

Biaxial Tensors for Anomalous Scattering of X-rays in Selenolanthionine

BY LIESELOTTE K. TEMPLETON AND DAVID H. TEMPLETON

Department of Chemistry, University of California, Berkeley, CA 94720, USA

(Received 8 February 1988; accepted 21 June 1988)

Abstract

X-ray pleochroism is observed near the Se *K* absorption edge in a monoclinic crystal of selenolanthionine monohydrate using linearly polarized synchrotron radiation and is explained by a simple molecular-orbital model. The complex anomalous-scattering tensor of selenium, measured by diffraction in a tetragonal crystal of the anhydrous compound, exhibits anisotropy nearly 6 for f' and 7 for f'' , the most yet found for a *K* edge. The crystal structure was determined for D-(-)-selenolanthionine, space group $P4_32_12$, $a = 6.651$ (2), $c = 21.758$ (5) Å, $Z = 4$, $R = 0.027$ for 304 unique reflections.

1. Introduction

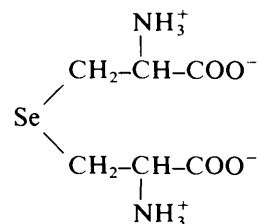
It is generally assumed, in derivations of scattering theories for X-rays, that for this frequency range the dielectric constant of matter has scalar rather than tensor character (e.g. Zachariasen, 1967). While this is often an accurate assumption, it is invalid for many materials for frequencies near absorption edges. Its failure gives tensor character to the absorption coefficient (dichroism, pleochroism) and refractive index (birefringence), phenomena which are familiar for visible light in crystals. Anomalous-scattering terms, which are closely related to the complex refractive index (James, 1982), also take on a tensor character. The anisotropy of these complex tensors is sufficient to cause substantial changes in diffraction intensity with polarization direction. The effects in both diffraction experiments and absorption spectra have been used to measure the tensors for linear UO_2^{2+} , trigonal-pyramidal BrO_3^{1-} , and square-planar $PtCl_4^{2-}$ (Templeton & Templeton, 1982, 1985*a*, 1985*b*). All these examples are uniaxial (with two independent principal values at each wavelength) because of the molecular symmetry. Here we report a more general example, a covalently bonded selenium compound in which the C_2 site symmetry of the Se atom demands a biaxial tensor, with three independent principal values of the complex atomic scattering factor for each wavelength.

The utility of anomalous-scattering effects in studies of molecular structure is well known. Hendrickson (1985) pointed out that selenium has special potential for phase determination for protein crystals

because it can be substituted for sulfur in them and the energy of its *K* absorption edge is good for experiments. The present study was undertaken to assist such applications. The polarization effects reported here may be useful for phasing, but can cause error if not taken into account.

2. Selenolanthionine

Zdansky (1968) prepared and characterized the L-(+), D-(-) and *meso* isomers of selenolanthionine (or 3,3'-selenobisalanine).



Recrystallization of the D and L isomers from aqueous solution yielded 'small, hexagonal plates' which were monohydrates according to chemical analysis. By X-ray diffraction, Hendrickson, Troup & Zdansky (1986) found two kinds of crystals, monoclinic and tetragonal: $C2$, $a = 9.501$, $b = 5.325$, $c = 9.618$ Å, $\beta = 98.15^\circ$, $Z = 2$; $P4_32_12$ or $P4_32_12$, $a = 6.653$, $c = 21.764$, $Z = 4$. In each case the Se atom is in a special position on a twofold axis. The structure of the monoclinic phase was determined as an example of the multiple-wavelength method (Hendrickson, 1985) and shows it to be the monohydrate. The molecular volumes are almost identical in the two phases, but as described in the next section the tetragonal crystals do not contain water. Samples of both phases of the D isomer were given us by Professor Hendrickson.

3. Crystal structure of tetragonal D-selenolanthionine

Crystal data: $C_6H_{12}N_2O_4Se$, $M_r = 255.13$, $P4_32_12$, $a = 6.651$ (2), $c = 21.758$ (5) Å, $V = 962.5$ (6) Å³, $Z = 4$, $D_x = 1.760$ (1) g cm⁻³, $\lambda(\alpha_1) = 0.70930$ Å, $\mu = 38.45$ cm⁻¹, $F(000) = 512$, $T = 301$ K, $R = 0.027$ for 304 unique reflections.

