AN ELECTRON DIFFRACTION STUDY OF THE SECOND SUPERLATTICE IN $PbBi_4Te_7$

A. G. Talybov and B. K. Vainshtein

Institute of Crystallography, Academy of Sciences, USSR,
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Superlattice II of $PbBi_4Te_7$ has a hexagonal cell (a = 4.44, c = 71.7 A, space group D_{3d}^3) and has 36-layer cubic packing (four sets of nine layers). The sets differ in the array of Pb atoms, which randomly populate alternate layers in a set.

The pseudobinary phase diagram for PbTe and Bi_2Te_3 contains the compound $PbBi_4Te_7$ (composition 1 : 2), which has been demonstrated by x-ray phase analysis[1]. Our electron-diffraction measurements [2] show that there are structures having hexagonal unit cells:

I. $a = 4.50 \pm 0.02$ A, $c_I = 17.60 \pm 0.05$ A,
II. $a = 4.44 \pm 0.02$ A, $c_{II} = 71.7 \pm 0.2$ A $= 4c_I$,
III. $a = 4.44 \pm 0.02$ A, $c_{III} = 107.4 \pm 0.3$ A $= 6c_I$.

$$(1)$$

The volume per molecule of $PbBi_4Te_7$ is 407 A^3, which is almost exactly the sum of the molecular volumes for PbTe ($64 A^3$) and Bi_2Te_3 (2 · 169 A^3) [3, 4], this sum being 402 A^3.

Structures I-III may be considered as those of a single phase having differing degrees of order; the latter two are superlattices with respect to I, which is a known structure [2]. The simple structure I is as follows (Fig. 1); it consists of nine layers stacked in a close-packed cubic array ABCABCABC ... . This is fitted to the formula $PbBi_4Te_7$, which contains 12 atoms, by virtue of a joint random distribution over certain layers for the Te and Pb atoms. The formula for this is:

$$\overset{\leftarrow \, c_I \, \rightarrow}{}$$

A_1	B_1	C_1	A_2	B_2	C_2	A_3	B_3	C_3	A_1	
Bi_I	Te_I	Bi_{II}	Te_{II}	Te_{III}	Te_{III}	Te_{II}	Bi_{II}	Te_I	Bi_I	(2)
	(Pb)		(Pb)		(Pb)		(Pb)			

This centrosymmetric array is described by group D_{3d}^3 $-P\bar{3}m1$. Layers A_1 and C_1 - B_3 are uniformly populated by Bi atoms; Te atoms do the same in layers B_1 - C_3, while Te and Pb together populate $A_2B_2C_2B_3$ in the proportions $Te_{3/16} Pb_{13/16}$. This gives us the formula

$$Bi_3Te_2 \; (Te_{13/16} Pb_{3/16}) \, 4 = {}^3/_4 \, (Pb \, Bi_4 \, Te_7).$$

Here we present structure II, which is produced when the alloy is distilled onto NaCl at room temperature and the film is annealed at 200°C for 40 min.

Fig. 1. Structure I of $PbBi_4Te_7$.

Figure 2a shows an oblique-texture pattern from structure II; all strong reflections correspond to one for structure I, which shows that structure II is very similar to structure I. Some of the ellipses also show reflections corresponding to a period $c_{II} = 4c_I$; some of these reflections are shown in Fig. 2b (a section of Fig. 2a enlarged).

Systematic absences occur only on the zero layer line, which contains only reflections having h - k = 3n.

The possible space groups are:

$$D_{3d}^3 - P\bar{3}m1, \qquad D_3^2 - P321,$$
$$C_{3i}^1 - P\bar{3}, \qquad C_{3v}^1 - P3m1.$$

The strongest reflections lie on the layer lines having $l = 12n$, and they obey the rhombohedral condition h + k - $l/12$ = 3n, as for structure I [2]. This implies a cubic ABC ... pseudoperiod of

