

average obtained from the two orientations of the carboxylic acid group.

#### References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- BENGHIAT, V., LEISEROWITZ, L. & SCHMIDT, G. M. J. (1972). *J. Chem. Soc. Perkin II*, pp. 1769–1772.
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478–483.
- CROMER, D. T. & LARSON, A. C. (1973). *J. Chem. Phys.* In the press.
- CROMER, D. T., LARSON, A. C. & ROOF, R. B. (1960). *Acta Cryst.* **13**, 913–918.
- CROMER, D. T. & WABER, J. T. (1973). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. In the press.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- LARSON, A. C. & CROMER, D. T. (1973). *J. Chem. Phys.* In the press.
- MCWEENY, R. (1951). *Acta Cryst.* **4**, 513–518.
- STEWART, R. F. (1969). *J. Chem. Phys.* **51**, 4569–4577.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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## Crystalline Structures of $\text{As}_2\text{Se}_3$ and $\text{As}_4\text{Se}_4$

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Tentative lattice parameters and fractional coordinates for crystalline  $\text{As}_4\text{Se}_4$  have been determined and the parameters for crystalline  $\text{As}_2\text{Se}_3$  have been revised. X-ray diffraction data from polycrystalline samples were employed. The peak positions yielded lattice parameters, and the radial distribution functions along with a Monte Carlo technique were used to obtain fractional coordinates. In addition some information regarding thermal vibrations at room temperature was obtained.  $\text{As}_4\text{Se}_4$  is isomorphic with realgar,  $\text{As}_4\text{S}_4$ , with space group  $P2_1/c$  and four molecules per cell. The parameters for the monoclinic lattice are  $a_0 = 6.69$ ,  $b_0 = 13.86$ ,  $c_0 = 10.00$  Å,  $\beta = 113.2^\circ$ . The mean As–Se distance is 2.38 Å and the mean As–As distance is 2.44 Å. For  $\text{As}_2\text{Se}_3$  the previously published structure has been slightly modified. The revised parameters for the monoclinic lattice,  $P2_1/c$ , are  $a_0 = 4.30$ ,  $b_0 = 9.94$ ,  $c_0 = 12.84$  Å,  $\beta = 109.1^\circ$ . The mean As–Se distance is 2.40 Å.

### Introduction

The determination of crystal structures by diffraction methods generally requires samples in the form of perfect single crystals. For many materials this presents a major experimental difficulty. In addition it is necessary to determine very accurate integrated intensities for a large number of reflections and subsequently to perform a rather involved analysis. However it is possible, in certain cases, to simplify the procedure considerably and to employ polycrystalline samples. Such a procedure has been used by Strong & Kaplow (1968) to determine the structure of  $\text{B}_2\text{O}_3$  and was subsequently verified by single crystal techniques (Gurr, Montgomery, Knutson & Gorres, 1970; Strong, Wells & Kaplow, 1971). In the course of studies of glasses in the arsenic–selenium system diffraction patterns from polycrystalline samples of  $\text{As}_2\text{Se}_3$  and  $\text{As}_4\text{Se}_4$  were obtained and structures determined using these techniques. As the structure of  $\text{As}_2\text{Se}_3$  was only a slight refinement of previous determinations while the  $\text{As}_4\text{Se}_4$  structure was previously unpublished, the bulk of this paper will be concerned with the latter determination.

### Experimental procedure

Samples of  $\text{As}_2\text{Se}_3$  and  $\text{As}_4\text{Se}_4$  were supplied by the Xerox Research Laboratory where they had been prepared by annealing amorphous samples of 40 at. % As–60 at. % Se and 50 at. % As–50 at. % Se respectively. The samples were ground to –200 mesh and placed on glass slides using a collodion–amyl acetate base. Subsequent analysis revealed no obvious amorphous content and comparison with known  $\text{As}_2\text{Se}_3$  reflection intensities indicated no preferred orientation. Since data was desired over as great a reciprocal-space range as possible, two radiations were employed. For the region from  $k = 0.40$  to  $k = 6.0$  Å<sup>-1</sup>,  $\text{Co K}\alpha$  ( $\lambda = 1.790$ ) was used with a pre-specimen LiF monochromator, proportional counter and pulse-height analyzer. From  $k = 2.0$  to  $k = 19.0$  Å<sup>-1</sup>,  $\text{Rh K}\alpha$  ( $\lambda = 0.6147$ ) was employed with a post-specimen highly oriented pyrolytic graphite monochromator, scintillation counter and pulse-height analyzer. Rhodium tube operation was held below 41 kV to eliminate  $\lambda/2$  components. The spectrometer alignment was verified by using Ag powder peaks and gave low-index peak widths of 15' for both systems. Data were taken by point counting

and multiple passes with an interval of 0.01 in  $k$  for Co and 0.05 for Rh above  $k=6 \text{ \AA}^{-1}$ . At least  $10^3$  counts/point of background regions were accumulated. The rhodium data served primarily to reduce termination effects in the radial distribution function analysis.

