## DETERMINATION OF THE CRYSTAL STRUCTURE OF THE HEXAGONAL PHASE IN THE SILVER-TELLURIUM SYSTEM R. M. Imamov and Z. G. Pinsker

Institute of Crystallography, Academy of Sciences of the USSR Translated from Kristallografiya, Vol. 11, No. 2, pp. 182-190, March-April, 1966 Original article submitted May 18, 1965

The structure of the hexagonal phase with lattice spacings a = 13.48 and c = 8.49 A in the Ag<sup>-</sup>Te system was studied in thin films. By using the method of three dimensions of  $\Phi^2$  and  $\Phi$  series it was shown that the unit cell of this phase contained five molecules of Ag<sub>7</sub>Te<sub>4</sub>. The Ag and Te atoms occupy the following positions in the D<sup>1</sup><sub>6h</sub> space group: 12 AgI - 12 (q) with x = 0.454 and y = 0.120, 12 AgI - 12 (o) with x = 0.237 and z = 0.181,  $6 \text{ Ag}_{\Pi} - 6 \text{ (l)}$  with x = 0.125,  $3 \text{ Ag}_{IV} - 3 \text{ (f)}$ ,  $2 \text{ Ag}_{V} - 2 \text{ (e)}$  with z = 0.181,  $12 \text{ Te}_{I} - 12 \text{ (n)}$  with x = 0.330 and z = 0.181,  $6 \text{ Te}_{\Pi} - 6 \text{ (k)}$  with x = 0.217,  $2 \text{Te}_{\Pi} - 2 \text{ (c)}$ .

For determining the structure of the hexagonal phase in the Ag<sup>-</sup>Te system, we used electron-diffraction photographs obtained by Chou Ching-liang.

According to the phase diagram [1], the Ag-Te system contains one high-temperature form  $\beta$ -Ag<sub>2</sub>Te and at least two or possibly three low-temperature forms. Rahlfs obtained [2] a face-centered cubic structure with lattice spacing a = 6.572 A for the high-temperature phase  $\beta$ -Ag<sub>2</sub>Te; the space group was  $Fm3m = O_{h}^{5}$ . The basis of the structure is a face-centered lattice of Te atoms. The silver atoms are disposed in disorder over several (tetrahedral and octahedral) positions. Contradictory data exist regarding the crystal system and unit cells of the low-temperature phases. According to Rowland and Berry [3] the low-temperature phase  $\alpha$ -Ag<sub>2</sub>Te belongs to the rhombic system with lattice spacings a = 16.28, b = 26.68, c = 7.55 A and space group Immm. These data disagree with those of Koern [4] and Tokody [5]. According to Koern  $\alpha$ -Ag<sub>2</sub>Te also belongs to the rhombic system, but with different spacings, namely a = 13.0, b = 12.7, c =12.2 A. Tokody considers that the low-temperature phase  $\alpha$ -Ag<sub>2</sub>Te must be monoclinic, with spacings a = 6.57, b = 6.14, c = 6.10 A,  $\beta = 61^{\circ}15'$ , and space group Pm, P2, or P2/m. A complete structural determination of the low-temperature phase of Ag<sub>2</sub>Te was given by A. J. Frueh [6]. According to this author, the structure of  $\alpha$ -Ag<sub>2</sub>Te constitutes an ordered phase and has a unit cell

with spacings a = 8.09, b = 4.48, c = 8.96 A,  $\beta = 123°20'$ . The number of molecules per cell is Z = 4, and the symmetry P2<sub>1</sub>/c. All the atoms lie in general, four-fold positions. An electron-diffraction study of the structure of  $\alpha$ -Ag<sub>2</sub>Te [7] confirmed the x-ray structural data for large-scale samples of the monoclinic phase Ag<sub>2</sub>Te for thin layers.

