

DETERMINATION OF THE STRUCTURE OF Tl_2S BY THE ELECTRON DIFFRACTION METHOD

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The electron diffraction method was used to perform a repeat determination of the atomic structure of the semiconductor compound Tl_2S . The coordinates of the Tl atoms were refined and the S atoms were localized. The nine-layer Tl_2S structure is the closest to the CdI_2 type. The Tl atoms, strictly speaking, do not form dense packing; one part of the atomic layers of the structure is corrugated.

Numerous compounds of the $A^{III}-B^{VI}$ type form a group of semiconductors, which are interesting from the crystallochemical point of view, and which possess a number of valuable properties. From among the works dealing with the structures of the compounds of this class, such as Tl_2Se [1], In_2Se [2], and Tl_2S [3-6], the investigation [3] is attracting special attention, since it contains an obvious error in the allocation of the S atoms. The authors describe the rhombohedral structure ($a = 13.61 \text{ \AA}$, $\alpha \approx 82^\circ$) of the phase Tl_2S in the hexagonal aspect with $a = 12.20 \pm 0.07$, $c = 18.17 \pm 0.06 \text{ \AA}$, space group $C_3^4 - R3$, and $Z = 27$. The Tl atoms are allocated in six general positions 9(b), namely $(000; \frac{1}{3}, \frac{2}{3}, \frac{1}{3}; \frac{2}{3}, \frac{1}{3}, \frac{2}{3}) + x, y, z; \bar{y}, x - y, z; y - x, \bar{x}, z$ with the parameters $x_1 \approx x_2 \approx x_3 \approx 0.12; x_4 \approx x_5 \approx x_6 \approx 0.23; y_1 \approx y_2 \approx y_3 \approx 0.20; y_4 \approx y_5 \approx y_6 = 0.09; z_1 = z_2 - \frac{1}{3} = z_3 - \frac{2}{3} = 0; z_4 = z_5 - \frac{1}{3} = z_6 - \frac{2}{3} = 0.152 \pm 0.002$. For the S atoms there were determined three general positions 9(b) with the parameters $x_1 = \frac{1}{3}, x_2 = \frac{2}{3}, x_3 = 0; y_1 = \frac{1}{3}, y_2 = 0, y_3 = \frac{2}{3}; z_1 = z_2 - \frac{1}{3} = z_3 - \frac{2}{3} = 0.243 \pm 0.002$. It can easily be seen that the values for the coordinate parameters of the three basal S atoms as presented in [3] are indeed associated with the group symmetry and pertain to a single correct system of the 9(b) points $(\frac{1}{3}; 0; 0.243)$. Thus, in [3], only 9 out of 27 atoms of S were allocated. The error permitted by the authors of [3] naturally poses a question concerning a new structural determination of the phase Tl_2S .

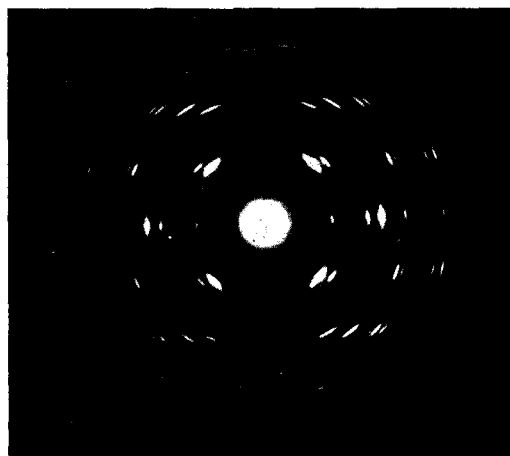


Fig. 1. Electron diffraction pattern of the oblique texture type obtained from Tl_2S films. The angle of filming was $\sim 60^\circ$.

We established the atomic structure of this compound by the electron diffraction method.

