The Crystal Structure and Optical Activity of Tellurium

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Abstract

The element tellurium has a crystal structure made up of spiral chains of bonded atoms packed in a hexagonal array. Its symmetry leads to the existence of enantiomorphic forms containing spirals of opposite handedness, the right-handed one belonging to space group $P3_121$ and the other to $P3_221$, which have opposite optical rotatory powers. The normal methods of crystal structure determination cannot distinguish between the enantiomorphs, nor is this feasible using anomalous dispersion unless there is sufficient asphericity in the tellurium electron density due to bonding. Such asphericity also gives rise to small but measurable differences from unity in the flipping ratios for polarized neutron scattering due to the polarization dependence of the Schwinger scattering. This effect is easier to measure than is the intensity difference between Bijvoet pairs and it has been used to determine the absolute structural configuration that corresponds to a particular sense of optical rotation in a tellurium single crystal. The plane of polarization of the transmitted light rotates in the same sense as the bonded atoms in the spiral chains. This observation disagrees with a previous theoretical calculation based on the single polarizable ion model.

1. Introduction

The elements tellurium and selenium have the crystal structure illustrated in Fig. 1, made up of spiral chains of bonded atoms packed in a hexagonal array. The spiral chains may be of either hand and consequently the symmetry of the structure is enantiomorphic. The right-handed form belongs to space group $P3_121$ and the other to $P3_221$. Crystals of tellurium exhibit strong optical rotatory power, the two enantiomorphs having opposite senses for the rotation (Nomura, 1960). The normal methods of crystal structure determination cannot distinguish between enantiomorphs, nor is this possible using anomalous dispersion if the tellurium electron density is spherical (Chandrasekaran, 1968). More recently, McIntyre (1978) has shown that Bijvoet intensity differences in X-ray diffraction can arise because of asphericity in the tellurium electron density. It has, however, not yet been possible to determine experimentally which particular enantiomorph gives which sense of optical rotation.

Forsyth & Brown (1992) have shown that the polarization dependence of the intensity of Schwinger scattering can be a sensitive probe of electronic structure in acentric crystals and it is worth considering whether it could be used as an alternative to X-ray diffraction to determine the absolute structural configuration corresponding to a particular sense of optical rotation in enantiomorphic crystals. The difference from unity of the flipping ratio, R, due to Schwinger scattering is given by

$$R - 1 = 4[\Re(N^*X_s)/NN^*][(\kappa \times \kappa')/|\mathbf{k}|^2] \cdot \mathbf{P} = 4\gamma, \tag{1}$$

where $\Re$ denotes the real part of a complex quantity, N is the nuclear structure factor, N^* its complex conjugate and X_s is the Schwinger structure factor given by

$$X_s = i(\gamma_n e^2/mc^2)(m/m_o)$$
$$\times \sum_n [Z_n - f_n(\mathbf{k})] \exp(\mathbf{k} \cdot \mathbf{r}_n). \tag{2}$$

In the above equations, γ_n is the neutron magnetic moment in nuclear Bohr magnetons, m and m_o are the electron and neutron masses, κ and κ' are the incident and scattered wave vectors, $\mathbf{k}$ the scattering vector and $\mathbf{P}$ the neutron polarization vector. The summation is over all atoms n with atomic numbers Z_n, X-ray
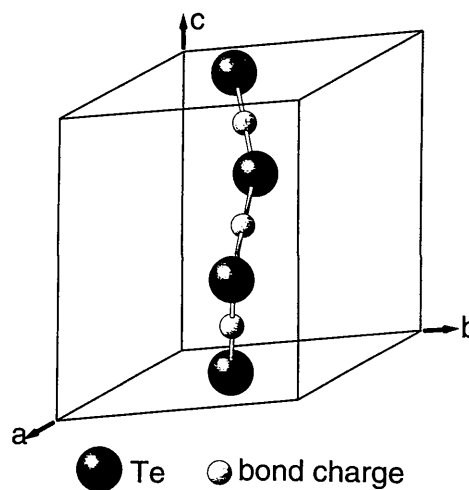

Fig. 1. The crystal structure of tellurium showing the positions of the bond charges used to model the acentric charge density.

form factors $f_n(\mathbf{k})$ and positions $\mathbf{r}_n$. The value of γ depends on the geometry of measurement through the term $[(\boldsymbol{\kappa} \times \boldsymbol{\kappa}')/|\mathbf{k}|^2] \cdot \mathbf{P}$ and it is convenient to define a quantity γ',

$$\gamma' = \gamma\{[(\boldsymbol{\kappa} \times \boldsymbol{\kappa}')/|\mathbf{k}|^2] \cdot \mathbf{P}\}^{-1}, \qquad (3)$$

to allow comparison of measurements made at different wavelengths.

