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ON THE CRYSTAL STRUCTURE OF INDIUM SELENIDE In_2Se_3

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Indium selenide In_2Se_3 belongs to an interesting group of semiconductors of the type $A_2^{III}B_3^{VI}$ (compounds of Al, Ga, and In with S, Se, and Te), the majority of which possess a structure of the ZnS type. A characteristic feature of these structures is their defective nature, i.e., the presence in them of a large number of statistically distributed vacant sites. Thus, for example, in 1 cm^3 of indium telluride In_2Te_3 there are about $5 \cdot 10^{21}$ sites which, for a composition of $1:1$, would have to be occupied by indium atoms. The presence of such an enormous number of defects leads to large distortions of the periodic distribution of the lattice potential and has a strong effect on the electrical properties of the compounds under consideration. In this connection, the structure of the compound In_2Se_3, unknown up to the present time and studied in a number of works, is of great interest.

In the first report(1) on the structure of In_2Se_3 it was indicated that this compound has some low-symmetry structure—many lines were observed on its Debye photographs, which could not be indexed. In a later work(2) the supposition was made that two modifications of In_2Se_3 may exist, and the periods of the hexagonal lattice of the high-temperature modification were given: $a = 3.99$ Å, $c = 19.24$ Å. Analysis of subsequent works(3–5) leads to the conclusion that at least three different modifications of In_2Se_3 exist: a graphite-like α-modification, stable at room temperature; a β-modification, stable above 200°; and a γ-modification, stable above 500–600°. It should be noted that in(2,3) (apparently erroneously), in contrast to(4,5), it is stated that the graphite-like form of In_2Se_3 is stable at temperatures above 200°.

In the present work an electron-diffraction investigation was carried out on thin films of In_2Se_3, which were obtained by sublimation of small charges of an In_2Se_3 alloy from a tungsten spiral. The photographs described below were obtained from In_2Se_3 films prepared by sublimation onto mica sheets kept at room temperature, with subsequent annealing in vacuum.

Figure 1 presents an electron-diffraction pattern obtained from a specimen annealed for 2 hours at 180°, i.e., below the temperature of the first phase transformation described in(4,5). A characteristic feature of this electron-diffraction

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

pattern is the presence of two types of reflections—sharp and strongly diffuse. As a result of indexing the electron-diffraction pattern it was established that all the strongest reflections belong to a hexagonal cell with periods $a' = 4.00$ Å, $c' = 19.24$ Å, established in$^{(2,3)}$. However, in addition to these reflections, weaker reflexes, also arranged along ellipses, are quite clearly visible in the photograph. It proved possible to index all reflections of the electron-diffraction pattern on the basis of a hexagonal cell with periods $a = 16.00$ Å, $c = 19.24$ Å.

Fig. 1. Electron diffraction pattern of the low-temperature α-modification of In_2Se_3

Fig. 2. Electron diffraction pattern of the β-modification of In_2Se_3, stable above 200°.

Fig. 3. Electron diffraction patterns of the cubic *(a)* and low-symmetry *(b)* modifications of In_2Se_3

Fig. 2 gives an electron diffraction pattern of a specimen annealed after sublimation at 350–400°, i.e., above the temperature of the first phase transition described in (4, 5). In contrast to the preceding electron diffraction pattern, here all reflections have normal sharpness. The transition $\alpha \to \beta$ proceeds very slowly—for complete transformation of a film 400–600 Å thick, annealing for 7–8 hr at 350° is required. The electron diffraction pattern in Fig. 2 was indexed on the basis of a hexagonal cell with periods $a = 7.11 \pm 0.01$ Å, $c = 19.30 \pm 0.04$ Å. These values of the periods are in a simple relation to the periods of the α-modification: $a_\beta \approx a_\alpha \cdot \sqrt{3}$, $c_\beta \approx c_\alpha$.

The high-temperature β-modification of In_2Se_3 is prone to supercooling and is fairly stable at room temperature—after storage of β-In_2Se_3 specimens for 4 months at room temperature, no signs of the transformation $\beta \to \alpha$ were observed. This agrees with the data of (5) on the tendency of macroscopic specimens of β-In_2Se_3 to supercool.

In addition to the electron diffraction patterns of oblique-texture type described above, we also obtained electron diffraction patterns from a polycrystal (Fig. 3). These photographs were obtained from specimens annealed for 10–12 hr at 500–

Figure 3

Figure 3: Figure 3

600°. The electron diffraction pattern in Fig. 3a is indexed on the basis of a cubic primitive lattice with periods $a = 10.10$ Å; in the electron diffraction pattern in Fig. 3b, a multitude of lines is observed, which indicates the low symmetry of this phase.

Thus, in addition to two hexagonal modifications of In_2Se_3, there also exists a cubic γ-modification with periods $a = 10.1$ Å and a second, as yet undeciphered, apparently monoclinic δ-modification. At present the determination of the crystal structure of the α- and β-modifications may be regarded as complete.

The clearest electron diffraction patterns were obtained from β-In_2Se_3; therefore the structure determination was begun with this phase. On electron diffraction patterns from textures of the β-modification taken in transmission, no systematic extinctions are observed; in photographs obtained by the reflection method, of the reflections $000l$ only those with $l = 6n$ are present, which leads to four (two pairs, left- and right-handed) space groups: $C_6^2 = C6_1$ ($C_6^3 = C6_5$) and $D_6^2 = C6_{12}$ ($D_6^3 = C6_{52}$).

According to the data of (2), the In_2Se_3 cell with periods $a = 4.00$ Å and $c = 19.24$ Å contains 2 formula units; consequently, the β-In_2Se_3 cell must contain 6 formula units, i.e., 18 Se atoms and 12 In atoms (the area of the base of the β-phase cell is three times greater than the base area of the α-phase pseudocell).

