

Structure and Properties of the New Phase of the Pseudo One-Dimensional Compound TaS₃

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The structure of a new form of tantalum trisulfide has been determined from single crystal X-ray diffraction data and refined to an R value of 0.025. The unit cell is monoclinic with space group $P2_1/m$: $a = 9.515(2)$ Å, $b = 3.3412(4)$ Å, $c = 14.912(2)$ Å, $\beta = 109.99(2)^\circ$. The structure consists of sulfur triangular prisms stacked on top of each other by sharing triangular faces. The tantalum atoms are located close to the center of the prisms which are parallel to the b twofold axis. The prisms are linked together in the c direction to form slabs parallel to the b - c plane. This arrangement is very like that observed in NbSe₃. The physical properties, especially the metal-semiconductor transition at 240 K, are discussed according to the structural features such as metal-metal distances and the existence of different S-S pairs.

Introduction

In a previous paper (1) a new form of tantalum trisulfide was characterized with a monoclinic unit cell: $a = 9.515(2)$ Å, $b = 3.3412(4)$ Å, $c = 14.92(2)$ Å, $\beta = 109.99(2)^\circ$. This compound exhibits a metal-semiconductor transition at 240 K and another transition in the semiconducting state at 160 K. TaS₃ was previously known in an orthorhombic form (2, 3) with $a = 36.804$ Å, $b = 15.173$ Å, $c = 3.340$ Å. This variety presents a similar transition at 210 K but none at 160 K. No structural determination had been made for both compounds and this has prevented any critical discussion of the observed physical properties. In the present work, the structure of the monoclinic form has been determined and refined down to $R = 0.025$. The results permitted us to propose some interpretations of the physical properties of both TaS₃

phases and introduce a more general discussion about chalcogenides of IV_B and V_B elements.

Experimental Details

On the basis of preliminary precession and Weissenberg photographs, TaS₃ could be assigned to the monoclinic system; the only systematic absences, namely, OkO for k odd, are consistent with space groups $P2_1$ and $P2_1/m$.

For data collection a crystal was mounted on a NONIUS CAD 3 automatic diffractometer. Experimental data are given in Table I.

Reflections (4179) were measured by the θ - 2θ scan mode in the interval $4^\circ < \theta < 38^\circ$. After having scaled and averaged the intensities, 1766 independent reflections with $\sigma(I)/I \leq 0.20$ were used for the refinement.

TABLE I
EXPERIMENTAL DATA

Space group: $P2_1/m$
Calculated density: 6.20
Crystal
<i>b</i> axis mounted
μ : 406 cm ⁻¹
Data collection
Number of units per unit cell: 6
Radiation: $\lambda\text{MoK}\alpha$
Max θ : 38.00°
Min θ : 4.00°
Scan width: $S_2 = a_2 + b_2 \tan \theta$ $\begin{cases} a_2 = +1.14^\circ \\ b_2 = +0.30^\circ \end{cases}$
Scan type: θ - 2θ coupled
Standard reflections: 208, 415
Periodicity: 30
$I_{\text{min.}} - I_{\text{max.}}$: 400-6000
Maximum number of cycles: 5

The repartition of reflections according to the $\sigma(I)/I$ criterion is given in Table II.

$$\sigma(I)/I = [I_0 + \tau^2(F_1 + F_2)]^{1/2} / [I_0 - \tau(F_1 + F_2)]$$

τ is a ratio of scanning time for the counter $I_0/(F_1 + F_2)$; here $\tau = 0.50$.

These 1766 reflections were corrected for Lorentz and polarization factors. Absorption corrections ($\mu = 406 \text{ cm}^{-1}$) were made with the DATAPH program (4). The crystal shape is approximated as a parallelepiped, the dimensions of which are $0.007 \times 0.02 \times 0.46 \text{ mm}$.

Refinement of the Structure

The structure was refined with the assumption that the atoms were in the $2(e)$ positions of the $P2_1/m$ space group. The SFLS-5 refinement program (5) was used. The function $\sum \omega(|F_0| - K|F_c|)^2$ was minimized; (F is the structure factor and ω the weight assigned to the reflection). Scattering factors for neutral tantalum and sulfur were taken from the International Tables (6) and corrected for anomalous dispersion.

