

The System Titanium-Sulfur. II. The Structures of Ti_3S_4 and Ti_4S_5

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The crystal structures of rhombohedral Ti_3S_4 and hexagonal Ti_4S_5 were determined by X-ray powder diffraction methods. The structures are based on close packings of sulfur atoms of the types $(chchch)_3$ and $(chch)_2$, respectively; the metal atoms lie in part of the octahedral holes of these packings. The occupancies of the various metal positions were determined; they can be described by *occupation waves*. Correlations of the compositions of titanium sulfides in the range Ti_2S_3 -TiS with the observed interatomic distances, stacking sequences and occupation waves are given and discussed.

Introduction

The system titanium-sulfur is a complicated one (1). The phase relations in the composition range TiS_2 -TiS were studied by Jeannin (2), (3), and (4) who found the phases listed in Table I. The disulfide TiS_2 has a trigonal structure of the $Cd(OH)_2$ type, the monosulfide TiS a hexagonal structure of the NiAs type (1); in both these structures the metal atoms lie in octahedral holes of a hexagonal-close-packed sulfur lattice (Fig. 1). The structures of the sulfides with compositions between TiS_2 and TiS are more complicated, however.

Hahn and Harder (5) found the structures of hexagonal Ti_2S_3 and rhombohedral Ti_8S_9 (which they called Ti_3S_4 and high-temperature-TiS) to be based on sulfur packings of the types $chch$ and $chhchhchh$, respectively, again with titanium in part of the octahedral holes in the sulfur lattice. [For a

discussion of the *c-h* symbolism see, e.g., (6)]. Wadsley (7) confirmed the outlines of the proposed structures. However, he (8) found the vacancies in the metal positions of Ti_2S_3 not to be randomly distributed over all octahedral holes in the sulfur packing [as Hahn and Harder (5) had assumed], but to be confined to alternate layers of metal sites (Fig. 1). This partial ordering of occupied and vacant metal sites was confirmed by Bartram (9) and by us (1), who also found the vacancies in the metal positions in Ti_8S_9 to be confined to some of the sites, as shown in Fig. 1 and Table IV.

In a previous communication (10) we described the structure of the rhombohedral phase Ti_5S_8 . It is based on a close packing of sulfur of the type $cchh\ cchh\ cchh$, again with titanium in part of the octahedral holes. The vacancies in the metal positions are confined to every second layer, as in Ti_2S_3

TABLE I

SPACE GROUPS AND UNIT-CELL DIMENSIONS OF TITANIUM SULFIDES Ti_pS ($0.5 < p \leq 1$)

| Phase | Composition Ti_pS | Space Group | a in Å | c in Å | Ref. |
|-----------|------------------------|----------------|----------|---------------------------|------|
| TiS_2 | $p = 0.519$ | $P\bar{3}m$ | 3.408 | $5.698 = 2 \times 2.849$ | (2) |
| | 0.550 | | 3.413 | $5.714 = 2 \times 2.857$ | (2) |
| Ti_5S_8 | 0.60 | $R\bar{3}m$ | 3.418 | $34.36 = 12 \times 2.863$ | (10) |
| Ti_2S_3 | 0.629 | $P6_3mc$ | 3.422 | $11.442 = 4 \times 2.860$ | (2) |
| | 0.726 | | 3.442 | $11.431 = 4 \times 2.858$ | (2) |
| Ti_3S_4 | 0.77 | $R\bar{3}m$ | 3.441 | $60.48 = 21 \times 2.880$ | |
| Ti_4S_5 | 0.81 | $P6_3/mmc$ | 3.439 | $28.93 = 10 \times 2.893$ | |
| Ti_8S_9 | 0.89 | $R\bar{3}m$ | 3.425 | $26.493 = 9 \times 2.944$ | (9) |
| TiS | | $P6_3/mmc$ | 3.299 | $6.380 = 2 \times 3.190$ | (9) |

