A Prediction of Bijvoet Intensity Differences in the Noncentrosymmetric Structures of Selenium and Tellurium

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The presence of an antisymmetric component of the non-spherical atomic charge distribution results in a more general breakdown of Friedel's law in polyatomic noncentrosymmetric structures. That this is also true in the case of noncentrosymmetric structures of elements is demonstrated directly for the case of the trigonal structures of Se and Te.

Introduction

The extension of the substructure description (Iwasaki, 1974) to include the antisymmetric atomic features incorporated within the generalized structure factor formalism (Dawson, 1967) leads to generalized expressions for the Bijvoet ratio (McIntyre & Barnea, 1978). These expressions imply that, in general, Friedel's law (Friedel, 1913) breaks down for all noncentrosymmetric structures. In particular, it is predicted that because of the antisymmetric contribution of the non-spherical charge distribution due to bonding, noncentrosymmetric structures of elements do not obey Friedel's law, regardless of the exact details of the structure which determine the specific angular forms of the atomic scattering factors. Because of the important implications of this prediction, it is of considerable interest to demonstrate the breakdown of Friedel's law for a particular elemental structure.

In this paper we discuss the structure of trigonal Se and Te, the simplest of the known noncentrosymmetric structures of elements. Following Dawson (1967), the atomic charge density is expanded in a series of symmetry-allowed functions. Inclusion of the deformation density in the expression for the Bijvoet intensity difference for this structure then demonstrates explicitly the breakdown of Friedel's law.

The generalized intensity difference

In the generalized structure factor formalism (Dawson, 1967) the structure factor $F(S)$ for a particular scattering vector S can be written in terms of the atomic scattering factors f_p and the thermal-vibration factors T_p of the atoms at nuclear positions r_p in the unit cell:

$$F(S) = \sum_p f_p(S)\, T_p(S) \exp (2\pi i S \cdot r_p)$$

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where f_p and T_p are the Fourier transforms of the atomic charge distribution ρ_p and nuclear smearing amplitude t_p respectively.

In general, both ρ_p and t_p are noncentrosymmetric and hence f_p and T_p are complex. For X-rays we also include the effects of anomalous dispersion:

$$f_p(S) = f_{c,p}(S) + i f_{a,p}(S) + f'_p + i f''_p$$

$$T_p(S) = T_{c,p}(S) + i T_{a,p}(S),$$

where f'_p and f''_p are the real and imaginary dispersion corrections of atom p, and the subscripts c and a refer to the centrosymmetric and antisymmetric components respectively.

The Bijvoet intensity difference between the Friedel pair of reflections defined by:

$$\Delta I(S) = |F(S)|^2 - |F(-S)|^2$$

is [suppressing (S)]:

$$
\begin{aligned}
\Delta I = {} & 4 \sum_p f_{a,p} f''_p [T^2_{c,p} + T^2_{a,p}] \\
& + 4 \sum_p \sum_{q \neq p} \{ f_{a,p} f''_q [(T_{c,p} T_{c,q} \\
& + T_{a,p} T_{a,q}) \cos 2\pi S \cdot (r_p - r_q) \\
& + (T_{c,p} T_{a,q} - T_{a,p} T_{c,q}) \sin 2\pi S \cdot (r_p - r_q)] \\
& + f'_{c,p} f''_q [-(T_{c,p} T_{a,q} - T_{a,p} T_{c,q}) \cos 2\pi S \cdot (r_p - r_q) \\
& + (T_{c,p} T_{c,q} + T_{a,p} T_{a,q}) \sin 2\pi S \cdot (r_p - r_q)] \}.
\end{aligned} \quad (1)
$$

In obtaining equation (1), all functions for the reflection at $-S$ are evaluated in terms of the functions for the reflection at S by using the fact that in going from S to $-S$ all centrosymmetric functions are unchanged while all antisymmetric functions are changed in sign alone. It is emphasized that regardless of the presence of the antisymmetric atomic functions f_a and T_a, a non-zero

f'' is still a necessary condition for Friedel's law ($\Delta I = 0$) to break down.

If we assume a centrosymmetric charge distribution for each atom (*i.e.* $f_{a,p} = 0$ for all p), and that all atoms have the same f_c, f' and f'', it is obvious from equation (1) that ΔI will vanish. Hence anharmonicity in the thermal vibration cannot itself lead to a break-down in Friedel's law for noncentrosymmetric structures of elements. This results from the presence of a centrosymmetric, imaginary term (necessary to lead to a breakdown in Friedel's law) in the expression for f_p, but not for T_p. A more detailed discussion of the consequences of equation (1) is given elsewhere (McIntyre & Barnea, 1978).