At the end of the refinement, anisotropic

thermal factors were fitted to all atoms using the expression:

$$\exp \left\{ - [h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}] \right\}.$$

An isotropic extinction correction was applied during refinement ($g = 0.266 \times 10^{-6}$). F values are weighted by using the scheme of Hughes (7) with the values:

$$F_1 = 38; F_2 = 54; F_3 = 235; F_4 = 270.$$

The reliability factors stabilize at $R = 0.025$ and $R_w = 0.025$.

$$R = \frac{\sum ||F_0| - K|F_c||}{\sum |F_0|}$$

$$R_w = \frac{[\sum \omega(|F_0| - K|F_c|)^2 / \sum \omega |F_0|^2]^{1/2}}{1}$$

At this stage the variations of the refined parameters are less than 1% of the standard deviations.

The final positional and thermal parameters with their standard deviations are given in Table III; lists of observed and calculated structure factors are available from the authors on request.

Description and Discussion of the Structure

The structure can be regarded as built up with infinite chains of sulfur trigonal prisms stacked on top of each other by sharing triangular faces. The chains are parallel to the b axis and also linked together to form slabs parallel to the b - c plane (Figs. 1 and 2). The tantalum atoms are located close to the center of the prisms. There are six prisms in a unit cell, which are two by two identical (Fig. 1). Interatomic distances for each coordination polyhedron of tantalum are given in Table IV.

Each prism base exhibits a shorter S-S

TABLE II

$\sigma(I)/I$	0.50	0.40	0.30	0.25	0.20	0.15	0.10
Independent reflections	2313	2226	2054	1959	1766	1571	1284

TABLE III
 REFINED POSITIONAL AND THERMAL PARAMETERS^a

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Beq (\AA^2)
Ta I	0.64153(4)	0.25	0.11909(3)	138(3)	970(25)	53(1)	0	29(2)	0	0.43
Ta II	0.69498(4)	0.25	0.79811(3)	169(3)	734(25)	65(1)	0	46(2)	0	0.45
Ta III	0.29736(4)	0.25	0.45911(3)	143(3)	1268(26)	58(1)	0	37(2)	0	0.49
S ₁	0.5649(2)	0.25	0.9366(2)	169(18)	1021(139)	61(7)	0	27(9)	0	0.50
S ₂	0.1693(2)	0.25	0.8971(2)	186(19)	1136(145)	141(9)	0	86(11)	0	0.70
S ₃	0.2007(3)	0.25	0.7640(2)	263(20)	1493(153)	69(8)	0	31(10)	0	0.70
S ₄	0.1656(3)	0.25	0.0837(2)	248(20)	893(141)	87(8)	0	38(10)	0	0.64
S ₅	0.1785(2)	0.25	0.2765(2)	183(19)	1177(144)	75(8)	0	35(10)	0	0.57
S ₆	0.5162(2)	0.25	0.2465(2)	181(19)	1044(141)	69(8)	0	53(10)	0	0.51
S ₇	0.9104(3)	0.25	0.5685(2)	184(19)	1369(150)	99(8)	0	33(10)	0	0.68
S ₈	0.5553(2)	0.25	0.5943(2)	194(19)	719(133)	80(8)	0	49(10)	0	0.51
S ₉	0.7580(3)	0.25	0.4309(2)	295(21)	1238(148)	90(8)	0	77(11)	0	0.71

^a Estimated standard deviations are given in parentheses. Beq, Equivalent isotropic temperature factors; β_{ij} , $\times 10^5$; for space group $P2_1/m$ $\beta_{12} = \beta_{23} = 0$.

distance. Two of these distances, $S_2-S_3 = 2.105(4)$ \AA and $S_7-S_9 = 2.068(3)$ \AA , correspond to the usual S-S distance in the anion $(S_2)^{2-}$. For example, this distance is equal to 2.14 \AA in FeS_2 (8) and is to be compared to the value of 2.05 \AA found in NbS_3 , by Rijnsdorp and Jellinek (9). The third S-S distance $S_4-S_5 = 2.835(3)$ \AA is longer but remains smaller than the S-S distance in a compound such as 2H-TaS_2 for which the distance is equal to 3.315 \AA in the base of $[\text{TaS}_6]$ prisms.

Each tantalum atom (for instance Ta_{II}) is surrounded by six sulfur atoms at distances close to each other: two at 2.461 \AA , two at 2.529 \AA , and the last two at 2.522 \AA . These

sulfur atoms are located at the corners of a trigonal prism around the tantalum atoms. Two other Ta-S distances are not long enough to exclude a bonding. They correspond to two sulfur atoms belonging to two neighboring chains and are responsible of the formation of folded slabs or ribbons of fibers. Considering Ta_{II} these distances correspond to $\text{Ta}_{\text{II}}-S_1 = 2.747$ \AA and $\text{Ta}_{\text{II}}-S_8 = 2.870$ \AA .