TABLE. Calculated and Measured* Structure Factors

a) $l = 4n$

hk$l$	Φ	Φ_0
10.4	+1.18	0.65
10.12	+0.36	0
10.16	—0.43	0.76
10.24	+12.16	10.30
10.28	+0.18	0.22
10.32	—0.32	0.36
10.40	+1.47	1.13
10.44	+0.64	0.75
10.48	+0.20	0
10.52	—0.23	0.95
$\overline{1}$0.4	—0.46	0.26
$\overline{1}$0.12	+15.16	13.40
$\overline{1}$0.16	+0.24	0.34
$\overline{1}$0.24	+0.30	0.26
$\overline{1}$0.28	+0.82	1.08
$\overline{1}$0.32	+0.80	0.90
$\overline{1}$0.40	—0.29	0.22
$\overline{1}$0.44	+0.14	0.17
$\overline{1}$0.48	+7.42	6.36
$\overline{1}$0.52	+0.12	0.50
11.0	+11.82	11.10
11.16	+0.80	0.90
11.20	+0.80	0.65
11.36	+7.87	8.15
11.40	+0.15	0.92
11.52	—0.54	0.97
11.56	+0.47	0.77
11.72	+4.41	3.95
11.76	+0.08	1.00
20.4	+0.32	0.32
20.8	+0.58	0.30
20.12	+9.78	11.30
20.24	+0.24	0
20.28	+0.71	1.05
20.32	+0.64	0.77
20.40	—0.31	0.54
20.44	+0.14	0.20
20.48	+6.07	5.62
20.52	+0.11	0.30
20.60	+0.15	0
20.64	+0.42	1.23
$\overline{2}$0.4	+0.80	0.41
$\overline{2}$0.8	+0.80	0.41
$\overline{2}$0.12	+0.26	0
$\overline{2}$.024	+8.68	8.20
$\overline{2}$.028	+0.15	0.21
$\overline{2}$.032	—0.27	0.32
$\overline{2}$.040	+0.57	0.93
$\overline{2}$0.44	+0.56	0.76
20.48	+0.17	0

hk$l$	Φ	Φ_0
$\overline{2}$0.52	—0.20	0.58
$\overline{2}$0.60	+5.13	5.01
$\overline{2}$0.64	+0.10	0 28
21.4	+0.65	0.45
21.12	+0.20	0
21.24	+7.03	6.13
21.28	+0.12	0.17
21.32	—0.22	0.26
21.40	+0.49	0.80
21.44	+0.47	0.66
21.48	+0.15	0
21.52	—0.17	0.55
21.60	+4.59	3.86
21.64	+0.09	0.59
21.84	+0.09	0.22
21.88	+0.09	0.67
12.4	—0.26	0.19
12.12	+7.63	9.50
12.24	+0.19	0.55
12.28	+0.55	0.95
12.32	+0.57	0.69
12.40	—0.20	0.32
12.44	+0.10	0.14
12.48	+5.35	4.60
12.52	+0.09	0.84
12.60	+0.13	0
12.64	+0.40	0 90
12.84	+3.37	2.49
12.88	+0.07	0.52
30.0	+6.91	6.03
30.16	—0.56	0.79
30.20	—0.53	0.70
30.36	+0.31	1.46
30.40	+0.10	0.85
30.52	+0.40	0.77
30.56	+0.40	0.45
30.72	+3.60	2.96
30.76	+0.05	0.86
220	+5.83	5.20
22.16	+0.22	0.79
22.36	+0.28	1.65
31.12	+5,49	4.75
31.24	+0,14	0
31.28	+0.41	0.70
31.40	—0,16	0.35
32.48	+4,20	3.12
31.60	+0,11	0
31.64	+0.29	0.96
13.12	+0.15	0

hk$l$	Φ	Φ_0
13.24	+5.11	4.16
13.28	+0.08	0.45
13.40	+0.40	0.79
13.48	+0.13	0
13.60	+3.70	2.68
13.64	+0.07	0.74
40.12	+0.13	0
40.24	+4.59	3.66
40.60	+2.60	1.91
$\overline{4}$0.12	+4.79	3.85
$\overline{4}$0.24	+0.13	0
$\overline{4}$0.60	+0.09	0.22
32.12	+0.13	0
32.24	+0.04	3.36
32.48	+0.10	0
32.60	+3.21	2.71
23.12	+4.27	3.66
23.24	+0.12	0
23.48	+3.37	2.86
23.60	+0.10	0
410	+4.08	3.48
41.36	+3.60	3.06
50.12	+3.51	3.12
50.24	+0.10	0
50.48	+3.01	2.39
$\overline{5}$0.12	+0.10	0
$\overline{5}$0.24	+3.41	2.59
$\overline{5}$0.48	+0.09	0.24
330	+3.40	3.04
33.36	+3.18	2.88
42.12	+3.28	2.64
42.24	+0.09	0
42.48	+2.28	2.34
24.12	+0.09	0.26
24.24	+3.19	2.72
24.48	+0.09	0
51.12	+0.10	0
51.24	+3.03	2.83
51.48	+0.09	0
15.12	+3.09	3.04
15.24	+0.10	0
15.48	+2.70	1.48
600	+2.82	2.34
43.12	+0.09	0
34.12	+2.70	2.13
520	+2.68	2.04
52.3$_6$	+2.43	1.9$_0$