### Data analysis – $\text{As}_4\text{Se}_4$

Lattice parameters for  $\text{As}_4\text{Se}_4$  were determined from the polycrystalline peak positions. Indexing was accomplished by assuming isomorphism with realgar,  $\text{As}_4\text{S}_4$ , space group  $P2_1/c$ .<sup>\*</sup> This was justified by the known isomorphism of  $\text{As}_2\text{Se}_3$  with orpiment,  $\text{As}_2\text{S}_3$ . In this way 23 peaks in the  $2\theta$  range  $0-45^\circ$  were identified. Then, by using a computer program developed by Charles W. Burham of the Carnegie Institute of Washington, a set of trial parameters was refined to give a best fit in the least-squares sense. The refined parameters for crystalline  $\text{As}_4\text{Se}_4$  are:

$$\begin{aligned} a_0 &= 6.69 \pm 0.01 \text{ \AA} \\ b_0 &= 13.86 \pm 0.02 \\ c_0 &= 10.00 \pm 0.01 \\ \beta &= 113.2 \pm 0.07^\circ \end{aligned}$$

This leads to an X-ray density of  $4.79 \text{ g cm}^{-3}$  which compares well with a measured value of  $4.70 \text{ g cm}^{-3}$ . Furthermore unpublished results of Goldstein (1971) on single crystals have yielded the following parameters:

$$\begin{aligned} a_0 &= 6.72 \text{ \AA} \\ b_0 &= 13.80 \\ c_0 &= 10.00 \\ \beta &= 113.8^\circ \end{aligned}$$

in good agreement with our results.

The determination of fractional coordinates requires the use of a one-dimensional atomic distribution function for the material. This is obtained from the measured intensity by the Fourier transformation of the reduced intensity function:

$$F(k) = k \left( \frac{I - \langle f^2 \rangle}{\langle f \rangle^2} \right)$$

where

$$\begin{aligned} k &= 4\pi \sin \theta / \lambda \\ \langle f^2 \rangle &= (\sum_i x_i f_i) (\sum_i x_i f_i^*) \\ \langle f \rangle^2 &= \sum_i x_i f_i f_i^* \\ f_i &= \text{complex scattering factor of atom } i \\ x_i &= \text{atomic fraction of species } i \end{aligned}$$

\* We use here the notation of *International Tables for X-ray Crystallography* (1952). The literature for  $\text{As}_2\text{Se}_3$ ,  $\text{As}_2\text{S}_3$  and  $\text{As}_4\text{S}_4$  generally employs the notation of Wyckoff with this space group designated  $P2_1/n$ . The axial transformation matrix used here is

$$\begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix}$$

$f$  values were obtained from tables of Doyle & Turner (1968) and dispersion corrections from Cromer (1965).

The intensity,  $I$ , used in this relation, was obtained from the measured intensity  $I_m$  by first correcting for background, polarization, multiple scattering and absorption. In this case an absorption correction was not required but the multiple scattering correction of Warren & Mozzi (1966) was performed. Next the corrected intensity was scaled to electron units by multiplication by a normalization constant. This constant may be chosen by requiring that, at sufficiently high  $k$ , the corrected intensity oscillates about  $\langle f^2 \rangle + I_c$  where  $I_c$  is the Compton incoherent scattered intensity. Values of  $I_c$  were obtained by a calculation using Bewilogua's procedure as discussed by James (1948) and multiplied, for rhodium data, by an acceptance factor required by the use of a post-specimen monochromator. The determination of this acceptance factor has been discussed elsewhere. Subsequently the normalization constant obtained in this way was checked by the use of the integral technique of Norman (1957), which showed agreement to 0.5%.

The distribution of atom centers about an average atom was then related to the reduced intensity by the