The slabs are linked together by weak van der Waals bonds. The three shortest S-S distances between the slabs are 3.259(3) \AA , 3.499(3) \AA , 3.694(3) \AA .

According to its structure TaS_3 appears as a two-dimensional compound with a high

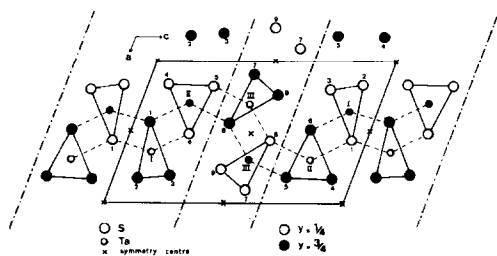


FIG. 1. Projection of the TaS_3 structure on the XOZ plane.

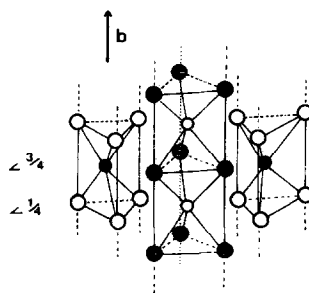


FIG. 2. Stacking of trigonal prisms along the b axis.

TABLE IV
INTERATOMIC DISTANCES (Å) AND STANDARD
DEVIATIONS

Ta polyhedron			
Ta I-2S ₁	2.495(2)		
2S ₂	2.527(2)	S ₁ -S ₂	3.605(3)
2S ₃	2.509(2)	S ₁ -S ₃	3.541(3)
1S ₄	2.564(2)	S ₂ -S ₃	2.105(4)
1S ₅	2.566(3)		
Ta II-2S ₄	2.461(1)		
2S ₅	2.529(2)	S ₆ -S ₄	3.389(3)
2S ₆	2.522(2)	S ₆ -S ₅	3.392(4)
1S ₇	2.747(3)	S ₄ -S ₅	2.835(3)
1S ₈	2.870(2)		
Ta III-2S ₇	2.512(2)		
2S ₈	2.481(2)	S ₈ -S ₇	3.530(4)
2S ₉	2.520(2)	S ₈ -S ₉	3.588(4)
1S ₅	2.566(2)	S ₇ -S ₉	2.068(3)
1S ₉	2.589(2)		
Ta I-Ta II	4.156	S ₂ -S ₄	2.796(4)
Ta II-Ta III	4.207	S ₆ -S ₉	2.920(3)
S-S distances between slabs			
S ₂ -S ₄	3.694(3)	S ₇ -S ₇	3.499(3)
S ₃ -S ₇	3.259(3)		

one-dimensional anisotropy within the slabs, and is related to the NbSe₃ structural type.

It is not possible to study the relationship between monoclinic TaS₃ and the previously known orthorhombic TaS₃ as the structure of the orthorhombic form has not been determined. However it can be seen (Table V: unit cell parameters) that $b_{\text{monoclinic}} = c_{\text{orthorhombic}}$. The b monoclinic parameter represents the Ta-Ta distance in the TaS₃ chains. From this observation it could be assumed that the orthorhombic form is built up with a stacking of similar triangular prisms. From this hypothesis the difference between both structures could stem from the dimensions of the bases of the prisms and their relative arrangement ($Z = 24$ in the orthorhombic form). However this is not the only possible scheme. One knows

that TaS₂ exists in a 1 T (octahedral) as well as a 2 H (trigonal prismatic) form, among several other possibilities; this is due to the fact that the Ta-S bond presents an ionicity close to the critical value separating the octahedral and trigonal prismatic domains in an ionicity diagram (10). In an octahedral structure we would have TaS₃ chains built up with [TaS₆] octahedra sharing faces as the VS₃ chains in BaVS₃ (11). The probability of having such an octahedral structure is in fact very low. The presence of X-X pairs makes it hard to compare with the dichalcogenides. In addition ZrSe₃ is built from trigonal prism units whereas ZrSe₂ present octahedral units.

Electrical Properties

Electrical resistivity measurements have been performed on single crystals with the applied current along the fibers (1). Figure 3 shows a typical curve which presents two transitions at 240 and 160 K. The former is a metal-semiconductor transition which was also observed in orthorhombic TaS₃ by Sambongi *et al.* (12). The latter appears in the semiconducting state and is not observed in orthorhombic TaS₃.

