

Some Consequences of the Presence of Antisymmetric Atomic Features in Noncentrosymmetric Structures

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Abstract

Noncentrosymmetric structures are considered in terms of a generalized substructure formulation. Inclusion of dispersion, bonding and anharmonicity leads to generalized expressions for Bijvoet ratios. Methods of numerically estimating the effects due to bonding and anharmonicity upon the Bijvoet ratios are suggested. Allowance for bonding and anharmonicity is shown to have wide implications for the breakdown of Friedel's law. Subsets of reflections that obey Friedel's law in the conventional approximation are now shown to violate it. These violations are of considerable importance for measuring antisymmetric contributions due to bonding and anharmonic thermal vibrations. The possibility that bonding effects will result in the appearance of Bijvoet differences in noncentrosymmetric structures of elements is explored.

Introduction

Early X-ray investigations of the zinc blende structure led Friedel (1913) to conclude that the X-ray diffraction pattern of a noncentrosymmetric structure cannot reveal the absence of a centre of symmetry. The intensities of a Friedel pair of reflections with Miller indices hkl and $\bar{h}\bar{k}\bar{l}$ are thus expected to be equal. This is often referred to as Friedel's law. Later work of Nishikawa & Matukawa (1928) and of Coster, Knol & Prins (1930) clearly demonstrated the breakdown of Friedel's law when the effects of anomalous dispersion are appreciable. Peerdeman, van Bommel & Bijvoet (1951) showed that the non-equivalence of the intensities of Friedel pairs of reflections could be exploited not only to determine the absolute configuration of noncentrosymmetric crystals but also as a significant aid in the determination of phases in structure analysis.

Useful measures of the breakdown of Friedel's law are provided by the Bijvoet intensity difference, defined as the difference in intensity between a Friedel pair of reflections or their equivalents, and the Bijvoet intensity ratio, obtained by dividing the Bijvoet intensity difference by the average intensity of the pair of

reflections. The latter is particularly convenient because it is independent of scale factor and its measurement is relatively free of other types of systematic errors.

Accurate measurements of these quantities are of considerable importance in the determination of phases and absolute configurations and also in tests of the theoretically calculated values of the dispersion corrections (Zachariasen, 1965). For a review of current anomalous-scattering techniques, the reader is referred to Ramaseshan & Abrahams (1975).

It is the purpose of this paper to show that the Bijvoet difference and the Bijvoet ratio may also yield significant information about the atomic features of nonspherical charge distributions and anharmonic thermal vibrations. Moreover, these features may themselves lead to further restrictions on the validity of Friedel's law, and thereby provide a particularly sensitive measure of the parameters describing these features.

Generalized substructure formulation

In the generalized structure factor formalism (Dawson, 1967*a*) the structure factor $F(\mathbf{S})$ for a particular scattering vector \mathbf{S} can be written in terms of the atomic scattering factors f_j and the thermal vibration factors T_j of the atoms at nuclear positions \mathbf{r}_j in the unit cell:

$$F(\mathbf{S}) = \sum_j f_j(\mathbf{S}) T_j(\mathbf{S}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}_j) \quad (1)$$

where f_j and T_j are the Fourier transforms of the atomic charge distribution ρ_j and nuclear smearing amplitude t_j respectively.

In general, both ρ_j and t_j are noncentrosymmetric and hence f_j and T_j are complex:

$$f_j(\mathbf{S}) = f_{c,j}(\mathbf{S}) + i f_{a,j}(\mathbf{S}) \quad (2a)$$

$$T_j(\mathbf{S}) = T_{c,j}(\mathbf{S}) + i T_{a,j}(\mathbf{S}) \quad (2b)$$

where the subscripts c and a refer to the centrosymmetric and antisymmetric components respectively. For X-rays we also include the effects of anomalous dispersion:

$$\begin{aligned} f_j(\mathbf{S}) &= f_{c,j}(\mathbf{S}) + i f_{a,j}(\mathbf{S}) + f_j' + i f_j'' \\ &= f_{c,j}'(\mathbf{S}) + i f_{a,j}'(\mathbf{S}) + i f_j'' \end{aligned} \quad (3)$$

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where f'_j and f''_j are the real and imaginary dispersion corrections of atom j . Since f'_j has the same centrosymmetric properties as $f_{c,j}(\mathbf{S})$, they can be combined in a single term $f'_{c,j}$; this is obviously not the case for f''_j . (For simplicity we have disregarded any \mathbf{S} dependence of the dispersion corrections.)

Rather than use equation (1) in its present form, it is more convenient to extend Iwasaki's (1974) substructure description to include anharmonicity and the non-spherical charge distribution due to bonding.

Let us consider a crystal with N types of atoms divided into N substructures such that the p th substructure, \mathcal{S}_p , is composed of atoms of only the p th type. Atoms are in general of the same type only if they are of the same chemical species and have identical atomic environments in both chemical species and orientation, and hence identical values of f_j and T_j .

For example: (i) in diamond we have two substructures, corresponding to the two orientations of environments about the C atoms (Fig. 1); (ii) in zinc blende we also have two substructures; however, each of these consists of a different chemical species in a different environment; (iii) in the wurtzite structure, there are four substructures, one for each atom in the unit cell; here each atom has a different atomic environment either in chemical species or orientation (Fig. 2).