For crystals containing a single atomic species that scatters isotropically, the nuclear and Schwinger geometrical structure factors are in exact quadrature, in which case the flipping ratios of Bijvoet pairs will be identical. However, in the case of tellurium, the electron density, and hence the Schwinger form factor, is expected to be anisotropic due to bonding effects and this can shift the phase of the Schwinger scattering with respect to that from the nuclei and give rise to a polarization-dependent cross section that is different for hkl and $\bar{h}\bar{k}\bar{l}$.

2. Schwinger scattering in tellurium

An order-of-magnitude calculation was made to see whether the difference from unity in the flipping ratios due to bonding might be measurable. The unit-cell parameters of tellurium at 300 K are $a = 4.4572$, $c = 5.9290$ Å with $Z = 3$. In space group $P3_121$, the atomic position (Cherin & Unger, 1967) is

$$\text{Te} \quad \text{in} \quad 3(a) \quad (x, 0, \tfrac{1}{3}) \quad \text{with} \quad x = 0.2633\,(5).$$

Schwinger structure factors were calculated for a model in which point bonding charges of 0.05 electrons [the value found in our study of GaAs (Forsyth & Brown, 1992)] were placed at the centres of the Te—Te bonds in $3(b)$ positions $(x_1, 0, \tfrac{5}{6})$ with $x_1 = 1 - x/2$. These
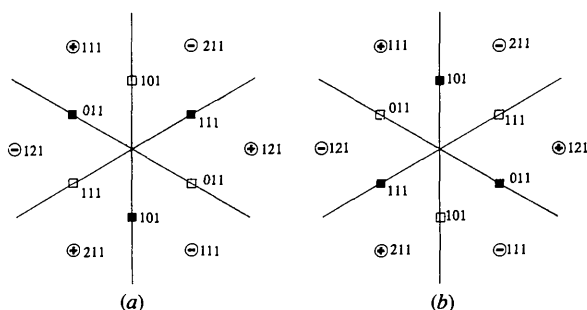

Fig. 2. Diagram of the $(hk1)$ plane of reciprocal space for the two enantiomorphs of Te. The positions of the 101 and 111 reflections are indicated. In the point group $P3_121$, the 12 101 reflections are divided into two groups of six, which for Te have very different structure factors. For each enantiomorph, the squares marking the sets with strong (s) or weak (w) structure factors are filled or open, respectively. The positions of the 111 reflections are marked with positive or negative signs indicating the expected sense of γ'. It can be seen that for enantiomorph (a) the sequence on rotating the diagram clockwise from 111 is $-w +s -w +s\ldots$ whereas for (b) it is $-s +w -s + w\ldots$.

Table 1. *The differences from unity of the observed flipping ratios R and their signs $\pm$ as calculated for the space group $P3_121$*

hkl	hkl	$\pm$	$hk\bar{l}$	$\pm$	$\bar{h}kl$	$\pm$	$\bar{h}k\bar{l}$	$\pm$
$\lambda = 0.84$Å								
110	$-9\,(7)$	$-$					$10\,(4)$	$+$
111	$35\,(11)$	$+$	$31\,(12)$	$+$	$-16\,(10)$	$-$	$-9\,(11)$	$-$
003	$2\,(5)$	$+$	$-1\,(5)$	$+$				
112	$14\,(11)$	$-$	$-2\,(11)$	$-$	$-31\,(17)$	$+$	$-4\,(15)$	$+$
$\lambda = 0.51$Å								
111	$-55\,(21)$	$+$	$40\,(20)$	$+$	$-59\,(26)$	$-$	$-31\,(21)$	$-$
003	$14\,(6)$	$+$	$9\,(6)$	$+$				

show that a null effect persists for reflections of the form $h0l$, but that for more general reflections including the form hhl a difference from unity should be observed. The numerical estimate gives a value for the absolute magnitude of γ' of about 2×10^{-4}. Furthermore, the calculations show that there is a characteristic sequence of positive and negative γ', shown in Fig. 2, which distinguishes between enantiomorphs. Measurement of such a small effect is possible only with a large crystal and a high-intensity polarized neutron source, since approximately 10^8 neutrons must be counted to obtain 25% accuracy in the value of γ' estimated above.

