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The Crystal Structure of the Mineral Tetradymite, Bi_2Te_2S.

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(With 2 figures.)

The mineral tetradymite is described by Dana as a substance occurring in small, acutely rhombohedral crystals resembling hexagonal prisms. The crystals cleave perfectly on the basal plane into flexible laminae with a metallic luster. The variety found in Hungary has compositions of which the following is typical:

Bismuth 59,0%, Tellurium 36.4%, Sulfur 4.6%.

The density is 7.500. In accordance with this analysis the formula can be written $Bi_2(Te, S)_3$ or Bi_2Te_2S. The sample of tetradymite used in the research to be described was from Hungary. The data lead to the adoption of a rhombohedral unit cell with the dimensions: $a_0 = 10.31$ Å, $a = 24° 10'$. This cell was found to contain one atom of sulfur, two atoms of bismuth, and two atoms of tellurium. An arrangement of these atoms in the cell is proposed which is compatible with all the observed experimental data and leads to the adoption of the formula Bi_2Te_2S.

The Determination of the True Unit Cell: The flexibility of the cleavage laminae of tetradymite made the production of good Laue photographs impractical. However, oscillation photographs, each showing an equator of good sharp lines and definite layers of rather diffuse lines, were easily prepared by reflection from the basal plane. Molybdenum $K\alpha$ radiation filtered through zirconia was used. Layer line measurements on these photographs gave $a_0 \cong 4.3$ Å and measurements of the equatorial lines gave $c_0 = 10.0$ Å for the dimensions of a hexagonal unit. Using these figures in connection with the composition and density given above, the contents of the unit cell is calculated to be:

2.05 atoms Bi, 2.08 atoms Te, 1.05 atoms S.

A powder photograph taken with the molybdenum $K\alpha$ doublet gave the data recorded in Table II. An attempt to assign indices to the observed lines on the basis of the hexagonal unit described above was unsuccessful. However, it was found possible to index all the observed lines on the basis of a hexagonal unit with $a_0 = 4.317$ Å and $c_0 = 30.01$ Å; that is, one with the *c*-axis tripled. On examination it was found that all lines for which $H + 2I + L = 3K$, $K = 0, 1, 2, \ldots$, were absent, an observation which shows the lattice to be rhombohedral and leads to the adoption of a rhombohedral unit cell with $a_0 = 10.31$ Å and $\alpha = 24^\circ\, 10'$. The volume of this cell is the same as that of the original small hexagonal unit and it therefore contains the same numbers of the same atoms. No reflections requiring a larger unit were observed on any photograph. This cell may then be accepted as the true unit.

Arrangement of Atoms in the Unit Cell: There are two alternatives to be considered: either tetradymite is a solid solution of Bi_2Te_3 and Bi_2S_3, by which is meant that the sulfur and tellurium atoms replace each other at random, the overall ratio being one sulfur atom to two tellurium atoms, or the substance is a true compound with the formula Bi_2Te_2S.

A. The Solid Solution Hypothesis: (i) If all the sulfur and tellurium atoms are crystallographically equivalent they must all lie in the same plane. They would then be at most only 2.49 Å apart. This small distance makes such a structure very improbable.

(ii) A more reasonable structure is one in which the five atoms form five different layers. This possibility is suggested by the similarity between the dimensions of tetradymite and those of bismuth and tellurium, both of which crystallize in the hexagonal system. These dimensions are:

	a_0(Å)	c_0(Å)	No. of layers	Length of *c*-axis for five layers (Å)
Tetradymite	4.32	30.0	15	10.0
Bismuth	4.54	11.4	6	9.5
Tellurium	4.45	5.91	3	9.9

Two possibilities present themselves under this assumption: The structure makes the *c*-axis either polar or non-polar. In the first case the five layers are not equivalent and the arrangement of the layers is determined by five parameters, one of which may be taken arbitrarily as zero. In the second case the structure is determined by two parameters, one atom of *Te, S* being at 0, 0, 0, two atoms of *Bi* at $\pm(u, u, u)$, and two atoms of *Te, S* at $\pm(v, v, v)$, where the coordinates refer to the rhombohedral axes. In view of the difficulty attending the rigorous discussion of a four-parameter structure such as provided by the first case, this possibility was neglected, a procedure ultimately justified by the agreement with the experimental data afforded by the use of a two-parameter structure.