The arrangement of the atoms in the structure of β-In_2Se_3 was determined mainly from projections and sections of the Patterson function. However, for an unambiguous interpretation of these syntheses, the author made extensive use of the ideas of the theory of closest packings and of methods of geometrical analysis of the structure. As a result it was established that the structure of the β-modification is based on a two-layer hexagonal packing of Se atoms, while the In atoms are located in tetrahedral voids of this packing, not statistically but in an ordered manner—they occupy voids associated with a sixfold screw axis (space group $C_3^3 = C6_5$).

To determine the parameter z of the In atoms, minimization of the R factor of the $h0hl$ reflections was carried out. As a result it was established that the minimum value of R (22%) is observed at $z_{\mathrm{In}} = 0.130$. In this case the shortest distance between In and Se atoms is 2.51 Å. This distance is somewhat smaller than the sum of the tetrahedral covalent radii of In and Se ($1.44+1.14 = 2.58$ Å). However, if the tetrahedral radius of In is calculated from the defect structure In_2Te_3, it will be equal not to 1.44 but to 1.35 Å (the tabulated value 1.44 Å was obtained from the structures InAs and InSb with a component ratio of 1 : 1), and the sum of the radii of In and Se will be $1.35 + 1.14 = 2.49$ Å, i.e., it practically coincides with the value obtained experimentally.

Thus, it may be considered that the interaction between In and Se atoms in the structure of β-In_2Se_3 is predominantly covalent. This structure is in fact a superstructure based on a wurtzite-type structure. An analogous structure was established earlier for one of the modifications of Ga_2S_3 (^{6}).

In work (^{5}), for the α-modification of In_2Se_3 the space group D^4_{6h}–$C6/mmc$ was proposed. In the electron-diffraction patterns obtained by us from this phase, only reflections of the type $000l$ with $l \neq 2n$ are extinguished, which, in contrast to (^{5}), leads to the following groups: C^6_6–$C6_3$; D^6_6–$C6_32$ and C^2_6–$C6_3/m$. The pseudocell of α-In_2Se_3 contains 2 formula units; accordingly, the cell with quadrupled period a contains 32 formula units, i.e., 96 Se atoms and 64 In atoms—a total of 160 atoms. It is clear that it is extremely difficult to determine the structure with such a number of atoms, especially from photographs with blurred reflections. However, this problem is greatly simplified owing to the presence of a pseudoperiod and a simple relation between the lattice periods of the α- and β-modifications, as was mentioned above.

To determine a model of the structure of the α-modification, Patterson projections $P(xy0)$ and a Patterson-Harker section $P(x0z)$ were constructed. In doing so, because of the different sharpness of the reflections, integral intensities were determined, and the transition to Φ_2 was made according to formula (^{7})

$$\Phi_2 = \frac{I}{pd'}, \quad \text{where } d' = \frac{L\lambda}{R\sin\varphi}.$$

In calculating the indicated syntheses, weak reflections were not taken into account; in other words, the syntheses were constructed for the pseudocell. As a result of the interpretation of these syntheses and application of the trial method, the following model of the structure of the α-modification was established. The basis of the structure, as in the case of the β-modification, is a two-layer hexagonal packing of Se atoms (space group C^6_6–$C6_3$); the main mass of In atoms is located in the tetrahedral voids of this packing, and 1/16 in the octahedral voids. At the same time, two layers of occupied voids alternate with one vacant layer, which leads to a strongly pronounced layered character of the structure: it is built of five-layer packets Se In Se In Se, with two similar packets fitting along the c axis of the cell. The bonding between packets is evidently van der Waals in character—the corresponding distance between Se atoms located at the boundary of two packets (3.55 Å) is even somewhat greater than the distance between atoms located in neighboring chains of the structure of elemental selenium (3.46 Å). The indicated five-layer packets are arranged in the structure of α-In_2Se_3 according to the law of hexagonal packing $BCBC$ ..., and in this respect this structure is very similar to the structure of InSe, where the same arrangement of the packets Se In In Se is observed (^{8}).

As indicated above, a characteristic feature of the electron-diffraction pattern from α-In_2Se_3 is the different sharpness of the reflections. In this case, all reflections lying on ellipses with h–$k \neq 3n$ (with the exception of $hk0$ reflections) prove to be blurred; all reflections lying on ellipses with $h - k = 3n$ have normal sharpness. A similar picture was observed earlier on electron-diffraction patterns of InSe and was explained by the presence of faults in the arrangement of the packets (^{8}). Since the regularity of the blurring of reflections in photographs from α-In_2Se_3 is exactly the same as in the case of InSe, it is obvious that the reason for this phenomenon is also the same, i.e., the presence of faults in the arrangement of the five-layer packets. A consequence of the layered character of the structure is the perfect cleavage of α-In_2Se_3 crystals along the basal plane.

The interatomic distances in the structure of the α-modification proved to be as follows: In—Se = 2.51 Å (in a tetrahedron), In—Se_2 = 2.95 Å (in an octahedron), Se—Se = 3.55 Å (between packets).

Despite its apparent complexity, the structure of α-In_2Se_3 is similar to the wurtzite structure (the arrangement of the main mass of In atoms in tetrahedral vacancies of the double-layer hexagonal packing). Its principal difference lies in the layered character and in the placement of 1/16 of the In atoms in octahedral vacancies.

The sharp decrease in the electrical conductivity of In_2Se_3 specimens, which occurs during the $\alpha \to \beta$ transformation (^{4,5}), is apparently connected chiefly with the transition of 1/16 of the In atoms from octahedral vacancies (bonds with p-electrons) to tetrahedral ones (sp^3-bonds).

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