
6	23.9	24.4		(3, 0, L)						(4, 1, L)		11	13.2	-13.1
*8	42.9	58.4					(1, 1, L)					12	6.7	-6.6
10	13.4	-14.3	*0	41.7	44.0				0	26.7	26.6	13	8.3	8.3
12	7.1	-7.2	2	12.2	-11.5	*0	55.7	67.6	2	7.4	-6.7	14	9.0	8.7
14	14.6	-14.6	4	5.6	-5.2	2	19.3	-18.9	4	3.2	-2.9	15	4.2	-4.2
16	26.9	28.1	6	12.0	-12.2	4	4.1	-4.5	6	7.6	-7.6	16	1.7	-1.8
18	7.8	-7.9	8	34.1	35.1	6	17.8	-18.0	8	22.5	22.2	17	3.8	3.4
20	3.7	-4.5	10	8.7	-8.6	*8	42.5	47.4	10	5.9	-5.8	18	5.0	5.1
22	9.4	-9.5	12	4.9	-5.0	10	11.6	-11.6	12	2.9	-2.5	19	8.1	-8.1
24	11.5	12.0	14	10.3	-10.4	12	6.7	-6.7	14	7.3	-7.2	20	3.0	-3.4
26	4.7	-4.5	16	20.4	20.1	14	12.7	-12.9	16	13.8	13.5			
			18	6.2	-6.2	16	24.4	25.0	18	4.6	-4.5		(4, 2, L)	
	(1, 0, L)		20	2.7	-2.9	18	7.3	-7.3						
			22	7.2	-7.3	20	4.1	-3.8		(5, 1, L)		0	2.2	-2.3
0	10.2	-8.8				22	8.7	-8.7				1	3.4	-3.4
1	17.7	16.2		(4, 0, L)		24	10.4	10.9	0	1.7	-2.2	2	8.5	8.5
2	35.1	35.6							1	3.0	3.1	3	11.9	11.6
*3	42.9	-46.0	0	2.8	-2.7		(2, 1, L)		2	7.6	7.5	4	7.1	-7.1
4	28.4	-27.5	1	5.4	5.1				3	10.7	-10.6	5	10.0	-9.9
5	35.1	35.6	2	13.8	13.7	0	4.6	-4.5	4	6.5	-6.4	6	8.9	8.6
6	27.5	29.2	3	17.9	-17.6	1	8.4	8.4	5	8.8	9.0	7	3.8	3.9
7	12.9	-13.0	4	11.0	-10.8	2	20.2	20.6	6	7.9	7.7	8	2.0	-2.1
8	5.5	-5.4	5	15.1	15.0	3	26.5	-26.8	7	3.6	-3.6	9	3.0	-2.9
9	9.0	9.2	6	14.1	13.6	4	16.8	-16.5	8	1.7	-2.0	10	6.2	6.2
10	18.5	19.0	7	5.4	-5.4	5	22.2	22.4	9	2.4	2.6	11	10.0	9.9
11	25.1	-26.2	8	2.4	-2.6	6	20.3	20.0	10	5.7	5.6	12	5.1	-5.0
12	13.3	-13.4	9	4.3	4.4	7	7.9	-8.0	11	9.4	-9.1	13	5.9	-6.2
13	16.3	16.4	10	10.0	9.9	8	4.0	-3.4	12	4.5	-4.5	14	6.5	6.4
14	16.8	17.2	11	14.7	-14.4	9	6.4	6.5	13	5.4	5.6	15	3.2	3.4
15	7.2	-6.9	12	7.5	-7.4	10	14.5	14.4	14	5.9	6.0	16	1.4	-1.5
16	2.8	-2.8	13	9.2	9.2	11	20.4	-19.9	15	3.2	-3.1			
17	6.4	6.4	14	10.0	9.7	12	10.4	-10.3					(5, 2, L)	
18	9.5	9.9	15	4.5	-4.6	13	12.8	12.7		(6, 1, L)				
19	13.8	-13.9	16	1.9	-2.0	14	13.6	13.5				0	14.5	14.6
20	5.8	-6.1	17	4.0	3.8	15	5.8	-5.7	0	1.6	-1.8	2	4.2	-3.8
21	7.2	7.5	18	5.7	5.6	16	2.5	-2.4	1	2.0	-2.2	4	0.8	-0.6
22	8.4	8.5	19	8.9	-8.8	17	5.0	5.1	2	5.0	5.0	6	4.1	-4.3
23	4.3	-4.0	20	3.8	-3.7	18	7.6	7.8	3	7.5	7.4	8	12.6	12.5
24	2.1	-1.4	21	4.6	4.7	19	11.6	-11.5	4	4.6	-4.5	10	3.3	-3.4
25	3.9	4.2				20	4.4	-5.0	5	6.2	-6.3			
26	4.5	4.7		(5, 0, L)		21	6.1	6.1	6	5.4	5.3		(3, 3, L)	
						22	6.8	7.0	7	2.7	2.6			
	(2, 0, L)		0	2.7	-2.4	23	3.6	-3.5				0	21.2	21.5
			1	4.0	-3.7	24	0.7	-1.2		(2, 2, L)		2	5.9	-5.5
0	6.5	-6.3	2	9.4	9.5							4	2.1	-1.7
1	11.0	-11.1	3	13.1	12.8		(3, 1, L)		2	10.3	-9.7	6	6.3	-6.3
2	23.3	24.9	4	8.0	-7.8				4	5.2	-4.9	8	18.4	18.2
3	31.7	33.1	5	11.0	-10.9	0	2.8	-3.0	6	10.6	-10.6	10	4.8	-4.8
4	20.1	-20.3	6	9.9	9.6	1	5.9	-5.8	8	30.3	31.0	12	1.9	-1.8