On discussing the two-parameter structure for the solid solution it was not found possible to assign values to u and v which accounted for the observed intensities of even the first six orders of reflection from the basal plane. (The scattering factor $f_{(Te,S)}$ was taken to be $\frac{2}{3} f_{Te} + \frac{1}{3} f_S$ as given in the Pauling and Sherman table of atomic scattering factors.) Consequently the assumption of a solid solution is incorrect, provided the c-axis is non-polar.

B. The Hypothesis of a Compound, Bi_2Te_2S. There is another arrangement of the atoms in a five-layer structure with a non-polar c-axis, namely: one S at 0,0,0, two Bi at $\pm(u, u, u)$, and two Te at $\pm(v, v, v)$. It was found that for $u = 0.065$, 0.392 or 0.725 and $v = 0.121$, 0.455 or 0.788 the intensities of all twelve of the observed basal plane reflections were accounted for exactly, as shown in Table I and Figure 1[1]). The formula from which the intensities were calculated is:

$$I_{(hhh)} = h\left(\frac{1+\cos^2 2\theta}{2\sin 2\theta}\right) e^{-2B\left(\frac{\sin\theta}{\lambda}\right)^2} \left[f_s + 2 f_{Bi} \cos 2\pi \cdot 3hu + 2 f_{Te} \cos 2\pi \cdot 3hv\right]^2 .$$

Pauling and Sherman f values were used. In the Debye-Waller temperature factor B was taken as 1.5×10^{-16}, corresponding to a characteristic temperature of 130° K, a not unreasonable value for such a soft substance.

Table I.

Calculated and Observed Intensities and Observed $d_{(111)}$ from Spectral Photograph No. 8 ($MoK\alpha$ Radiation, ZrO_2 filter).

Reflection	Angle of Reflection	$d_{(111)}$ Å	$I/1000$ (calc.)	$I_{\text{obs.}}$
111	2° 02′	9.99	6.7	v. v. v. w.
222	4° 04′	10.00	108.2	s.
333	6° 05′	10.02	54.5	m.
444	8° 07′	10.03	121.0	v. s.
555	10° 10′	10.03	182.2	v. v. s.
666	12° 15′	10.01	196.6	v. v. v. s.
777	14° 21′	10.01	13.2	w.
888	16° 26′	10.01	5.9	v. w.
999	18° 37′	10.00	46.7	m. w.
10.10.10	20° 46′	10.00	2.0	v. v. v. w.
11.11.11.	22° 58′	10.00	85.1	m. s.
12.12.12	25° 12′	9.99	5.6	v. v. w.
		Mean = 10.01 Å		

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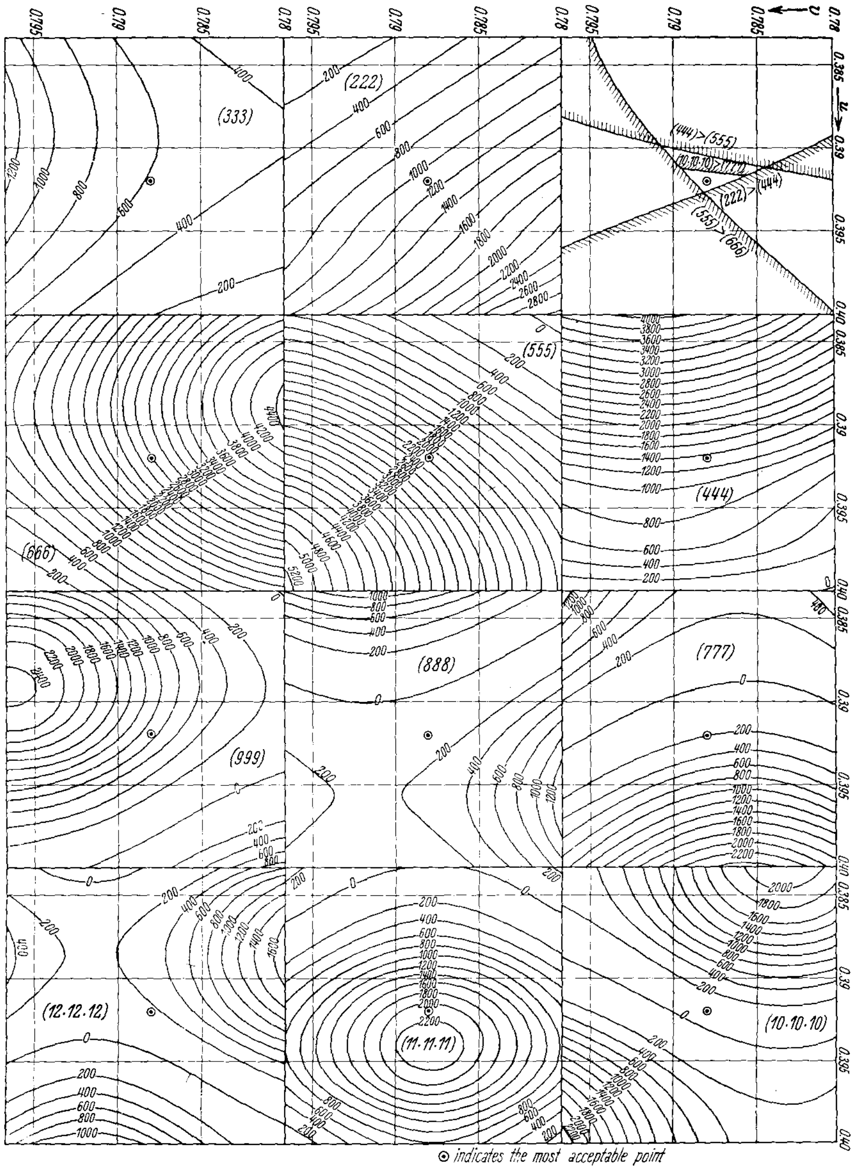
1) The intensities shown in figure 1 were calculated without the use of the Debye-Waller temperature factor.



