Zeitschrift für Kristallographie 173, 185–191 (1985)

The crystal structure of arsenic selenide, As_2Se_3

A. C. Stergiou and P. J. Rentzeperis

Applied Physics Laboratory, Aristotle University of Thessaloniki, Thessaloniki, Greece

Received: June 27, 1985

Crystal structure / **As_2Se_3**

Abstract. Single crystals of As_2Se_3 were prepared hydrothermally. The crystal structure was determined by using the intensities of 1014 independent reflections, measured on a computer-controlled single-crystal diffractometer. The cell constants, refined by least-squares, are: $a = 12.0774(4)$, $b = 9.9037(6)$, $c = 4.2835(6)$ Å, $\beta = 90.458\,^{\circ}(9)$; $Z = 4$; space group $P2_1/n$.

The structure was solved by using MULTAN combined with successive Fourier syntheses. The final R value was 0.038 and $R_w = 0.037$.

Each As atom is surrounded by a composite polyhedron of seven Se atoms, consisting of a tetragonal pyramid and a triangular prism, one face of which coincides with the base of the pyramid. Two centrosymmetrically equivalent composite polyhedra are linked by a common prismatic face, forming thus a double composite polyhedron, which is further linked on either side to two centrosymmetrically equivalent composite polyhedra through common prismatic faces. Thus a block of four composite polyhedra is formed. This combination of the polyhedra is repeated along the c axis, forming infinite chains. These chains are further linked to four similar adjacent chains by common Se, Se edges.

Introduction

The elucidation of the structure of As_2Se_3 was undertaken within the framework of our program for a systematic and accurate determination of structures of arsenic chalcogenides and arsenic chalcohalogenides, several members of which show interesting physical properties. Approximate structure determinations ($R = 0.138$ and $R = 0.14$) have been reported by Vaipolin (1966) and by Renninger and Averbach (1973). The latter used crystals prepared by anealing amorphous samples.

Table 1. Crystal data for As_2Se_3. (In all the tables of this paper, standard errors, given in parentheses, refer to the last digit)

As_2Se_3
Space group: $P2_1/n$
$a = 12.0774(4)$ Å
$b = 9.9037(6)$ Å
$c = 4.2835(6)$ Å
$\beta = 90.458°(9)$

$Z = 4$
$F(000) = 672$
$\varrho_{calc} = 5.012\ g \cdot cm^{-3}$
$\varrho_{meas} = 4.85\ g \cdot cm^{-3}$
$\mu = 364.45\ cm^{-1}$
$\lambda(MoK\alpha) = 0.71069$ Å

Experimental

Cherry-red needle-like single crystals of As_2Se_3 were prepared hydrothermally in the way already described (Stergiou and Rentzeperis, 1985). The quartz-glass ampoule ($\sim$ 3 mm diameter) placed in the autoclave was filled up to 70% with a HCl 25% w/w solution and a stoichiometric mixture of powdered As and Se. The system was heated at 365 °C for 3 days and then cooled to room temperature at a rate of approximately 2 °C/h. Needle-like crystals of As_2Se_3 grew in the upper part of the ampoule. The calculated pressure in the autoclave for the space factor 0.70 and temperature 365 °C was about 640 bars.

A prismatic single crystal, with dimensions $0.40 \times 0.07 \times 0.92$ mm, was selected and centred on our computer-controlled, four-circle, single-crystal diffractometer (Philips PW 1100). With Mo*Kα* radiation the cell constants were determined by measuring the ϑ angles of 106 strong reflections with large ϑ values directly on the diffractometer and subsequently processing them with the least-squares program LATCON (part of the X-Ray System by Stewart, Kruger, Ammon, Dickinson and Hall, 1976). The final values for the unit cell are given in Table 1. Three-dimensional intensity data were measured with a scintillation counter on the diffractometer in the ω-scan mode, using Mo*Kα* radiation monochromated with a graphite monochromator. The intensities of 4721 reflections in the range $\vartheta = 2-30°$ (maxima $h = \pm 12$, $k = \pm 10$, $l = \pm 6$) were measured and examined. Of the resulting 1218 unique reflections, 1014 with intensities greater than $2\,\sigma$ were included in all subsequent calculations.

For further calculations the programs of the X-Ray System (Stewart et al., 1976) were used.