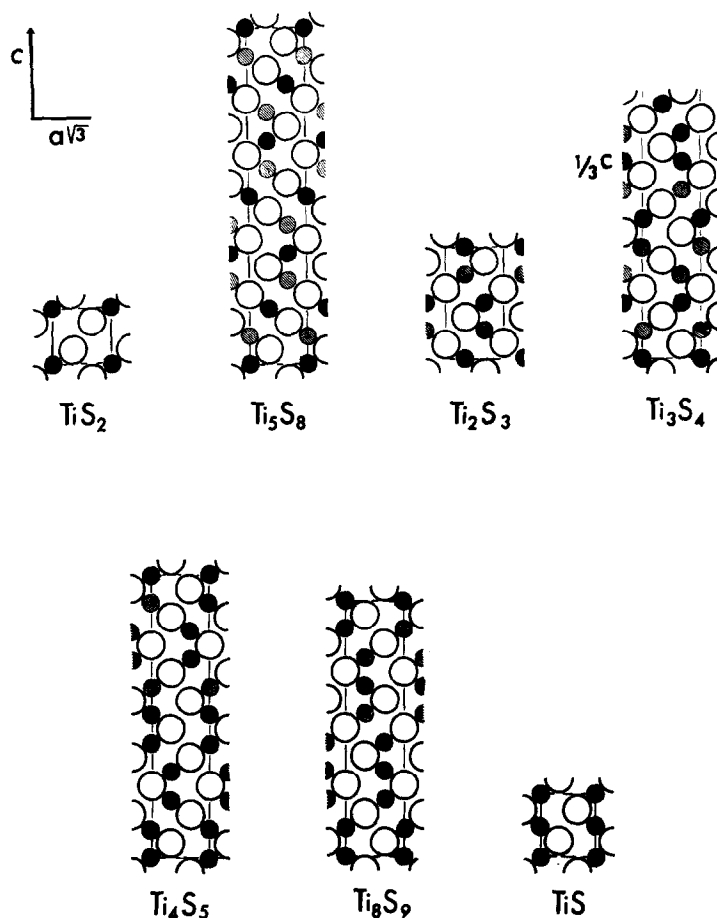


FIG. 1. Sections through the hexagonal (110) planes of titanium sulfides in the range TiS_2 - TiS . Open circles indicate sulfur positions, black circles (nearly) fully occupied metal positions, and hatched circles partly occupied metal positions. For Ti_3S_4 only one third of the unit cell is shown.

(Fig. 1). In the same paper (10) we showed the phase Ti_4S_5 to be hexagonal or trigonal and Ti_3S_4 to be rhombohedral [not monoclinic as Jeannin (3) had proposed]. The unit-cell dimensions are included in Table I.

The present communication describes the structures of Ti_3S_4 and Ti_4S_5 and discusses the structures and the distribution of the metal atoms in the titanium sulfides in the range TiS_2 - TiS .

Experimental

The samples were prepared by heating weighed quantities of titanium sponge and sulfur at 1000°C in evacuated quartz tubes, the inner walls of which had been covered by a carbon film. The samples were quenched to room temperature and studied by X-ray diffraction. While single crystals of Ti_2S_3 and Ti_8S_9 were frequently obtained, the phases

Ti_3S_4 and Ti_4S_5 were always polycrystalline. The pure phase Ti_3S_4 was obtained in a sample of composition $\text{Ti}_{0.77}\text{S}$. Almost pure Ti_4S_5 was obtained in a sample of composition $\text{Ti}_{0.81}\text{S}$; it was slightly contaminated by Ti_3S_4 .

X-ray powder patterns were registered by a Philips diffractometer (CuK_α radiation); the intensities of the powder lines were measured by planimetry of the diffractograms. Atomic positions and site occupation numbers (for Ti only) were refined by means of the least-squares program T 53 C written by Dr. H. M. Rietveld (R.C.N., Petten, the Netherlands). This full-matrix program permits to include overlapping powder lines in the calculations. Most of the calculations were carried out on the Telefunken TR 4 computer of this University. Atomic scattering factors were taken from Moore (11).