The trigonal selenium structure

The crystal structure of trigonal Se and Te consists of helical chains which spiral around axes parallel to the c axis and are arranged in a hexagonal array (Unger & Cherin, 1969). The space group is $P3_121$ (D_3^4) or $P3_221$ (D_3^6) depending on the sense of rotation of the helical chains. In the following discussion we shall assume a left-handed spiral. The three atoms in the unit cell are situated at the special positions: $P3_121$: $(u,0,0)$; $(0,u,-\frac{1}{3})$; $(-u,-u,\frac{1}{3})$. The site symmetry at these positions is 2. The structural parameter u has been determined by X-ray techniques to be 0·2254 (10) for Se (Cherin & Unger, 1967a) and 0·2633 (5) for Te (Cherin & Unger, 1967b).

Since the atoms in the Se structure are identical in all respects, except in the orientation of their atomic environment, inclusion of anharmonicity in the thermal vibration will not lead to a breakdown in Friedel's law. We shall, therefore, for simplicity assume that the vibrations are harmonic and consider only the consequences of allowing the charge distribution to reflect the symmetry of the atomic site. Similarly, we shall also neglect the anisotropy in the harmonic vibrational motion observed in X-ray structure refinements of Se and Te (Cherin & Unger, 1967a,b). Inclusion of the anisotropy leads to no new conditions for the breakdown of Friedel's law and would needlessly complicate our expressions. Within our assumptions T_c is the same for all three atoms, and for a structure of an element $f'(f'')$ is of course identical for all atoms.

The scattering-factor model

The electron density distribution may be represented by a variety of models differing predominantly in the functions used to express the radial dependence of the distribution about each atomic site; the angular dependences of the various models must be identical if they are to fully reflect the site symmetry. Here the

desired result may be readily demonstrated by application of the pseudo-atom model of Stewart (1976), whose notation we follow.

In this model each atom is assumed to have an invariant core, and a deformable valence density that obeys the symmetry of the site. The valence charge density $\rho(\mathbf{r} - \mathbf{r}_p)$ of atom p at $\mathbf{r}$ is expressed as a finite multipole expansion about the atomic site $\mathbf{r}_p$:

$$\rho(\mathbf{r}_p') = \sum_{l=0}^{L} \left[\sum_{m=0}^{l} C_{plm}^e B_{plm}^e(\mathbf{r}_p') + \sum_{m=1}^{l} C_{plm}^o B_{plm}^o(\mathbf{r}_p') \right], \quad (2)$$

where C_{plm}^e and C_{plm}^o are electron-population coefficients and $\mathbf{r}_p' = \mathbf{r} - \mathbf{r}_p$. The basis functions B_{plm}^e and B_{plm}^o are

$$B_{plm}^e(\mathbf{r}_p') = (4\pi)^{-1} R_{pl}(r_p') P_l^m(\cos\theta_p) \cos(m\varphi_p)$$

$$B_{plm}^o(\mathbf{r}_p') = (4\pi)^{-1} R_{pl}(r_p') P_l^m(\cos\theta_p) \sin(m\varphi_p),$$

where $R_{pl}(r_p')$ is a radial function for the lth order multipole of pseudo atom p, $P_l^m(\cos\theta_p)$ is an associated Legendre function, and θ_p and φ_p are the angular components of the vector $\mathbf{r}_p'$. The superscripts e and o denote the even and odd functions respectively.

The representation for the scattering factor $f_p(\mathbf{S})$, omitting the anomalous-scattering contributions, is obtained from the Fourier transform of equation (2):

$$f_p(\mathbf{S}) = \sum_{l=0}^{L} \left[\sum_{m=0}^{l} C_{plm}^e f_{plm}^e(\mathbf{S}) + \sum_{m=1}^{l} C_{plm}^o f_{plm}^o(\mathbf{S}) \right],$$

where

$$f_{plm}^e(\mathbf{S}) = i^l f_{pl}(S) P_l^m(\cos\theta_s) \cos(m\varphi_s)$$

and

$$f_{plm}^o(\mathbf{S}) = i^l f_{pl}(S) P_l^m(\cos\theta_s) \sin(m\varphi_s)$$

are the generalized X-ray scattering factors and θ_s and φ_s are the angular components of the Bragg vector. The radial function is

$$f_{pl}(S) = \int_0^\infty R_{pl}(r_p') j_l(Sr_p') r_p'^2 \, dr_p',$$

where $j_l(x)$ is an lth-order spherical Bessel function. The form of the radial distribution function does not concern us here since it is the angular components of the generalized X-ray scattering factors [the tesseral harmonics,

$$P_l^m(\cos\theta_s) \begin{Bmatrix} \cos(m\varphi_s) \\ \sin(m\varphi_s) \end{Bmatrix}]$$

that reflect the symmetry of the site.

Stewart (1973, 1976) has presented the symmetry constraints for the multipole basis functions up to fourth order in l for all point groups. The several multipoles up to fourth order that obey the symmetry of point group 2 in reciprocal space are listed in Table 1.

