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Structure of Solid Carbon Diselenide (CSe_2) at 17·5, 50 and 200K

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Abstract. $M_r = 169·9$, orthorhombic, *Cmca*, $Z = 4$. At 17·5 K: $a = 6·5021$ (4), $b = 5·7599$ (4), $c = 8·9907$ (7) Å, $V = 336·71$ (9) Å^3, $D_x = 3·35$ Mg m^{-3}, $R_{wp} = 9·7\%$. The crystal structure of CSe_2 has been determined at 17·5, 50 and 200 K using neutron powder profile refinement with a wavelength of 1·9887 Å. The C–Se bond is 1·689 (3) Å, oriented at 41·60 (10)° to the *b* axis in the *bc* plane. The structure is similar to that of CS_2 and the lattice parameter *c* shows the same anomalous temperature dependence.

Introduction. As part of a programme to investigate interatomic potentials in solids composed of simple linear molecules, we have recently studied the structure and intermolecular dynamics of CS_2 (Pawley, Dolling, Powell & Torrie, 1981; Powell, Dolling & Torrie, 1982; Powell, Dolling, Torrie & Pawley, 1982). An analogous solid composed of simple, linear, triatomic molecules which might be expected to have properties similar to those of carbon disulphide is CSe_2. As an extension of the investigation of such molecular solids we have determined the crystal structure of solid CSe_2. Little is known about this material since it is highly noxious, poisonous and unstable at normal storage temperatures (253 K or above). We proceeded on the assumption that CSe_2 has the same structure as CS_2 and determined the structure at three widely separated temperatures, 17·5, 50 and 200 K, as a check on possible phase transitions (the melting temperature is 227·7 K). In a companion study, we have measured the frequencies of the Raman and infrared active lattice modes (Torrie, Andrews, Anderson & Powell, 1983).

Experimental. Liquid carbon diselenide was supplied by Strem Chemicals. After shipping and storage in a refrigerator for several weeks the liquid was black in appearance with black deposits on the sides of the vials. The black precipitate is believed to be a polymerized form of CSe_2. Purification of the sample was carried out by vacuum distilling the liquid into a container immersed in liquid nitrogen. No heat was applied to avoid further polymerization of the CSe_2. The end product of the distillation process was a golden yellow liquid, which was used to prepare the polycrystalline sample.

The liquid was dripped into a thin-walled vanadium can immersed in liquid nitrogen. The solid formed in the can was mechanically ground into a fine powder before more liquid was added. Several grinding steps were carried out until the vanadium can (7·5 cm long by 1·2 cm diameter) was almost filled. The resulting sample was mounted in a cryostat and cooled to 17·5 K. The quality of the polycrystalline nature of the sample was checked by measuring the intensity of the 111 Debye–Scherrer peak as a function of specimen orientation about the cylinder axis (*i.e.* an axis perpendicular to the scattering plane). Measurements of the peak intensity were made at intervals of 10° in specimen orientation and the intensities were distributed about their mean value with a standard deviation of 14%. The sample was rotated continuously throughout the experiment to minimize possible residual errors in the intensities due to the finite grain size of the sample.

The powder diffraction measurements were made on the L3 triple-axis spectrometer at the NRU reactor, Chalk River. The monochromator was Ge (133) and the analyser, graphite (002), was set to reflect elastically scattered neutrons. Soller-slit collimators with horizontal divergences of 0·33 and 0·36° were placed before and after the sample respectively. Calibration of the spectrometer was performed using Ge powder. The wavelength was determined to be 1·9887 Å and initial values for the zero of the scattering-angle scale and initial values for the line-shape parameters were also derived. The spectrometer resolution (FWHM) at zero scattering angle was determined to be 0·32°. The intensity of the diffracted neutrons was measured as a function of scattering angle (2θ) in steps of 0·1° from 20 to 120° (at 17·5 K), 23 to 120° (at 200 K) and from 23 to 53·6° (partial run at 50 K). Each complete run lasted for four days. The powder profiles for the two complete runs are shown in Fig. 1.*

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* Lists of observed and calculated intensities corresponding to Figs. 1(*a*) and 1(*b*) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38581 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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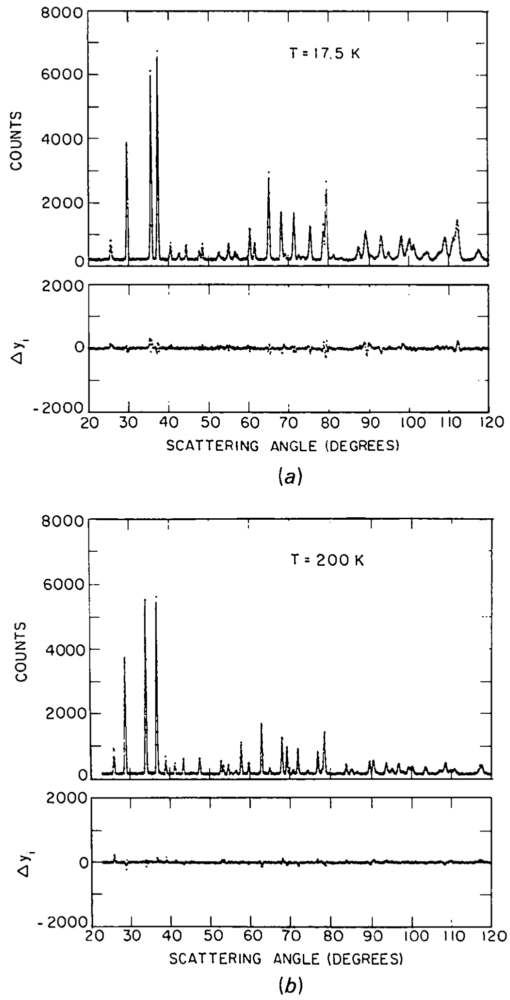