Experimental: A $0.14 \times 0.11 \times 0.05$ mm triangular plate (11 faces) was mounted on the end of a glass

Table 1. Atomic coordinates and thermal parameters for tetragonal D-selenolanthionine

	$B_{\text{eq}} = \sum B_{ii}/3.$			$B_{\text{eq}} (\text{\AA}^2)$
	x	y	z	
Se	0.12976 (13)	0.12976	0	4.24
O1	0.6205 (10)	0.1387 (10)	-0.0597 (2)	4.21
O2	0.5562 (9)	-0.1900 (11)	-0.0515 (2)	3.58
N	0.4963 (11)	-0.1778 (12)	0.0685 (3)	2.53
C1	0.5790 (12)	-0.0152 (20)	-0.0293 (4)	2.43
C2	0.5355 (13)	0.0177 (13)	0.0384 (4)	1.61
C3	0.3676 (17)	0.1640 (14)	0.0515 (3)	3.26

fiber on an Enraf-Nonius CAD-4 diffractometer (at Berkeley) equipped with graphite monochromator and Mo $K\alpha$ radiation. Cell dimensions were derived from 24 reflections in the range $10 < \theta < 19^\circ$. Of 761 measured intensities [$h, -5$ to $5, k, 0$ to $5, l, 0$ to $18, (\sin \theta)/\lambda < 0.436 \text{ \AA}^{-1}$], 121 (some of which were forbidden by the space group) were rejected as too weak ($I < \sigma$). After analytical correction for absorption ($1.179 < A < 1.340$) reflections which were equivalent by the point-group symmetry were averaged giving 304 unique ones; $R_{\text{int}} = 0.078$. The members of each Bijvoet pair were considered to be independent. Periodic measurements of three standard reflections were constant within about 2% with no systematic trend; no correction was made. The structure was solved using the Patterson function to find the Se atom and electron density maps for other atoms. It was refined by least squares (on F) with weights $w = \sigma(F)^{-2}$; $p = 0.03$ in calculation of $\sigma(F^2)$. An empirical correction for extinction increased F by 5% for the strongest reflection (004). H-atom parameters were refined, but to avoid physically unrealistic values some limitations were necessary. The isotropic thermal parameters were constrained to a common value for the three H atoms on N and to another common one for the two H atoms on C3. Distances were restrained to 0.95 and 1.00 \AA respectively for N-H and C-H and to 1.55 \AA for H1...H2, H1...H3, and H2...H3, all with $\sigma = 0.05 \text{ \AA}$. With anisotropic thermal parameters for non-H atoms, 81 parameters were refined subject to nine distance restraints; $wR = 0.030$; $S = 1.23$; maximum final shift 0.14σ ; extremes of electron density difference function, 0.28 and -0.21 e \AA^{-3} . Atomic scattering factors including anomalous-scattering terms were taken from *International Tables for X-ray Crystallography* (1974). Calculations were made with unpublished local programs. Atomic parameters are listed in Table 1 and bond lengths and angles in Table 2.* The same structure was found

* Lists of anisotropic displacement parameters, coordinates and isotropic displacement parameters for H atoms, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51085 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

Se-C3	1.95 (1)	C1-C2	1.52 (1)
C1-O1	1.25 (1)	C2-N	1.48 (1)
C1-O2	1.27 (1)	C2-C3	1.51 (1)
C3-Se-C3'	98.1 (6)	C1-C2-N	109.7 (8)
O1-C1-O2	125.2 (8)	C1-C2-C3	114.7 (8)
C2-C1-O1	116.0 (10)	C3-C2-N	110.7 (7)
C2-C1-O2	118.6 (10)	C2-C3-Se	114.6 (6)

independently by Pähler & Hendrickson (1987) using direct methods.

The enantiomorphic space groups $P4_12_12$ and $P4_32_12$ are both consistent with the diffraction symmetry. The structure solution was started arbitrarily in $P4_12_12$. After the non-H atoms had been located, a refinement in which f'' of Se was varied gave $-2.0(4)$, the correct magnitude but wrong sign ($+2.223$, Cromer & Liberman, 1970). Because f'' is 0.006 or less for the other atoms, this method is nearly the same as the η test of Rogers (1981). This result indicates that $P4_32_12$ is the correct space group for this D(-) isomer, and it was used for the final calculations. The L(+) isomer will crystallize in $P4_12_12$. The same result is given even more decisively by the synchrotron experiments. The molecular configuration plotted in Fig. 1 is consistent with accepted amino acid structures and is a check that the specimen was indeed the D isomer.