On analyzing the published data, we come to the conclusion that a hexagonal phase (or several phases) also exists in the Ag – Te system at room temperature. Thus Peacock [8] studied the compound Ag<sub>2-x</sub>Te<sub>1+x</sub> (where 0.1 < x < 0.5) and assigned it a hexagonal symmetry with spacings a = 13.49 and c = 8.480 A, associated with space group D<sup>4</sup><sub>6h</sub>. Koern [4] gives hexagonal spacings for  $\alpha$ -Ag<sub>12</sub>Te<sub>7</sub>: a = 13.456 and c = 8.468 A, with space group D<sup>1</sup><sub>6h</sub>. Chou Ching-liang studied thin films in the Ag – Te system by electron diffraction [9] and also established the existence of a hexagonal phase with spacings very close to those given in [4] and [8]; he also showed that a hexagonal phase of the Ag – Te system was always formed in the presence of excess Te.

Most reliably of all,a lamellar texture of hexagonal-phase crystallites was obtained on the surface of rocksalt crystals. Oblique photographs of these films (Fig. 1) in the presence of standard NH<sub>4</sub>Cl lines gave the lattice spacings of this phase:  $a = 13.48 \pm 0.05$  and  $c = 8.49 \pm 0.05$  A, which are close to those of the hexagonal phases obtained by Peacock [8] and Koern for alloys with formulas



Fig. 1. Electron-diffraction photograph of the hexagonal phase Ag<sub>7</sub>Te<sub>4</sub>.

 $Ag_{2-x}Te_{1+x}$  and  $Ag_{12}Te_7$  respectively. With this unit cell we were able to index electron-diffraction photographs of the Fig. 1 type completely and establish the absence of any extinctions, which supports Koern's proposed space group P6/mmm $^{-}D_{6h}^{1}$ . In addition to the centrosymmetric space group  $D_{6h}^{1}$ , however, the same condition is satisfied by other space groups, both centrosymmetric and noncentrosymmetric.

For further examination of the structure, the hexagonal phase had to be identified. We had no data on the exact composition of this phase. As mentioned earlier, however, hexagonal crystallites were obtained in the presence of excess Te. A deviation from the stoichiometric composition of Ag<sub>2</sub>Te is also confirmed by the ratio of the unit-cell volumes of the hexagonal and monoclinic phases:  $\Omega_{\rm hex} / \Omega_{\rm mon} = 1330/271.4 = 4.89 < 5$ . Thus it would appear that the unit cell contains less than 20 molecules of Ag2Te. As indicated earlier, Peacock assigned this phase the composition  $Ag_{2-x}Te_{1+x}$  and Koern Ag<sub>12</sub>Te7. Other compositions are given in [1]:  $Ag_3Te_2$  and  $Ag_7Te_4$ . There are no experimental data, however, to support the existence of the compound Ag<sub>3</sub>Te<sub>2</sub>. Compounds Ag<sub>7</sub>Te<sub>4</sub> and Ag<sub>12</sub>Te<sub>7</sub> differ by only 0.15 at.% Te; points in favor of the former include the simpler atomic ratio and the fact that the x-ray data which suggested the existence of compound  $Ag_{12}Te_7$  are not entirely reliable. Thus at the very beginning of our study of the hexagonal phase we may assume that its composition corresponds to the formula  $Ag_7Te_4$  and that the unit cell contains five molecules of this composition, although the final composition of the phase can only

be ascertained by analyzing the heights of the potential peaks.

The reflection intensities on the electron-diffraction picture of the hexagonal phase were determined visually, the intensities of the hk0 reflections [texture axis (0001)] as measured on an MF-4 microphotometer serving as standards. The intensities were translated into experimental structure amplitudes by the kinematic-theory formula  $\Phi =$  $(I/pd_{hk0}d_{hkl})^{1/2}$ . Altogether some 400 reflections were measured on the diffraction photograph of Fig. 1. In some of these, however, two or sometimes three reflections were merged together. In these cases the experimental intensity values were divided by two (or three), allowing for the repetition factor of the reflections. In this way values of  $\Phi^2_{exp}$  were obtained for around 450 reflections (up to sin  $\theta/\lambda \approx 0.72 \text{ A}^{-1}$ ). Statistical analysis of the experimental intensities gave no convincing evidence in favor of either centrosymmetric or noncentrosymmetric space groups. Even the first stage in the structural investigation, however, viz., the projection of the  $\Phi^2$  series P(xy), the Harker sections P(xy0), P(xy<sup>1</sup>/<sub>2</sub>), and the one-dimensional sections  $P[^{1}/_{3}0z]$ ,  $P[^{1}/_{3}^{2}/_{3}z]$ ,  $P[^{14}/_{60}^{28}/_{60}z]$ ,  $P[^{13}/_{60}0z]$ , etc., convinced us of the existence of a center of symmetry.

