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DETERMINATION OF THE CRYSTAL STRUCTURE OF THE LOW-TEMPERATURE PHASE α-Ag_2Se

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The structure of the low-temperature phase α-Ag_2Se with spacings a = 7.05, b = 7.85, c = 4.33 A, Z = 4, and space group $P222_1$ is established by electron diffraction. In the phase α-Ag_2Se there is a completely new combination of covalent bonds inside chain molecules in the three-dimensional framework of a diamond-type lattice of silver with metallic bonds.

According to the phase diagram [1], the Ag–Se system does not contain any marked concentration range for solid solutions based on either of the components. The only compound is Ag_2Se, forming a high-temperature β-phase and a low-temperature α-phase with a transformation point at about 133°C. The structure of the β-phase is body-centered cubic with spacing a = 4.98 A and two Ag_2Se molecules in the unit cell. The Se atoms are positioned in an ordered fashion, while the Ag statistically occupy several positions with an overall multiplicity of 42.

There are no x-ray data on the structure of the α-phase. Electron-diffraction examination of thin, sublimed Ag–Se films [3, 4] yielded photographs of oriented α-Ag_2Se samples giving this phase a rhombic unit cell with dimensions: a = 7.05, b = 4.325, c = 7.82 A. Furthermore, the existence of cubic phases richer in silver than Ag_2Se, a face-centered β'-phase (a = 6.92 to 6.96 A) and a silver-base solid solution (a = 4.10 to 4.11 A) was observed in [4].

The present paper is devoted to determining the crystal structure of α-Ag_2Se. Thin films of α-Ag_2Se were obtained by vacuum sublimation of the components onto a NaCl face or a celluloid film. In the majority of the experiments the selenium was sublimed first (usually in excess), and then the silver. The atomic beams were condensed either on substrates at room temperature or on heated substrates. After sublimation, the films were annealed for homogenization and the formation of the α-Ag_2Se phase by mutual diffusion (the excess of Se atoms meanwhile evaporated). Electron-diffraction examination showed that films obtained with a not-too-intense evaporation of the components on a NaCl substrate at room temperature, followed by annealing, comprised α-Ag_2Se crystals. Figure 1 shows an electron-diffraction photograph of a textured film (exposure angle ~60°)

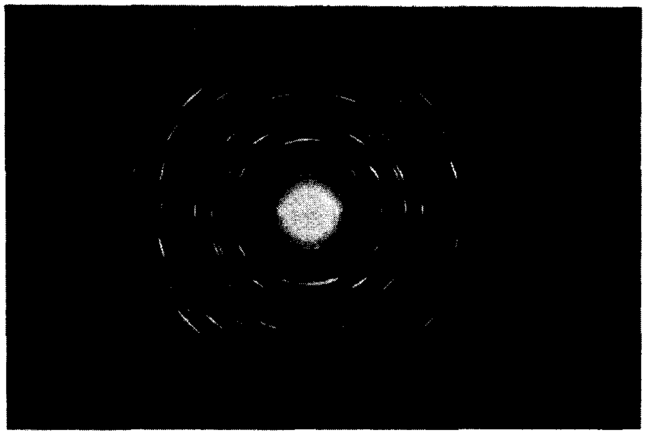

Fig. 1. Oblique-texture electron-diffraction photograph of the α-phase of Ag_2Se.

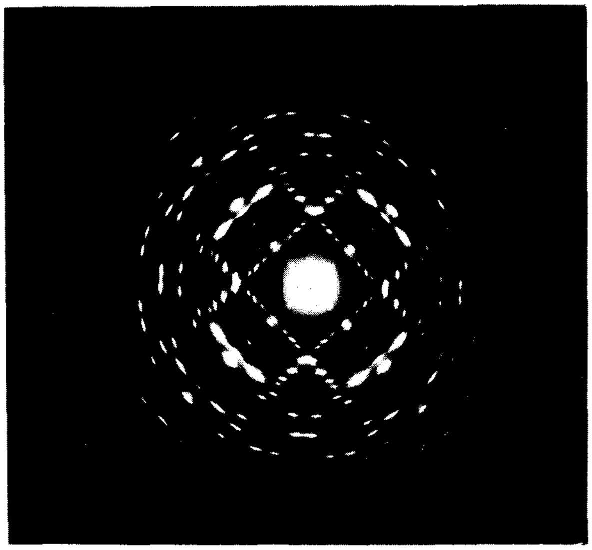

Fig. 2. Electron-diffraction photograph of mosaic crystals of the α-phase of Ag_2Se. Plane (011) parallel to the substrate.