4. X-ray pleochroism of monoclinic selenolanthionine monohydrate

Because the monohydrate crystals contain a single orientation of the molecules, the absorption coefficient tensor of the crystal is the same as that of the molecule. Molecular axes are designated z for the twofold axis bisecting the C-Se-C angle, x for the direction perpendicular to both Se-C bonds, and y for the direction perpendicular to x and z . By symmetry the z axis coincides with the b axis of the crystal, and the other two are in the ac plane. Absorption spectra (Fig. 2) near the Se K absorption edge were recorded by the X-ray fluorescence method for various directions of polarization with a small crystal

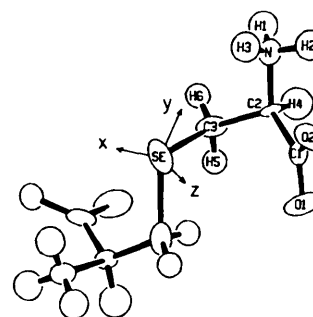


Fig. 1. Molecular structure of D-selenolanthionine (ORTEP, Johnson, 1965).

mounted on the CAD-4 diffractometer at SSRL (Phillips, Cerino & Hodgson, 1979) and a scintillation counter which detected the Se *K* radiation. The best position of this counter for minimum scattered radiation is horizontal at a right angle to the beam. Because space was limited it was about 30° from this direction. It is possible for Bragg reflections to contaminate spectra when measured in this way, but we found no evidence for them. The available crystals were too small for the transmission technique to be used. The orientation matrix of the crystal was determined with the diffractometer in the usual way. The diffractometer software is convenient for setting various crystal directions, specified by reciprocal-lattice coordinates, coincident with the horizontal direction of the major polarization component of the radiation. The monochromator at Beam Line I-5 contained two Si(220) crystals.

As the crystal is rotated, keeping the polarization direction in the *ac* plane, the strong absorption line at 12 658 eV varies in intensity. On the basis of several spectra not displayed here, the minimum was estimated to occur in the direction 2, 0, -3 (reciprocal-lattice coordinates), or 126° from the positive *a* axis past *c*, with a precision of 3°. For reasons given in § 8 below, this minimum was expected to occur for polarization in the *x* direction. Subsequent calculation from the coordinates of the β -C atom (Hendrickson, Troup & Zdansky, 1986) gives this direction as 125° from *a*. The 2, 0, 1 spectrum shown in Fig. 2 was measured with polarization close to the *y* direction.

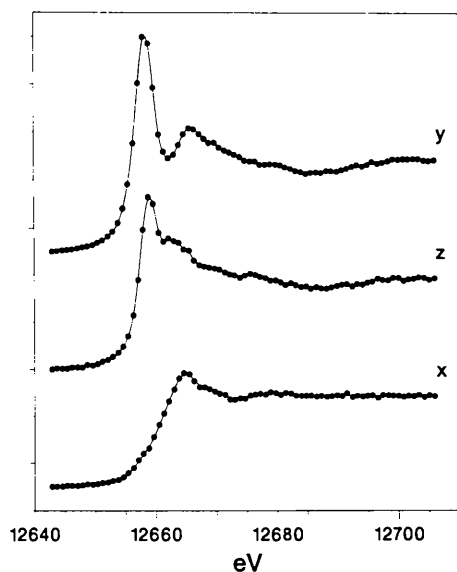


Fig. 2. Absorption spectra for monoclinic selenolanthionine with electric vector in reciprocal-lattice direction 2, 0, 1 = *y* (top), 0, 1, 0 = *z* (middle), 2, 0, -3 = *x* (bottom). The ordinate is intensity of fluorescence radiation on arbitrary scales.

This experiment shows how the method can be used to find molecular orientation in advance of a detailed determination of crystal structure.

The polarization of the EXAFS spectra (Stern, 1974) gives another way to assign the 2, 0, -3 spectrum to the *x* direction. In Fig. 2 it is quite evident which of the three spectra is least modulated at energies above the edge and thus has polarization perpendicular to the nearest-neighbor vectors.

No correction of these spectra has been made for the incomplete polarization of the radiation, estimated as 94%. Thus the true anisotropy of absorption is somewhat greater than shown here.

5. Anomalous-scattering tensors from diffraction data

Diffraction experiments with the monoclinic crystals near the absorption edge are hindered, except for special classes of reflections or very tiny crystals, by the complexity and large anisotropy of absorption effects. The tetragonal crystals are more suitable. The macroscopic absorption tensor, which is uniaxial in this case, is the average of the four orientations of the molecular tensor and is much more nearly isotropic. Absorption spectra measured by the fluorescence technique show only minor differences for polarization parallel and perpendicular to *c*. However, the anisotropy of the molecular tensor continues to influence the diffraction intensities, as was shown earlier with cubic crystals of sodium uranyl acetate and sodium bromate (Templeton & Templeton, 1982, 1985*a*).