Figure 2 shows the projection of the  $\Phi^2$  series along the c axis, calculated from 68 hk0 reflections. Characteristics of this projection include maxima at the points  $(\frac{1}{3}, 0)$ ,  $(\frac{1}{3}, \frac{1}{3})$ ,  $(\frac{14}{60}, \frac{28}{60})$  and certain others  $(\frac{13}{60}, 0)$ ,  $(\frac{7.5}{60}, \frac{15}{60})$ ,  $(\frac{28}{60}, \frac{8}{60})$ , etc. We see from Fig. 2 that this projection is insufficient to determine the structure of the hexagonal



Fig. 2. Projection of the  $\Phi^2$  series along the c direction.



Fig. 3. Section of three-dimensional  $\Phi^2$  series, P(xy0).



Fig. 4. Section of three-dimensional  $\Phi^2$  series,  $P(xy^1/_2)$ .

phase. The picture is complicated by the fact that the silver and tellurium atoms are not very different in atomic number (47 and 52 respectively). Onedimensional sections of the  $\Phi^2$  series were constructed from almost all the observed maxima of Fig. 2. The one-dimensional section  $P[^{1}/_{3}0z]$ ,  $P[^{14}/_{60} \, {}^{28}/_{60}z]$  gave peaks for z = 0.185. The sections  $P[^{7.5}/_{60}, \, {}^{15}/_{60}, \, z]$ ,  $P[^{1}/_{2}0z]$ , and also  $P[^{1}/_{3} \, {}^{2}/_{3} \, z]$ gave no maxima apart from the peak at zero. As regards the sections  $P[^{13}/_{60}0z]$  and  $P[^{28}/_{60} \, {}^{8}/_{60} \, z]$ , these gave a peak at z = 0.500.

We may thus suppose that the silver and tellurium atoms are disposed in planes perpendicular to the c axis with the following z values: 0.000, 0.185, 0.500, 0.815. Accordingly, we calculated the three-dimensional sections of the  $\Phi^2$  series, P(xy0),  $P(xy^{1}/_{2})$ , as shown in Figs. 3 and 4. Figure 3 shows strong maxima at points  $(^{7.5}/_{60}, \frac{15}{60}), (\frac{15}{60}, \frac{7.5}{60}),$ etc., associated with the six-fold position of the atoms in one of the following space groups:  $D_{3d}^3$ ,  $D_6^1$ , and  $D_{6h}^{1}$ . Maxima at  $\binom{1}{3}$ ,  $\binom{2}{3}$  and  $\binom{1}{2}$ , 0) apparently correspond to the two- and three-fold position in the same space groups. In Fig. 4 strong maxima are found at  $\binom{13}{60}$ , 0),  $\binom{13}{60}$ ,  $\frac{13}{60}$ , etc. These may also be related to the six-fold position in one of the space groups mentioned. The maxima at  $\binom{28}{60}$ ,  $\frac{8}{60}$ ,  $\binom{28}{60}$ ,  $\binom{28}{60}$ ,  $^{20}/_{60}$ ), etc., apparently correspond to the twelvefold position: x, y, 1/2; y, x-y, 1/2; y-x, x, 1/2; x-y,  $\overline{y}$ , 1/2;  $\overline{x}$ , y-x, 1/2; y, x, 1/2;  $\overline{x}$ ,  $\overline{y}$ , 1/2;  $\overline{y}$ , y-x, 1/2;  $\overline{y}$ ,  $\overline{x}$ , 1/2; x-y, x, 1/2; x, x-y, 1/2; y-x, y, 1/2. Of all the space groups mentioned earlier, only  $D_{6h}^{1}$  has such a 12(q) position. Thus, we are left with only one space group,  $D_{6h}^1$ , with which to describe the phase in question.