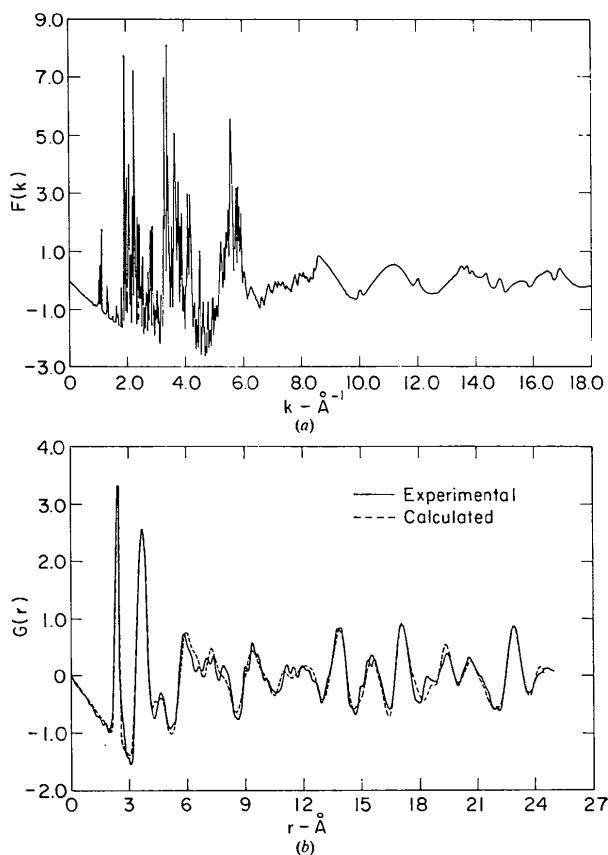


Fig. 1. Data for  $\text{As}_4\text{Se}_4$ . (a) Corrected reduced measured intensity  $F(k)$ . (b) Comparison of reduced distribution functions,  $G(r) = 4\pi r [\rho(r) - \rho_0]$ .

Fourier transformation:

$$G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^{\infty} F(k) \sin kr dk$$

where

$G(r)$  = reduced distribution function

$\rho_0$  = average atomic density

$$\rho(r) = \sum_i x_i K_i K_j \rho_{ij}(r)$$

with

$\rho_{ij}(r)$  = density of atoms of type  $j$  at a distance  $r$  from an average atom of type  $i$

$$K_i = f_i / \langle f \rangle.$$

The assumption that  $K_i K_j$  be independent of  $k$ , required for this derivation, is well satisfied for the As-Se system.

In general, several corrections must be made in the process of obtaining reliable distributions from the reduced intensity. These include corrections for errors in normalization, a termination correction and corrections for slowly varying errors. A procedure developed by Kaplow, Strong & Averbach (1965) for performing these corrections has been employed here.

Once the one-dimensional atomic distribution function has been obtained it is possible to determine fractional coordinates for  $\text{As}_4\text{Se}_4$  by a Monte Carlo procedure. This involves assuming some initial set of fractional coordinates, calculating an atomic distribution from the resulting structure, comparing with the experimental distribution, varying one of the fractional coordinates at random and recomputing the atomic distribution. If the change improves the fit to the experimental distribution, it is retained, otherwise, it is rejected. Random changes are thus introduced in all the fractional coordinates until an adequate match with the experimental distribution is obtained. This is indicated by the value of the mean-square difference defined to be the average squared difference between the calculated and experimental functions.

The atomic distribution of the model is calculated from the relation,

$$4\pi r \rho(r) = \sum_i \frac{C_i}{r_i (2\pi\sigma_i^2)^{1/2}} \exp \left[ -\frac{(r-r_i)^2}{2\sigma_i^2} \right]$$

where

$C_i$  = weighted number of atoms in a spherical shell of width  $\Delta r_i$  at a distance  $r_i$  from an average atom,

$\sigma_i^2$  = relative mean-squared thermal displacement of atoms separated by a distance  $r_i$ .

The  $C_i$  are determined from the crystalline lattice positions of the model utilizing the previously assumed symmetry of the structure. For  $\text{As}_4\text{Se}_4$  the assumed isomorphism with realgar yielded the required symmetry and in addition the fractional coordinates for realgar were employed as convenient initial values for

the Monte Carlo procedure. A shell width of 0.05 Å was employed and unit weights were assigned since the  $K_i K_j$  for this system do not differ by more than 6% for any pair in the material. The  $\sigma_i^2$  are determined in the course of modeling. These quantities are related to the mean-squared thermal displacement of atoms in the structure in a given direction,  $\langle u_s^2 \rangle$ , as follows

$$\sigma_i^2 = \gamma_i \sigma_\infty^2 = \gamma_i \langle 2u_s^2 \rangle$$

where the  $\gamma_i$  are coupling coefficients describing the degree of independence of the thermal vibrations of a pair of atoms separated  $r_i$ . If  $\gamma=0$  the two atoms vibrate parallel to each other and their distance of separation remains constant. If  $\gamma=1$ , then the thermal vibrations are independent.

One limitation of the Monte Carlo procedure is that the time required for computation of distributions is rather great because a large number of atomic positions are involved in order to obtain all correlations to distances like 20 Å from a set of basis atoms. Thus the procedure is modified somewhat in that initially only a distribution to about 5 Å is used and a best fit achieved in this region. The resulting fractional