obtained from a sample annealed at 100°C for 2 h. The crystals in these films were oriented with the (001) plane parallel to the NaCl cleavage surface. All the reflections on the electron-diffraction photograph were indexed on the basis of a rhombic cell with spacings $a = 7.05$, $b = 4.33$, $c = 7.85$ A. On these photographs no regular extinctions were noted, so that we have the following space groups to choose from: Pmmm, Pmm2, P222. In order to decide between the first centrosymmetrical and the two noncentrosymmetrical groups, we attempted to use statistics in the distribution of structure amplitudes with respect to moduli. No definite results, however, could be achieved. If we omit three very weak reflections (010, 030, and 050) from consideration, then the only possible space group is the $P222_1$ in the system $a = 7.05$, $b = 7.85$, $c = 4.33$ A (subsequently, unless otherwise stipulated, we shall be considering the arrangement $a = 7.05$, $b = 7.85$, $c = 4.33$ A). The proximity of the cubic and rhombic cells to a multiple relationship ($V_{cub} = 123.5$, $V_{rhomb} = 239.6$ A^3) shows that the unit cell of α-Ag_2Se contains four Ag_2Se molecules. Apart from this, we note the simple ratios between the spacings: $a_{rhomb} = a_{cub}\sqrt{2}$, $c_{rhomb} = a_{cub}\sqrt{3/2}$.

In order to establish the structure of this phase, we measured the reflection intensities on the electron-diffraction photograph. The intensities of the $h0l$ reflections (zero layer line) were measured microphotometrically and served as blackening standards for the visual estimate of intensity in the other reflections. It is known that one of the demerits of texture electron-diffraction photographs is the existence of a dead zone, i.e., a cone around the texture axis, the angles of which remain outside the interference field of the photograph. In order to reduce the "dead zone" somewhat, we obtained diffraction photographs at angles of 70 to 80°. In this way we were able to collect the 120, 140, 150, 240, 250, 260, etc., reflections.

The intensities of the reflections lying on the texture axis (0k0) were estimated from the electron-diffraction photographs of a mosaic single crystal (Fig. 2) obtained from a film evaporated onto a heated NaCl substrate with subsequent annealing at 150°C for 2 h. The crystallites were disposed with the (011) plane parallel to the substrate. As blackening marks for estimating the intensities of the (0k0) reflections we used reflection (0kl), which was also present in the photograph of Fig. 1. By further comparison of the intensities of reflections found in both diffraction photographs (Figs. 1 and 2), we found the mean transfer coefficient for bringing the intensities to the same scale. In this way we obtained the intensities of around 275 reflections (up to $\sin\vartheta/\lambda \sim 0.800$ A^{-1}). Transformation from the intensities to the $|\Phi|$ values was effected by the kinematic-theory formula.

The small value of the c spacing of the unit cell as compared with the a and b enabled us to obtain a good Patterson projection along the c axis, without undesirable overlapping of maxima. This projection was calculated from 68 hk0 reflections. Characteristics of the projection include strong maxima at the points (0; ½) and (~0.3; 0) and certain others: (¼; ½), (½; ¼), and (~0.15; 0.28) (Fig. 3). In order to determine the structure, we used chiefly the method of deciphering this Φ^2

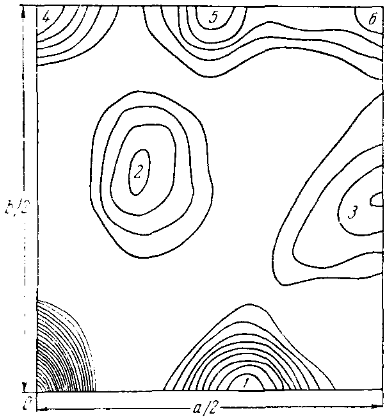

Fig. 3. Projection of the Φ^2 series on the (xy0) plane.