3. Polarized neutron measurements

The experiment was carried out on the D3 polarized neutron diffractometer at the ILL Grenoble. For a given reflection and wavelength, γ' is maximized if it is measured in the plane perpendicular to $\mathbf{P}$ since then $\boldsymbol{\kappa} \times \boldsymbol{\kappa}'/|\mathbf{k}|^2$ is perpendicular to $\mathbf{P}$ and numerically equal to $\tfrac{1}{2}\cot\theta$. A large $6 \times 4.5 \times 10$ mm single crystal of tellurium was mounted in an ILL Orange cryostat, with its long $\langle 1\bar{1}0\rangle$ axis vertical and parallel to $\mathbf{P}$, and maintained at 100 K throughout the experiment. A vertical magnetic field of 0.14 T was applied using an electromagnet at the sample position to preserve the neutron polarization. The incident wavelength was 0.843 Å with $|\mathbf{P}| = 0.9387\,(3)$. The choice of indexing was such that the 101 and $0\bar{1}1$ reflections in the first layer were strong and the $10\bar{1}$ and $0\bar{1}\bar{1}$ reflections were weak, corresponding to space group $P3_121$.

Initially, the sign of γ' was determined for the four 111 reflections in the $[1\bar{1}0]$ zone. The peak intensity in these reflections was $\sim 15\,000$ counts s^{-1} and the reflections were measured sequentially for periods of 1 h during which six background–peak–background sequences were recorded giving a total peak count of 22×10^6 for each incident polarization state. The statistical accuracy of each determination of R was 3.2×10^{-4}. Data collected over 40 h were averaged to give the values of γ' in Table 1. It may be seen that, although the symmetry of positive and negative values corresponds to that in Fig. 2, the absolute values of γ' for the positive pair of reflections is greater than that for the

negative one. The origin of this difference lies in the contribution to the Schwinger scattering made by the imaginary part of the Te nuclear scattering length. This effect is more noticeable because the magnitude of the bonding contribution is smaller than estimated above.

The flipping ratios of three further sets of reflections were measured at 0.843 Å and two, the 111 and 003 sets, were remeasured with a wavelength of 0.514 Å. The final averaged set of flipping ratios are given as their differences from unity $(R-1)$ in Table 1. The values for equivalent reflections are consistent with one exception; the 111 reflection measured at 0.514 Å differs from the equivalent 11$\bar{1}$ and from the 111 at 0.843 Å by more than four times its standard deviation. It was concluded that this measurement was subject to systematic error and it was excluded in the subsequent analysis. Apart from this measurement and the 112 set, which could not be very well determined, the signs of all the $R-1$ values correspond to those calculated for space group $P3_121$.

Finally, in order to be able to estimate the extinction that is expected to be present in such a large crystal, the integrated intensities of all reflections for which flipping ratios had been obtained were measured, together with those of the 101 and 011 sets at both 0.843 and 0.514 Å.

4. Data analysis

The sum over the atomic positions

$$\sum_n \exp(\mathbf{k} \cdot \mathbf{r}_n) = A + iB$$

occurs in the expressions for both N and X_s:

$$N = (b + ib')(A + iB)$$
$$X_s \propto i\{[Z_n - f_n(\mathbf{k})](A + iB) + (x + iy)\}. \tag{4}$$

b and b' are the real and imaginary parts of the Te nuclear scattering length while $(x + iy)$ is the structure factor of the bonding charge:

$$x + iy = \sum_b -q_b f_b(\mathbf{k}) \exp(\mathbf{k} \cdot \mathbf{r}_b),$$

where q_b, f_b and r_b give the magnitude, form factor and positions of the bonding charges. The term in (1) that gives the Schwinger flipping ratio can be expanded to second order as:

$$\Re(N^*X_s) \simeq \text{constant} \times \{[Z_n - f_n(\mathbf{k})](A^2 + B^2)b' - (Ay - Bx)b\}. \tag{5}$$

The value of the constant is 2.95×10^{-18} m. The corresponding term for the Bijvoet partner is

$$\Re(N^*X_s) \simeq \text{constant} \times \{[Z_n - f_n(\mathbf{k})](A^2 + B^2)b' + (Ay - Bx)b]\}. \tag{6}$$

The first term, which is symmetric between the two equations, comes from interference between the

Table 2. *Observed and calculated values of the symmetric and antisymmetric contributions to* γ' *(× 10^6)*

The calculated values are for space group $P3_121$ with a bond charge of 0.032 electrons, using values of b' from Garber & Kinsey (1976).