The thin films to be used for the present investigation were prepared by fast sublimation in vacuum of the alloy Tl_2S onto a collodion substrate at room temperature, with subsequent annealing at $T \approx 30-40^\circ C$ for 30 min. A typical electron diffraction pattern as obtained from films prepared in such a fashion is presented in Fig. 1. The electron diffraction pattern is indexed on the basis of the hexagonal lattice with $a = 12.20 \pm 0.04$ and $c =$

18.17 ± 0.06 Å, and is characterized by the rhombohedral extinction law for the $-h + k + l \neq 3n$ reflections, which corresponds to the data of [3].¹ The coincidence of the translation groups and the lattice parameters demonstrates that the composition of the phase studied by us is indeed close to Tl₂S. The axis of the texture is the [0001] direction. Under these conditions it would be natural to start the analysis by following [3] and taking the noncentrosymmetric group $C_3^4 - R3$ for Tl₂S. The determination of the intensities of the reflections of the hk0 type was performed microphotometrically. These reflections of the zero layer line were used as a mark of darkening during visual determination of the intensities of the reflections on other layer lines. A verification of the nature of the scattering by the method proposed in [7] showed that the scattering has an intermediary character. The transition from the intensities to the Φ^2 values was worked out following the kinematic scattering formula $|\Phi|^2 = I/pd_{hkl} d_{hk0}$, whereupon the correction was entered for dynamic scattering.

The symmetry group R3 of the compound Tl₂S pertains to the groups for which there is characteristic the presence of systems of planes not related by symmetry and with equal interplanar spacings. The investigation of the atomic structure from electron diffraction patterns of the oblique texture type is in this case made difficult, since the experiment gives only the total intensity of the reflections from the planes with equal d_{hkl} . For brevity, we shall call the magnitudes $|\Phi_{hkl}|^2$, obtained by the dividing of the total intensity into a number of merging independent reflections, "averaged" structural factors.

The indexing of the Tl₂S structure was done from Patterson projections $P(x, y)$, $P(x, z)$, and from the three-dimensional potential series. The fact that the reflections lying on the layer lines with $l = 3n$ are considerably stronger than the remaining ones (the pseudoperiodicity $c' = c/3$) pointed to the lamellar nature of the structure. The projection of the function of the interatomic vectors $P(x, y)$ showed that the x and y coordinates as proposed in [3] for the Tl atoms are acceptable. By the trial and error method, the following positions were chosen for the S atoms: S₁ at 3(a) and $00z_1$; S₂ at 3(a) and $00z_2$; S₃ at 3(a) and $00z_3$; S₄ at 9(b) and $x_4 = 2/3, y_4 = 2/3, z_4$; S₅ at 9(b) and $x_5 = 1/3, y_5 = 2/3, z_5$. The projection of the potential $\varphi(x, y)$ confirmed the correctness of the proposed model. The divergence factor $R_{hk0}^* = 0.264$.

The more accurate determination of the x, y atoms from the projections of the potential $\varphi(x, y)$ and $\varphi(x, z)$ and, in particular, the determination of the z -coordinates of the atoms turned out to be a rather complex task since, on the one hand, the crystallographically independent atoms very accurately overlap on the $\varphi(x, y)$ projection, and on the other hand, as has already been pointed out, some nonequivalent reflections cannot be distinguished on the electron diffraction patterns.

For the space group R3 such merging reflections are the hk0 and kh0; h0l and $\bar{h}0l$ at $h, l = 3n$; hhl and $\bar{h}\bar{h}l$; hkl, $\bar{h}\bar{k}l$, kh \bar{l} , and $\bar{k}\bar{h}l$, at $l = 3n$. By taking into consideration the indices for the systems of equal structural amplitudes for the space group R3 as presented in [8], the indices of the independent reflections were determined, which were merging into one spot, and also the number of such reflections. The divergence factor, as calculated by the use of the "averaged" structural factors, gave the value $R_{hk0}^* = 0.264$, and after the separation of $|\Phi_{hk0}|_{\text{exp}}^2$ and $|\Phi_{kh0}|_{\text{exp}}^2$ in the ratio of $|\Phi_{hk0}|_{\text{calc}}^2$ and $|\Phi_{kh0}|_{\text{calc}}^2$ its value decreased to $R_{hk0} = 0.243$.

