

CRYSTAL STRUCTURE OF BISMUTH SELENIDES AND BISMUTH AND ANTIMONY TELLURIDES

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Single crystals of the bismuth selenides and the bismuth and antimony tellurides were studied by x-ray diffraction. The crystal structures of Bi_2Se_2 and Sb_2Te_2 were determined. After studying the structures of alloys with compositions $\text{A}_2\text{VX}_3\text{VI}$, $\text{A}_2\text{VX}_2\text{VI}$ and $\text{A}_4\text{VX}_3\text{VI}$, a model was developed for the structure of the solid solutions in the Bi-Se, Sb-Te, and Bi-Te systems. The regions of solid solutions were in fact regions of ordering, in which double A_2 layers, connected together covalently, were uniformly distributed between five-layer packs of the X-A-X-A-X type.

Bismuth selenides and bismuth and antimony tellurides have found wide application in semiconductor technology. Many of these compounds are found in the form of minerals. A study of the phase diagrams of the Bi-Se, Sb-Te, and Bi-Te systems by the method of microstructural and thermal analysis [1-4] has shown that these systems contain compounds of the $\text{A}_2\text{VX}_3\text{VI}$ type melting with an open maximum and also ranges of solid solutions formed by peritectic reactions. The A_2X_3 compounds belong to the structural type of tetradimite [5, 6]. Attempts to discover the nature of the solid solutions by examining the Debye photographs of the alloys have not given any positive results [7]. For this reason we have now made an x-ray study of single crystals of various compositions obtained from the regions of solid solutions.

TABLE 1. Theoretical and Experimental Structure Amplitudes of Bi_2Se_2 ($B = 1.2 \text{ \AA}^2$)

$h0l$	$F_{\text{theor.}}$	$F_{\text{expt.}}$	$h0l$	$F_{\text{theor.}}$	$F_{\text{expt.}}$	$h0l$	$F_{\text{theor.}}$	$F_{\text{expt.}}$
00.1	-22,1	—	00.30	-2,1	—	10.28	-52,4	68,2
00.2	-10,2	15,5	10.0	0	—	10.1	+82,2	80,9
00.3	-33,7	26,2	10.1	-28,2	—	10.2	-8,2	—
00.4	-9,1	—	10.22	-1,6	—	10.3	-63,7	63,5
00.5	-133,0	123,2	10.33	+21,6	—	10.4	+5,0	—
00.6	-2,2	—	10.4	-278,0	254,0	10.5	-20,2	29,5
00.7	+53,0	58,1	10.5	+19,8	—	10.6	-14,8	—
00.8	-10,4	—	10.6	+27,2	29,4	10.7	-21,8	—
00.9	31,8	35,3	10.7	+35,3	25,7	10.8	+232,0	206,0
00.10	-24,8	15,9	10.8	+8,8	—	10.9	-20,4	—
00.11	+24,0	27,2	10.9	+100,0	82,4	10.10	-41,1	37,7
00.12	-205,0	209,0	10.10	+2,3	—	10.11	-41,9	26,3
00.13	+18,6	20,5	10.11	-37,3	42,1	10.12	-13,3	—
00.14	+44,0	56,7	10.12	+15,1	—	10.13	-100,0	92,8
00.15	+42,4	39,0	10.13	-33,0	29,9	10.14	-1,5	—
00.16	+0,9	—	10.14	+18,7	—	10.15	+36,6	34,7
00.17	+90,6	92,6	10.15	+18,9	—	10.16	-8,8	—
00.18	+0,1	—	10.16	+145,8	125,5	10.17	+34,6	129,3
00.19	-34,7	42,5	10.17	-19,2	—	10.18	-13,1	—
00.20	+8,1	—	10.18	-43,5	57,6	10.19	+21,9	—
00.21	-32,8	37,8	10.19	-42,3	36,5	10.20	-108,0	106,0
00.22	+10,3	—	10.20	+2,6	—	10.21	+18,2	—
00.23	-16,1	15,5	10.21	-75,0	84,5	10.22	+38,4	49,2
00.24	+87,5	80,0	10.22	+3,3	—	10.23	+39,2	54,5
00.25	-15,7	—	10.23	+36,8	51,1	10.24	-7,6	—
00.26	-32,2	29,5	10.24	-2,6	—	10.25	+60,2	78,1
00.27	-35,6	27,6	10.25	+33,3	44,4	10.26	-3,7	—
00.28	-10,0	—	10.26	-2,0	—	10.27	-37,6	52,6
00.29	-51,4	48,9	10.27	+14,3	—			