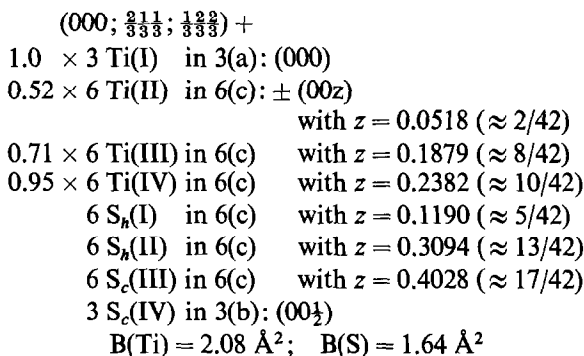
The Structure of Ti_3S_4

It has been shown by us (10) that Ti_3S_4 is rhombohedral; the unit-cell dimensions in hexagonal setting (Table I) indicate that the repeating unit is $3 \times 7 = 21$ sulfur layers thick. The close packings of sulfur with such a repeating unit could readily be derived by applying Zhdanov's symbolism (12). The titanium atoms were (statistically) placed in the octahedral holes of the various possible sulfur packings and diffraction intensities were calculated for these hypothetical models. Satisfactory agreement of calculated and observed intensities was found for the model with a sulfur packing of the type $(chchch)_3$, or in Zhdanov's notation $(2221)_3$.

This model (with space group $R\bar{3}m$) was taken as the starting point for a refinement of the structure by means of the program T 53 C; the refinement was based on the intensities of 22 observed powder lines and of eight lines with zero intensity. Since the occupation numbers of the Ti sites and the thermal parameters of Ti atoms are strongly correlated, all titanium atoms were assumed to have the same (isotropic) temperature factor. Another (isotropic) temperature factor was assigned to all sulfur atoms. Furthermore, six positional parameters, four occupation numbers, and one scaling factor were refined. The final agreement of observed and calculated intensities (Table II) is good; $R_I =$

$100 \Sigma |I_o - I_c| / \Sigma I_o = 5.4\%$ (nonobserved lines included).

The final structure (Fig. 1) can be described in space group $R\bar{3}m$ with the atomic positions and occupation numbers of metal sites given below. (The z parameters of the "ideal" structure from which the refinement was started, are given in brackets; sulfur atoms in h -packed layers are indicated as S_h , sulfur atoms in c -packed layers as S_c .)



Taking into account that the number of adjustable parameters (thirteen) is not small compared with the number of experimental intensities, the standard deviations of the z parameters are calculated as about 0.0007, that of the occupation numbers of the

TABLE II

OBSERVED AND CALCULATED POWDER DIFFRACTOMETER DATA OF Ti_3S_4 ; CuK_α RADIATION

| hkl | θ_o | θ_c | I_o | I_c | hkl | θ_o | θ_c | I_o | I_c |
|-------|------------|------------|-------|-------|-------|------------|------------|-------|-------|
| 009 | 6.61 | 6.58 | 10 | 12 | 10.19 | 20.75 | 20.74 | 10 | 17 |
| 00.12 | 8.79 | 8.79 | 30 | 35 | 01.20 | 21.29 | 21.28 | 70 | 77 |
| 00.15 | 10.97 | 11.01 | 10 | 0 | 10.22 | } 22.42 | 22.41 | 60 | { 63 |
| 00.18 | — | 13.25 | 0 | 5 | 00.30 | | 22.46 | | |
| 101 | } 15.02 | 15.00 | 37 | { 28 | 01.23 | 23.00 | 23.00 | 5 | 4 |
| 012 | | 15.05 | | | 10 | 10.25 | 24.23 | 24.21 | 55 |
| 104 | 15.28 | 15.28 | 37 | 31 | 01.26 | } 24.86 | 24.84 | 55 | { 48 |
| 015 | } 15.47 | 15.44 | 18 | { 18 | 00.33 | | 24.85 | | |
| 00.21 | | 15.51 | | | 1 | 10.28 | 26.15 | 26.13 | 10 |
| 107 | — | 15.87 | 0 | 0 | 110 | — | 26.60 | 260 | { 247 |
| 018 | 16.15 | 16.13 | 21 | 19 | 113 | 26.62 | 26.70 | | |
| 10.10 | 16.78 | 16.75 | 140 | 139 | 01.29 | — | 26.80 | } | 2 |
| 01.11 | 17.11 | 17.10 | 150 | 151 | 116 | — | 27.01 | | |
| 00.24 | — | 17.80 | 0 | 4 | 00.36 | — | 27.29 | 0 | 0 |
| 10.13 | — | 17.88 | 0 | 0 | 119 | — | 27.53 | 0 | 2 |
| 01.14 | 18.31 | 18.30 | 67 | 64 | 10.31 | } 28.21 | 28.16 | 43 | { 37 |
| 10.16 | 19.23 | 19.22 | 230 | 230 | 11.12 | | 28.23 | | |
| 01.17 | 19.72 | 19.71 | 210 | 207 | 01.32 | 28.87 | 28.86 | 28 | 27 |
| 00.27 | — | 20.11 | 0 | 1 | | | | | |

titanium positions as about 0.12. Interatomic distances in Ti_3S_4 are included in Table V; their standard deviations are about 0.05 Å for Ti-Ti and 0.04 Å for Ti-S distances.