In order to plot the Patterson projection $P(x, z)$ we made use of the reflections of the h0l and $\bar{h}0l$ type at $h, l = 3n$, merging into one spot. Since the contribution of each of such reflections to the total intensity is not known, it turned out to be in no way possible to interpret carefully the Patterson projection $P(x, z)$, as plotted by means of the averaged structural factors. The averaged structural factors $|\Phi_{h0l}|^2$ and $|\Phi_{k0l}|^2$ are considerably stronger than $|\Phi_{hk0}|^2$ and $|\Phi_{kh0}|^2$, which were used for the plotting of the projection $P(x, z)$, which results in a considerably greater distortion of the synthesis of $P(x, z)$ as compared to the projection $P(x, y)$.

To find the z coordinates of the atoms, the successive sorting method was employed. The starting model for the lamellar structure was selected under the proposition that the layers of the atoms Tl₁, Tl₂, Tl₃; Tl₄, Tl₅, Tl₆, and S are arranged strictly through $c/3$: $z_1 = 0$; $z_2 = 1/3$; $z_3 = 2/3$; $z_4 = 0.133$; $z_5 = 0.466$; $z_6 = 0.800$ for the Tl atoms, and $z_1 = 0.208$, $z_2 = 0.541$, and $z_3 = 0.874$ for the S atoms. By keeping in mind the possible

¹We should mention that in [3] the extinction law $h - k + l \neq 3n$, and, correspondingly, the $(000; 1/3, 2/3, 1/3; 2/3, 1/3, 2/3)$ alignment, were used. In the present work we used the alignment which is shown in the International Tables; the changeover from it to the aspect of [3] is accomplished by replacing the z coordinates by the $-z$ coordinates.

TABLE 1. Coordinates of the Atoms in the Tl₂S Structure

Atom	Position	x/a	y/b	z/c	Atom	Position	x/a	y/b	z/c
Tl ₁	9(b)	0.119	0.191	0.957	S ₁	3(a)	0	0	0.195
Tl ₂	9(b)	0.122	0.201	0.321	S ₂	3(a)	0	0	0.519
Tl ₃	9(b)	0.118	0.209	0.656	S ₃	3(a)	0	0	0.853
Tl ₄	9(b)	0.233	0.103	0.140	S ₄	9(b)	0.665	0.657	0.226
Tl ₅	9(b)	0.227	0.093	0.474	S ₅	9(b)	0.333	0.337	0.195
Tl ₆	9(b)	0.233	0.096	0.808					

interatomic spacings, we varied within reasonable limits the coordinate z of the first atom (with the spacing of $0.004c$), by pinning thereby all the remaining ones, and we then calculated the value for R_{h0l} . Upon attaining the minimum R_{h0l} value we went on with the separation of the merging reflections and calculated the intrinsic R_{h0l} value for the given model. Thereupon we varied the coordinate z of the following atom, again performed the separation, and so on. Parallel to this, we plotted the $\varphi(x, z)$ projections, during the examination of which it was significant that the peaks of the potential be considered. For the final $\varphi(x, z)$ projection, as plotted with the separation of the $h0l$ and $\bar{h}0l$ reflections, $R_{h0l} = 0.294$.

Further refinement of the coordinates of the atoms was performed from the three-dimensional selection of the structural amplitudes, with the separation of the merging reflections. The calculations were performed on a "BÉSM-4" machine according to the programming complex "kristall." For the separation of the averaged $|\Phi|_{\text{exp}}^2$ in agreement with $|\Phi|_{\text{calc}}^2$ and for the calculation of the divergence factor, special programming was compiled by A. B. Tovbis.

After six stages of the refining of the parameters following the three-dimensional syntheses the divergence factor of the structure $R_{hkl} = 0.300$. The introduction of the dynamic correction [9], and also the more accurate determination of the coefficient by the reduction to the absolute scale² and the more accurate determination of the temperature factor by the least mean-square method ($B = 0.84$) decreased the value of the divergence factor to $R_{hkl} = 0.258$. Unfortunately, existing programs do not allow us to perform a more accurate determination of the coordinate parameters by the least mean-square method during the requirement of separating the merging reflections.