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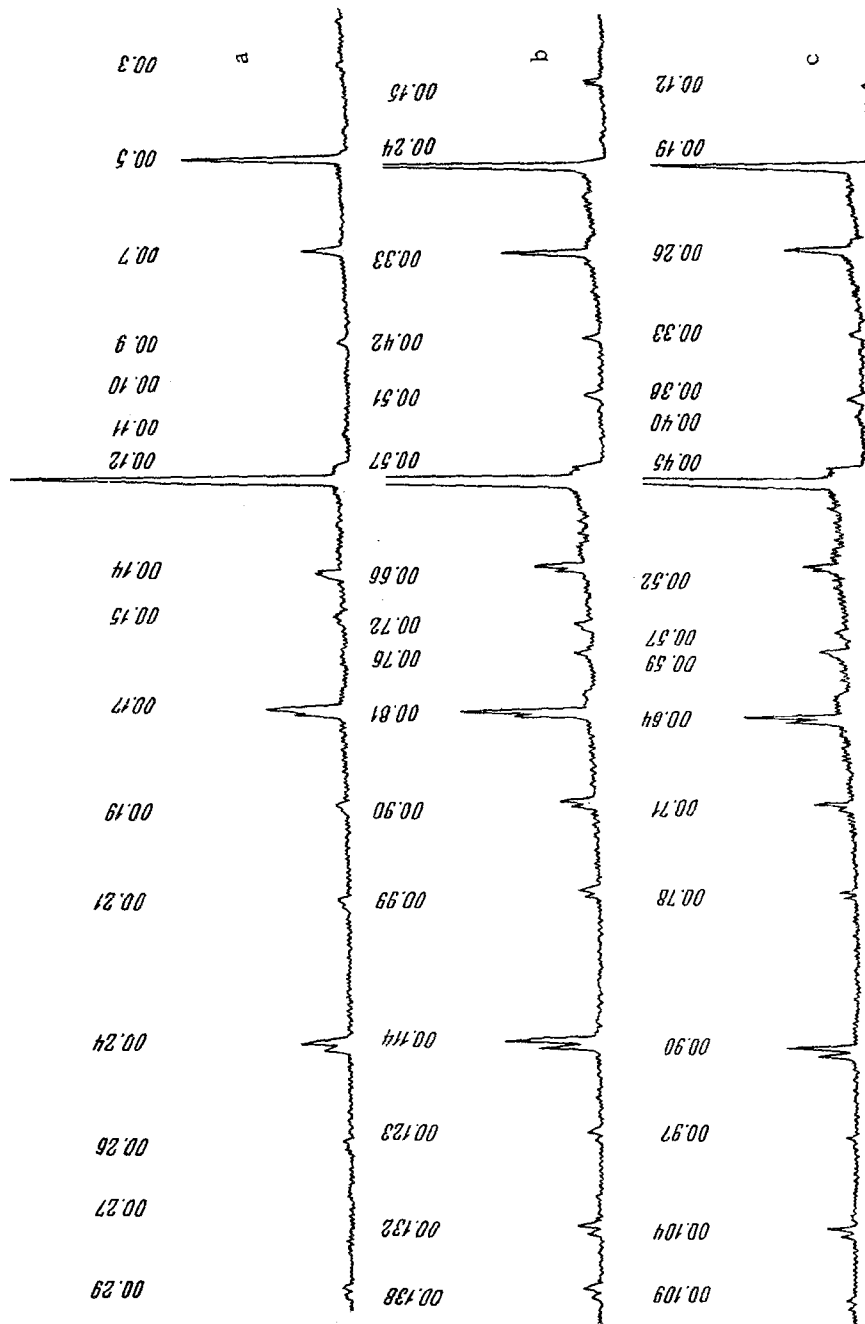