Determination of the structure and refinement

The systematic absences were unambiguously consistent with space group $P2_1/n$. At first the atomic positions of the orpiment-type structure determination of As_2Se_3 reported by Vaipolin (1966) were used, as a starting point, but refinement with an overall temperature factor gave $R = 0.46$ (for an

Table 2. Atomic coordinates, anisotropic temperature coefficients $U_{ij}(\times 10^4)$ and equivalent isotropic temperature coefficients in As_2Se_3. $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq} [Å^2]
As(1)	0.2362(1)	0.1967(1)	0.1113(3)	149(7)	184(7)	182(7)	6(5)	1(5)	−11(6)	1.27
As(2)	0.0108(1)	0.3253(1)	0.3810(3)	159(6)	164(7)	183(8)	−11(5)	−13(5)	−9(6)	1.18
Se(1)	0.0977(1)	0.1182(1)	0.4726(3)	172(6)	144(7)	232(8)	19(5)	19(5)	3(6)	1.38
Se(2)	0.1534(1)	0.4104(1)	0.0257(3)	201(7)	159(8)	236(8)	−27(5)	−31(5)	−2(5)	1.48
Se(3)	0.3785(1)	0.2981(1)	0.4436(3)	143(6)	205(8)	193(7)	−6(5)	−5(5)	−5(6)	1.29

explanation see below). Next, the atomic positions obtained by Renninger and Averbach, 1973) were tried, but again refinement as above gave $R = 0.42$. This necessitated a new ab initio structure determination. Use of MULTAN (Main, Lessinger, Woolfson, Germain and Declercq, 1977), followed by successive Fourier syntheses, gave all the atomic positions. A structure-factor calculation with the obtained parameters and an overall isotropic temperature factor $B = 1.044$ Å^2 gave $R = 0.127$.

Refinement of the structure was carried out by full-matrix least-squares calculations with the X-Ray System. At first the non-ionized state was assumed for all atoms, and probable individual isotropic temperature factors were assigned to them. Atomic scattering factors and anomalous dispersion corrections for all atoms were obtained from Ibers and Hamilton (1974). A single scale factor was used for the whole set of reflection data.

Refinement with individual isotropic temperature factors and unit weights reduced R to only 0.123. Since the absorption coefficient was large ($\mu = 364.45$ cm^{-1}), an empirical absorption correction of F_{obs} was applied, with the special program CORABS, written for this purpose (Stergiou, 1984). The program is based on the same principles as DIFABS (Walker and Stuart, 1983) and works in an analogous way. After the absorption correction, the R factor was reduced to 0.052. Further refinement with anisotropic temperature coefficients gave $R = 0.038$ and $R_w = 0.049$. At this stage a systematic weight analysis was carried out, which led to the adoption of the weighting scheme $w = 1/\sigma^2(F_{rel})$, best suiting the experimental data. However the R factor remained unchanged, but R_w converged to 0.037.

The final positional and thermal parameters for the atoms are given in Table 2. The interatomic distances and bond angles are shown in Tables 3 and 4[1] respectively. In these tables the indices in parentheses refer to the atoms in Figures 1 and 2. Structure factor tables have been deposited[1].

---

[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 51332, names of the authors and the title of the paper

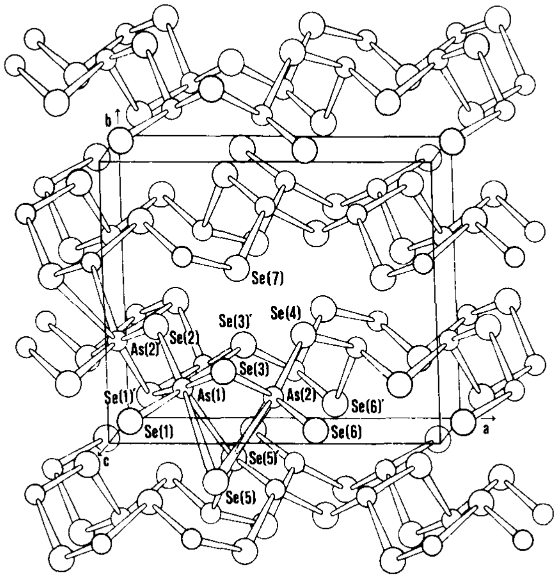

Fig. 1. Clinographic projection of the unit cell of As_2Se_3 parallel to [001]

Description of the structure and discussion

Comparison of the atomic parameters given in Table 2 with those of Vaipolin (1966), which virtually coincide with those of Renninger and Averbach (1973), showed that while the y and z coordinates were comparable, the x coordinates of the atoms are connected by $x_v + x = 1/2$, where x_v is the coordinate given by Vaipolin. Obviously the two structures refer to two different origins i.e. 000 and $\frac{1}{2}00$.

In Vaipolin's description of the structure the basic unit is a trigonal pyramid of composition $AsSe_3$ with the As atom at its apex. Adjacent pyramids are linked together with common Se atoms to form infinite chains along the c axis. As shown in Figure 1 the chains are bridged together by Se atoms, forming thus a layer structure with "crinkled" layers parallel to (010). Inside the layers the atoms are connected by strong covalent bonds.