b) $l = 2n$

hk$l$	Φ	Φ_0	hk$l$	Φ	Φ_0	hk$l$	Φ	Φ_0
10.10	—3.54	3.61	01.22	—3.35	1.71	11.38	+0.63	1.85
01.10	—1.27	1 30	10.26	+0.97	0.63	20.26	+1.96	2.35
10.14	+3.90	4.25	01.26	+2.75	1.80	02.26	+0.70	0.85
01.14	+1.22	1.32	10.50	+1.86	1.97	21.50	+1.37	1.41
10.22	—1.05	0.53	01.50	+0.58	0.61	12.50	+0.43	0.44

c) $l \neq 2n$

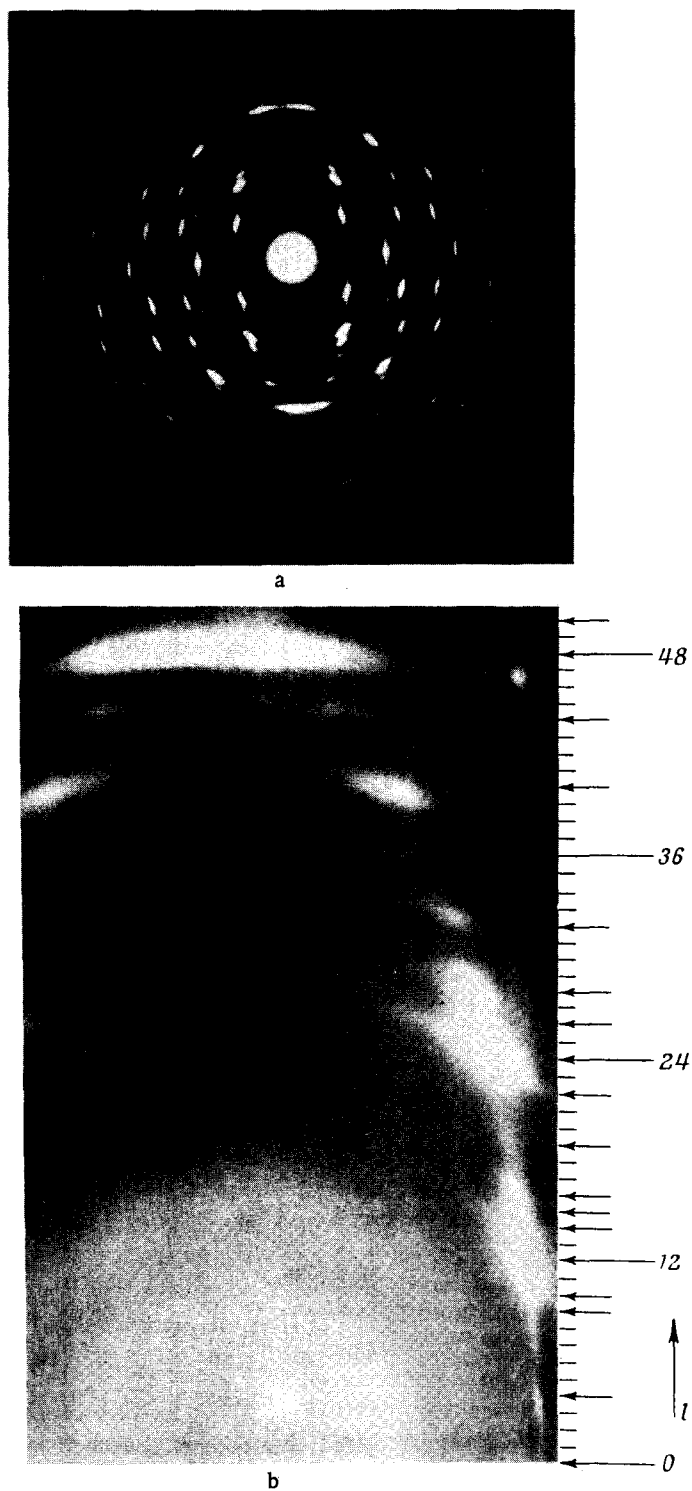| hk$l$	A	B	Φ	cos α	sin α	Φ_0
109	—1.21	—1.21	1.71	0.708	0.708	1.3
10.15	+0.79	—0.79	1.21	0.707	1.707	1.71
10.19	—0 45	+0.45	0 63	0.712	0 712	0.58
0.19	+0.32	—0.32	0.44	0.714	0.714	0.35
01.15	+0.28	—0.28	0.40	0.714	0.714	0.62
01.19	—0.59	+0.59	0.84	0.708	0 708	0.76