Fig. 1. Diffraction records of alloys obtained from the solid-solution region of the Bi-Se system: a) 50.0 at% Se(Bi_2Se_2), b) 47.4 at% Se($\text{Bi}_{10}\text{Se}_9$), c) 46.6 at% Se(Bi_8Se_7).

TABLE 2. Theoretical and Experimental Structure Amplitudes of Sb_2Te_2 ($B = 1.0 \text{ \AA}^2$)

$h0l$	$F_{\text{expt.}}$	$F_{\text{theor.}}$	$h0l$	$F_{\text{expt.}}$	$F_{\text{theor.}}$
00.1	— 0,5	—	00.16	+ 0,3	—
00.2	— 10,7	12,1	00.17	+84,6	81,5
00.3	— 7,2	—	00.18	—17,6	12,2
00.4	— 2,4	—	00.19	+46,3	53,3
00.5	— 44,7	42,5	00.20	— 4,5	—
00.6	+ 8,9	10,0	00.21	—12,5	15,0
00.7	— 49,0	49,8	00.22	— 6,1	—
00.8	— 2,5	—	00.23	+ 7,4	—
00.9	— 3,8	—	00.24	+55,6	47,7
00.10	— 15,1	18,9	00.25	— 4,3	—
00.11	— 3,1	—	00.26	—58,4	67,0
00.12	—174,0	173,4	00.27	—30,5	21,4
00.13	+ 5,6	—	00.28	+ 9,2	—
00.14	+ 62,0	69,0	00.29	—53,1	48,5
00.15	+ 31,6	32,4	00.30	—14,8	—

TABLE 3. Coordinates of the Atoms in the Bi_2Se_2 and Sb_2Te_2 Structures

Bi_2Se_2			Sb_2Te_2		
Atoms	Position in sp. gr. P3m1	z	Atoms	Position in sp. gr. P3m1	z
Bi_1	2(c)	0,126	Sb_1	2(c)	0,126
Bi_2	2(d)	0,291	Sb_2	2(d)	0,292
Bi_3	2(d)	0,541	Sb_3	2(d)	0,533
Se_1	2(d)	0,056	Te_1	2(d)	0,055
Se_2	2(d)	0,789	Te_2	2(d)	0,789
Se_3	2(c)	0,362	Te_3	2(c)	0,364

TABLE 4. Shortest Interatomic Distances in the Bi_2Se_2 and Sb_2Te_2 Structures

Bi_2Se_2		Sb_2Te_2	
Atoms in neighboring layers	Distance, Å	Atoms in neighboring layers	Distance, Å
Bi_3 — Bi_3	3,06	Sb_3 — Sb_3	2,92
Bi_1 — Se_1	2,90	Sb_1 — Te_1	2,98
Bi_1 — Se_2	3,10	Sb_1 — Te_2	3,18
Bi_2 — Se_2	3,03	Sb_2 — Te_2	3,13
Bi_2 — Se_3	2,91	Sb_2 — Te_3	3,00
Bi_3 — Se_3	3,27	Sb_3 — Te_3	3,48
Se_1 — Se_1	3,52	Te_1 — Te_1	3,60

EXPERIMENTAL

For the most detailed x-ray study we took the Bi—Se system, since its components had considerably differing scattering powers.