Diffraction data were measured at Beam Line I-5, SSRL, using the crystal described in § 3 above, the CAD-4 diffractometer, and Si(220) monochromator crystals. Harmonic wavelengths were largely avoided by the combined effects of slight missetting of the monochromator, discrimination of the scintillation-counter signals, and the reduced intensity of high-energy photons in the source spectrum. Reflections selected in 'zigzag' mode, with θ limited between 2.5 and 20 or 25°, were each measured at three azimuths separated by 30 or 40° with the objective of reducing correlation of polarization effects with other variables. How many were measured depended on the time available. The always-changing intensity of incident radiation was monitored first by an ion chamber in front of the diffractometer and checked by repetition of a standard reflection after each 10 to 20 measurements. Scan times were adjusted to attain 3% statistical accuracy with an upper limit variously 60 to 120 s. Each reflection was scanned twice (forward and backward) as a protection against short-term instability, and a third time if necessary for agreement. Of 2169 reflections measured, four flagged as not checking were discarded. Another 152 were discarded because each was too weak to measure according to a fast prescan. Intensities were multiplied by a

Table 3. Anomalous-scattering tensor components from diffraction data

$$N = \text{number of reflections, } R = 100(\sum |\Delta F| / \sum |F_o|).$$

E (keV)	N	R	f'_{11}	f'_{33}	f'_{12}	f'_{13}	f''_{11}	f''_{33}	f''_{12}	f''_{13}
12-6403	154	3.6	-6.7 (1)	-7.0 (1)	-0.8 (2)	-1.1 (2)	0.2 (3)	0.9 (3)	1.0 (2)	0.2 (1)
12-6445	219	3.4	-7.1 (1)	-7.4 (1)	-0.7 (1)	-1.0 (1)	0.6 (3)	1.0 (3)	0.0 (2)	0.0 (1)
12-6470	245	3.1	-7.7 (1)	-8.1 (1)	-0.7 (1)	-1.0 (1)	1.3 (2)	1.0 (3)	-0.3 (2)	0.1 (1)
12-6515	132	3.1	-10.0 (1)	-10.5 (2)	-0.6 (1)	-1.1 (1)	1.1 (4)	0.4 (9)	0.3 (2)	0.3 (1)
12-6515	181	3.6	-9.6 (1)	-9.4 (1)	-0.7 (1)	-1.0 (2)	1.3 (3)	1.6 (3)	0.0 (2)	0.2 (1)
12-6549	387	4.7	-11.2 (1)	-13.3 (2)	-1.0 (1)	-1.8 (1)	4.4 (2)	4.8 (3)	0.6 (2)	2.4 (1)
12-6579	165	3.0	-7.3 (3)	-7.7 (3)	0.0 (2)	1.1 (2)	5.8 (4)	6.5 (3)	1.4 (1)	1.7 (1)
12-6579	107	2.7	-7.5 (2)	-7.3 (3)	0.3 (3)	1.4 (2)	5.7 (3)	4.9 (6)	0.7 (2)	2.1 (1)
12-6587	116	4.8	-7.7 (3)	-8.2 (4)	0.4 (3)	1.7 (2)	5.2 (4)	4.0 (6)	0.5 (3)	1.3 (2)
12-6602	260	3.1	-7.8 (1)	-7.4 (2)	0.6 (1)	0.6 (1)	5.2 (2)	5.3 (2)	0.9 (1)	0.5 (1)

Lorentz-polarization factor

$$(\sin 2\theta)/(1 + 0.0309 \cos^2 2\theta).$$

Analytical corrections for absorption, using coefficients estimated from absorption spectra, ranged from 1.06 to 1.12 for $\mu = 13 \text{ cm}^{-1}$ and 1.60 to 2.40 for $\mu = 110 \text{ cm}^{-1}$.

The independent elements of the anomalous-scattering tensor, four real and four imaginary terms, and a scale factor were determined as the parameters of a least-squares fitting of observed and calculated structure factors. All the coordinates and displacement parameters were kept fixed at the values found in the structure determination with Mo $K\alpha$ radiation. The computer program was a straightforward but tedious extension of that used earlier for simpler cases. The problem has much in common with refinement of anisotropic displacement parameters: unit vectors for polarization directions take the place of the \mathbf{h} vector in a bilinear form:

$$f = \sum_{j,k} e_1^j e_2^k f_{jk}, \quad (1)$$

which for convenience of calculation with real variables is written

$$f = f_0 + \sum_{j,k} e_1^j e_2^k f'_{jk} + i \sum_{j,k} e_1^j e_2^k f''_{jk}. \quad (2)$$