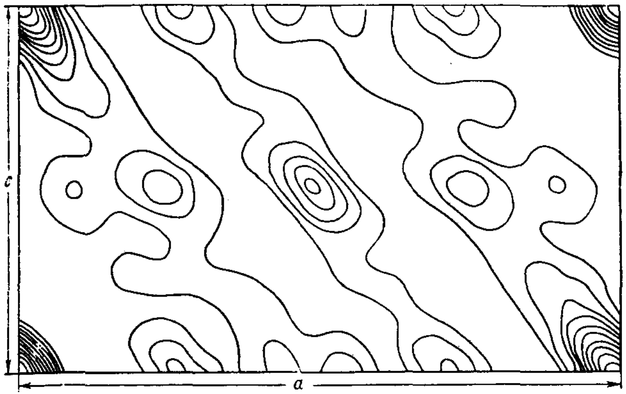

Fig. 4. Projections of the Φ^2 series on the (x0z) plane.

projection on the basis of probable space groups. In this we naturally ascribed the two strong maxima mainly to the Ag–Ag vectors. In deciphering the xy0 Patterson projection, we turned first to the centrosymmetrical space group Pmmm. It is not difficult to see that we cannot use the eightfold (a) position for the disposition of the eight available silver atoms, since the pairs of positions (connected with the plane of symmetry perpendicular to the c axis) existing in them are unacceptable. Actually, the spacing c = 4.33 A is considerably smaller than $4R_{Ag}$ ($R_{Ag} \approx 1.4$ to 1.5 A). Thus the positions of smaller multiplicity on the mirror planes $z = 0$ or $z = \frac{1}{2}$ remain to be considered. However, even the existence of planes perpendicular to the x axis creates difficulties in placing the atoms if we consider the vector $(0;\ 0 \rightarrow {}^{17}/_{60};\ 0)$ on the Patterson projection. This vector, in fact, is only possible on choosing $x \approx \frac{1}{8}$, which for the value of R_{Ag} mentioned requires $\Delta y \approx 0.3$-0.35, whereas in the present case $\Delta y = 0$. Thus the Pmmm space group falls out.

In considering the group Pmm2, it is convenient to change the nomenclature of the axes and select the arrangement $a = 7.85$ A, $b = 4.33$ A, $c = 7.05$ A. In fact, for the first pair of silver atoms (Ag_I) we choose, for example, position 2(f): $x\frac{1}{2}z$ and $\bar{x}\frac{1}{2}z$; bearing in mind the above-mentioned maxima $(0;\ 0 \rightarrow {}^{17}/_{60};\ 0)$ on the Patterson projection in the new axes $(0;\ 0 \rightarrow {}^{17}/_{60};\ 0)$ we choose $z_1 \approx 0.14$. Bearing in mind the maximum $(0;\ 0 \rightarrow \frac{1}{2};\ 0)$, we choose $x_1 \approx 0.25$. For Ag_{II} we choose 2(e) with $x_2 \approx 0.25$ and $z_2 \approx 0.86$. The remaining four Ag atoms we place on the projection in two pairs on the straight lines: $x_3 = 0$ and $x_4 = \frac{1}{2}$; Ag_{III} and Ag_{IV} on $x_3 = 0$, and Ag_V and Ag_{VI} on $x_4 = \frac{1}{2}$. For $\Delta z \approx 0.25$ and $\Delta y = \frac{1}{2}$, distances of the Ag_I–Ag_{II} type are of the order of 2.78 A and distances of the Ag_I–Ag_{IV} type with $\Delta z \approx 0.25$ and $\Delta x = \frac{1}{4}$ are of the order of 2.62 A, which is somewhat smaller than the Ag–Ag distance in the Ag_2Se structure. The Se atoms we again place in twofold positions: Se_I in 2(e) with $x_5 \approx 0.25$ and $z_5 \approx 0.25$; Se_{II} in 2(e) with $x_6 \approx 0.25$ and $\Delta z_6 \approx 0.75$. The model described must still be slightly deformed, since it has too great symmetry as compared with the Pmm2 group. In fact, perpendicular to the c axis, there appears a b glide plane, which corresponds to the D^5_{2h} group in the Pmmb arrangement, with origin of coordinates on the rotational axes. The deformation of the structure may be achieved by slight changes in the parameters $z_{Ag_{II}}$, $z_{Ag_{III}}$, $z_{Ag_{IV}}$, and also x_{Se} and z_{Se}, without an undesirable change in the interatomic distances.