⊙ indicates the most acceptable point

Fig. 1. $I_{(hhh)}$ as a function of u and v. (Calculated without the Debye-Waller temperature factor.)

There are now nine structures to be discussed, one of which is the correct one. They cannot be distinguished by means of the intensities of reflection from the basal plane, but the observed intensities of the

Table II. Observed and Calculated Distances and Intensities for Powder Photograph No. 12.

hkl	$d_{\text{obs.}}$	$d_{\text{calc.}}$ 1)	$I_{\text{obs.}}$	$I_{\text{calc.}}$	
222	5.06	5.00	0.85	0.42	
100	3.74	3.71	0.65	0.65	
110	3.57	3.63	0.30 2)	0.08	
333	3.36	3.33	0.20	0.12	0.54
211	3.36	3.35		0.42	
221	3.20	3.17	3.75	3.75 3)	
322	2.84	2.82	0.35	0.28	
332	2.65	2.65	0.50	0.26	
444	2.52	2.50	0.25	0.15	
433	2.35	2.34	0.80	1.26	
443	2.21	2.20	0.15	0.16	
01$\bar{1}$	2.16	2.16	1.10	1.30	
120	absent	2.11	absent	0.01	
555	1.99	2.00	0.60	0.14	0.57
231	1.99	1.98		0.12	
544	1.99	1.96		0.31	
554	1.86	1.86	0.13	0.03	0.14
11$\bar{1}$	1.86	1.87		0.09	
200	1.86	1.86		0.02	
220	1.79	1.81	0.40	0.06	0.79
342	1.79	1.81		0.04	
311	1.79	1.79		0.69	
331	1.72	1.71	0.02	0.08	
665	1.68	1.68	0.25	0.05	0.24
666	1.68	1.67		0.12	
422	1.68	1.67		0.07	
453	1.63	1.63	0.13	0.13	
665	1.59	1.60	0.35	0.18	0.56
442	1.59	1.59		0.38	
533	1.54	1.54	0.06	0.06	

lines on the powder photographs afford a means of eliminating all but one of the nine structures. This remaining structure is, therefore, the correct one. The following data are obtained from powder photograph no. 12 (see Table II).

Indices	(100)	(122)	(223)	(233)
Observed Intensity	0.65	3.75	0.35	0.50

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1) $a_0 = 10.31$ Å; $\alpha = 24° 10'$.

2) β (221) falls here with ~ 1/10 intensity of (221) or $I\,\beta$ (221) = 0.38. This gives $I\,(110)_{\text{Obs.}} = -0.08 \sim 0$.

3) Agreement forced for this line.