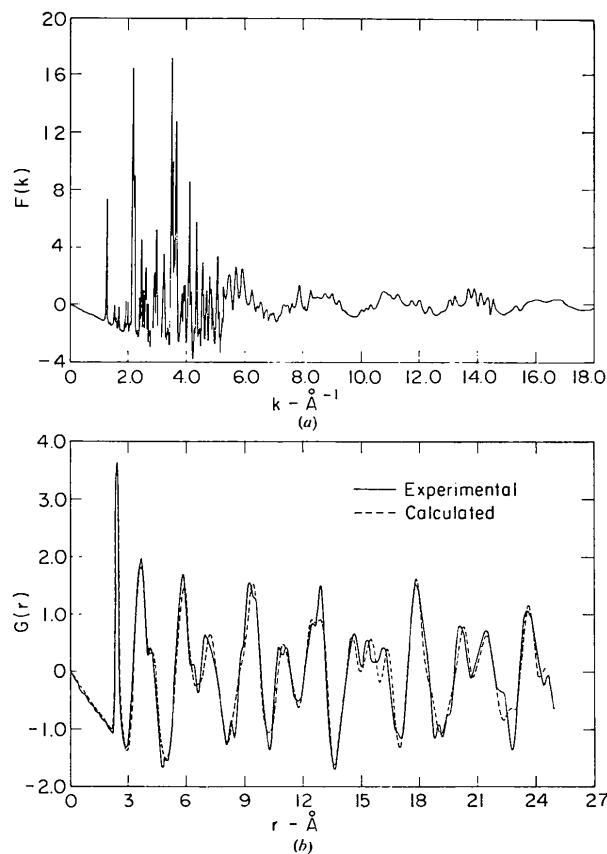


Fig. 2. Data for  $\text{As}_2\text{Se}_3$ . (a) Corrected reduced measured intensity  $F(k)$ . (b) Comparison of reduced distribution functions,  $G(r) = 4\pi r [\rho(r) - \rho_0]$ .

coordinates are then used to generate the entire distribution and the overall fit obtained. This final fit may not prove satisfactory in which case a new low- $r$  fit must be generated. In general the final result is simply the best overall fit obtained and could be improved on by additional refinement.

The final set of fractional coordinates for  $\text{As}_4\text{Se}_4$  is given in Table 1 and the fit of the experimental and calculated distributions in Fig. 1. There appears to be regular oscillation in the experimental curve with a period of about  $0.5 \text{ \AA}$  which could indicate an error in the reduced intensity at

$$k = 2\pi/\Delta r = 12.5 \text{ \AA}^{-1}.$$

However all of the principal correlation peaks are well reproduced.

Table 1. *Crystalline*  $\text{As}_4\text{Se}_4$

Space group  $P2_1/c$

Lattice parameters  $a_0 = 6.69 \pm 0.01 \text{ \AA}$   $b_0 = 13.86 \pm 0.02 \text{ \AA}$   
 $c_0 = 10.00 \pm 0.01 \text{ \AA}$   $\beta = 113.2 \pm 0.07^\circ$

Fractional coordinates M.S.D. = 0.018

	$x$	$y$	$z$
As(1)	0.3595	0.0185	0.1088
As(2)	0.5627	-0.1420	0.4337
As(3)	0.1718	-0.1293	0.3325
As(4)	0.3380	-0.1528	0.0364
Se(1)	0.6601	0.0077	0.3374
Se(2)	0.0930	0.0240	0.2130
Se(3)	0.6080	-0.2250	0.2450
Se(4)	0.0670	-0.2150	0.1150

Equivalent positions:

$$\pm(x, y, z); (-x, \frac{1}{2} + y, \frac{1}{2} - z); (x, \frac{1}{2} - y, \frac{1}{2} + z)$$

Near-neighbor distances

As(1)-Se(1)	2.38 $\text{\AA}$	As(3)-Se(2)	2.39 $\text{\AA}$
As(1)-Se(2)	2.39	As(3)-Se(4)	2.33
As(2)-Se(1)	2.48	As(4)-Se(3)	2.38
As(2)-Se(3)	2.33	As(4)-Se(4)	2.40
As(1)-As(4)	2.47	As(2)-As(3)	2.41

Mean As-Se distance = 2.38  $\text{\AA}$

Mean As-As distance = 2.44

Bond angles

As(1)-Se(1)-As(2)	100.0°	Se(1)-As(1)-Se(2)	94.4°
As(1)-Se(2)-As(3)	97.7	Se(1)-As(2)-Se(3)	87.8
As(2)-Se(3)-As(4)	101.9	Se(2)-As(3)-Se(4)	93.5
As(3)-Se(4)-As(4)	97.7	Se(3)-As(4)-Se(4)	88.4
Se(1)-As(1)-As(4)	98.6	Se(2)-As(3)-As(2)	105.3
Se(2)-As(1)-As(4)	101.0	Se(4)-As(3)-As(2)	103.4
Se(1)-As(2)-As(3)	100.6	Se(3)-As(4)-As(1)	102.2
Se(3)-As(2)-As(3)	99.3	Se(4)-As(4)-As(1)	102.3