It is not hard to see that the projection of this structural model along the y axis does not have a center of symmetry. Thus calculation of the Fourier projection requires introduction of the phases of the structure amplitudes, which makes objective verification of the model and selection of parameters from the experimental intensities more difficult. Since attempts made to improve the structural model failed to reduce the R factor below 60%, this variant was abandoned.

Another variant of the structure was a model based on the positions of points in a space group with rotational axes, P222. In this group the fourfold position corresponds to a rhombically-distorted tetrahedron. Let us retain the old nomenclature of the axes ($a = 7.05$, $b = 7.85$, and $c = 4.33$ A). We select for Ag_I the position 4(u) with $x \approx 0.14$, $y = 0.25$, and $z = 0.25$. For the other four silver atoms the fourfold position is unsuitable. In fact, in placing the silver atoms near the points $(\frac{3}{8}\frac{3}{8})$ we should choose for them $z = \frac{3}{4}$, and then difficulties are created with the disposition of Se atoms satisfying the Patterson projection. Thus we choose twofold positions on the lines $y = 0$ and $y = \frac{1}{2}$. In contrast to the Pmm2 group, however, in the present case these pairs of silver atoms lie on the z level. This does not allow them to approach closer than 2.65 to 2.70 A, which corresponds to $x \approx 0.34$: Ag_{II} in 2(i) and Ag_{III} in 2(e). Difficulty arises in placing the Se atoms. In the triangle of silver atoms Ag_I, Ag_{II}, and Ag_{III}, the height with respect to z is $\frac{1}{4}$, $\frac{1}{2}$, and 0. In order to place the Se atoms anywhere near the point $\frac{3}{8}\frac{1}{4}$, we must (so as to obtain the proper Ag_I–Se distance) choose $z = \frac{3}{4}$ for Se, but in this case the Ag_{II}–Se distance will be of the order of 2.14 A.

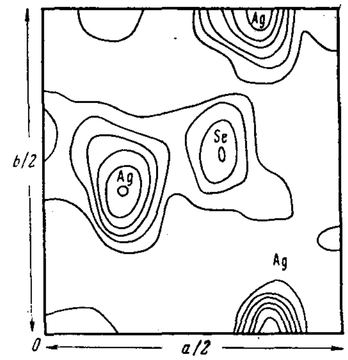

Fig. 5. Projection of Φ series on the (xy0) plane.

Calculation of the projection of the structure along the z axis is here facilitated by the presence of a center of symmetry in this projection. Examination enabled us to place the atoms in the positions indicated with the parameters

$$\mathrm{Ag_I},\ 4(u): x = 0.14,\ y = 0.23,\ z = 0.14,$$
$$\mathrm{Ag_{II}},\ 2(k): x = 0.32,$$
$$\mathrm{Ag_{III}},\ 2(j): x = 0.32,$$
$$4\,\mathrm{Se},\ 4(u): x = 0.27,\ y = 0.33,\ z = 0.63.$$

These values of parameter z, however, are hard to reconcile with the projection of the Φ^2 series along the b axis (Fig. 4), where the maxima are only situated near the levels z = 0 and z = ½. Here, however, some interatomic distances still remain impermissibly small: $\mathrm{Ag_{III}}-\mathrm{Ag_{III}}$ 2.33 A, $\mathrm{Ag_I}-$Se 2.38 A. The possibilities of displacing atoms in this space group are extremely limited. The structural model is strained and improbable; hence this variant also was abandoned.