Fig. 1. Comparison of the observed and calculated profiles. The crosses show the experimental intensities and the line through them is the calculated intensity. The plot of Δy_i *versus* $2\theta_i$ is a quantitative measure of the discrepancies between the observed (y_i^{obs}) and calculated (y_i^{calc}) intensities at $2\theta_i$. (*a*) $T = 17{\cdot}5$ K, (*b*) $T = 200$ K.

Analysis

The powder diffraction profiles were analysed by means of the program *EDINP* (Pawley, 1980) which is a modified Rietveld profile-analysis program (Rietveld, 1969) in which the molecular orientation and C—Se bond length can be constrained during the initial cycles of refinement. In the present case we have chosen to refine the bond length and the molecular orientation rather than the atomic coordinates (y,z) of the Se atom (the C atom is at the origin).

As a result of the good resolution used in this experiment, the Debye–Scherrer peaks are well separated even at high angles, so the background level and peak shapes can be accurately determined. The intensity due to inelastically scattered neutrons was minimized by the analyser and a linearly sloping (two-parameter) background was found to be adequate for all runs. All well separated peaks could be fitted to Gaussian profiles with half-widths given by H where $H^2 = U\tan^2\theta + V\tan\theta + W$. Initial values for the parameters U, V and W were derived from the calibration of the spectrometer. These parameters were allowed to vary during the refinement of the low-temperature structure and the final values obtained at this temperature were used during the refinement of the structure at 50 K. For the final refinement of the structure at 200 K it was necessary to allow these parameters to vary to eliminate obvious misfits in line widths. This may indicate that there was grain growth at this temperature. A reflection was considered to contribute to the profile over a range of 4σ.

It was clear from preliminary calculations that CSe_2 has a structure very similar to that of CS_2, so the analysis of the data was started with this assumption. Initial values for the lattice parameters were calculated from the low-angle peaks and initial values for other parameters were taken from the CS_2 results. First the scale and background parameters were varied and then lattice parameters and the effective zero of the scattering angle were added. Next, the molecular orientation and C—Se bond length were allowed to vary, followed by U, V and W and finally the thermal parameters (isotropic or anisotropic) were adjusted. At each step R_{wp} (defined below) reached a constant value after three cycles of refinement. However, visual comparison of the observed and calculated diffraction profiles for the data at 17·5 K showed that the fit was not particularly good, with the most obvious discrepancy being the low calculated value for the 200 peak at $2\theta \simeq 36°$. In order to reduce this discrepancy a preferred-orientation parameter, G, was introduced in the form discussed by Rietveld (1969). The preferred-orientation direction was chosen to be [014] since preliminary calculations showed that this choice would improve the fit and this direction tended to be a preferred growth direction for the single crystals of CS_2 which we examined previously. Some difficulties were

Table 1. *The parameters determined from the refinements of the crystal structure of* CSe_2

The R factors, lattice parameters, unit-cell volume, the isotropic thermal parameters B(C) and B(Se), the C—Se bond length, the orientation angle, θ, between the molecular axis and the **b** direction and the preferred-orientation parameter, G, are given.

Temperature (K)	17·5	50*	200
R_{wp}(%)	9·7	7·0	8·4
R_p(%)	7·2	5·4	6·3
R_{expected} (%)	4·8	4·9	6·0
a (Å)	6·5021 (4)	6·6298 (19)	6·7666 (3)
b (Å)	5·7599 (4)	5·8526 (20)	5·9513 (3)
c (Å)	8·9907 (7)	8·8924 (22)	8·8451 (5)
Unit-cell volume (Å^3)	336·71 (9)	345·04 (30)	356·19 (5)
B(C) (Å^2)	0·88 (11)	—	3·46 (11)
B(Se) (Å^2)	0·73 (7)	—	5·01 (9)
Orientation angle θ(°)†	41·60 (10)	40·19 (17)	39·86 (10)
C—Se bond length (Å)†	1·689 (3)	1·678 (6)	1·676 (3)
G	0·26 (4)	0·26	0·26

* Data collected over a limited range of angles.