The Structure of Ti_4S_5

The unit-cell dimensions of hexagonal Ti_4S_5 (Table I) indicate a repeating unit of 10 close-packed sulfur layers thick; this conclusion was supported by a Patterson synthesis. The possible models with such a repeating unit were deduced by applying Zhdanov's symbolism (12), as described for Ti_3S_4 . Again, the titanium atoms were statistically distributed over the octahedral holes in the close packings of sulfur. Best agreement of calculated and observed intensities (and also of the theoretical and experimental Patterson syntheses) was given by the model with a sulfur packing of the type $(chchh)_2$, or in Zhdanov's notation $(221)_2$.

This model (with space group $P6_3/mmc$) was taken as the starting point for the refinement of the structure by program T 53 C. The refinement was carried out as described for Ti_3S_4 ; it was based on the intensities of 18 observed powder lines and of seven lines with zero intensity. The number of adjustable parameters was nine (four z parameters, three occupation numbers of Ti positions, one over all temperature factor and one scaling factor). The final agreement of observed and calculated intensities (Table III) is satisfactory; $R_f = 13\%$, including nonobserved reflections. The standard

deviations are calculated as about 0.0012 for the z parameters and about 0.05 for the occupation numbers of the titanium positions given below.

The final structure (Fig. 1) can be described in space group $P6_3/mmc$ with the following parameters. (Again, sulfur atoms in h -packed layers are indicated as S_h , sulfur atoms in c -packed layers as S_c ; the z parameters of the *ideal* structure which was the starting point of the refinement, are given in brackets.)

1.00×2 Ti(I) in (2a): 000; $00\frac{1}{2}$

0.62×4 Ti(II) in 4(e): $\pm(00z; 0, 0, \frac{1}{2} + z)$
with $z = 0.105 (\approx 2/20)$

0.88×4 Ti(III) in 4(f): $\pm(\frac{2}{3}\frac{2}{3}z; \frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z)$
with $z = 0.195 (\approx 4/20)$

4 S_h (I) in 4(f) with $z = 0.053 (\approx 1/20)$

4 S_c (II) in 4(f) with $z = 0.650 (\approx 13/20)$

2 S_h (III) in 2(b): $\pm(00\frac{1}{2})$

$$B(Ti) = B(S) = 1.02 \text{ \AA}^2$$

Interatomic distances in Ti_4S_5 are included in Table V; their standard deviations are about 0.04 Å for Ti-Ti and 0.03 Å for Ti-S distances.

Discussion

The determination of the crystal structures of Ti_3S_4 and Ti_4S_5 completes our picture of the structures of the titanium sulfides in the range

TABLE III
OBSERVED AND CALCULATED POWDER DIFFRACTOMETER DATA OF Ti_4S_5 ; $CuK\alpha$ RADIATION

| hkl | θ_o | θ_c | I_o | I_c | hkl | θ_o | θ_c | I_o | I_c |
|-------|------------|------------|-------|-------|-------|------------|------------|-------|-------|
| 004 | — | 6.11 | 0 | 2 | 10.10 | 21.78 | 21.79 | 82 | 125 |
| 006 | 9.20 | 9.19 | 40 | 43 | 00.14 | | 21.88 | | |
| 008 | — | 12.30 | 0 | 0 | 10.11 | 22.98 | 23.00 | 53 | 61 |
| 100 | 15.10 | 14.99 | 127 | 24 | 10.12 | 24.26 | 24.27 | 115 | 108 |
| 101 | | 15.07 | | 75 | 00.16 | 25.20 | 25.21 | 10 | 13 |
| 102 | 15.34 | 15.31 | 107 | 93 | 10.13 | 25.60 | 25.60 | 15 | 18 |
| 00.10 | | 15.44 | | 3 | 110 | 26.61 | 26.66 | 420 | 387 |
| 103 | — | 15.70 | 0 | 2 | 112 | — | 26.81 | 0 | 0 |
| 104 | 16.26 | 16.24 | 50 | 55 | 10.14 | 26.98 | 26.98 | 15 | 22 |
| 105 | 16.92 | 16.91 | 350 | 324 | 114 | — | 27.42 | 0 | 0 |
| 106 | 17.72 | 17.70 | 70 | 93 | 116 | 28.39 | 28.40 | 123 | 8 |
| 107 | 18.59 | 18.59 | 119 | 142 | 10.15 | | 28.41 | | |
| 00.12 | | 18.63 | | 0 | 00.18 | — | 28.63 | 0 | 0 |
| 108 | 19.59 | 19.57 | 600 | 568 | 118 | — | 29.73 | 0 | 0 |
| 109 | 20.65 | 20.64 | 156 | 196 | 10.16 | 29.89 | 29.89 | 7 | 4 |