One must rotate the tensor for each member of an equivalent set of atoms just as the displacement tensor is transformed. A complication is that the relation of the polarization directions to the crystal orientation must be carried forward for each reflection from the initial data file. Equivalent reflections are not averaged because their settings are not equivalent with respect to polarization. The constraints of the site symmetry ($f_{11} = f_{22}$; $f_{13} = -f_{23}$ in this case) are the same as for thermal motion and are imposed in the same way. For the geometry of this experiment (scattering in the vertical plane) most of the intensity is in the s component of scattering from the s component of incident radiation, to which selenium contributes with scattering factor f_{ss} and other atoms with their ordinary scattering factors. Only these terms were considered in the calculation of derivatives

$\partial|F|/\partial f_{ij}$. The p' component scattered from incident s radiation depends on f_{sp} and was included in the calculated structure-factor magnitude:

$$|F_{\text{cal}}| = (|F_{ss}|^2 + |F_{sp}|^2)^{1/2}. \quad (3)$$

In measurements at 12.6549 keV, where the greatest anisotropy was found, the mean and maximum values were 2.6 and 11.8 for $|F_{sp}|$ and 29 and 153 for $|F_{ss}|$. Thus, the effect of F_{sp} is rather small for most reflections, but it is the dominant term for a few of them. Least-squares refinement with and without these extra terms gave very similar parameters for the scattering factor. Terms for the p component of incident radiation were omitted from the calculated intensity. With the polarization correction mentioned above, this is equivalent to assuming that the p radiation (estimated as 3% of the total) is scattered like the s radiation except for reduction by a factor $\cos^2 2\theta$, which is true for all atoms except Se. The result is that the anisotropy is underestimated by a small and unknown amount.

Results of the least-squares calculations are listed in Table 3. The principal values of the f' and f'' tensors (Table 4 and Fig. 3) were calculated after values measured at the same wavelengths were averaged.

6. Tensors from fluorescence data

The anomalous-scattering tensor was also estimated by assuming that the connection of f' and f'' to the absorption cross section σ (James, 1982; Wagenfeld, 1975):

$$f''(\omega) = mc\omega\sigma(\omega)/4\pi e^2, \quad (4)$$

$$f'(\omega) = (2/\pi) \int_0^\infty [\omega' f''(\omega') / (\omega^2 - \omega'^2)] d\omega', \quad (5)$$

is valid for each tensor component. It was also assumed that the Cromer & Liberman (1970) model describes f'' correctly at wavelengths outside the range of our experiment. The scale of each spectrum measured by fluorescence was adjusted to fit values of f'' from Cromer's (1983) program at wavelengths where pleochroism was assumed to be insignificant.

Table 4. Principal values of anomalous-scattering tensors and angles Φ' , Φ'' ($^\circ$) between the c crystallographic axis and f'_x, f''_x

E (keV)	f'_x	f'_y	f'_z	f''_x	f''_y	f''_z	Φ'	Φ''
12.6403	-4.8 (2)	-8.1 (1)	-7.6 (2)	-0.8 (4)	1.0 (3)	1.2 (3)	55 (3)	[79]*
12.6445	-5.4 (1)	-8.3 (1)	-7.7 (1)	0.6 (4)	1.0 (3)	0.6 (4)	55 (2)	[88]
12.6470	-6.0 (1)	-9.1 (1)	-8.4 (1)	1.0 (3)	1.5 (3)	1.0 (3)	55 (2)	[12]
12.6515	-8.0 (1)	-11.1 (1)	-10.4 (1)	0.6 (4)	1.5 (4)	1.3 (3)	52 (2)	46 (2)
12.6549	-8.8 (2)	-14.7 (2)	-12.2 (1)	0.8 (4)	7.7 (4)	5.1 (3)	60 (1)	49 (2)
12.6579	-9.3 (3)	-5.7 (3)	-7.2 (3)	2.4 (5)	7.9 (5)	6.8 (3)	45 (3)	51 (3)
12.6587	-10.6 (5)	-5.7 (5)	-7.2 (4)	2.5 (7)	6.2 (7)	5.7 (5)	44 (3)	[40]
12.6602	-8.9 (2)	-6.8 (2)	-7.2 (1)	3.9 (2)	5.7 (2)	6.1 (2)	60 (4)	62 (5)

* Brackets indicate angles which are very uncertain.

The integration was confined to the range of experiment, with the quantity $(f''_s - f''_{CL})$ substituted for f'' in (5); the subscripts indicate values derived from the spectra and from Cromer's program, respectively. Each result of the integration was added to Cromer's value for f' at that wavelength.