TABLE 5 (continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
5	26.7	-27.1	7	4.0	4.2	2	15.6	15.6	10	7.8	-7.7	14	6.0	-6.1
6	23.1	23.5	8	2.2	-2.2	3	19.9	19.9	12	4.3	-4.3	16	11.2	11.3
7	9.6	9.8	9	3.3	-3.2	4	12.5	-12.2	14	9.5	-9.5			
8	4.1	-4.1	10	6.9	6.9	5	16.9	-16.9	16	17.9	18.2		(4, 3, L)	
9	7.5	-7.6	11	11.0	10.9	6	15.7	15.3	18	5.8	-5.7			
10	16.3	16.4	12	5.5	-5.5	7	5.9	6.0	20	2.6	-2.5	0	2.1	-2.0
11	22.2	22.6	13	6.6	-6.8	8	2.5	-2.7	22	6.6	-6.8	1	2.0	2.6
12	11.7	-11.6	14	7.5	7.1	9	5.2	-5.0				2	6.0	6.1
13	14.6	-14.4	15	3.6	3.7	10	11.2	11.1		(3, 2, L)		3	8.9	-8.8
14	15.1	15.2	16	1.1	-1.6	11	16.2	15.9				4	5.4	-5.3
15	6.4	6.3	17	2.6	-2.9	12	8.4	-8.2	0	2.5	-2.6	5	7.1	7.4
16	3.0	-2.6	18	4.0	4.3	13	10.3	-10.2	1	4.7	4.6	6	6.5	6.3
17	5.6	-5.7				14	11.1	10.7	2	10.3	12.1	7	2.8	-3.1
18	8.5	8.8		(6, 0, L)		15	5.0	4.9	3	15.8	-15.8	8	1.7	-1.8
19	12.8	12.7				16	2.5	-2.1	4	9.7	-9.6	9	2.4	2.1
20	5.3	-5.5	0	16.0	16.0	17	4.3	-4.2	5	13.5	13.4	10	4.5	4.6
21	6.8	-6.8	2	4.6	-4.1	18	6.3	6.2	6	12.2	12.0	11	7.5	-7.7
22	7.4	7.7	4	1.2	-0.8	19	9.7	9.6	7	4.7	-4.9	12	3.9	-3.8
23	3.7	3.7	6	4.6	-4.8	20	4.1	-4.1						

a large number of "vacancies" rather than collapsing to form a new structure with lower sulphur coordination (e.g., tetrahedral) suggests the existence of a bonding feature. It is seen that the Ti(1) and Ti(2) sites on a triad next to a S(1) atom constitute a trigonal prism *geometrically*. In  $Nb_2Se$ , ordered "holes" were shown to exist (14) completing trigonal prisms around the chalcogen atom. In the same way it is here believed that the geometric shape of the trigonal prisms and octahedra of Ti atoms around S is maintained by a disordered arrangement of holes. These are not, however, void space, but are thought to contain electrons in directed nonbonding orbitals.

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