ELECTRON DIFFRACTION STUDY OF THE COMPOUND $AgBiTe_2$

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As a result of an electron diffraction study of thin films of $AgBiTe_2$, the existence of cubic (a = 6.16 A, NaCl type) and hexagonal modifications of this compound was established, the latter having ordered dispositions of the Ag and Bi atoms (space group $D_{3d}^5-R\bar{3}m$, a = 4.24, c = 20.67 A). The atoms occupy the positions: 6Te : 6(c) with z = 0.25; 3Ag : 3(a); 3Bi : 3(b). An interpretation was obtained for the point electron diffraction patterns, indicating the orientation of the $AgBiTe_2$ crystallites with the $(10\bar{1}4)$ face parallel to the NaCl cube face.

Recent papers devoted to the physics of semiconductors have concentrated attention on three-component compounds of the $A^1B^5X_2^6$ type (A^1 = Ag or Cu, B^5 = Bi or Sb, X^6 = S, Se, or Te). One of the most important problems involving these compounds is the detailed study of the ordered and disordered phases, the aim being to accumulate data for establishing the crystallochemistry of multicomponent semiconducting compounds.

The present paper is devoted to the electron diffraction study of thin films of $AgBiTe_2$. The samples for investigation were prepared by vacuum volatilization (10^{-4} mm Hg) of $AgBiTe_2$ alloy onto freshly cloven rock salt faces. Different electron diffraction photographs were obtained for various conditions of volatilization and substrate temperatures. Slow volatilization of the alloy onto a substrate at room temperature resulted in the formation of amorphous films. Crystalline films were obtained by rapid volatilization or by annealing the amorphous films, and also by sputtering the alloy onto heated NaCl crystals. We further obtained electron diffraction photographs from polycrystalline samples (annealing for 20 min at 120°C), laminar textures, and a mosaic single crystal (by sputtering onto heated NaCl crystals with subsequent annealing for an hour at 160°C). The diffraction photographs from the laminar textures were obtained in two forms: with a small number of reflections (annealing 1 h at 130°C), and with an extremely large number of reflections (annealing 2 h at 180°C). It is interesting to note that, whereas the first form showed very weak reflections from monoclinic Ag_2Te [1] on the electron diffraction photographs, the second form gave weak reflections from the hexagonal phase $Ag_{2-x}Te_{x+1}$.

The electron diffraction photographs from the polycrystalline sample and the laminar texture of the first type were indexed on the basis of a cubic face-centered cell with spacing a = 6.16 ± 0.02 A (NH_4Cl standard), which is in conformity with published data [2]. The crystallites in the films giving electron diffraction patterns of the first type were disposed with the octahedral face parallel to the plane of the substrate (fiber axis [111]). Simple analysis of the intensity of electron diffraction reflections for the cubic form of $AgBiTe_2$ (all reflections with even indices are strong and those with odd indices weak) indicates that this belongs to the NaCl type structure.

It proved feasible to index the electron diffraction picture of the second type of laminar texture (Fig. 1) on the basis of a hexagonal (rhombohedral) cell with spacings a = 4.24 and c = 20.67 A. Proceeding from the cell volumes of the cubic and hexagonal forms of $AgBiTe_2$ (233.6 A^3 and 321.4 A^3 respectively), we determined the number of molecules in the hexagonal cell Z = 3; the space group was $D^5_{3d}-R3m$. A characteristic mark of this electron diffraction pattern was the paired disposition of reflections on the ellipses $h - k \neq 3n$, associated with the existence of the rhombohedral ex-

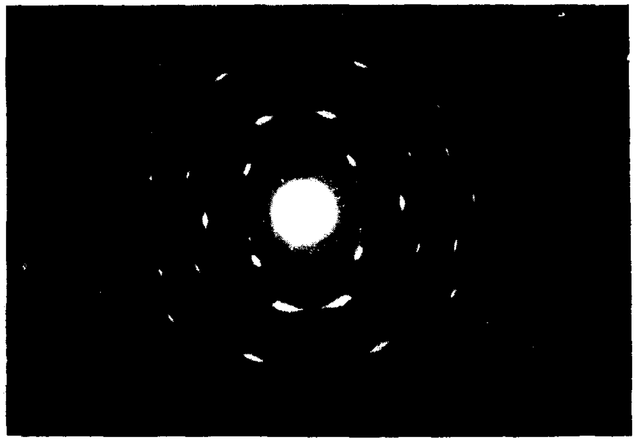

Fig. 1. Electron diffraction pattern from the rhombohedral form of $AgBiTe_2$ (taken at 60° angle).