However, if we neglect the three very weak 00*l* reflections (in the arrangement *a* = 7.05, b = 7.85, c = 4.33 A), the only possible space group is the $P222_1$. Supposing that the structure under investigation belongs to this group, we were easily convinced that our model was most simply described by means of the atomic positions in the $P222_1$ group. Here the projection of the structure along the c axis is centrosymmetrical, just as in the P222 group. In accordance with the positions of the maxima in the projections of the Φ^2 series along the c and b axes, we choose the atomic positions

$$\mathrm{Ag_I} - 4(e): x \approx 0.13,\quad y \approx 0.20;\quad z \approx 0.05,$$
$$\mathrm{Ag_{II}} - 2(a): x \approx 0.40,\quad \mathrm{Ag_{III}} - 2(b): x \approx 0.36;$$
$$\mathrm{Se} - 4(e): x \approx 0.31,\quad y \approx 0.24;\quad z \approx 0.55.$$

It must be noted that the values of $z_{\mathrm{Ag_I}}$ and z_{Se} must (slightly) differ from 0 or ½, since this would lead to the extinction of reflections 0k*l* with *l* ≠ 2n (i.e., to the space group Pcmm).

It should be noted that all three variants of the structure here considered are essentially very similar. Although they are described by three different space groups, and hence differ in symmetry, these differences are associated with only slight variations in the coordinates of the atoms.

We calculated the signs of the structure amplitudes on the basis of the last model. Ascribing these signs to Φ_{exp}, we constructed the projection of the Φ series on the xy0 plane (Fig. 5). The picture obtained fully satisfied the proposed model with certain variations of parameters. Comparison between Φ_{exp} and Φ_{calc} indicates the partially dynamic character of the scattering. After introduction of the dynamic correction by the method used in [6], the deviation factor R equalled 32%. Several cycles of improving the xy0 projection reduced to R to 27%. The final value of R after introducing the temperature factor, using the value B = 1 A^2, was 25% (Fig. 6), reflections with zero intensities in the electron-diffraction picture also being taken into consideration.

The projection of the Φ series on the x0z plane also fully confirmed the present model (Fig. 7). For this projection, however, it was not possible to determine the z parameter exactly for $\mathrm{Ag_I}$ and Se owing to the overlapping of atoms. Parameter z for both silver and selenium was improved by the R-minimization method. The final R value for h0*l* reflections (after introducing temperature and dynamic corrections) was 22% (Fig. 8). The improved parameters of the Ag and Se atoms as well as the interatomic distances in α-$\mathrm{Ag_2Se}$ are given in Tables 1 and 2.

Our structure for α-$\mathrm{Ag_2Se}$ may be described in the following way. The silver atoms form a somewhat distorted diamond structure. Tables 3 and 4 show the ratios and the relative directions of the axes in these structures, together with the interatomic distances inside the tetrahedra around $\mathrm{Ag_I}$, $\mathrm{Ag_{II}}$, and $\mathrm{Ag_{III}}$. The closest coordination around the silver atoms, however, is determined by a pair of neighboring Se atoms, standing at 2.54 A from the silver. Figure 9 shows the way in which infinite plane zigzag ...–Ag–Se–Ag–Se–.. chains pass through the silver tetrahedra. These chains stretch parallel to the c axis, and the Se–Ag–Se link of the chain forms the lattice spacing c = 4.33 A. The plane of the chain approximately