It must be mentioned that the employment of the zero layer line, on which strong reflections are located, as the mark for the blackening of the reflections does not provide the possibility to determine within the same accuracy the intensities of

TABLE 2. Shortest Interatomic Spacings in the Tl₂S Structure

Tl - Tl spacings in Å		Tl - S spacings in Å		
In between the layers	Tl ₁ -Tl ₁	3.52	Tl ₁ -S ₃	2.78
	Tl ₁ -Tl ₂	4.05	Tl ₁ -S ₄	2.92; 3.28
	Tl ₁ -Tl ₃	3.90	Tl ₁ -S ₅	2.91
	Tl ₂ -Tl ₂	3.70	Tl ₂ -S ₁	3.14
	Tl ₂ -Tl ₃	4.00	Tl ₂ -S ₄	3.28
	Tl ₃ -Tl ₃	3.84	Tl ₂ -S ₅	3.22
	Tl ₄ -Tl ₄	4.28	Tl ₃ -S ₂	2.78
	Tl ₄ -Tl ₅	3.73; 4.33	Tl ₃ -S ₄	3.08
	Tl ₄ -Tl ₆	3.63; 4.31	Tl ₃ -S ₅	3.23
	Tl ₅ -Tl ₅	4.18	Tl ₄ -S ₁	2.66
	Tl ₅ -Tl ₆	4.35	Tl ₄ -S ₄	2.67
	Tl ₆ -Tl ₆	4.29	Tl ₄ -S ₅	2.68
In the layer	Tl ₁ -Tl ₄	3.96; 4.11	Tl ₅ -S ₂	2.55
	Tl ₁ -Tl ₅	4.29	Tl ₅ -S ₄	2.51
	Tl ₂ -Tl ₅	3.58; 3.62	Tl ₅ -S ₅	2.70
	Tl ₂ -Tl ₆	3.76	Tl ₆ -S ₁	2.61
	Tl ₃ -Tl ₄	3.64	Tl ₆ -S ₄	2.51
Tl ₄ -Tl ₆	3.59; 3.66	Tl ₆ -S ₅	2.70	

the weak reflections of the layer lines with $l \neq 3n$, containing the information as to the deviations from pseudoperiodicity in the structure, which showed up in the divergence factor value.

The final coordinates of the atoms and the interatomic spacings are presented in Tables 1 and 2. The accuracy in the determination of the coordinates of the Tl atoms was 0.001, and that of the S atoms was 0.003. The structure can be ascribed to the CdI₂ type (with $a = 4.24$, and $c = 6.84$ Å). A simple relationship exists between the unit cell parameters of these compounds, namely $a_{\text{Tl}_2\text{S}} \approx 3a_{\text{CdI}_2}$ and $c_{\text{Tl}_2\text{S}} \approx 3c_{\text{CdI}_2}$. In the first approximation it can be considered that the Tl atoms occupy the positions I, and the S atoms the positions Cd ("triple" layers). The layer of the S atoms is enclosed between two layers of the Tl atoms forming octahedra. The octahedra occupied by the S atoms alternate in layers with vacant octahedra. The octahedra themselves have common sides and are stacked according to the CdI₂-type. The coordination number of the Tl atoms is 3. However, if the I atoms form in hexagonal closest packing, then

²The tables showing the atomic scattering functions for the electrons were used in this work.

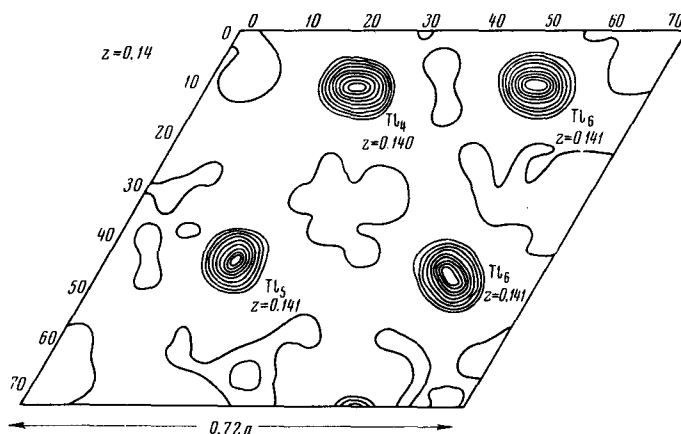


Fig. 2. Profile of the three-dimensional series of the potential $\varphi(x; y; 0.14)$.