The curves for principal values of the f' and f'' tensors derived in this way are compared with results of the diffraction method in Figs. 4-6. The minimum f' values are considerably more negative according to the latter method and more anisotropy is indicated, but the general trends are the same. In bromate and in tetrachloroplatinate we also found greater anisotropy when it was measured by diffraction. The fit would be better if some of the diffraction values were shifted 1 or 2 eV toward higher energy. This is evidence of a systematic error or drift in the wavelength, which was set at the beginning of each diffraction experiment extending over several hours. We do not know if this error comes from changes of

electron orbits or the positions or temperatures of the monochromator crystals, or if it has some other cause.

7. Calibration of energy scale

Photon energies are selected by rotation of the monochromator crystals with a stepping motor [2000 steps ($^\circ$) $^{-1}$] and calibrated frequently with absorption spectra. At 12.7 keV, each step is 0.42 eV with Si(220). Often the energies of inflection points of absorption edges, tabulated by Bearden (1967), are used for this purpose. We prefer to use centers of white lines because their locations are less likely to be influenced by wavelength resolution, non-linearity of detection or ambiguity due to complex structure in the edge. Here the strong sharp K -edge line of selenium measured by transmission through a polycrystalline sample of sodium selenate was used as the working

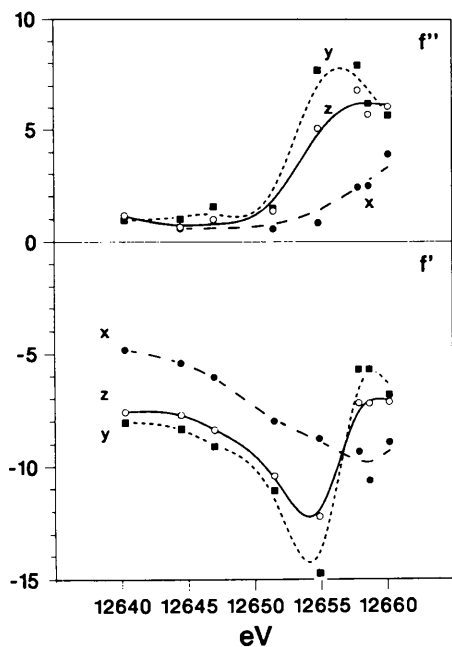


Fig. 3. Principal values of tensors from diffraction data.

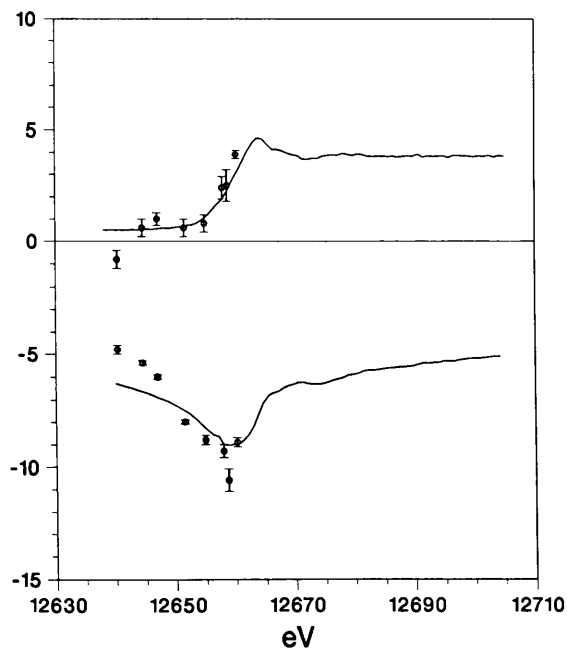


Fig. 4. Curves for f'' (upper) and f' (lower) from the absorption spectrum with x polarization (perpendicular to Se-C bonds); points with error bars were measured by diffraction.

standard. Its location is $+7.9$ (4) eV from the edge peak or about $+9.8$ from the edge inflection measured in powdered elemental selenium. The elemental peak is $+4.5$ eV from the $K\beta_2$ emission line according to the spectra of Deslattes & deBen (1959). The selenate peak is thus $12\,664.6$ (7) eV according to Bearden's value and error estimation for the $K\beta_2$ line and

$12\,664.3$ according to his value for the elemental edge. We adopted the former value because we are uncertain how to define the edge inflection in our spectra.

An independent calibration based on cell dimensions measured for a spherical ruby crystal by the method described by Templeton & Templeton (1985*a*) gave $12\,666.5$ (10) eV for the selenate line. The agreement is less than perfect, but is in the range of plausible systematic errors.

8. Discussion

The extreme values, -14.7 for f' and 7.9 for f'' , make selenium in this chemical state attractive for applications in structure analysis. The maximum anisotropy, 5.9 for f' and 6.9 for f'' , is the most yet measured for a K edge. As a percentage of f_0 it exceeds the L_3 -edge effects found in platinum. Even larger effects may occur with more nearly monochromatic radiation because the energy spread here (FWHM about 2 eV) is comparable to the natural K -level width (2.33 eV, Krause & Oliver, 1979).