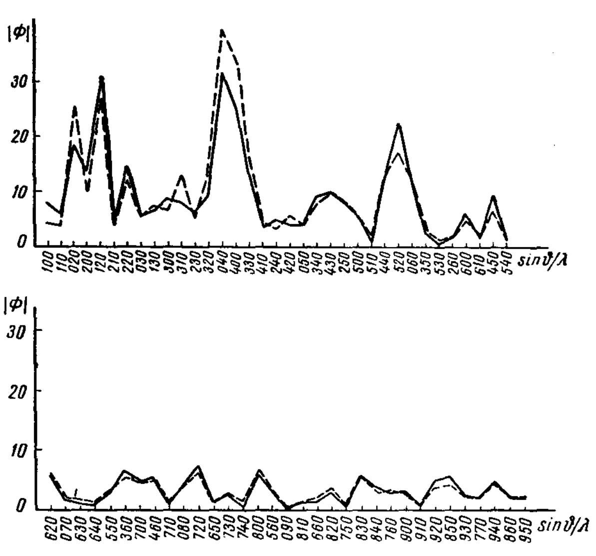

Fig. 6. Graphs comparing Φ_{exp} with Φ_{calc} for hk0 reflections.

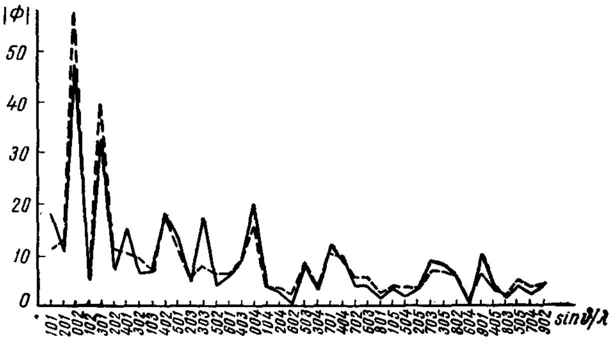

Fig. 8. Graph comparing Φ_{exp} with Φ_{calc} for h0l reflections.

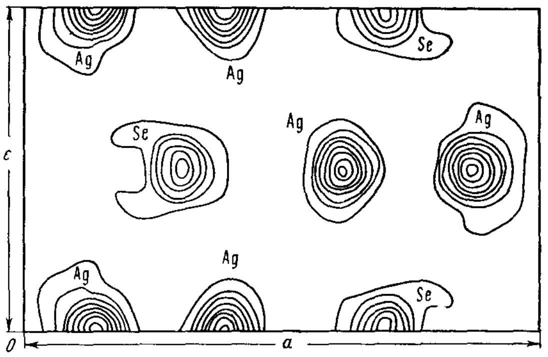

Fig. 7. Projection of Φ series on the (x0z) plane.

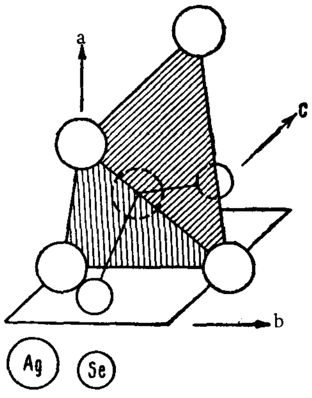

Fig. 9. Coordination group of silver.

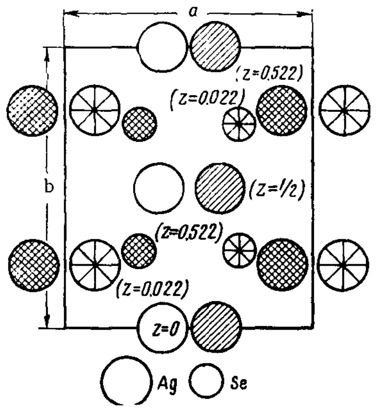

Fig. 10. Projection of the structure of the α-phase of Ag_2Se on the (001)

TABLE 1

Atom	Coordinates		
	x	*y*	*z*
Ag_I	0.121	0.225	0.022
Ag_{II}	0.393	0	0
Ag_{III}	0.378	0.500	0
Se	0.298	0.275	0.522