### Data analysis - $\text{As}_2\text{Se}_3$

For  $\text{As}_2\text{Se}_3$  attempts to generate a distribution from Vaipolin's (1966) previously reported structure parameters did not give a satisfactory fit to the experimental function even when fractional coordinates were allowed to vary. In part the differences were the result of the displacement of calculated correlation peaks

beyond  $10 \text{ \AA}$  to smaller distances. This suggested that the lattice parameters might require revision and so the intensity peaks were indexed and optimum lattice parameters were obtained. The revised values and previous values are (space group  $P2_1/c$ ):

	This work	Vaipolin (1966)
$a_0 =$	$4.30 \pm 0.01 \text{ \AA}$	$4.227 \text{ \AA}$
$b_0 =$	$9.94 \pm 0.01$	$9.890$
$c_0 =$	$12.84 \pm 0.01$	$12.82$
$\beta =$	$109.1 \pm 0.03^\circ$	$109.1^\circ$

This gives an X-ray density of  $4.96 \text{ g cm}^{-3}$  whereas the previous values give a density of  $5.06 \text{ g cm}^{-3}$ . Chernov, Dembovskii & Chistov (1968) have noted experimental densities ranging from  $4.75$  to  $4.90 \text{ g cm}^{-3}$  while our value was  $4.85 \text{ g cm}^{-3}$  so that the present results would seem to give better agreement than that of Vaipolin.

The resultant fit to the experimental distribution is shown in Fig. 2. There are still some notable differences though all correlations are represented. The differences do not seem to point to any one error in the experimental function and it may be that further refinement of the structure would improve the fit. The final fractional coordinates, near-neighbor distances and bond angles are given in Table 2.

Table 2. *Crystalline*  $\text{As}_2\text{Se}_3$

Space group  $P2_1/c$

Lattice parameters  $a_0 = 4.30 \pm 0.01 \text{ \AA}$   $b_0 = 9.94 \pm 0.01 \text{ \AA}$   
 $c_0 = 12.84 \pm 0.01 \text{ \AA}$   $\beta = 109.1 \pm 0.03^\circ$

Fractional coordinates M.S.D. = 0.048

	$x$	$y$	$z$
As(1)	0.1483	0.1977	0.2637
As(2)	0.8512	0.3180	0.4847
Se(1)	-0.0699	0.1143	0.3987
Se(2)	0.3720	0.4092	0.3539
Se(3)	0.3468	0.3037	0.1153

Equivalent positions:

$$\pm(x, y, z); (-x, \frac{1}{2} + y, \frac{1}{2} - z); (x, \frac{1}{2} - y, \frac{1}{2} + z)$$

Near-neighbor distances

As(1)-Se(1)	2.37 $\text{\AA}$	As(2)-Se(1)	2.32 $\text{\AA}$
As(1)-Se(2)	2.44	As(2)-Se(2)	2.37
As(1)-Se(3)	2.56	As(2)-Se(3)	2.36

Mean As-Se distance = 2.40  $\text{\AA}$

Bond angles

As(1)-Se(1)-As(2)	101.0°	Se(1)-As(1)-Se(2)	98.2°
As(1)-Se(2)-As(2)	97.1	Se(1)-As(1)-Se(3)	104.8
As(1)-Se(3)-As(2)	85.1	Se(2)-As(1)-Se(3)	95.9
Se(1)-As(2)-Se(2)	102.7°		
Se(1)-As(2)-Se(3)	91.8		
Se(2)-As(2)-Se(3)	105.0		

Additional evidence of the accuracy of these determinations is provided by reliability factors calculated for each structure. The usual procedure is to define a

reliability index,  $R$ , by

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

where

$F_o$  = experimentally determined structure factor,  
 $F_c$  = calculated structure factor.

In this case it was not possible to completely separate a large enough number of lines to make such a calcula-