tinction conditions, and the disposition of the strongest reflections on the layer lines with $l = 4n$. The latter indicates periodicity in four layers, inherent to the structure, and this agrees well with the chemical formula $AgBiTe_2$. The four-layer packing arrangement, three times repeated by the rhombohedral conditions, leads to a total number of $3 \times 4 = 12$ layers per cell. The reflections of the strong layer lines with l equal to a multiple of four ($l' = l/4$) by themselves form the characteristic rhombohedral extinction law ($h - k + l' = 3n$), corresponding to the superposition of layers in cubic packing. Forgetting for a moment the different atomic types, we may write the packing formula ABC ABC ABC ABC.

Further analysis was carried out by constructing Φ^2- and Φ-series. The intensity of the reflections was determined microphotometrically and visually. Transformation from intensities to structure amplitudes was effected by means of the kinematical theory formula. By this means we obtained experimental amplitude values of up to about 85 structurally independent reflections (up to $\sin\vartheta/\lambda \sim 0.88$ A^{-1}). The one-dimensional cross section of the Φ^2-series along the 00z (Fig. 2) showed that the peaks in this section were disposed practically at distances of c/4 from one another.

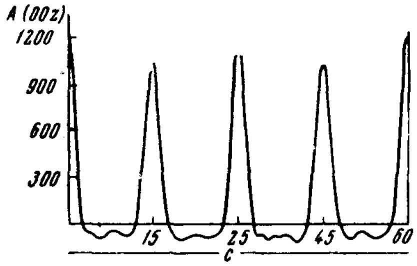

Fig. 2. Section of Φ^2-series A(00z).

The 12 atoms in the space group D^5_{3d} may be displayed as follows:

3 Ag in position (a) with coordinates
$000;\ \frac{1}{3}\frac{2}{3}0;\ \frac{2}{3}\frac{1}{3}0;$
3 Bi in position (b) + $00\frac{1}{2}$; 6 Te in (c)
$\pm 00z$, with $z = 0.25$.

On the basis of this model we calculated the theoretical values of structure amplitude, allowing for the temperature factor ($B = 1\ A^2$). Having determined the signs of the experimental amplitudes, we constructed a one-dimensional section of the three-dimensional series $\varphi(00z)$ and $\varphi(\frac{1}{3}\frac{2}{3}z)$. The section $\varphi(\frac{2}{3}\frac{1}{3}z)$ gave atoms which were inversion-equivalent to the atoms of the $\varphi(\frac{1}{3}\frac{2}{3}z)$ section. All three sections are assembled in Fig. 3. The heights of the peaks in these sections at once showed the correctness of the selected model. The Fourier syntheses were constructed without the zero term Φ_{000}. The contribution of this term may approximately be evaluated as equal to the mean negative potential value in the syntheses of Fig. 3; we therefore took the potential shown by the dotted line in Fig. 3 as the base for calculating peak heights.

Analysis of the potential peak heights showed that whereas for the Ag and Te atoms, agreement between φ_{exp} (1200 V, allowing for reflections falling in the "dead zone") and φ_{theor} (for Ag 1240 V and for Te 1270 V) was satisfactory, yet for the Bi atoms φ_{exp} constituted roughly 85% of φ_{theor} ($\varphi^{Bi}_{exp} = 1680$ V, $\varphi^{Bi}_{theor} = 2000$ V). Deviation from stoichiometrical composition of the hexagonal form of $AgBiTe_2$ was also confirmed by the ratio between the volumes of the elementary cells of the hexagonal and cubic phases:

$$\frac{\Omega_{hex}}{\Omega_{cub}} = \frac{321.4}{233.6} \approx 1.375 < 1.5.$$

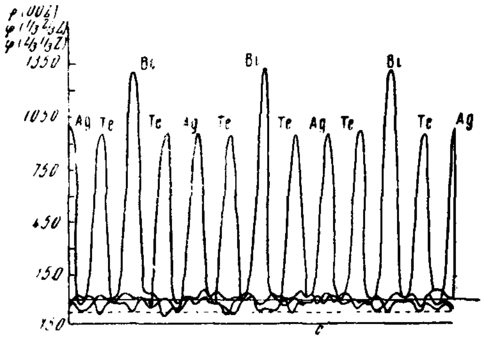

Fig. 3. Assembled sections of the three-dimensional series $\varphi(00z)$, $\varphi(\frac{1}{3}\frac{2}{3}z)$, and $\varphi(\frac{2}{3}\frac{1}{3}z)$.

Experimental and Theoretical Values of Φ (in Volts)

Serial no.	*hkl*	Φ_{theor}	Φ_{exp}	Serial no.	*hkl*	Φ_{theor}	Φ_{exp}
1	$10\bar{1}$	—1,26	—1,66	43	3012	3.4	3,23
2	102	0,83	1.63	44	$31\bar{5}$	—0.39	—0.42
3	$10\bar{4}$	12.42	8.93	45	317	—0.38	—0,45
4	105	—1.10	—1.54	46	$31\bar{8}$	3.21	3,16
5	$10\bar{7}$	—0.93	—1.45	47	$21\bar{1}6$	3.16	3.02
6	110	9,26	8,15	48	2117	—0.35	—0.38
7	108	9,24	8,72	49	3015	—0.35	—0.33
8	113	—0,91	—1,01	50	3110	0.25	0,43
9	201	—0.83	—1.02	51	$40\bar{4}$	2.56	2.91
10	$20\bar{2}$	0,65	0,95	52	2212	2.50	2.91
11	116	0.56	1.52	53	$31\bar{1}1$	—0.31	--0.36
12	204	8.16	8,57	54	408	2.27	2,70
13	$20\bar{5}$	—0,77	—0.96	55	$21\bar{1}9$	—0.31	—0.32
14	207	—0,69	—0.99	56	3113	—0,30	—0,37
15	119	—0.70	-0.75	57	$31\bar{1}4$	0.21	0,37
16	$20\bar{8}$	6.30	5,95	58	3018	0,2	0,41
17	$21\bar{1}$	—0,67	—0.87	59	$32\bar{4}$	2,5	2,04
18	212	0.42	0,88	60	2120	2,46	2,21
19	2010	0,43	0,83	61	328	2.3	1.64
20	$21\bar{4}$	5,42	5,64	62	410	2.24	1.94
21	1112	5.38	4,97	63	3116	1,92	2.30
22	215	-0,57	0.80	64	2218	0.23	0.38
23	2011	—0.57	—0.62	65	416	0,17	0,47
24	217	—0,55	0.71	66	4016	2,00	1.64
25	300	4.74	4.85	67	4112	1.84	1.50
26	218	4.75	4.95	68	$31\bar{2}0$	1.38	1.83
27	303	—0.52	—0,44	69	504	1.86	1.80
28	2013	—0,52	—0,56	70	$50\bar{8}$	1,74	1.48
29	306	0,36	0.46	71	330	1,74	1.43
30	$21\bar{1}0$	0.35	0.53	72	$32\bar{1}6$	1.74	1.43
31	$20\bar{1}4$	0.25	0.48	73	336	0.15	0.23
32	2111	--0.48	—0.55	74	424	1,71	1,35
33	309	- 0.45	—0,38	75	4020	1.64	1.38
34	220	3.81	3.24	76	428	1,58	1.13
35	2016	3.76	3.64	77	514	1,47	1.02
36	223	—0,43	—0.23	78	3312	1,45	1.08
37	$21\bar{1}3$	—0.43	—0.53	79	3220	1.41	1.05
38	311	—0.42	—0.53	80	518	1.39	1.00
39	226	0.29	0.33	81	5016	1.23	1.23
40	$31\bar{2}$	0.29	0.48	82	4216	1.18	0,99
41	2114	0,28	0,45	83	3318	0,13	0.29
42	314	2,91	3,44	84	$51\bar{1}6$	1.09	0.87

If we allow for the deficit of Bi atoms in the structure, then the divergence factor R is 18% (table).