Coarse-crystalline samples were obtained by horizontal zone melting. After passing through the zone, the composition of the crystals along the sample varied regularly with respect to position in the phase diagram. Thus, if the original two-phase sample for zone melting contained 33.3 at. % Se, on passing the zone the alloy became single-phased; at the beginning of the bar crystals of Bi_2Se_2 (50.0 at. % Se) were formed, then further along the bar the composition of the crystals changed in the sense of increasing bismuth content. After passing the zone, all the crystals were easily cleaved into individual plates in the direction of crystallization. By choosing single-crystal plates from various parts of the sample, we were able to study crystals of any composition within the range of the solid solution. In order to check the composition of the single-crystal samples we took Debye photographs of cast annealed single-phase alloys, the composition of which was strictly known.

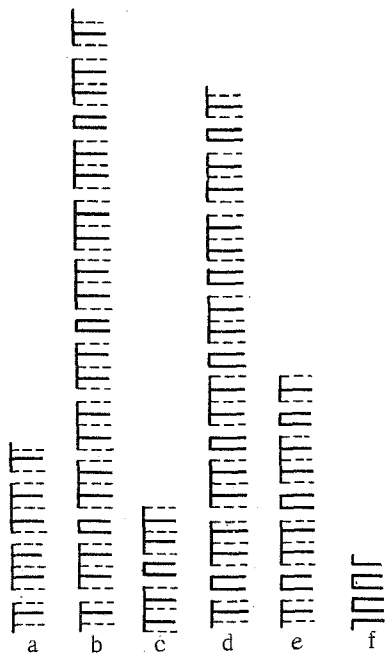


Fig. 2. Manner in which the structure is formed in the region of the solid solution of the Bi-Se system: a) Bi_2Se_3 , b) Bi_8Se_9 , c) Bi_2Se_2 , d) Bi_8Se_7 , e) Bi_4Se_3 , f) Bi_2 .

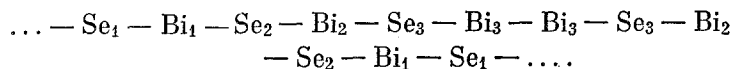
perpendicularly to the planes of the plates showed that all the crystals belonged to the $3m$ diffraction class. The reciprocal-lattice photographs of all the crystals studied had strong reflections determining rhombohedral subcells and weak superstructural reflections.

Crystal Structure of Bi_2Se_2

The structure of Bi_2Se_2 has lattice parameters $a = 4.18$, $c = 22.8 \text{ \AA}$ and a pseudo-period along the c axis equal to 5.71 \AA . The unit cell contains three Bi_2Se_2 formula units. Analysis of the reciprocal-lattice photographs shows that the following space groups without extinctions are possible: $P3m1$, $P3m1$ and $P32$. However, there are some pseudo-extinctions in the $hk0$ plane, only reflections with $-h+k=3n$ being present.

The small value of the parameter a suggests that the structure consists of layers formed by translationally-identical atoms of one sort. In the space groups selected, this arrangement of the atoms is only possible if we place the atoms on the verticals $00z$ (layers A), $1/3^2/3z$ (layers B), and $2/3^1/3z$ (layers C) in the unit cell.

In order to determine the crystal structure of Bi_2Se_2 we must consider all possible sequences of the layers of bismuth and selenium atoms in the cell and find the coordinates of the atoms and the order of the A, B, and C layers. Since the atomic radii of bismuth and selenium are similar, while their scattering powers differ widely, in calculating the structure factors of the initial model we may suppose that the distances between the layers equal $c/12$. Making this assumption, we calculated the F_{00l} of all possible dispositions of the six layers of bismuth and six layers of selenium in the 12-layer cell, and chose a form giving the best agreement with the experimental structure amplitudes:



This arrangement of the layers is confirmed by the projection of the F^2 series on the $x0z$ plane and may be described within the centrosymmetric space group $P3m1$. We further employed the method of successive approximations for the projection of the structure on the z axis by reference to the $00l$ reflections; this enabled us to reduce the reliability factor with respect to the nonzero $00l$ reflections to 10.1% (Tables 1 and 3). In order to establish the type of layer stacking in the structure, we used the reflections of the $10l$ reciprocal-lattice photograph. Calculation of the

A detailed study of the structure of the crystals was made with alloys containing 50.0 at. % of the chalcogen (Bi_2Se_2 , Sb_2Te_2) and also 42.8 at. % of the chalcogen (Bi_4Se_3 [8]). Using single-crystal plates, we obtained reciprocal-lattice photographs of the $h0l$ and $h1l$ types and ordinary diffraction photographs of the $00l$ reflections in $\text{MoK}\alpha$ radiation (Fig. 1). In calculating the intensities from the diffraction photographs, we introduced a correction for the dead time of the counter and allowed for the variation in the cross-sectional area of the beam reflected from the face for various angles of reflection. The intensities of the $10l$ reflections were estimated from the reciprocal-lattice photographs. Crystals of all the alloys studied were very soft and inelastic. The imperfection of the crystals and the existence of superstructure led to the absence of many reflections from the reciprocal-lattice photographs. Nevertheless, it was mainly the $00l$ reflections which were required in order to determine the layer structures of the bismuth selenides and the bismuth and antimony tellurides. The remaining reflections were only used to confirm the existence of layer stacking of the close cubic type ABC ... in all the structures.

Determination of Crystal Structure

In an earlier x-ray-diffraction study of single-crystal solid solutions belonging to the Bi-Se, Bi-Te, and Sb-Te systems, we observed layer structures with large periods, transforming one into the other [9]. The number of layers N in the unit cells of these structures was related to the chemical formula of the alloy. Thus, if the composition of the alloy were expressed by the formula $A_{2n}^V X_m^{\text{VI}}$, the number of layers in the unit cell equalled $N = 3(2n + m)$ [10]. Laue photographs taken per-

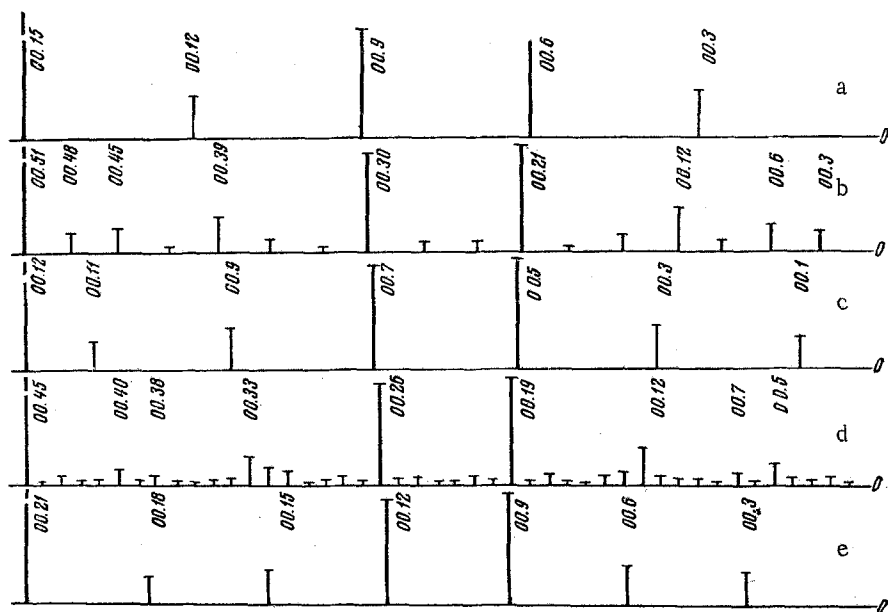


Fig. 3. Theoretical diffraction pictures of the structures: a) Bi_2Se_3 , b) Bi_8Se_9 , c) Bi_2Se_2 , d) Bi_8Se_7 , e) Bi_4Se_3 .