* As modified by dynamic corrections.

Fig. 2. a) Oblique-texture pattern from phase II of $PbBi_4Te_7$; b) the first $\bar{1}01l$ ellipse enlarged. The reflections are indicated by arrows.

$$c' = \frac{c_I}{3} = \frac{c_{II}}{12} = 5{,}97 \text{ A.}$$

The cell contains four sets each of nine layers (36 layers in all).

Each layer is 71.7/36 = 1.98 A thick (i. e., about 2 A), which is characteristic of other semiconductor phases containing Bi and Te [5, 6].

We used Φ^2 and Φ series in the analysis of structure II.

The intensities of reflections on the oblique-texture patterns were measured visually and by means of a microphotometer [6]; the observed intensities were converted to the structure factors by means of the formula [7]:

$$\Phi^2_{hkl} = \frac{I_{hkl}}{p d_{hko} \cdot d_{hkl}} . \qquad (3)$$

A dynamic correction was applied [8]; the mean size of the scattering regions was found to be 400 A.

The superlattice reflections for structure II were much weaker than the reflections for structure I, which is described by (2), so the superlattice must be based on four sets of type (2), but these must all differ slightly. The Φ^2 and Φ constructions showed that the differences lie in the distribution of the Pb atoms over the layers A$_2$B$_2$C$_2$A$_3$ (2) (Fig. 1), in which the atoms are uniformly distributed in structure I. These differences in distribution give rise to slight differences in the scattering power of the sets relative to that power for I or for any given power for II.

Structure II gives reflections with $l \neq 4n$ as a result of these changes in scattering power; we may consider structure I (disordered) as a zero matrix (see [9]), whose alterations are responsible for the reflections with $l \neq 4n$.

A Φ^2 series [an A (00z) section] constructed from reflections with $l = 4n$ gave almost exactly the picture found for structure I; the complete A (00z) section (Fig. 3a) is not very different, because the reflections with $l \neq 4n$ are relatively weak. The complete picture has peaks separated by 5.97 A (every third layer), which confirms that the packing is cubic.

The most reliable information on the changes is found from the A (00z) synthesis from the superlattice reflections only (Fig. 3b); this is a component part of Fig. 3a. Most of these reflections have l even; the table shows that few have l odd. This indicates that the four-set structure has a two-set substructure; for this reason, the component derived from the odd l is shown separately in Fig. 3b.

The superlattice synthesis gives a strong peak at $c_{II}/2$ on account of the substructure; there is a minimum at $c_{II}/4$, which shows that the distance between identical points in adjacent sets is $c_{II}/4 = c_I$, which means that the distributions are entirely different (other distances of $c_{II}/4$ would otherwise occur). The strongest peak lies at $c_{II}/12 = 5.97$ A, which corresponds to the distance between layers separated by two others. The
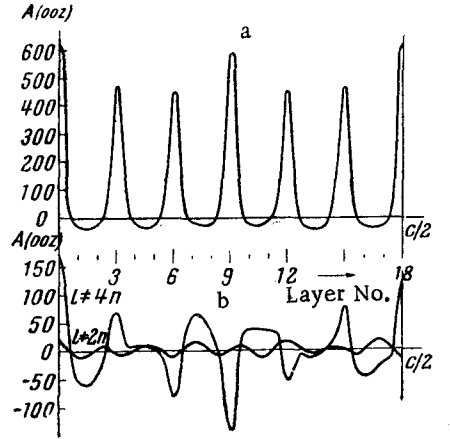
Fig. 3. A(00z) section (a) and components thereof as constructed from reflections with $l \neq 4n$ and $l \neq 2n$.