The established $AgBiTe_2$ structure belongs (as do $TlBiTe_2$, $TlSbTe_2$ [3], and $TlBiSe_2$ [4]) to the $NaInO_2$ structural type. Thus the crystal structure of the ordered phase of $AgBiTe_2$ is formed from four blocks of form AgTeBiTeAg . . . (see Fig. 4). The shortest interatomic distances (sums of atomic radii given in brackets) in the hexagonal phase of $AgBiTe_2$ are as follows (in A): Ag to Te 2.991 (for $R_{Ag} + R_{Te} = 3.14$; with correction* 2.99); Bi to Te 2.99 (for $R_{Bi} + R_{Te} = 3.52$; with correction* 3.35); Te to Te, 3.85. The small value of the Bi to Te distance is evidently linked with the lack of Bi in the elementary cell.

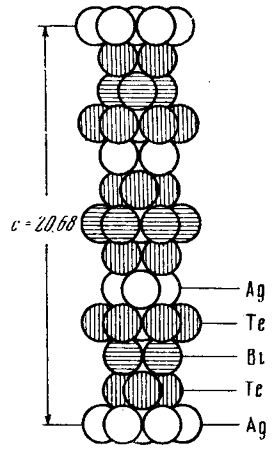

Fig. 4. Rhombohedral structure model of $AgBiTe_2$.

As mentioned earlier, on volatilizing $AgBiTe_2$ alloy onto a heated NaCl crystal we observed the formation of films with a mosaic single crystal structure. Electron diffraction photographs of these films taken perpendicularly had a fourth-order symmetry axis, but in contrast to diffraction photographs of cubic or tetragonal crystals the majority of the reflections were split. These diffraction photographs were very similar in form to

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* The corrections to the atomic radii as functions of coordination number were introduced in Table 13 [5].

those of cubic crystals oriented with the (100) face parallel to the substrate, so that the properties described above are doubtless connected with the orienting effect of the NaCl crystals.

Interpretation of the electron diffraction patterns obtained from the mosaic single crystals showed that they could be indexed on the basis of the same hexagonal cell as the photographs from the laminar textures of the second kind (basic coarse network of reflections). Moreover, for the diffraction photographs obtained under perpendicular conditions, the most characteristic are the four $10\overline{14}$ spots disposed on the horizontal and vertical lines of the pattern; further off there are four $10\bar{1}8$ spots and so forth. It must be noted that just such an orientation of crystallites was observed earlier in studying $TlBiSe_2$ [4]. Similar orientations are possible when hexagonal crystals are disposed on the face of an NaCl crystal cube with a certain face parallel to the z-axis or making an acute angle with it [i.e., face $(10\overline{14})_{AgBiTe_2} \parallel (100)_{NaCl}$]. The dihedral angles ψ formed by the planes $10\bar{1}\bar{4}$ and $0\bar{1}1\bar{4}$ and calculated by a well known formula are 89°50' and 90°10', which corresponds to the observed square network of reflections. This leads to the idea that the $\{1014\}$ planes correspond to the $\{100\}$ faces of the cubic form of $AgBiTe_2$. Transformation of the axes and indices of the cubic system to the hexagonal confirms this supposition. Thus the $\{10\overline{14}\}$ type faces of the hexagonal form are the former cube faces of the disordered $AgBiTe_2$ phase, and for this reason the hexagonal crystallites have their $\{10\overline{14}\}$ face lying on the rock salt. Further, the cell dimensions of the cubic and hexagonal forms fairly well obey the obvious equations $a_{hex} = a_{cub}/\sqrt{2}$ and $c_{hex} = 2a_{cub}\sqrt{3}$; moreover, $[0001]_h \parallel [111]_c$, $[1010]_h \parallel [110]_c$, and $[01\bar{1}0]_h \parallel [\bar{0}11]_c$.

As in the ordered structure, so also in the disordered structure the atoms retain octahedral coordination, and the ordering is accompanied only by the necessary (re)distribution of Ag and Bi atoms in the dense cubic packing formed by the Te.

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