		Symmetric		Antisymmetric	
	hkl	Obs.	Calc.	Obs.	Calc.
$\lambda = 0.84$Å					
	110	1 (11)	4	−17 (11)	6.3
	111	14 (11)	2	35 (11)	23
	003	2 (10)	5		
	112	−11 (14)	5	14 (14)	−11
$\lambda = 0.51$Å					
	111	−2 (12)	7	34 (12)	23
	003	14 (8)	7		

Schwinger scattering from the centrosymmetric part of the tellurium charge density and the imaginary part of its nuclear scattering length. The antisymmetric term on the other hand comes from interference between the bonding charge and the real part of the scattering length.

The phase of the Schwinger scattering $(\pm\pi/2)$ depends upon the geometric factor $\kappa \times \kappa' \cdot \mathbf{P}$ determined by the configuration of the diffractometer. In the present experiment, however, the correct phase is implicit in the sign of the symmetric part of γ' measured for Bijvoet pairs. With the crystallographic phase convention used in structure-factor calculations, the imaginary parts of neutron scattering lengths are positive (Sears, 1984). With this convention, the scattering length of Te is $5.43 + 0.0036i$ fm at 0.84 Å and $5.43 + 0.0054i$ fm at 0.514 Å.

The measured integrated intensities were averaged over equivalent reflections and a set of observed structure factors calculated for each of the two wavelengths. These were used in a least-squares refinement to obtain the scale factors and the two extinction parameters of the Becker & Coppens (1974) model. Satisfactory ageement between the observed and calculated structure factors was obtained: with a mosaic spread of 15 (5) × 10^{-4} rad^{-1} and a domain radius of 0.49 (5) μm, the R factor for structure factors was 0.034. These parameters were used to calculate extinction-corrected values of γ' from the observed flipping ratios using the method described by Delapalme, Lander & Brown (1978). The extinction corrections that had to be applied varied from 0.87 for the 111 reflection measured at 0.514 Å to 0.46 for the 003 reflection at 0.843 Å.

The symmetric and antisymmetric parts of γ' for all measured reflections are listed in Table 2. The weighted mean value of the ratio between the observed and calculated values of the symmetric contributions is 1.0 (6). The fact that this ratio is unity shows that the extinction has been correctly estimated and its positivity determines the phase of the geometric factor as $+\pi/2$. The signs of the antisymmetric parts of the Schwinger scattering in the 111 reflections relative to the strong and weak members of the 101 set is characteristic of the space

group $P3_121$, suggesting that the spiral chains in our crystal are right handed.

The weighted mean value of the ratio between the observed values of the antisymmetric terms and those calculated for a bond charge of 0.05 electrons is 0.64 (32) so that the best estimate of the bond charge is 0.032 (15) electrons. Since neither the symmetric nor the antisymmetric ratio is determined with very good precision, it is worth considering whether the data really allow the two possible configurations to be distinguished. For this purpose, a χ^2 value was calculated for the model with a bond charge of 0.032 electrons and for one with zero bond charge. The former χ^2 is 1.35 and the latter 3.0 indicating that the model with a bond charge characteristic of a right-handed spiral is to be preferred. (The value of χ^2 for a bond-charge model of a left-handed spiral is 5).

5. The optical rotation

The optical rotation of our crystal was measured at the Clarendon Laboratory, University of Oxford, England, using two infrared Fourier transform spectometers, a Perkin–Elmer Model 1710 and a Bruker Model IFS 66V. In the latter instrument, the beam path is *in vacuo* giving the cleaner spectra of Fig. 3, which shows the [001] transmitted intensity as a function of wavelength in the range 1000–2600 μm for three different orientations of the analyser with respect to the input polarizer. These data have been normalized by dividing by the intensity detected when the sample is absent. The positions of the maxima are given in Table 3. The wavelengths corresponding to the maxima in the transmited intensity are given in Table 1, together with the corresponding rotation assuming that the sense of rotation is to the right as viewed in the direction of the beam. The corresponding values for the optical rotatory power are also given in Table 1: they have the same functional form as the measurements of Nomura (1960), as may be seen from Fig. 4, but indicate a somewhat higher rotatory power at all wavelengths. Our sample is therefore laevorotatory, since it rotates the light to the left as seen by an observer looking through the crystal towards the light source.