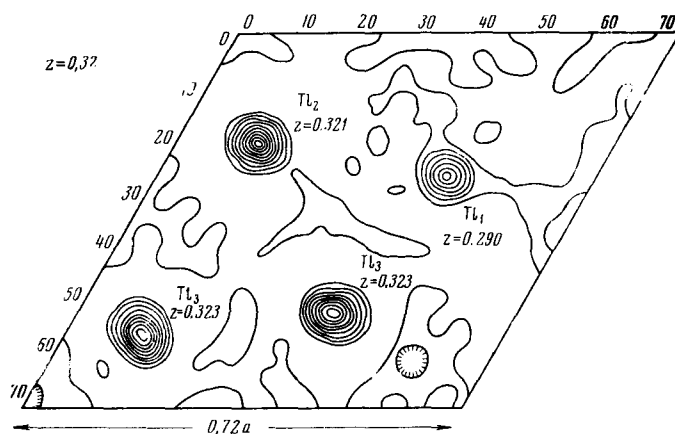


Fig. 3. Profile of the three-dimensional series of the potential $\varphi(x; y; 0.32)$.

the Tl atoms—strictly speaking—do not form such packing. The hexagonal packing of the Tl atoms differs from the ideal ball-packing in that it is extended in the flat (0001) layers (Tl—Tl = 3.52–4.35 Å). While the Tl₄, Tl₅, and Tl₆ as a matter of fact lie in a single layer (Fig. 2), the layer consisting of Tl₁, Tl₂, and Tl₃ atoms is like a corrugated one (Fig. 3). The S atoms form analogous layers. The octahedra of the Tl atoms making up the structure are to a significant degree distorted, whereas the S atoms occupy positions which are not strictly in the centers of the octahedra. This circumstance makes for a rather considerable scatter in the interatomic Tl—Tl and Tl—S spacings. Nevertheless, these spacings are in agreement with the analogous spacings in the compound TlS (Tl—S = 2.59; 3.33 Å) [11] and TlAsS₂ (Tl—S = 2.80; 2.99; 3.00; 3.12; 3.25 Å) [12]. It is obvious that the fundamental interaction in the Tl₂S structure is ac-

complished inside the Tl—S—Tl layers. The sum of the ionic radii Tl¹⁺ and S²⁻ (1.49 + 1.82 = 3.31) is somewhat higher than that of the Tl—S spacings observed in the structure. This interaction is apparently stronger than the ionic one and has a covalent component. The binding forces inside the mentioned triple Tl—S—Tl layers are considerably higher than those between two such layers, as a result of which there is observed in case of Tl₂S an almost perfect cleavage parallel to the base. It can be assumed that the characteristic lamellar nature of the Tl₂S crystals, manifesting itself in the capability of giving oriented residues during the condensation from the vapors, is also explained by the difference in the interaction forces.

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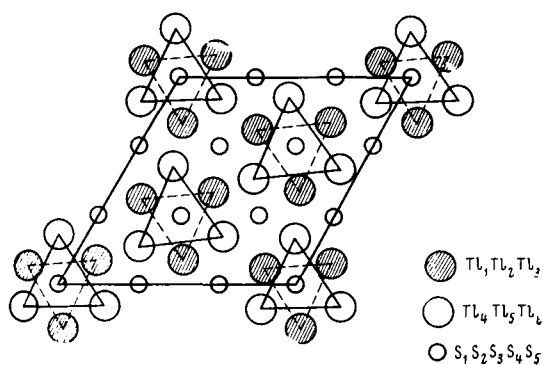


Fig. 4. Projection of the Tl_2S structure onto the (0001) plane.

of the reflections, and also R. M. Imamov, who has displayed great interest in the present work.

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