peak for the fifteenth layer is placed symmetrically with respect to the first; the sole explanation for this is as follows. The redistribution occurs within a set of four layers A$_2$B$_2$C$_2$A$_3$; the distance between such layers in adjacent sets is at least six layers, so the three-layer distance is one within a set, which cannot be other than the A$_2$-A$_3$ distance. Then, in one set at least, the Pb atoms populate mainly the A$_2$ and A$_3$ layers, leaving the B$_2$C$_2$ layers free (the substructure implies that this occurs in every alternate set). If we denote each layer by a number only (then A$_1$B$_1$C$_1$A$_2$B$_2$ ... = 0, 1, 2, 3, 4...), these layers are 3 and 6 (first set) and 3 + 18 = 21, 6 + 18 = 24 (third set; Fig. 6).

The next strong peak in Fig. 3b gives a distance of seven or eight layers (also 10-11, which is symmetrically placed). This is clearly a distance between layers in different sets, because the largest distance within a set is that for three layers. If we consider the layers A$_2$B$_2$C$_2$A$_3$ as two adjacent nine-layer sets:

$$
\begin{array}{l}
\text{A}_2\text{B}_2\text{C}_2\text{A}_3 \ldots \ldots \ldots \ldots \text{A}_2\text{B}_2 \quad \text{C}_2\text{A}_3 \\
\end{array}
$$

first (third) set   second (fourth) set   (4)
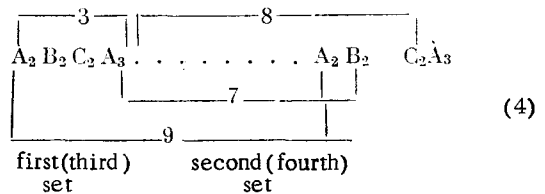
then the distances of seven and eight layers are A$_3$-B$_2$ and A$_3$-C$_2$, which automatically gives A$_2$-B$_2$ and A$_2$-C$_2$ as 10- and 11-layer distances.

The repeat distance of four sets can arise only if the second set differs from the fourth, because the first and third are the same. This is simple to provide if we assume, for example, that the 7- (or 10-) layer distance is that between Pb atoms in the first and second sets, while the 8- (or 11-) layer distance is the same between third and fourth sets. The A (00z) section indicates that the Pb atoms occur preferentially in layers 3 and 6 (first

set), 13 (second set), 21 and 24 (third set), and 32 (fourth set). The differences between these numbers give all the distances between layers observed in Fig. 3b.

This gives us six positions for Pb, whereas the four-set formula $4 \cdot \frac{3}{4}$ (PbBi$_4$Te$_7$) gives only three Pb for 36 layers. We may suppose that each of these positions is taken with a probability $\frac{1}{2}$ by a Pb atom and also with a probability of $\frac{1}{2}$ by a Te atom. Other possible arrays do not give satisfactory agreement with the observed superlattice intensities, so the above model was used. There is a further point here that has been glossed over so far. The Φ^2 series of Fig. 3b in principle gives only distances between atoms lying on the same vertical line, such as A−B, B−B, and C−C. These distances are ascribed to layers A−B, A−C, and so on in (4). The reason is that the resolving power of the Φ^2 series in the horizontal plane is small. One might assume that the cubic packing law is violated in the second set [see (4)], the order being B$_2$A$_2$ instead of A$_2$B$_2$. The seven-layer distance would then be between A$_3$ in the first set and A$_2$ in the second; the same applies to the fourth set (permutation C$_2$A$_3$ → A$_3$C$_2$).

We used the series φ (00z) and $\varphi(\frac{1}{3} \frac{2}{3} z)$ in the subsequent analysis; the space group is $D_{3d}^3 - P\overline{3}m1$, which has centers of symmetry at 000 and 00$\frac{1}{2}$. Now (2) and (4) indicate that these centers coincide with the centers of the first and third sets, which lie between B$_2$C$_2$ layers. The calculations are made much simpler if we bear in mind that each set has the symmetry D_{3d}^3 (if we neglect the redistribution of the Pb atoms). This means that the structure factors for l = 4n are precisely those for structure I; all are real. The reflections with $l \neq 4n$ arise from the randomly distributed Pb atoms among the Te atoms in layers 3, 6, 13, 21, 24, and 32. The zero matrix does not give reflections with $l \neq 4n$, but the modified structure has the above layers filled by effective difference atoms ($\frac{1}{2}$ Pb + $\frac{1}{2}$ Te)−Te = $\frac{1}{2}$(Pb−Te), which gives rise to an effective atomic scattering factor for electrons of $f' = [f(Pb) - f(Te)]/2$ for the reflections with $l \neq 4n$.