The intensities of each of the above lines was calculated for each of the nine structures by means of the formula:

$$I_{(hkl)} = z\left(\frac{1+\cos^2 2\theta}{2\sin 2\theta}\right) d_{hkl}\left[f_s + 2f_{Bi}\cos 2\pi(h+k+l)\,u + 2f_{Te}\cos 2\pi\,(h+k+l)\,v\right]^2 .$$

Pauling and Sherman f values were used. z is the number of planes in a form and d_{hkl} is the interplanar distance. The results of this calculation are as follows:

Structure	u	v	$\frac{I_{(100)}}{8000}$	$\frac{I_{(122)}}{8000}$	$\frac{I_{(223)}}{8000}$	$\frac{I_{(233)}}{8000}$
a	0.065	0.121	653	152	52	17
b	0.065	0.455	72	48	72	221
c	0.065	0.788	423	5	295	164
d	0.392	0.121	27	88	22	229
e	0.392	0.455	495	217	12	20
f	0.392	0.788	102	571	43	42
g	0.725	0.121	29	264	276	122
h	0.725	0.455	137	117	237	0
i	0.725	0.788	0	3	30	6

There is only one structure which satisfies all the requirements $I(221) > I(100)$, $I(221) > I(223)$, and $I(221) > I(233)$. This is the structure f above for which $u = 0.392$ and $v = 0.788$. A complete set of calculations for the intensities of the lines appearing on powder photograph No. 12 was made on the basis of structure f. The results are shown in Table II. From the very satisfactory agreement it can safely be concluded that f is the structure of tetradymite.

Description of the Structure: Analytically the structure is described as follows:

Rhombohedral lattice; $a_0 = 10.31$ Å, $\alpha = 24° 10'$.
One sulfur atom at 0,0,0; two bismuth atoms at $\pm(u,u,u)$ with $u = 0.392$;
Two tellurium atoms at $\pm(v,v,v)$ with $v = 0.788$.

The structure consists of layers of atoms of one kind in the order *S, Bi, Te, Te, Bi, S, Bi* etc. where each layer is in the relation to its neighboring layers found in cubic close-packing. The relative positions of the atoms are shown in Figure 2. The shortest interatomic distances compare with the normal-valence radius sums calculated from Pauling and Huggins' table as follows:

Atoms	*Bi-S*	*Bi-Te*	*Te-Te*
Shortest distance in tetradymite (Å)	3.05	3.12	3.69
Normal-valence radius sum (Å)	2.55	2.88	2.74

Each S has six Bi at the Bi-S distance, each Bi has three S and three Te at the Bi-S and Bi-Te distances and each Te has three Bi and three Te at the Bi-Te and Te-Te distances.

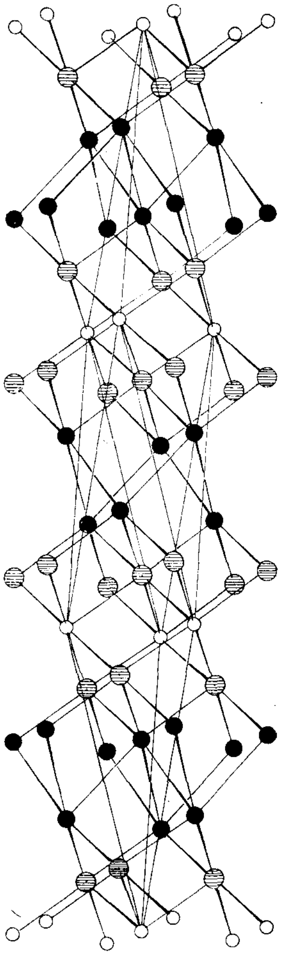

Fig. 2. Structure of Tetradymite.

The only result which can be correlated with existing data is the Te-Te distance which is very near the shortest distancebetween two nonbonded tellurium atoms in elementary tellurium; namely, 3.74 Å.

It might have been expected that the structure would be such as to place each sulfur atom nearest to two bismuth atoms and each bismuth atom nearest to one sulfur and two tellurium atoms as a result of covalent bond formation. A distortion of the tetradymite structure such as to meet these requirements would result in a structure demanding a larger unit cell for its description than that found experimentally. Such a distortion, therefore, if it exists, must be too small to give any effects observable by means of the experimental technique used. The absence of covalent bonds and the physical properties of tetradymite suggest that this substance is an example of the metallic state.

Summary: The unit cell of tetradymite is found to be rhombohedral with $a_0 = 10.31$ Å and $\alpha = 24° 10'$. Atomic positions:

$1\,S$ at $0,0,0$; $2\,Bi$ at $\pm(u,u,u)$, $u = 0.392$;
$2\,Te$ at $\pm(v,v,v)$, $v = 0.788$.

The formula of tetradymite may accordingly be written Bi_2Te_2S. It is suggested that tetradymite is an example of the metallic state.

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