TiS₂-TiS (Fig. 1). These structures have several features in common; in all cases the sulfur atoms form a close packing, while the titanium atoms lie in octahedral holes of this packing. Table IV gives a survey of the sulfur packings in the various phases and of the occupancies of the metal positions.

In TiS₂, Ti₅S₈ and Ti₂S₃ completely occupied and partly occupied metal layers alternate, as in many other transition-metal chalcogenides. (Superstructures, probably due to ordering of the vacancies within the partly occupied metal layers, have been observed for Ti₂S₃ (9) and Ti₅S₈, but not for the more metal-rich compounds.) In Ti₃S₄, Ti₄S₅ and Ti₈S₉, the occupancy sequence of the metal layers is more complex. Indeed, a preliminary account (13) of the present study has given rise to the comment (14): "It is hard to believe that such an 'irregular' order is reproducible." However, the order is not so irregular as it looks on first sight, as is illustrated by Fig. 2.

Figure 2 gives a plot of the fractional occupancies P_M of consecutive metal layers in TiS, Ti₈S₉, Ti₄S₅, Ti₃S₄ and Ti₂S₃. It is seen that the occupancy of the metal layers can be described by occupation waves. The structural repeat unit consisting of $(2n + 1)$ metal layers and an equal number of sulfur layers,

contains n wavelengths of the occupation waves. For the compounds mentioned $n = 0, 1, 2, 3$, and ∞ , respectively; attempts to prepare compounds with $n = 4, 5$ etc. (their expected structures can readily be derived from the data in Table IV) have failed so far. Similar modulations in the occupancy of metal sites have recently been found in the orthorhombic modifications of Ni_{3±x}Te₂ and Cu_{3-x}Te₂ (15).

TABLE IV
SULFUR PACKINGS AND FRACTIONAL OCCUPANCY OF METAL SITES IN TITANIUM SULFIDES

| Phase | Sulfur Packing | Zhdanov Symbol | Occupancy of Metal Sites |
|--------------------------------|-----------------------|---------------------|---|
| TiS ₂ | hh | (11) | $h\ 1.0\ h\ 0.05\ \dots$ |
| Ti ₅ S ₈ | (cchh) ₃ | (31) ₃ | $c\ 1.0\ c\ 0.2\ h\ 1.0\ h\ 0.2\ \dots$ |
| Ti ₂ S ₃ | (ch) ₂ | (2) ₂ | $c\ 1.0\ h\ 0.4\ \dots$ |
| Ti ₃ S ₄ | (chchch) ₃ | (2221) ₃ | $c\ 0.95\ h\ 0.7\ c\ 0.7\ h\ 0.95$ $c\ 0.5\ h\ 1.0\ h\ 0.5\ \dots$ |
| Ti ₄ S ₅ | (chchh) ₂ | (221) ₂ | $c\ 0.9\ h\ 0.9\ c\ 0.6\ h\ 1.0$ $h\ 0.6\ \dots$ |
| Ti ₈ S ₉ | (chh) ₃ | (21) ₃ | $c\ 0.83\ h\ 1.0\ h\ 0.83\ \dots$ |
| TiS | h ₂ | (1) ₂ | $h\ 1.0\ \dots$ |