We have given the layers the above logical numbering , for which the origin (000) lies at the center of atom B$_{II}$ in the first set and the z (the coordinates of the other atoms) are N/36 (in which N is the number of the set); on this basis we have calculated the superlattice reflections from the formulas for group C_{3v}^1 whose points have coordinates 00 $\frac{3}{36}$; 00 $\frac{6}{36}$; $\frac{1}{3} \frac{2}{3} \frac{3}{36}$; 00 $\frac{21}{36}$; 00 $\frac{24}{36}$; $\frac{2}{3} \frac{1}{3} \frac{32}{36}$. These formulas take the form

$$A_{hkl} = f \left[\cos 2\pi \frac{l}{12} + \cos 2\pi \frac{l}{6} \right. $$
$$ + \cos 2\pi \frac{7l}{12} + \cos 2\pi \frac{2l}{3} $$
$$ + \cos \pi i \cdot \cos \pi \left(\frac{k-h}{3} + \frac{13\,l}{18} \right) $$
$$ \left. + \cos \pi i \cdot \cos \pi \left(\frac{h-k}{3} + \frac{16\,l}{18} \right) \right], \quad (5)$$

while the analogous expression for B$_{hkl}$ has all cosines (except cos πi) replaced by sines. The table gives the signs and phases so calculated, as well as the corresponding $| \Phi_0 |$:

	A$_I$	B$_I$	C$_I$	A$_2$	B$_2$	C$_2$	A$_3$	B$_3$	C$_3$
Set I	Bi	Te	Bi	Te$_{1/2}$	Te *	Te	Te$_{1/2}$	Bi	Te
				Pb$_{1/2}$			Pb$_{1/2}$		
Set II	Bi	Te	Bi	Te	Te$_{2/3}$	Te$_{5/6}$	Te	Bi	Te
					Pb$_{1/3}$	Pb$_{1/6}$			
Set III	Bi	Te	Bi	Te$_{1/2}$	Te *	Te	Te$_{1/2}$	Bi	Te
				Pb$_{1/2}$	Pb$_{1/2}$	Te$_{2/3}$	Pb$_{1/2}$		
Set IV	Bi	Te	Bi	Te	Te$_{5/6}$	Pb$_{1/2}$	Te	Bi	Te
					Pb$_{1/6}$				

(6)

(Asterisks denote the centers of symmetry in group D_{3d}^3). The hk$l$ and $\overline{h}$kl reflections are fused in these texture patterns from PbBi$_4$Te$_7$ although the structure factors are always different. The contribution from each $|\Phi_0|$ in each pair was calculated theoretically.

Figure 4 shows φ(00z) with its components as broken lines; that for l = 4n is the main one, while that for $l \neq 4n$ arises from the altered distribution of the Pb. This reveals atoms whose x and y coordinates are 0. The result for $l \neq 4n$ shows clearly the altered distribution of
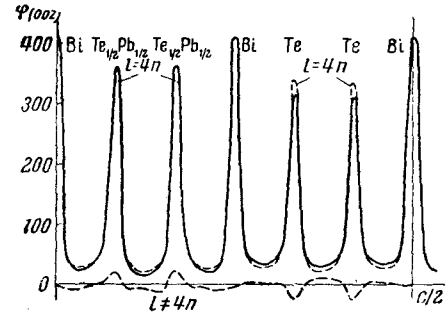

Fig. 4. One-dimensional δ(00z) section (full line), and components (broken lines) constructed from reflections with l = 4n and $l \neq 4n$.
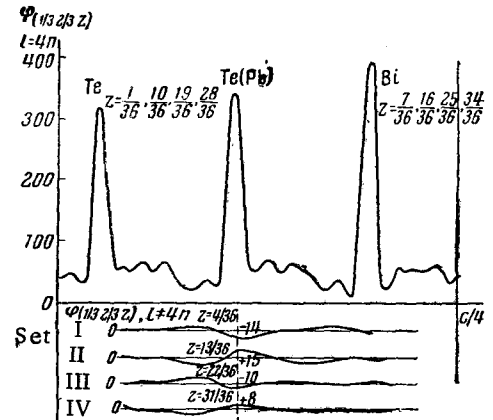