The orientation of the x molecular axis, calculated from the C3 coordinates in the tetragonal crystal, is 49 (3) $^\circ$ from the c axis. The averages of the angles listed in Table 4 are 53 (6) $^\circ$ for Φ' and 52 (7) $^\circ$ for Φ'' if four poorly determined ones are omitted.

A simple molecular-orbital model of the electronic structure of the molecule gives an explanation of the pleochroism. By analogy with oxygen and sulfur compounds, one expects the bonding of selenium to be largely based on the $4p_y$ and $4p_z$ electrons, with lone pairs occupying orbitals consisting mainly of the $4p_x$ and $4s$ atomic orbitals. Approximations of the bonding molecular orbitals are:

$$b_1 = p_y(\text{Se}) + sp^3(\text{C}) - sp^3(\text{C}') \quad (6)$$

$$a_1 = p_z(\text{Se}) + sp^3(\text{C}) + sp^3(\text{C}'). \quad (7)$$

The corresponding antibonding orbitals are empty and have the correct symmetry for allowed transitions from the K shell for polarizations respectively in the y and z directions:

$$b_1^* = p_y(\text{Se}) - sp^3(\text{C}) + sp^3(\text{C}'), \quad (8)$$

$$a_1^* = p_z(\text{Se}) - sp^3(\text{C}) - sp^3(\text{C}'). \quad (9)$$

The first resonance line is missing for x -polarized radiation because no such vacant orbital exists for $4p_x$ electrons. Absorption can be different for the other two polarizations because the b_1^* and a_1^* orbitals are not equivalent. The spectra (Fig. 2) indicate that energy level b_1^* is lower than a_1^* by about 0.5 eV. The most nearly analogous molecule for which we have found energy-level calculations is dimethyl sulfide (Thompson, Carroll, Watson, O'Donnell & McGlynn, 1966) where these levels were estimated to be in the same order but 1.83 eV apart.

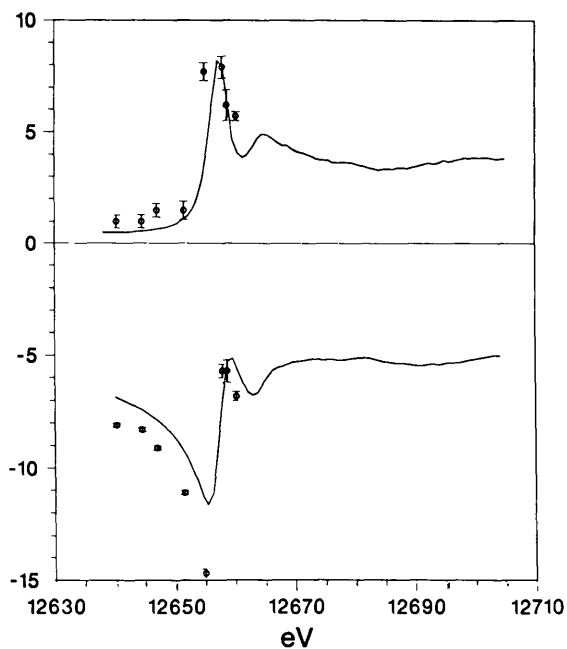


Fig. 5. Same as Fig. 4, but y polarization (C-C direction).

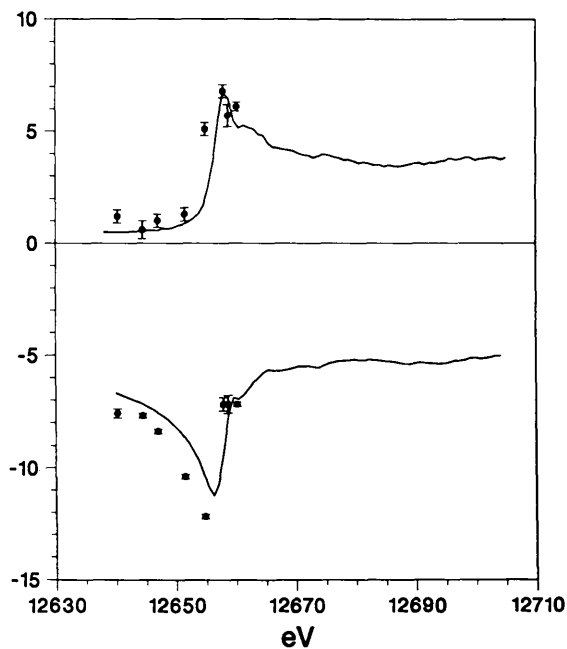


Fig. 6. Same as Fig. 4, but z polarization (bisector of C-Se-C bond angle).