† The molecule lies in a mirror plane with the C atom at a centre of symmetry, as illustrated in Fig. 2.

experienced in refining G and the thermal parameters together since they are highly correlated. So the value of G was manually stepped through a broad range and, for each value of G, all other parameters were varied to minimize R_{wp}. The value of G which minimized R_{wp} was then added to the variables to produce the final parameter values listed in Table 1 using a weighting factor of (Intensity)$^{-1}$. For the various fits G was constant within the limits of error, but the most reliable value of G is expected to be that obtained at 17·5 K with isotropic temperature factors since temperature factors are small and correlations are minimized. Therefore the results in Table 1 were obtained using this 'best value' of G.

A correction for the effective absorption of the cylindrical specimen was made. The transmission of the sample was measured to be 52%, which gives an effective correction to the overall temperature factor, $\Delta B = -0{\cdot}204$ Å^2 (Hewat, 1979). Isotropic temperature factors for C and Se are increased by $-\Delta B$ and smaller increases are distributed among the anisotropic temperature factors.

The resulting anisotropic temperature factors had reasonable average magnitudes and signs but the individual components varied somewhat erratically between 17·5 and 200 K. Also, U_{11}(Se), U_{22}(Se) and U_{11}(C) are very strongly correlated with the preferred-orientation parameter. For these reasons we decided to quote only the isotropic temperature factors. Note that temperature factors cannot be adequately determined from the partial run at 50 K. The fitted profiles for the full runs are compared with the experimental data in Fig. 1. A quantitative measure of the difference between the observed and fitted profiles is given by the difference $\Delta y_i = y_i^{\rm obs} - y_i^{\rm calc}$. At both temperatures it is clear that the mean value of Δy_i is essentially zero, which indicates that the variation of background with scattering angle has been adequately described. The variations of Δy_i about zero thus show the discrepances between the fitted structural model and the data. The general magnitude of Δy_i is rather similar for both temperatures and is slightly larger than the corresponding quantity in CS_2 (Powell, Dolling & Torrie, 1982).

Discussion. The structural parameters obtained from refinements with a linear sloping background, isotropic thermal parameters and weighting factor proportional to (Intensity)$^{-1}$ are given in Table 1. Also shown are two R factors defined by $R_{wp} = \{\sum_i[(y_i^{\rm obs} - y_i^{\rm calc})^2/y_i^{\rm obs}]/\sum_i y_i^{\rm obs}\}^{1/2}$ and $R_P = \sum_i|y_i^{\rm obs} - y_i^{\rm calc}|/\sum_i y_i^{\rm obs}$, where $y_i^{\rm obs}(y_i^{\rm calc})$ is the observed (calculated) intensity at scattering angle $2\theta_i$, while $R_{\rm expected} = (N/\sum_i y_i^{\rm obs})^{1/2}$ where N is the number of values of y_i. Correlations among the listed parameters are small.

The errors quoted in the table are the standard deviations produced by the profile-refinement program. As discussed in a previous paper (Powell, Dolling & Torrie, 1982), we feel that the quoted standard deviations should be multiplied by a factor of approximately three to give reasonable estimates of the errors in the parameters. The bond lengths determined from the refinement should be corrected for foreshortening due to the librational motion of the CSe_2 molecule. It is impossible to do this directly using only isotropic thermal parameters, but by comparison with CS_2 we expect that the bond-length correction at 17·5 K is smaller than the quoted standard deviation. A comparison of the isotropic thermal parameters and bond-length corrections between the two substances indicates that most, if not all, of the apparent temperature variation of the C—Se bond length is due to the foreshortening correction. The structures of CSe_2 at 17·5 and 200 K are shown schematically in Fig. 2.

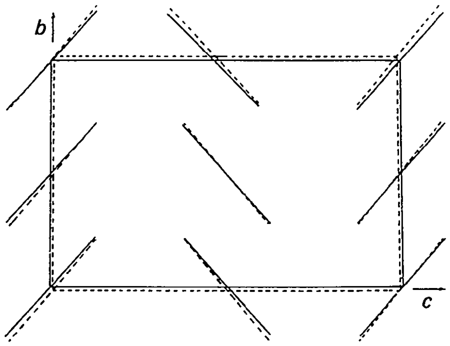

Fig. 2. Projection of the unit cell of CSe_2 on to the bc plane, The linear molecules are represented by lines and molecules at the centre of each edge are at $a/2$. The solid line is for $T = 17{\cdot}5$ K and the dashed line for $T = 200$ K.

The present results indicate that CSe_2 has the same crystal structure as CS_2, space group *Cmca*, in the temperature range investigated and the lattice parameters show the same type of variation with temperature. The a and b lattice parameters increase with increasing temperature whereas the c lattice parameter decreases. Also, the CSe_2 molecule rotates clockwise with increasing temperature as viewed in Fig. 2 as does the CS_2 molecule from a similar perspective. In all cases the variations with temperature for CSe_2 are smaller than for CS_2, as might be expected with a heavier molecule.

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