tion meaningful. Instead a modified reliability index,  $R'$ , was defined by

$$R' = \frac{\sum |F'_o - F'_c|}{F'_o}$$

using modified structure factors as follows

$$F'_c = (\sum m F_c^2)^{1/2}$$

$$F'_o = \left( \frac{KA}{P \exp(-2M)} \right)^{1/2},$$

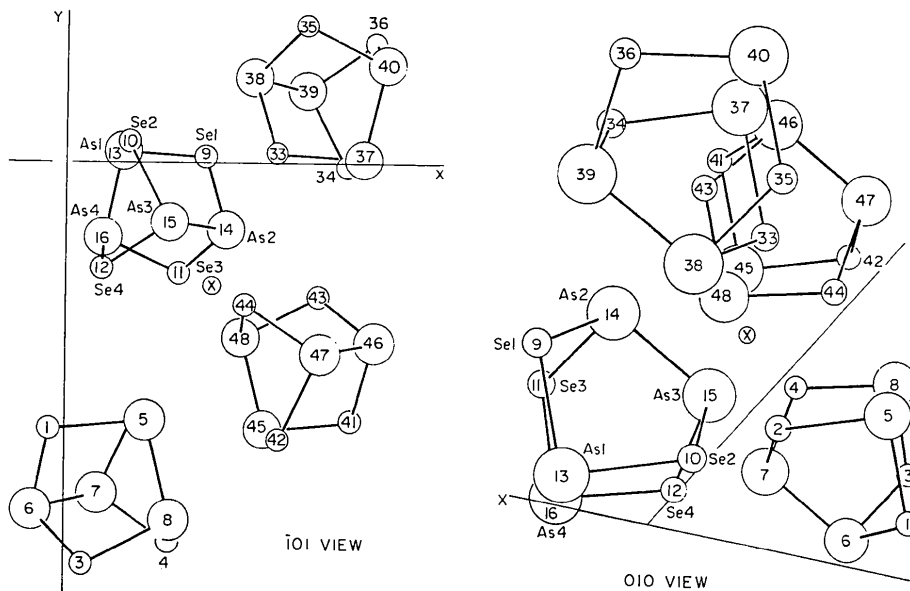


Fig. 3. Perspective plots of  $As_4Se_4$ . Large circles are As, small circles Se.

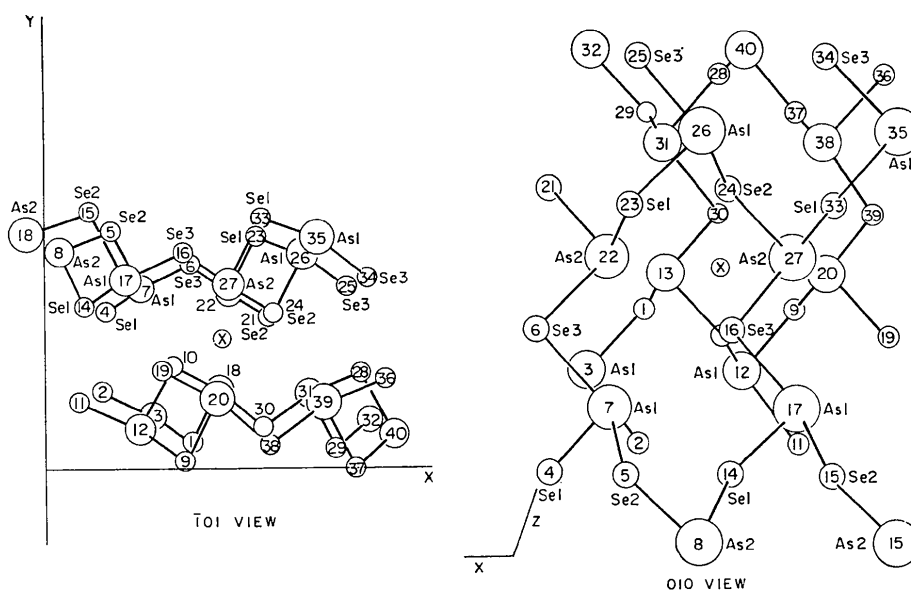


Fig. 4. Perspective plots of  $As_2Se_3$ . Large circles are As, small circles Se.

where

$A$  = peak area,  
 $P$  = Lorentz-polarization correction

$$= \frac{\sin^2 \theta \cos \theta}{1 + \cos^2 2\theta \cos^2 2\theta_m}$$

$2\theta$  = polycrystalline reflection angle,

$2\theta_m$  = monochromator reflection angle,

$\exp(-2M)$  = Debye-Waller temperature factor  
 $= \exp(-2B \sin^2 \theta / \lambda^2)$ ,

$K$  = normalization constant,

$m$  = reflection multiplicity.

The sum is over all reflections within plus or minus the full width at half maximum (FWHM) of the experimental peak. Only those peaks were used which were sufficiently resolved so that the FWHM could be accurately determined. Relative peak areas were determined from an  $I$  vs.  $k$  plot and converted to  $I$  vs.  $2\theta$  by dividing by  $\cos \theta$ . The normalization constant was taken as an average over all peaks of  $F'_c/F'_o$ . The Debye constant  $B = 2.41 \text{ \AA}^2$  for both crystals as determined from  $\sigma_\infty^2$ .

For  $\text{As}_4\text{Se}_4$  the reliability index determined in this way was 0.07 while for  $\text{As}_2\text{Se}_3$  it was 0.14. The latter value is the same as that obtained by Vaipolin (1966). The modified structure factors are shown in Tables 3 and 4. The lines listed for each peak are those which contribute 90% or more to the total modified structure factor squared.