The one-dimensional sections  $P[{}^{1}_{3}0z]$ ,  $P[{}^{14}_{60}$ ,  ${}^{28}_{60}$ , z], etc., show that the maxima at  $({}^{4}_{3}$ , 0, 0.185), etc., and at  $({}^{44}_{60}$ ,  ${}^{28}_{60}$ , 0.185), etc., correspond to two twelve-fold positions, 12(n) and 12(o) in the space group  $D_{5h}^{4}$ . Thus, of the 55 silver and tellurium atoms (supposing that the cell contains five  $Ag_{7}Te_{4}$  molecules) we have fixed the positions of 53. The two remaining atoms may be placed in the two-fold position 2(e) with  $z \approx 0.185$ .

It was further necessary to distinguish the positions occupied by the Ag and Te atoms. We started with the following: the Te atoms in the monoclinic form of  $\alpha$ -Ag<sub>2</sub>Te lying in planes with y = 0.159, y = 0.841, y = 0.659, y = 0.341 form an approximately hexagonal pattern with side  $a \sim 8.09$ -8.96 A. The b spacing of the monoclinic phase of  $\alpha$ -Ag<sub>2</sub>Te is 4.48 A and the c spacing of the hexagonal phase, 8.49 A, i.e., chex  $\approx 2b_{mon}$  ( $\beta = 123^{\circ}20^{\circ}$ ). On this basis, we placed Te atoms in positions 12(n) and 6(k). The silver atoms were placed in positions

12(q), 12(0), 6(l), and 3(f). From crystal-chemical considerations we placed two Te atoms in 2(c): if we put silver atoms in the position, we obtain a trihedral prism of Ag atoms with a silver atom inside, which is not very probable. We regard the 2(e) position as silver-occupied. For this arrangement of Ag and Te atoms in the structure of the hexagonal phase, the interatomic distances, Ag-Ag~2.80, Ag-Te ~ 2.70, and Te-Te ~ 2.8 to 3.2 A, as well as the coordination of the Ag atoms relative to the Te and vice versa, are in good agreement with published data [10, 11].

Thus, on the basis of  $\Phi^2$  series, geometrical analysis, and crystal-chemical considerations, we came to the conclusion that the atoms in the structure of the hexagonal phase  $Ag_7Te_4$  occupied the following positions in the space group  $D_{6h}^{1}$ :  $12Ag_I -$ 12(q) with  $x \approx \frac{28}{60}$  and  $y \approx \frac{8}{60}$ ,  $12Ag_{II} - 12$  (o) with  $x \approx \frac{14}{60}$  and z = 0.185,  $6Ag_{III} - 6(l)$  with  $x \approx$  $7.5/_{60}$ ,  $3Ag_{IV} - 3(f)$ ,  $2Ag_V - 2$  (e) with  $z \approx 0.185$ ,  $12Te_I - 12$  (n) with  $x \approx \frac{1}{3}$  and  $z \approx 0.185$ ,  $6Te_{II} - 6$  (k) with  $x \approx \frac{13}{60}$ ,  $2Te_{III} - 2$  (c).

On the basis of this model we calculated the theoretical structure amplitudes for the hk0 reflections. As mentioned earlier, in the first stage of the structural investigation the intensities of overlapping reflections were divided in a ratio allowing for the repetition factor. After calculating the  $\Phi_{calc}$ , the intensities of these reflections were also divided in a ratio determined by theoretical calculation of the corresponding pair of amplitudes.