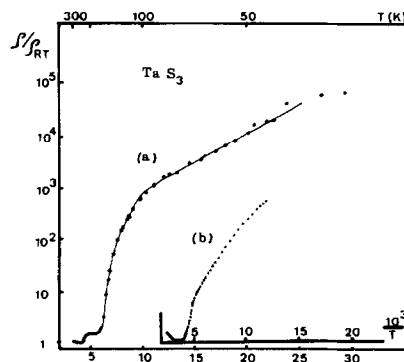


FIG. 3. Semi-log plot of the resistivity of TaS₃ normalized to the room temperature as a function of $10^3/T$: (a) monoclinic TaS₃; (b) orthorhombic TaS₃ (after Sambongi *et al.* (12)).

TABLE V
LATTICE PARAMETERS OF MONOCLINIC AND ORTHORHOMBIC TaS₃

Compound	a (Å)	b (Å)	c (Å)	β (°)	Z	Space group
Monoclinic	9.515(2)	3.3412(4)	14.912(2)	109.99(2)	6	P2 ₁ /m
Orthorhombic ^a	36.804	15.173	3.340		24	C222 ₁

^a These results are from Refs. (2) and (3).

Discussion and Conclusion

In the TaS₃ monoclinic structure it is possible to recognize two types of MX₃ chains according to the length of the S–S pairs in the triangular bases. In the first type the chains correspond to short S–S distances equal to 2.068 and 2.105 Å; in the second type the chains exhibit longer S–S distances of 2.835 Å. As said above, the short distances are explained by the occurrence of (S₂)²⁻ anions. In these chains tantalum atoms would be present as tetravalent cations (Ta⁴⁺ in ionic terms, i.e., d¹). The conducting properties would be linked to these chains. For the second type the longer S–S distance corresponds to a weakening of the bond which implies a higher valence state for the tantalum atoms. We cannot verify the occurrence of a pentavalent cation (Ta⁵⁺ in ionic terms, i.e., d⁰) in these chains as no references exist in this field. This is related to the discussion on trichalcogenides given by Wilson (13) and Jellinek *et al.* (14) (see Fig. 4).

In the more simple case as typified by ZrSe₃, there is only one kind of chain with a short Se–Se distance equal to 2.34 Å. ZrSe₃ can be described by the ionic formula Zr⁴⁺ Se²⁻ (Se₂)²⁻. ZrSe₃ is thus a nonmetallic compound according to the d⁰ configuration.

In the TaSe₃ model, two kinds of chains are observed with the following distances: Se–Se = 2.58 and 2.90 Å. None of the distances fits in with the 2.34

Å length of the (Se)₂ pairs. This suggests that in the corresponding prisms a more or less important ratio of Ta⁵⁺ atoms.

In the case of NbSe₃, one observed three kinds of chains corresponding to a short Se–Se distance of 2.374 Å, a mean distance of 2.485 Å, and a long distance of 2.909 Å. The short length of 2.374 Å is due to a (Se)₂²⁻ pair like in ZrSe₃ and would correspond to Nb⁴⁺. The two other distances correspond to a weakening of the Se–Se bond and a strengthening of the Nb–Se bond. This would bring about an intermediate situation for the niobium atoms (between Nb⁴⁺ and Nb⁵⁺).

This description in terms of the valence states of cations on different chains is a simplification but it can give a picture of the conduction electron density along the different chains. It could be said that the

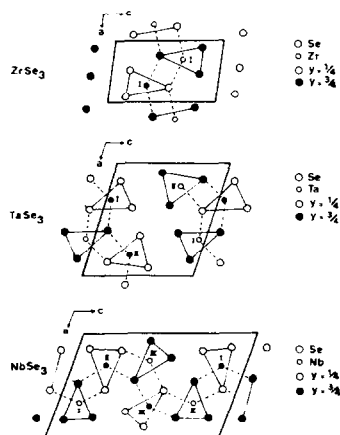


FIG. 4. Projections of the ZrSe₃, TaSe₃, and NbSe₃ structure types on the XOZ plane.

chalcogen pair behaves as "a reservoir of electrons" giving rise to a related variation of the electron density from chain to chain.

A deeper discussion would result from electron band structure investigations as given by Bullett (15) in the case of ZrSe₃, TaSe₃ and NbSe₃. The metal-insulator transition at 240 K, probably due to a "Peierls transition," should correspond to a pairing of tantalum atoms through the sharing of the d electrons. Consequently this pairing should take place on Ta⁴⁺ chains only. This hypothesis has been formulated in the same way by Wilson (13) to localize the two CDW for NbSe₃. No explanation can be put forward at the moment for the second transition at 160 K.

XPS studies (16) in progress must bring information on the valence state of Ta, whereas electronic diffraction studies at low temperature must allow us to determine the occurrence of a possible structural transition.

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