Table 3. Measured and calculated modified structure factors for  $\text{As}_4\text{Se}_4$

$k$	Lines included*	Measured	Calculated
0.81	011	67	72
0.90	020	68	83
1.01	100	152	205
1.07	$\bar{1}11$	233	251
1.13	110, 021	327	419
1.33	$\bar{1}02, \bar{1}21$	243	251
1.50	111, 031	170	141
1.64	022	207	167
1.81	040	297	254
1.93	032, $2\bar{1}\bar{1}$ , 041, $\bar{2}00$	836	902
2.00	102, $\bar{2}12$	578	630
2.09	013, $\bar{1}14, \bar{1}23, 22\bar{1}, \bar{1}41$	923	878
2.14	$\bar{2}22$	444	405
2.20	122	574	530
2.25	023, 042, $\bar{1}42, 051$	1040	1021
2.37	$\bar{2}32$	552	493
2.43	211, 033, 132, 230, $\bar{2}23$	658	647
2.55	$\bar{1}14, 221$	553	533
2.67	{ 113, $\bar{1}24, \bar{2}04$ }	580	537
	{ 052, 151, $\bar{2}33$ }		
2.72	004, 231, 043, 142, 060	628	576
2.80	123, $\bar{2}24, 302, 061$	757	679
2.88	{ 202, 212, 024 }	759	696
	{ $3\bar{1}\bar{1}, \bar{2}43, 162$ }		
3.31	{ 104, $\bar{1}25, \bar{2}25, 251$ }	1216	1162
	{ $\bar{1}63, \bar{3}24, 26\bar{1}$ }		
3.40	{ 124, $\bar{1}35, 242$ }	1364	1384
	{ 154, 063, 162 }		

\* Includes lines contributing to 90% of  $m|F_c|^2$ .

Table 4. Measured and calculated modified structure factor for  $\text{As}_2\text{Se}_3$

$k$	Lines included*	Measured	Calculated
1.21	012	101	136
1.26	020	306	290
1.55	$\bar{1}02, 100$	194	183
1.59	$\bar{1}01$	135	181
1.67	$\bar{1}12, 110$	179	240
1.93	$\bar{1}13, \bar{1}21$	221	275
2.00	023, $\bar{1}22, 120$	231	256
2.13	$\bar{1}04, 102$	434	454
2.16	032	664	481
2.19	$\bar{1}23, 121$	642	711
2.23	$\bar{1}14, 112$	568	663
2.40	024, $\bar{1}30$	319	375
2.46	$\bar{1}24, 033, 130$	469	452
2.53	040	315	196
2.61	$\bar{1}15, 113, \bar{1}33, 131, 041$	477	499
2.67	015	289	248
2.89	025, $\bar{1}34$	432	282
2.93	$\bar{2}02, \bar{1}41$	386	454
2.97	104, 043, $\bar{1}42, \bar{2}12$	527	492
3.17	016, $\bar{1}35, 133, \bar{2}14$	479	347
3.22	$\bar{1}26, 124, 035, \bar{2}23, 22\bar{1}$	575	543
3.48	$\bar{2}32, \bar{1}51$	957	815
3.54	{ $\bar{1}36, 134, 202, 143$ }	956	835
	{ $\bar{2}25, 053, \bar{2}33, 150$ }		
3.65	{ $\bar{1}27, 125, 036, \bar{2}06$ }	1186	1211
	{ $\bar{2}16, 212, \bar{2}34, 230$ }		
4.11	{ $\bar{1}28, 037, \bar{2}27$ }	822	683
	{ $\bar{2}23, 063, 160$ }		

\* Includes lines contributing to 90% of  $m|F_c|^2$ .

## Discussion

The resultant structure for  $\text{As}_4\text{Se}_4$  is shown in Fig. 3. The isomorphism with realgar as described by Ito, Morimoto & Sadanaga (1952) is evident. The primary differences lie in the relative As-Se and As-As distances which are more nearly equal than the corresponding As-S and As-As distances. The larger As-Se value is to be expected on the basis of the larger covalent radius of Se and in fact the resulting As-Se distance of 2.38 Å is the value expected from the sum of the covalent radii (as given by Pauling, 1960). However, the As-As distance is decidedly smaller than in  $\text{As}_4\text{S}_4$ , its value of 2.44 is also quite close to the covalent radii sum. The bond angle distributions for the two crystals are quite similar. Following Ito *et al.* (1952) the arsenic atoms may be described as being arranged in an elongated tetrahedron while the selenium atoms, in a nearly square-planar arrangement, bisect the arsenic tetrahedron along the elongated dimensions. More precise information regarding the  $\text{As}_4\text{Se}_4$  structure must await single-crystal measurements. Such a study is presently being conducted by Goldstein (1971) of the Xerox Research Laboratory whose preliminary results were cited earlier.

Fig. 4 shows the resulting structure for  $\text{As}_2\text{Se}_3$ . It is essentially the same as that described by Vaipolin. The As-Se distances are somewhat more broadly distributed, especially the As(1)-Se(3) distance. However the mean As-Se distance is the same. The bond angles

for As(1) and Se(3) are quite similar to the previous values but the angles for As(2), Se(1) and Se(3) are slightly larger so that the layers may be smoother than in Vaipolin's model and more like those of  $\text{As}_3\text{S}_3$  as described by Morimoto (1954).