We thank Professor Wayne Hendrickson for providing the crystals, for helpful discussions, and for data in advance of publication. This work would have been impossible without the assistance of many members of the staff of SSRL, especially Dr Ethan Merritt. This research was supported by the National Science Foundation under Grant CHE-8515298. It was done in part at SSRL which is supported by the Department of Energy, Office of Basic Energy Sciences; and the National Institutes of Health, Biotechnology Resource Program, Division of Research Resources. It used some facilities of the Lawrence Berkeley Laboratory, supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract No. DE-AC03-76SF00098.

References

- BEARDEN, J. A. (1967). *Rev. Mod. Phys.* **39**, 78-124.
 CROMER, D. T. (1983). *J. Appl. Cryst.* **16**, 437.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
 DESLATTES, R. D. & DEBEN, H. S. (1959). *Phys. Rev.* **115**, 71-74.
 HENDRICKSON, W. A. (1985). *Trans. Am. Crystallogr. Assoc.* **21**, 11-21.
 HENDRICKSON, W. A., TROUP, J. M. & ZDANSKY, G. (1986). Private communication.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 JAMES, R. W. (1982). *The Optical Principles of the Diffraction of X-rays*, p. 138. Woodbridge: Ox Bow.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 KRAUSE, M. O. & OLIVER, J. H. (1979). *J. Phys. Chem. Ref. Data*, **8**, 329-338.
 PÄHLER, A. & HENDRICKSON, W. A. (1987). Private communication.
 PHILLIPS, J. C., CERINO, J. A. & HODGSON, K. O. (1979). *J. Appl. Cryst.* **12**, 592-600.
 ROGERS, D. (1981). *Acta Cryst.* **A37**, 734-741.
 STERN, E. A. (1974). *Phys. Rev. B*, **10**, 3027-3037.
 TEMPLETON, D. H. & TEMPLETON, L. K. (1982). *Acta Cryst.* **A38**, 62-67.
 TEMPLETON, D. H. & TEMPLETON, L. K. (1985a). *Acta Cryst.* **A41**, 133-142.
 TEMPLETON, D. H. & TEMPLETON, L. K. (1985b). *Acta Cryst.* **A41**, 365-371.
 THOMPSON, S. D., CARROLL, D. G., WATSON, F., O'DONNELL, M. & MCGLYNN, S. P. (1966). *J. Chem. Phys.* **45**, 1367-1379.
 WAGENFELD, H. (1975). *Anomalous Scattering*, edited by S. RAMASESHAN & S. C. ABRAHAMS, pp. 13-24. Copenhagen: Munksgaard.
 ZACHARIASEN, W. H. (1967). *Theory of X-ray Diffraction in Crystals*, p. 114. New York: Dover.
 ZDANSKY, G. (1968). *Ark. Kemi*, **29**, 443-448.

Acta Cryst. (1988). **A44**, 1051-1055

Structure Analysis of Modulated Molecular Crystals. V. Symmetry Restrictions for One-Dimensionally Modulated Crystals

BY V. PETŘÍČEK* AND P. COPPENS

Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214, USA

(Received 11 March 1988; accepted 21 June 1988)

Abstract

Symmetry restrictions that apply to amplitudes of displacement waves when atoms or rigid molecules are located at special positions in a modulated structure are tabulated for various crystallographic symmetry elements. The tables can be used for both the atomic and molecular models and are valid for harmonics of arbitrary order.

Introduction

The (3+1) superspace-group formalism described by de Wolff (1974) and de Wolff, Janssen & Janner (1981) has found widespread application in the

description of one-dimensionally modulated crystals. For a given space group the amplitudes of the displacement waves are restricted when an atom or rigid molecule is located at a special position of the basic space group (e.g. Yamamoto, 1980, 1983; Kucharczyk, Paciorek & Uszynski, 1986; Gao, Gajhede, Mallinson, Petříček & Coppens, 1988). We present here a simple method for obtaining the restrictions and the derivation of general rules. The results are summarized in Table 1.

In order to illustrate our derivation, we will first summarize a number of relevant expressions given by de Wolff, Janssen & Janner (1981). A four-dimensional symmetry operation \hat{S} is defined by

$$\hat{S}(x_1, x_2, x_3, x_4) = (x'_1, x'_2, x'_3, x'_4)$$

where the x_i are the coordinates with respect to the four-dimensional bases. \hat{S} is described by the matrix

* Permanent address: Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, 180 40 Praha 8, Czechoslovakia.