Comparison between  $\Phi_{\exp}^{hk0}$  and  $\Phi_{calc}^{hk0}$  gave sat-isfactory results (R ~ 35%). The coordinates of the atoms on the projection of the  $\Phi$  series along the c direction only differed slightly from those of the model just derived. After four refinement cycles the R factor for the hk0 reflections fell to 29%. We also calculated  $\Phi_{calc}$  for the h0l reflections and compared with  $\Phi_{exp}$  (R ~ 34%). Five refinement cycles of the  $\varphi(xz)$  projection reduced the R factor for the h0l reflections to 28%. The Ag and Te atoms in the  $\Phi$  series projection  $\varphi(xz)$  were in fact disposed at z = 0,  $z = \pm 0.183$ , z = 0.500. Many atoms, however, overlapped in this projection. For exact determinations of the horizontal coordinates, we then calculated the three-dimensional  $\Phi$ -series sections  $\varphi(xy0)$ ,  $\varphi(xy^{1}/_{2})$ . The silver and tellurium atoms in these sections had almost the same coordinates as in  $\Phi$ -series projection  $\varphi(\mathbf{x}\mathbf{y})$ . In order to refine the z parameters of the Ag and Te atoms we constructed the one-dimensional sections  $\varphi[00z]$ ,  $\varphi$ [0.237, 0.474, z],  $\varphi$ [0.330, 0, z] (Fig. 5). The final coordinates of Ag and Te in the  $Ag_7Te_4$  structure are given in Table 1.

TABLE 1

A +	Coordinates of atoms			Atoms	Coordinates of atoms		
Aloins	x/a	<b>y</b> /b	z/c		x/a	y/b	z/c
$\begin{array}{c} \mathrm{Ag}_{\mathrm{I}}\\ \mathrm{Ag}_{\mathrm{II}}\\ \mathrm{Ag}_{\mathrm{III}}\\ \mathrm{Ag}_{\mathrm{IV}} \end{array}$	0.454 0.237 0.125 0.500	0, <b>12</b> 0 0 0 0	0.599 0.181 0 0	Ag <sub>V</sub> Te <sub>I</sub> Te <sub>II</sub> Te <sub>III</sub>	0 0,330 0,217 1/3	0 0 0 2/3	0.181 0.181 0.500 0



Fig. 5. ()ne-dimensional sections of the  $\Phi$  series:  $\varphi[00z], \varphi[0.330, 0, z], \varphi[0.237, 0.474, z].$ 

Naturally, other variants of the atomic positions of Ag and Te are possible. Thus, for example, we could put the Te atoms in position 12(o) and the Ag in 12(n), and so on. It should be emphasized, however, that the lowest value of the R factor, and also satisfactory agreement with the Ag-Ag and Ag-Te interatomic distances already published [10, 11], were obtained from our preferred model. The slight difference in the potential-peak heights of the Ag and Te atoms in the Fourier syntheses also indicated the correctness of our model.

The final values of the R factors for the hol and hk0 reflections were 23% (Fig. 6) and 24% (Fig. 7) respectively; for all the reflections observed on the electron-diffraction photographs (~450, allowing for reflections with zero indices), it was 23.2%. All these R factors were calculated with due allowance for the temperature factor (B =  $1.3 \text{ A}^2$ ).

Thus our structural study of the hexagonal phase leads to the composition  $Ag_7 Te_4$ , with five molecules in the unit cell. On considering the structure of  $Ag_7 Te_4$ , we find an extremely complicated coordination of the Ag and Te atoms. We see from Fig. 8 that the Te<sub>II</sub> atoms form  $Ag_2$ Te molecules with the Ag<sub>I</sub> (Ag – Te distance 2.765 A), lying in a plane perpendicular to the c axis at  $z = \frac{1}{2}$ . The Ag – Te – Ag bond angle is of the order of 61°. This layer of atoms is, as it were, isolated from the Ag and Te atoms in other planes. Figure 9 shows a projection of three layers of the Ag<sub>7</sub>Te<sub>4</sub> structure on the (0001) plane with the following z values: 0, 0.181, -0.181. We see from this figure that the









Fig. 8. Disposition of Ag and Te atoms in the plane z = 0.500.

TABLE 2. Interatomic Distances in A



Fig. 9. Projection of three layers of the  $Ag_7Te_4$  structure on the (0001) plane with the following z values: 0.000, 0.181, -0.181.