The structure of As_2Se_3 may be visualised in yet a different way. As shown in the clinographic projection of Figure 1, each As atom is surrounded by a composite polyhedron of seven Se atoms, which is formed by a distorted tetragonal pyramid and a triangular prism, one face of which coincides with the base of the pyramid. There are two different kinds of composite polyhedra $As(1)Se_7$ and $As(2)Se_7$ (Fig. 2). One composite polyhedron $As(2)Se_7$ is linked to a centrosymmetrically equivalent composite polyhedron by a common prismatic face. Thus, a double

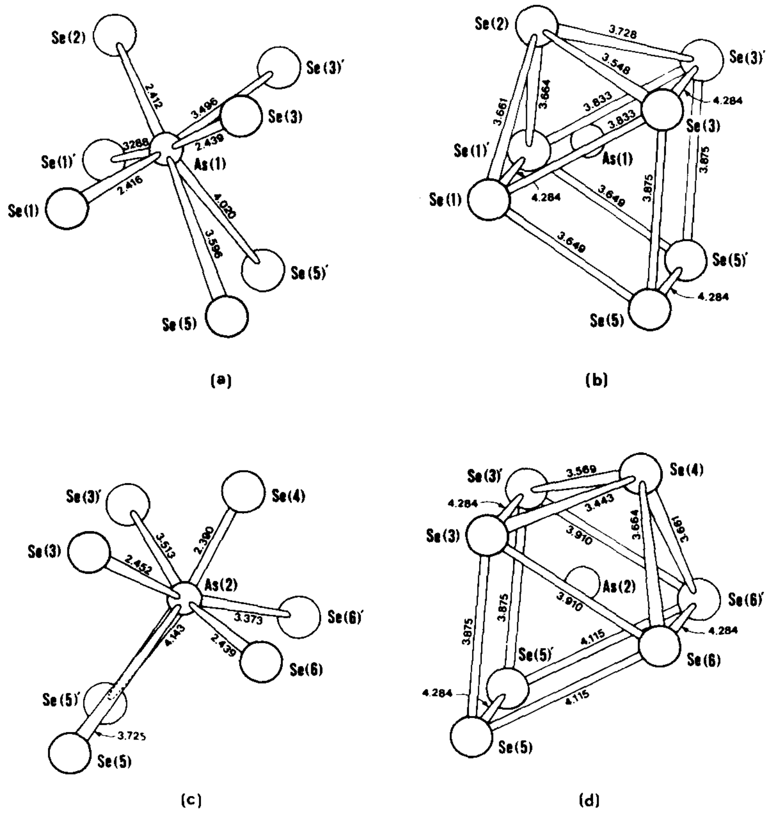

Fig. 2. Clinographic projection of the composite polyhedra with interatomic distances: (a) and (b): As(1)Se_7, (c) and (d): As(2)Se_7. (e.s.d's in all distances 0.002)

composite polyhedron unit is formed, while two centrosymmetrically equivalent composite polyhedra As(1)Se_7 are linked to the double polyhedron unit on either side through common prismatic faces. Thus a block of four composite polyhedron units is formed, which is repeated along the *c* axis, forming an infinite $\{As_4Se_{16}\}_n$ chain. Each chain is further linked to four similar adjacent chains by common Se, Se edges. Figure 3 shows the arrangement of the coordination polyhedra in clinographic projection parallel to [010]. Between the chains a tunnel of two composite polyhedra width is formed.

As can be seen from Figure 2, in the composite polyhedra around As(1) and As(2) three As – Se distances, namely the distance to the apical atom and those to two atoms forming the base of the tetragonal pyramid, are much shorter than the other four, averaging to 2.422 Å and 2.427 Å respec-