Fig. 5. One-dimensional $\varphi(\frac{1}{3} \frac{2}{3} z)$ section derived from the reflections with $l \neq 4n$, together with the contributions from those reflections for each of the four sets.
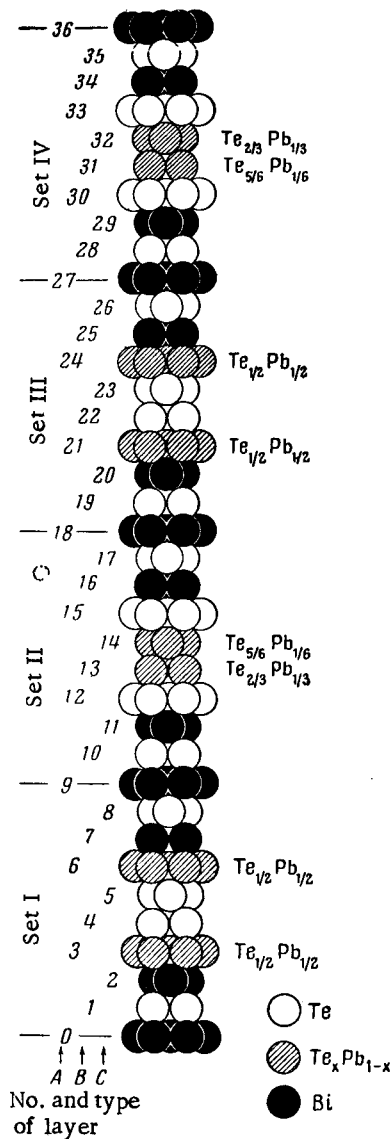
Fig. 6. Superlattice II of PbBi$_4$Te$_7$.

the Pb in positions $^3/_{36}$, $^6/_{36}$ ($^{21}/_{36}$, $^{24}/_{36}$) and the positions $^{12}/_{36}$; $^{15}/_{36}$ ($^{30}/_{36}$, $^{33}/_{36}$) thus left to the Te. The peak heights for the synthesis (full line) correspond precisely to the relation Bi, $^1/_2$ (Pb + Te), Te. (The heights of the middle peaks indicate a Pb content of 49%.)

Figure 5 shows φ ($^1/_3$ $^2/_3$ z), as constructed from the reflections with $l = 4n$, with the contribution from those with $l \neq 4n$. The latter shows the predicted reduced Te (Pb) peak heights for the first and third sets, as well as the increase in the second set; there is also a certain increase in the fourth set. This means that we were not quite correct in making the original assumption that the Pb from the A$_2$B$_2$C$_2$A$_3$ (2) layers in the initial structure passes only to position B$_2$ in the second set, because the same occurs to a smaller extent in the fourth set. That is, the second set contains in position B$_2$ ($^1/_3$ $^2/_3$ $^{13}/_{36}$) rather less than $^1/_2$Pb (about $^1/_3$), about $^1/_6$ being in posi-

tion C$_2$ ($^2/_3$ $^1/_3$ $^{14}/_{36}$); on the other hand, the fourth set has at position B$_2$ ($^1/_3$ $^2/_3$ $^{31}/_{36}$) about Pb/$_6$ and at C$_2$($^2/_3$ $^1/_3$ $^{32}/_{36}$) about Pb/ 3. Moreover, there is a possible change in the sequence of layers. We consider the model as proven, because the intensities (particularly those of the superlattice reflections) are in satisfactory agreement; again, there are no unexplained peaks on the Fourier synthesis.

To sum up, structure II of PbBi$_4$Te$_7$ has some of its layers randomly populated, but these are fewer than in structure I, the structure being as in (6).

The structure shows several repeat periods; the strongest is c' = 5.97 A = $c_{II}/12$(cubic packing), the next being $c_I = c_{II}/4$ (nine-layer sets), and the third $c_{II}/2$ (the two-set substructure). Figure 6 shows the structure.

The reliability factor computed from all the tabulated amplitudes is 22%.

All peaks lie almost exactly at the ideal positions (the z are multiples of $^1/_{36}$). The shortest distances between atoms in a layer are 4.44 A; those between atoms in adjacent layers (Bi—Te, Te (Pb)—Te, Te—Te, Te(Pb) —Bi) are 3.32 A.

Structure II is more highly ordered than structure I, but the order is not complete, although the structure is readily produced under certain conditions; this feature entitles us to consider it as a distinct phase.

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