In Table 1 the z axis is along the direction of maximum symmetry and the (q_x, q_y, q_z) are direction cosines of the Bragg vector in an arbitrary orthogonal coordinate system.

For atom 1 at $(u,0,0)$ the maximum symmetry direction is along the a axis of the unit cell. The required transforms relating (q_x, q_y, q_z) to the conventional hexagonal Miller–Bravais indices $hkjl$ of the reflection $\mathbf{S}$ are

$$q_x = \frac{k - j}{3^{1/2}aS}$$

$$q_y = \frac{l}{cS}$$

$$q_z = \frac{h}{aS},$$

where a and c are the lattice parameters and

$$S = |\mathbf{S}| = \left[\left(\frac{h}{a}\right)^2 + \left(\frac{k-j}{\sqrt{3}a}\right)^2 + \left(\frac{l}{c}\right)^2\right]^{1/2}.$$

The scattering factor for atom 1 is, to third order,

$$f_1(\mathbf{S}) = f_{\text{core}} + f_{10}(S)\,C_{10} + if_{11}(S)\,C_{113}\,\frac{h}{aS}$$

$$-f_{12}(S)\left\{3C_{121}\left[\frac{(k-j)^2}{3a^2} - \frac{l^2}{c^2}\,\frac{1}{S^2}\right]\right.$$

$$+ 6C_{122}\frac{(k-j)l}{3^{1/2}acS^2} + \frac{3}{2}C_{125}\left(\frac{h^2}{a^2 S^2} - \frac{1}{3}\right)\right\}$$

$$- if_{13}(S)\left\{15C_{133}\left[\frac{(k-j)^2}{3a^2} - \frac{l^2}{c^2}\right]\frac{h}{aS^3}\right.$$

$$\left. + 30C_{134}\frac{h(k-j)l}{3^{1/2}a^2 cS^3} + 2C_{137}\left(\frac{5h^2}{a^2 S^2} - 3\right)\frac{h}{aS}\right\}.$$

Table 1. *Non-vanishing multipole basis functions for point group 2 in reciprocal space*

Tesseral harmonic	Cartesian representation
$P_1^0(\cos\theta_s)$	q_z
$P_2^2(\cos\theta_s)\cos(2\varphi_s)$	$3(q_x^2 - q_y^2)$
$P_2^2(\cos\theta_s)\sin(2\varphi_s)$	$6q_x q_y$
$P_2^0(\cos\theta_s)$	$\frac{1}{2}(q_z^2 - \frac{1}{3})$
$P_3^2(\cos\theta_s)\cos(2\varphi_s)$	$15(q_x^2 - q_y^2)q_z$
$P_3^2(\cos\theta_s)\sin(2\varphi_s)$	$30q_x q_y q_z$
$P_3^0(\cos\theta_s)$	$\frac{1}{2}(15q_z^2 - 3)q_z$
$P_4^4(\cos\theta_s)\cos(4\varphi_s)$	$105(q_x^4 - 6q_x^2 q_y^2 + q_y^4)$
$P_4^4(\cos\theta_s)\sin(4\varphi_s)$	$420(q_x^2 - q_y^2)q_x q_y$
$P_4^2(\cos\theta_s)\cos(2\varphi_s)$	$\frac{15}{2}(7q_z^2 - 1)(q_x^2 - q_y^2)$
$P_4^2(\cos\theta_s)\sin(2\varphi_s)$	$15(7q_z^2 - 1)q_x q_y$
$P_4^0(\cos\theta_s)$	$\frac{3}{8}(7q_z^4 - 6q_z^2 + \frac{1}{5})$

The scattering factors for the other two atoms in the unit cell are obtained simply by cyclic interchange of the indices hkj. Since all atoms are identical apart from the orientation of the atomic environment, $C_{10} = C_{20} = C_{30}$, $C_{113} = C_{213} = C_{313}$ etc. Similarly, the corresponding radial functions are identical: $f_{10} = f_{20} = f_{30}$; $f_{11} = f_{21} = f_{31}$ etc.

The harmonic intensity difference for selenium

To demonstrate that $\Delta I(T_a = 0)$ is in general non-zero for this structure, it is sufficient to consider only the first-order effect of the valence electron density of f_p with:

$$f_{c,p} = \bar{f}_c + f_{10}(S)\,C_{10} \quad (p = 1, 2, 3)$$

$$f_{a,1} = f_{11}(S)\,C_{113}\,\frac{h}{aS}$$

$$f_{a,2} = f_{11}(S)\,C_{113}\,\frac{k}{aS}$$

and

$$f_{a,3} = f_{11}(S)\,C_{113}\,\frac{j}{aS},$$

where $\bar{f}_c$ is the conventional spherically symmetric atomic scattering factor.