The coupling coefficients required for these structures are shown in Fig. 5. In both cases  $\sigma_\infty^2 = 0.061 \text{ \AA}^2$ . The value of  $\sigma_\infty^2$  was established by initially setting all  $\gamma = 1.0$  and varying  $\sigma_\infty^2$  to achieve a best fit in the region beyond  $r = 20 \text{ \AA}$  where previous studies by Strong & Kaplow (1968), Lagneborg & Kaplow (1967), and Kaplow, Rowe & Averbach (1968) have indicated that the thermal vibrations are independent. This procedure is only approximate especially for  $\text{As}_4\text{Se}_4$  where the distribution is rather smooth and is only good to about 15%. Errors due to instrumental broadening, estimated by the technique of Lagneborg & Kaplow, are felt to be about 5%, at  $20 \text{ \AA}$ . There is some evidence of a distinction between intraplanar and interplanar coupling in  $\text{As}_2\text{Se}_3$  in the vicinity of  $4.3 \text{ \AA}$ . In fact the peak at that distance is a characteristic intraplanar correlation in contrast to the second peak which consists of correlations of both types. For  $\text{As}_4\text{Se}_4$  the second peak is more strongly intramolecular in nature while the third peak at  $4.5 \text{ \AA}$  is primary due to intermolecular correlations as evidenced by the behavior of the thermal coupling.

The results of the present investigation indicate that  $\text{As}_4\text{Se}_4$  is isomorphic with  $\text{As}_4\text{S}_4$ , realgar, with space group  $P2_1/c$ . The crystal is thus a molecular crystal with van der Waals bonding between the cradle molecules. The layer structure of  $\text{As}_2\text{Se}_3$  is confirmed and that structure is shown to be somewhat closer to orpiment,  $\text{As}_2\text{S}_3$ , than previously thought. Furthermore the procedure used for determining these structures, while not as precise as single-crystal methods and requiring, in practice, some *a priori* knowledge of the structure, is a significant simplification of the usual methods and ought to prove useful in many structure determinations previously limited by lack of single crystals of sufficient quality.

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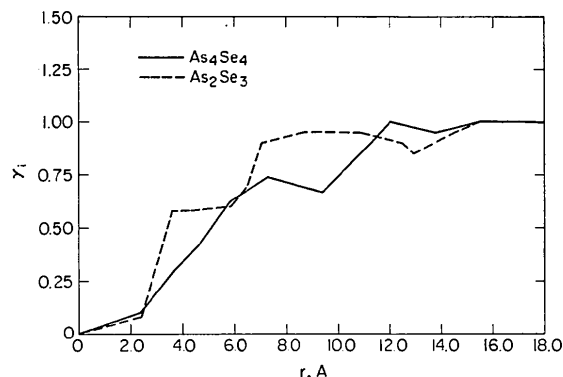


Fig. 5. Coupling coefficients for crystalline  $\text{As}_4\text{Se}_4$  and  $\text{As}_2\text{Se}_3$ .

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#### References

- CHEKNOV, A. P., DEMBOVSKII, S. A. & CHISTOV, S. F. (1968). *Izv. Akad. Nauk SSSR Neorg. Mater.* **4**, 1658–1663.
- CROMER, D. E. (1965). *Acta Cryst.* **18**, 17–23.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- GOLDSTEIN, P. (1971). Xerox Corp., private communication.
- GURR, G. E., MONTGOMERY, P. W., KNUTSON, C. D. & GORRES, B. T. (1970). *Acta Cryst.* **B26**, 906–915.
- International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.
- ITO, T., MORIMOTO, N. & SADANAGA, R. (1952). *Acta Cryst.* **5**, 775–782.
- JAMES, R. W. (1948). *The Optical Principles of the Diffraction of X-rays*, p. 462. London: Bell.
- KAPLOW, R., ROWE, T. & AVERBACH, B. L. (1968). *Phys. Rev.* **168**, 1068–1079.
- KAPLOW, R., STRONG, S. L. & AVERBACH, B. L. (1965). *Phys. Rev.* **138**, A1336–A1345.
- LAGNEBORG, R. & KAPLOW, R. (1967). *Acta Metall.* **15**, 13–24.
- MORIMOTO, N. (1954). *Miner. J.* **1**, 160–169.
- NORMAN, N. (1957). *Acta Cryst.* **10**, 370–373.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 225. Ithaca: Cornell Univ. Press.
- STRONG, S. L. & KAPLOW, R. (1968). *Acta Cryst.* **B24**, 1032–1036.
- STRONG, S. L., WELLS, A. F. & KAPLOW, R. (1971). *Acta Cryst.* **B27**, 1662–1663.
- VAIPOLIN, A. A. (1966). *Sov. Phys. Crystallogr.* **10** (5), 509–512.
- WARREN, B. E. & MOZZI, R. L. (1966). *Acta Cryst.* **21**, 459–461.