F_{00l} factors and comparison of these with the experimental structure amplitudes showed that the layers were arranged on the ABC... cubic close-packing law. The reliability factor R for the nonzero $10l$ reflections was 14.4%.

It follows from an analysis of the interatomic distances (Table 4) that the Bi_2Se_2 structure, like that of Bi_4Se_3 [8], contains double covalently-connected layers of bismuth lying between five-layer $\text{Se}_1\text{-Bi}_1\text{-Se}_2\text{-Bi}_2\text{-Se}_3$ packs. In the Bi_2Se_2 structure the double layer of bismuth atoms alternates with two five-layer packs, while in the Bi_4Se_3 structure it alternates with one five-layer pack (Fig. 2).

Crystal Structure of Sb_2Te_2

The Sb-Te systems contains atoms with almost equal scattering powers, and the development of a superstructure in this system only involves the nonuniform arrangement of the layers. The unit-cell parameters ($a = 4.26$, $c = 23.9$ Å) and the character of the x-ray diffraction photographs strongly suggest that the compound Sb_2Te_2 is isostructural with Bi_2Se_2 . Hence the Sb-Sb double layer should alternate with two five-layer packs of the form Te-Sb-Te-Sb-Te . For a preliminary calculation, the distances in the Sb-Sb double layers were taken the same as in the "corrugated" layers of elemental antimony, while the five-layer packs were constructed by analogy with the same packs in Sb_2Te_3 . The calculation was improved by the method of successive approximations by reference to the projection of the structure on the z axis. The final value of the R factor for the nonzero $00l$ reflections was 8.7% (Tables 2 and 3). The diffraction photograph of the compound Sb_4Te_3 contains three weak reflections (second-order superstructure) which means that we have to double the number of layers in the cell as compared with the 21-layer cell of Bi_4Se_3 . The large period $c = 82.8$ Å made it impossible to carry out a final refinement of the structure; however, the doubling of the period can only be associated with a layer arrangement in which two double layers of antimony atoms alternate with two five-layered Te-Sb-Te-Sb-Te packs (Table 4). In the Bi-Te system many superstructural reflections are absent from the diffraction photographs, and this impedes study of the structure.

DISCUSSION OF RESULTS

The establishment of a relation between the number of layers in the unit cells of the bismuth selenides and bismuth and antimony tellurides and the composition of these compounds, taken together with the crystal structures of analogous series of such compounds, enables us to set up some general laws governing their structures.

If we suppose that, by analogy with the compounds studied, the intermediate compounds contain also double A_2 layers, uniformly distributed between five-layered $X\text{-A-X-A-X}$ packs of the type characterizing the A_2X_3 structures (Fig. 2), we may calculate the theoretical diffraction pictures (F_{00l}) of the structures of various compositions in the Bi-Se system for interlayer distances equal to c/N , where N is the number of layers in the unit cell. The regular displacement of the reflections with alloy composition on the theoretical diffraction pictures (Fig. 3)

is analogous to the displacement of the superstructural $00l$ reflections on the diffraction pictures [10]. Refinement of the z coordinates of the layers of such models led to the true structures for compounds of compositions A_2X_3 , A_2X_2 , and A_4X_3 . Hence the ranges of homogeneity may be regarded as solid solutions of double layers of bismuth or anti-mony in A_2X_3 structures of the tetradimite type. The formation of the layer structures is the result of ordering in the solid solution. Between the regions of the solid solutions and the bounding structures (A_2X_3 and A_2) on the phase diagrams, there are distinct two-phase regions [1-4, 11]. It is clear that for small concentrations of A_2 or A_2X_3 , there is no ordering and the alloys remain in the two-phase state.

We may well imagine the existence of disordered structures, even within the regions of solid solutions, for very large dimensions of the unit cells; however, in view of the small difference between neighboring structures this lack of order cannot be observed experimentally.

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