The harmonic intensity difference [using equation (1)] is then:

$$\Delta I(T_a = 0) = 4T_c^2 f'' f_{11}(S)\,C_{113}\left(\frac{1}{aS}\right)$$

$$\times \left\{(h + j)\cos\left[2\pi(h - j)u - 2\pi\frac{l}{3}\right]\right.$$

$$+ (k + h)\cos\left[2\pi(k - h)u - 2\pi\frac{l}{3}\right]$$

$$\left. + (j + k)\cos\left[2\pi(j - k)u - 2\pi\frac{l}{3}\right]\right\}.$$

(3)

$\Delta I(T_a = 0)$ does not vanish identically, as may be seen by substitution of specific values of the indices $hkjl$.

Discussion

By expanding the atomic charge density as a series of symmetry-allowed functions we have demonstrated that non-zero Bijvoet intensity differences are allowed

in the noncentrosymmetric trigonal Se and Te structures. We have not attempted to predict the magnitude of the intensity differences. To determine whether these differences are measurable would require a knowledge of the form of the radial functions R_{pl} and an estimate of the electron-population coefficients for these structures.

Chandrasekaran (1968) has also suggested that Bijvoet intensity differences may be observed in the noncentrosymmetric elements. However, our arguments for their appearance are independent of Chandrasekaran's postulates.

The existence of the chain structure in trigonal Se and Te is manifested by the anisotropy ratio of intrachain to interchain bonding strength as reflected in lattice dynamic and electronic structure studies of these structures (Joannopoulos, Schlüter & Cohen, 1975; Martin, Lucovsky & Helliwell, 1976; and references therein). The atoms within each chain are tightly and covalently bonded to two neighbours; the interchain bonding is partly van der Waals in character with an admixture of some covalent bonding. This anisotropy in the bonding renders particularly desirable a more complete representation of the atomic charge density than the usual spherically symmetric representation, and gives credibility to our discussion.

As well as providing information of considerable value about bonding features, observation of Bijvoet intensity differences in noncentrosymmetric elemental structures may also aid the resolution of ambiguities in their symmetry. A possible example of such an ambiguity is the question as to whether the β-uranium structure possesses a centre of symmetry (Tucker, Senio, Thewlis & Steeple, 1956).

References

CHANDRASEKARAN, K. S. (1968). *Acta Cryst.* A**24**, 248–249.
CHERIN, P. & UNGER, P. (1967a). *Inorg. Chem.* **6**, 1589–1591.
CHERIN, P. & UNGER, P. (1967b). *Acta Cryst.* **23**, 670–671.
DAWSON, B. (1967). *Proc. R. Soc. London Ser. A*, **298**, 255–263.
FRIEDEL, G. (1913). *C. R. Acad. Sci.* **157**, 1533–1536.
IWASAKI, H. (1974). *Acta Cryst.* A**30**, 173–176.
JOANNOPOULOS, J. D., SCHLÜTER, M. & COHEN, M. L. (1975). *Phys. Rev. Sect. B*, **11**, 2186–2199.
MCINTYRE, G. J. & BARNEA, Z. (1978). *Acta Cryst.* Submitted.
MARTIN, R. M., LUCOVSKY, G. & HELLIWELL, K. (1976). *Phys. Rev. Sect. B*, **13**, 1383–1395.
STEWART, R. F. (1973). *J. Chem. Phys.* **58**, 1668–1676.
STEWART, R. F. (1976). *Acta Cryst.* A**32**, 565–574.
TUCKER, C. W., SENIO, P., THEWLIS, J. & STEEPLE, H. (1956). *Acta Cryst.* **9**, 472–474.
UNGER, P. & CHERIN, P. (1969). *Physics of Selenium and Tellurium*, edited by W. C. COOPER, p. 223. Oxford: Pergamon Press.

The Crystal Structure of 4Nb₂O₅.9WO₃ Studied by 1 MV High-Resolution Electron Microscopy

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Images of pale yellow crystals of 4Nb₂O₅.9WO₃, obtained with a 1 MV high-resolution electron microscope revealed twinned domains of a tetragonal tungsten bronze structure with a superlattice of 3 × 1 subcells. Comparison with computer calculations suggests that the cations filling the pentagonal tunnels include both Nb and W. Crystals darkened due to reduction on longer heating included no domains and were sensitive to electron irradiation; cations were knocked on from the filled to the vacant pentagonal tunnels. This suggests that some oxygens are released from the $-M-O-M-O-M-$ strings in the tunnels on reduction to weaken the chemical bonding. The number of deficient oxygens is known from the weight gain on oxidizing the crystal. Some additional experiments reveal that there is no '6Nb₂O₅.11WO₃' phase. The resolving power of the present microscope is discussed on the basis of the analysis of the chromatic aberration.