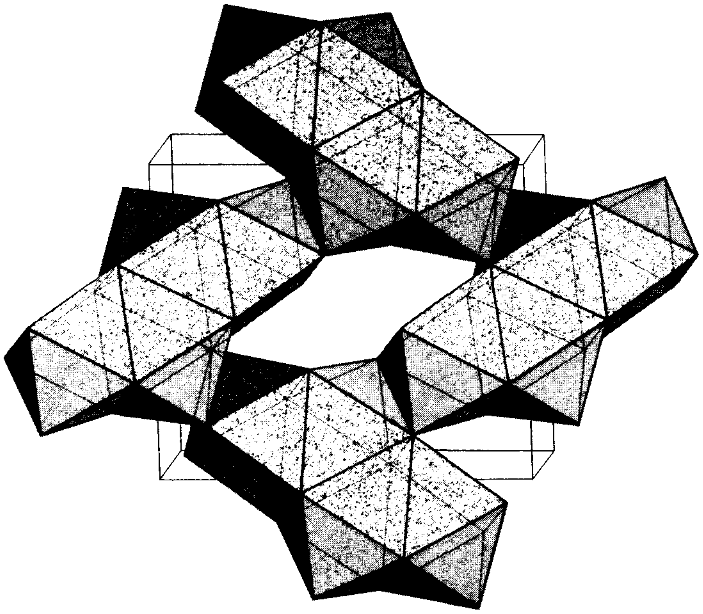

Fig. 3. Arrangement of the coordination polyhedra in clinographic projection parallel to [001]

tively. These values are very near the sum of the covalent radii of As and Se (2.38 Å in Pauling, 1960). Three other distances are considerably larger with an average 3.456 Å and 3.537 Å respectively and well below the sum of the van der Waals radii of the two atoms (3.75 Å in Bondi, 1964; 4.00 Å in Pauling, 1960). The seventh As – Se distance of each polyhedron, namely As(1) – Se(5)′ = 4.020 Å and As(2) – Se(5)′ = 4.143 Å is somewhat larger than the value of 4.00 Å.

This description of the structure with the help of the composite polyhedron, the existence of which has been ascertained in the crystal structures of antimony and bismuth chalcohalogenides (Voutsas and Rentzeperis, 1980, 1982, 1984; Papazoglou and Rentzeperis, 1983) permits a satisfactory explanation of the connection between the layers and also of the needle-like growth of the crystals along the *c* axis and their brittleness. It should be noted, however, that these crystal structures, as well as that of As_2Se_3, are formed only by composite polyhedra and are different from those of As_2Te_3 and As_5Te_7I (Stergiou and Rentzeperis, 1985), which are made up of composite polyhedra and octahedra.

Acknowledgement. Thanks are due to the Computing Center of the University of Thessaloniki for the use of its computing facilities.

References

Bondi, A.: Van der Waals volumes and radii. J. Phys. Chem. **68**, 441–451 (1964)

Ibers, J., Hamilton, W. C.: *International Tables for X-Ray Crystallography*, vol. IV, p. 72. Birmingham: The Kynoch Press (1974)

Main, P., Lessinger, L., Woolfson, M., Germain, G., Declercq, J.-P.: A system of computer programs for the automatic solution of crystal structures from X-Ray diffraction data (1977)

Papazoglou, A., Rentzeperis, P.: The crystal structure of antimony telluroiodide, SbTeI. Z. Kristallogr. **165**, 159–167 (1983)

Pauling, L.: *The Nature of the Chemical Bond*, 3rd edn. Cornell Univ. Press, Ithaca, N.Y. (1960)

Renninger, A., Averbach, B.: Crystalline structures of As_2Se_3 and As_4Se_4. Acta Crystallogr. **B29**, 1583–1589 (1973)

Stergiou, A.: Hydrothermal method for the growth of crystals and the crystal structure of As_2Se_3, As_5Te_7I, pp. 62–63. D. Sc. Thesis, University of Thessaloniki (1984)

Stergiou, A., Rentzeperis, P.: Hydrothermal growth and the crystal structure of arsenic telluride, As_2Te_3. Z. Kristallogr. **172**, 139–145 (1985)

Stergiou, A., Rentzeperis, P.: The crystal structure of arsenic telluroiodide, As_5Te_7I. Z. Kristallogr. **172**, 111–119 (1985)

Stewart, J., Kruger, G., Ammon, H., Dickinson, C., Hall, S.: The X-ray system of crystallographic programs for any computer. Technical Rep. 446, Computer Science Center, University of Maryland (1976)

Vaipolin, A.: Refining the structure of crystalline As_2Se_3 by finding probable corrections to the atomic coordinates. Sov. Phys. Crystallogr. **10**, no 5, 510–512 (1966)

Voutsas, G., Rentzeperis, P.: The crystal structure of the paraelectric bismuth thiocloride, BiSCl. Z. Kristallogr. **152**, 109–118 (1980)

Voutsas, G., Rentzeperis, P.: The crystal structure of antimony selenoidide, SbSeI. Z. Kristallogr. **161**, 111–118 (1982)

Voutsas, G., Rentzeperis, P.: The crystal structure of bismuth sulfide bromide, BiSBr. Z. Kristallogr. **166**, 153–158 (1984)

Walker, N., Stuart, D.: An empirical method for correcting diffractometer data for absorption effects. Acta Crystallogr. **A39**, 158–166 (1983)