6. Discussion

These experiments have shown conclusively that the plane of polarization of light transmitted parallel to [001] rotates in the same sense as the spiral chains of bonded Te atoms. The absolute values of rotatory power are 6% higher than reported by Nomura (1960). In addition, they allow a quantitative, although not very precise, determination of the degree of asymmetry in the charge-density distribution. Knowledge of this value allows the feasibility of an experiment to determine the sense of the spiral from X-ray integrated intensity measurements,

as suggested by McIntyre (1978), to be assessed. Using our simple bond-charge model and an X-ray wavelength close to the L absorption edge at 2.86 Å, we estimate the intensity difference between the 111 and $\bar{1}\bar{1}\bar{1}$ reflections as not more than 0.1%. The X-ray experiment might be feasible for selenium, which is more covalent and has fewer electrons, although the experiment would be significantly easier using the Schwinger scattering of neutrons.
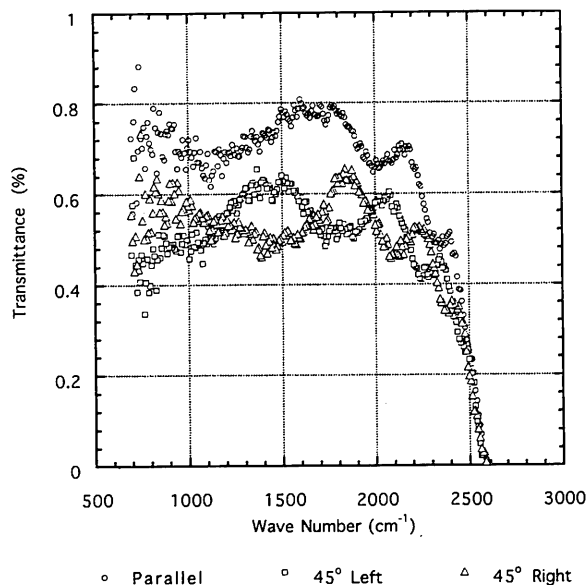

Fig. 3. Transmittance by a Te crystal of infrared radiation plotted against wave number with the analyser (*a*) oriented parallel (◯), (*b*) rotated 45° to the left (□) and (*c*) rotated 45° to the right (△) relative to the polarizer. The senses of the rotations are given travelling along the beam. The positions of the maxima are given in Table 3.
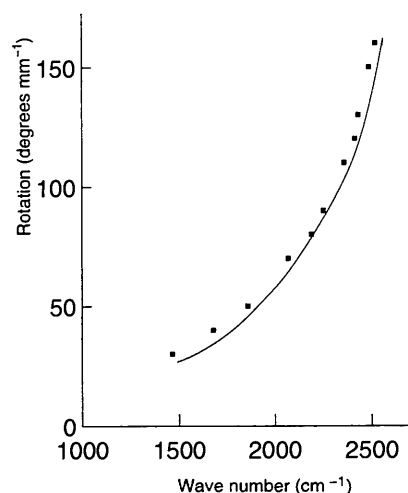

Fig. 4. The optical rotatory power in ° mm^{-1} deduced from the measurements illustrated in Fig. 3 and given in Table 3 compared with the observations of Nomura (1960) (solid curve).

Table 3. *Wave numbers at which maximum transmission occurs for three different settings of the analyser relative to the polarizer*

The tabulated angles are the absolute clockwise rotations of the plane of polarization when looking in the direction of the beam.

Parallel		45° left		45° right	
Wave number (cm^{-1})	Rotation (°)	Wave number (cm^{-1})	Rotation (°)	Wave number (cm^{-1})	Rotation (°)
1679	180	1465	135	926	45
2190	360	2068	315	1859	225
2413	540	2357	495	2251	405
2519	720	2487	675	2432	585

Glazer & Stadnicka (1986) and Devarajan & Glazer (1986) discuss the relationship between crystal structure and optical activity in a number of inorganic crystals using the classical polarizable ion model. They did not include the elements selenium and tellurium although these were previously treated by Reijnhart (1970) using essentially the same method. According to their analysis, four principles determine the sense of the optical rotation: (i) Only the most polarizable atoms need be considered. (ii) The directions of highest polarizability are the shortest vectors between these atoms. (iii) The optical activity is greatest for those helices with the shortest interatomic distances and the lowest pitches. (iv) The sense of the optical activity is determined by whether the polarizability in the plane perpendicular to the helical axis is greater in the direction radial or tangential to the envelope of the helix. The tangential direction gives optical rotation in the same sense as the helix. Although these principles are successful for the compounds studied by Glazer & Stadnicka (1986) and by Devarajan & Glazer (1986), Reijnhart's calculations for selenium and tellurium predict that the plane of polarization rotates in the opposite sense to the helix in contradiction with our observation. The opposing sense of the optical rotation follows from the principles enumerated above since the projections of the bond directions perpendicular to the helix at each atom site lie at ±30° to the radial direction. It is probable that this disagreement is due to the inadequacy of a single ionic polarizability to describe the highly anisotropic covalent structure of tellurium. We note that this simple model also leads to an infinite value for the parallel component of the dielectric constant.

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