TABLE 2. Interatomic Distances (in A) in α-Ag_2Se

Atom	Ag_I	Ag_{II}	Ag_{III}	Se
Ag_I	2.62; 2.91	2.61	2.82	2.54; 2.98
Ag_{II}	—	2.64	3.925	3.06; 3.19
Ag_{III}	—	—	2.77	2.89; 2.93
Se	—	—	—	3.53; 3.76

TABLE 3

α-Ag_2Se		Diamond	
direction	identity period	direction	identity period
[100]	7.05	[100]	3.56
[010]	$4.33=\frac{7.05}{1,63}$	$[\bar{1}10]$	$3.56/\sqrt{2}$
[001]	$7.85=7.05\cdot 1,11$	[110]	$3.56/\sqrt{2}$

TABLE 4

Atom	Interatomic distances, A
Ag_I	2.61; 2.62; 2.62; 2.82
Ag_{II}	2.61; 2.61; 2.64; 2.64
Ag_{III}	2.77; 2.77; 2.82; 2.82

coincides with the (130) plane, and the Se–Ag–Se angle is around 73°. The rows of the chains, considered along the *a* or c axes, are sandwiched by rows of silver atoms. The structural features indicated enable us to explain the ease of formation of oriented films with the b = 7.85 A axis as texture axis. In fact, this orientation must be connected with the lamellar form of the crystallites, which in turn usually corresponds to cleavage in the present case along the planes shown schematically in Fig. 10.

TABLE 5. Minimum Interatomic Distances

Composition of phase	Structure type	Distance
Ag_5Sr	Cu_5Ca	2.82—2.83
$AgBe_2$	$MgCu_2$	2.72
Ag_5Zn_8	γ-Brass	2.70
α-Ag_2Se	—	2.61—2.62

Considering the general appearance of the structure, it is interesting to compare it first of all with the structure of the monoclinic phase of Ag_2S [7]. We can see a similarity between these structures, in that Ag_2S also has plane zigzag ... –Ag–S–Ag–S–... chains running perpendicular to the (103) plane, though these are less clearly expressed. In the projection of this structure on the plane in question, just as in that of Ag_2Se (Fig. 10), we find rows of ... –Ag–S–... chains alternating with rows of silver atoms. The Ag–S interatomic distances of around 2.50 A are in reasonable accordance with the Ag–Se distances of 2.54 A.

A remarkable feature of α-Ag_2Se is the basic diamond structure of silver atoms. We may well remember, however, that this arrangement of silver atoms occurs in the structure of $AgBe_2$, which is of the $MgCu_2$ type. This $AgBe_2$ has cubic symmetry, as a result of which the silver atoms form an undistorted diamond structure, in contrast to the slightly distorted structure of α-Ag_2Se.

Finally it must be emphasized that α-Ag_2Se has small Ag – Ag interatomic distances: 2.61 and 2.62 A. These distances are considerably smaller than the Ag–Ag distances in the structure of metallic silver: 2.89 A. In this connection Table 5 shows values of Ag–Ag interatomic distances smaller than this latter value.

We note that in Ag_5Zn_8 there is normally ~ 65% of the amount of zinc indicated. In β-Ag_2Se there is a strongly ordered disposition of silver atoms occupying several positions in the structure, the overall multiplicity of which equals 42 in a unit cell for four silver atoms. In this structure there are Ag–Ag interatomic distances of 2.44 A.

Thus the structure of α-Ag_2Se which we have established is distinguished by the following characteristic features.

1. It is based on a fairly compact disposition of metal atoms forming a spatial "binding."
2. This structure, in which clearly the metallic bond should predominate, is penetrated by ... – Ag – Se – Ag – Se – ... chains with an undoubtedly covalent bond within the chain.

3. Finally, a characteristic of the structure is the small interatomic distance between some of the silver atoms: 2.61 and 2.62 A.

It is interesting to compare the structure studied with the chain structure of Se: in Se the covalent-bonded ... – Se – Se – ... chains are connected with each other by predominantly weak residual forces, while in α-Ag_2Se the corresponding chains are apparently linked through the silver atoms by a metallic bond. Some analogy with graphite is possible.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.