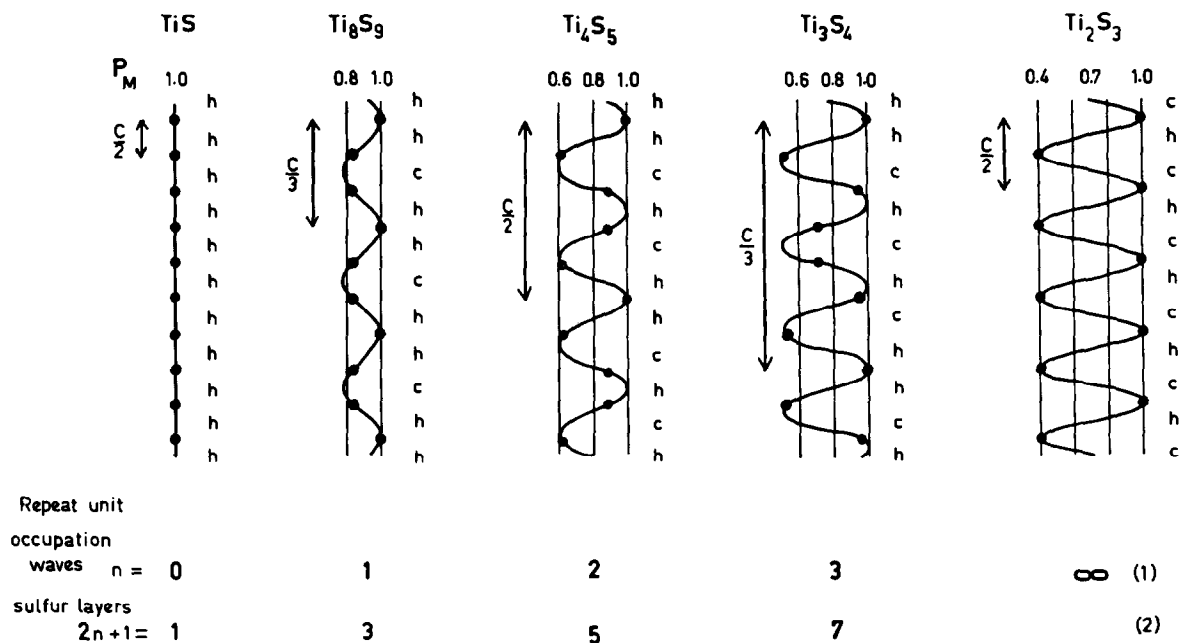


FIG. 2. Occupancy P_M of the metal layers in titanium sulfides in the range Ti₂S₃-TiS; observed fractional occupation numbers are indicated by black dots. The stacking of the sulfur layers is indicated by the symbols c and h . It is seen that the occupancies can be described by occupation waves; there are n such waves in the repeat unit consisting of $(2n + 1)$ metal layers and $(2n + 1)$ sulfur layers.

TABLE V

Ti-Ti AND Ti-S DISTANCES (IN Å) IN TITANIUM SULFIDES

The First Number in Brackets Gives the Multiplicity of Equivalent Distances, the Second Number (for Ti-Ti only) the Occupancy of the Neighboring Metal Positions