Compound	Ag — Ag	Ag — Te	Те — Те
Ag₃AuTe₂ AgAuTe₄	-	2.90, 2.95 2.69, 2.96, 3.20	3.91 2.87, 3.55, 3.65
(Ag, Au) Te <sub>2</sub> 1 (Ag, Au) Te <sub>2</sub> 11	-	2.68, 2.94 2.63, 2.66, 2.67, 2.87, 2.94, 2.95, 3.04, 3.15, 3.22	3, 19, -3.49 3.02, -3.08, 3.28, 3.34, -3.51, -3.54
α-Ag <sub>2</sub> Te	-	2.85, 2.90, 2.95, 3.04, 2.87, 2.91, 2.99, 3.04	More than 4.26
Ag7Te4	$\begin{array}{l} Ag_{I} & - Ag_{I}: 2.81, \\ & 2.88, \\ Ag_{III} - Ag_{III}: 2.92, \\ Ag_{II} & - Ag_{III}: 3.04, \\ Ag_{I} & - Ag_{II}: 3.08, \\ Ag_{III} - Ag_{V}: 3.30, \end{array}$	$\begin{array}{c} \mathbf{Ag_{II}} - \mathbf{Te}_{I}: 2.72, \\ \mathbf{Ag_{IV}} - \mathbf{Te}_{I}: 2.75, \\ \mathbf{Ag}_{I} - \mathbf{Te}_{II}: 2.765, \\ \mathbf{Ag}_{II} - \mathbf{Te}_{II}: 2.84, \\ \mathbf{Ag}_{II} - \mathbf{Te}_{I}: 2.87, \\ \mathbf{Ag}_{I} - \mathbf{Te}_{I}: 3.16, \end{array}$	$ \begin{array}{l} {\rm Te}_{\rm II} - {\rm Te}_{\rm II}; 2.92, \\ {\rm Te}_{\rm I} - {\rm Te}_{\rm II}; 3.11, \\ {\rm Te}_{\rm I} - {\rm Te}_{\rm I}: 4.45, \end{array} $
	$A_{g_{II}} - Ag_{II}$ : 3,90,	$Ag_V - Te_{II}$ : 3.95	

Te<sub>1</sub> atoms are surrounded by five silver atoms:  $2Ag_{III}$ ,  $2Ag_{II}$ ,  $Ag_{IV}$  (Ag - Te distances 2.87, 2.92, 2.75 A, respectively). The Ag<sub> $\Pi$ </sub> are surrounded by  $4\text{Te}_I$  and  $2\text{Ag}_{III}$  (Ag – Te and Ag – Ag distances 2.87 and 2.92 A). As regards the Ag<sub>IV</sub> atoms, these lie in the center of a rectangle formed by Teratoms, with Ag - Te distance 2.75 A. The remaining Ag - Ag, Ag - Te, and Te - Te interatomic distances are shown in Table 2. The Ag-Te distances in the  $Ag_7Te_4$  structure are in good agreement with those in the structures of  $\alpha$ -Ag<sub>2</sub>Te, Ag<sub>3</sub>AuTe<sub>2</sub>, AgAuTe<sub>4</sub>. The mean Ag – Te distance in Ag<sub>7</sub>Te<sub>4</sub> is  $\sim 3.00$  A; that in the other structures is  $\sim 2.95$  A. The Te – Te distances in  $Ag_7Te_4$  are 2.92 and 3.11 A. These quantities are comparable with the corresponding distances within the molecules in the structure of Te (2.87 A), but smaller than the Te - Te distances between molecules (3.74 A).

On comparing the structure of our  $Ag_7Te_4$  phase with that of  $\alpha$ -Ag<sub>2</sub>Te, we notice first of all a hexagonal pattern of Te atoms in both structures. Moreover, the Ag and Te atoms in  $\alpha$ -Ag<sub>2</sub>Te also (to a first approximation) form Ag<sub>2</sub>Te molecules with Ag-Te distances of 2.85 and 2.87 A.

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