| Phase | Metal Atom | Site Occupancy | Ti-Ti distances | | | Ti-S _h | Ti-S _c |
|---|------------|----------------|-----------------------------|-----------------------------|-----------------|-------------------|-------------------|
| | | | Across S _h Layer | Across S _c Layer | Within Ti Layer | | |
| Ti ₂ S ₃ ^a | (I) | 1.0 | 3.02(1 × 0.4) | 3.35(3 × 0.4) | 3.43(6 × 1.0) | | |
| | (II) | 0.4 | 3.02(1 × 1.0) | 3.35(3 × 1.0) | 3.43(6 × 0.4) | | |
| | average | | 3.02 | 3.35 | 3.43 | 2.49(3 ×) | 2.39(3 ×) |
| Ti ₃ S ₄ | (I) | 1.0 | 3.14(2 × 0.5) | — | 3.44(6 × 1.0) | 2.46(6 ×) | — |
| | (II) | 0.5 | 3.14(1 × 1.0) | 3.29(3 × 0.95) | 3.44(6 × 0.5) | 2.61(3 ×) | 2.26(3 ×) |
| | (III) | 0.7 | 3.04(1 × 0.95) | 3.24(3 × 0.7) | 3.44(6 × 0.7) | 2.55(3 ×) | 2.36(3 ×) |
| | (IV) | 0.95 | 3.04(1 × 0.7) | 3.29(3 × 0.5) | 3.44(6 × 0.95) | 2.45(3 ×) | 2.52(3 ×) |
| | average | | 3.09 | 3.27 | 3.44 | 2.52 | 2.38 |
| Ti ₄ S ₅ | (I) | 1.0 | 3.04(2 × 0.6) | — | 3.44(6 × 1.0) | 2.51(6 ×) | — |
| | (II) | 0.6 | 3.04(1 × 1.0) | 3.27(3 × 0.9) | 3.44(6 × 0.6) | 2.49(3 ×) | 2.37(3 ×) |
| | (III) | 0.9 | 3.18(1 × 0.9) | 3.27(3 × 0.6) | 3.44(6 × 0.9) | 2.54(3 ×) | 2.37(3 ×) |
| | average | | 3.09 | 3.27 | 3.44 | 2.51 | 2.37 |
| Ti ₈ S ₉ ^a | (I) | 1.0 | 3.11(2 × 0.83) | — | 3.42(6 × 1.0) | 2.48(6 ×) | — |
| | (II) | 0.83 | 3.11(1 × 1.0) | 3.27(3 × 0.83) | 3.42(6 × 0.83) | 2.55(3 ×) | 2.37(3 ×) |
| | average | | 3.11 | 3.27 | 3.42 | 2.52 | 2.37 |
| TiS | | 1.0 | 3.19(2 × 1.0) | — | 3.30(6 × 1.0) | 2.48(6 ×) | — |
| Ideal lattice ^b | | | 2.90 | 3.51 | 3.43 | 2.45 | 2.45 |

^a Distances calculated with parameters from (9).^b Layers equally spaced; $a = 3.43$ Å, $c = n \times 2.90$ Å.

In the titanium sulfides there are two kinds of sulfur layers, viz., *h*-packed layers and *c*-packed layers. The stacking sequence is correlated with the occupation waves: the *h*-packed layers are found near the maxima of these waves, the *c*-packed layers near the minima (Fig. 2). The proportion of *h*-packed layers increases with increasing metal contents of the compounds. Roughly speaking, one finds *c*-packed sulfur layers where the value of the P_M wave is less than about 0.8, *h*-packed layers where it is larger.

The occurrence of *c*-packed or *h*-packed sulfur layers determines the number and lengths of closest metal-metal approaches. The Ti-Ti distances are of three kinds:

(a) distances across a *h*-packed sulfur layer (one neighboring site);

(b) distances across a *c*-packed sulfur layer (three neighboring sites);

(c) distances within the same metal layer (six neighboring sites).

The Ti-Ti distances observed in the various titanium sulfides are collected in Table V†. The Table also includes the distances expected in *ideal* structures

(with $a = 3.43$ Å; $c = n \times 2.90$ Å), in which all (metal and sulfur) layers are equally spaced; the Ti-Ti distances across *h*-packed sulfur layers would be very short in these ideal structures. (In b.c.c. titanium metal Ti-Ti = 2.896 Å).

It is seen that the observed structures deviate significantly from the ideal ones. The metal and sulfur layers are displaced from their ideal positions in such a way that the Ti-Ti distances across *h*-packed sulfur layers become longer, the Ti-Ti distances across *c*-packed sulfur layers shorter than in the ideal structure. Nevertheless, the Ti-Ti distances across *h*-packed sulfur layers are still short enough to correspond to a strong metal-metal interaction; the frequency of occurrence of such distances increases with increasing metal contents of the compounds (Table V). Quite similar displacements of the atomic layers have been observed in TiP (16) which is isostructural with Ti₂S₃.

† In fact, the observed distances are distances between atomic sites—occupied or vacant—not between atoms. The positions of individual atoms will somewhat depend on the actual occupation of their neighboring sites. The fairly small observed temperature factors indicate that these *short-range distortions* of the (average) structures are not very large.

The displacements of the atomic layers from their ideal positions also affect the Ti-S distances, as is evident from Table V. Generally, the Ti-S_n distances are longer, the Ti-S_c distances shorter than in the ideal structures (where all Ti-S distances would be equal). The average distance of the six sulfur neighbors of each titanium atom is about 2.46 Å.

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