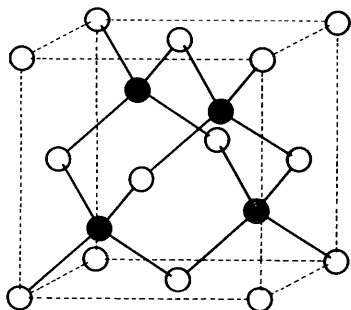


Fig. 1. The diamond structure. The two substructures are denoted by solid and open circles.

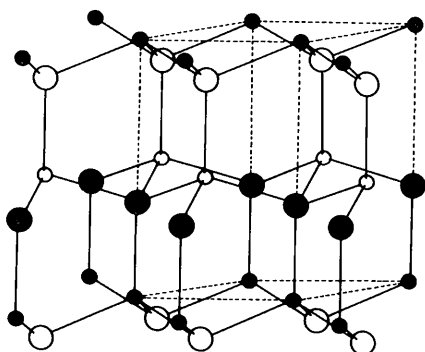


Fig. 2. The wurtzite structure. The size of each circle indicates the atomic species; the two substructures for each species are denoted by solid and open circles. The dashed line defines the hexagonal unit cell.

Equation (1) now becomes

$$F(\mathbf{S}) = \sum_p F_p(\mathbf{S}) \exp(2\pi i \mathbf{S} \cdot \mathbf{u}_p) \\ = \sum_p f_p(\mathbf{S}) T_p(\mathbf{S}) G_p(\mathbf{S}) \exp(2\pi i \mathbf{S} \cdot \mathbf{u}_p) \quad (4)$$

where \mathbf{u}_p is the vector from the origin of the unit cell to the chosen origin of the substructure \mathcal{S}_p ; f_p and T_p are the atomic scattering factor and thermal vibration factor for atoms in \mathcal{S}_p ; $F_p(\mathbf{S})$ and $G_p(\mathbf{S})$ are the structure factor and effective geometric factor respectively for \mathcal{S}_p .

In practice the number of substructures into which a given structure must be divided decreases with decreasing sophistication of the model. Introduction of bonding and anharmonic thermal motion, which depend on the environment of a given atom, will result in greater differentiation of atoms. This differentiation will depend on the number of terms retained in the expansions for f_p and T_p .

Introducing the appropriate quantities in terms of real and imaginary parts, we find that the square of the absolute value of the generalized structure factor is (suppressing \mathbf{S})

$$|F_{hkl}|^2 = \sum_p G_p^2 [f'_{c,p}{}^2 + f'_{a,p}{}^2 + f''_p{}^2 \\ + 2f'_{a,p}f''_p] [T_{c,p}^2 + T_{a,p}^2] \\ + \sum_p \sum_{q \neq p} G_p G_q \{ [f'_{c,p}f'_{c,q} + f'_{a,p}f'_{a,q} \\ + f''_p f''_q + 2f'_{a,p}f''_q] \\ \times [(T_{c,p}T_{c,q} + T_{a,p}T_{a,q})c_{pq} \\ + (T_{c,p}T_{a,q} - T_{a,p}T_{c,q})s_{pq}] \\ + 2[f'_{c,p}f'_{a,q} + f'_{c,p}f''_q] \\ \times [-(T_{c,p}T_{a,q} - T_{a,p}T_{c,q})c_{pq} \\ + (T_{c,p}T_{c,q} + T_{a,p}T_{a,q})s_{pq}] \}, \quad (5)$$

where

$$G_p(\mathbf{S}) = G_p \exp(i\gamma_p) \\ c_{pq} = \cos[2\pi \mathbf{S} \cdot (\mathbf{u}_p - \mathbf{u}_q) + \gamma_p - \gamma_q] \\ s_{pq} = \sin[2\pi \mathbf{S} \cdot (\mathbf{u}_p - \mathbf{u}_q) + \gamma_p - \gamma_q].$$

The generalized Bijvoet intensity ratio

The Bijvoet intensity ratio is defined as

$$B_{hkl} = \frac{\Delta I}{I_{av}} = \frac{|F_{hkl}|^2 - |F_{\bar{h}\bar{k}\bar{l}}|^2}{\frac{1}{2}(|F_{hkl}|^2 + |F_{\bar{h}\bar{k}\bar{l}}|^2)} \quad (6)$$

where I_{av} is the average kinematic intensity and ΔI is the intensity difference of a Friedel pair of reflections. Friedel's law, $\Delta I = 0$, is valid for all centrosymmetric crystals. As we have already pointed out, for a non-centrosymmetric crystal containing anomalous scatterers Friedel's law does not generally hold.

In general a crystal cannot contain only one substructure for which $f_{a,p}$ and $T_{a,p}$ are nonzero, regardless of how many centrosymmetric substructures it also contains. Furthermore, a noncentrosymmetric crystal contains no centrosymmetric site symmetry. It follows, therefore, that a noncentrosymmetric crystal must consist of at least two substructures and for these $f_{a,p}$ and $T_{a,p}$ are nonzero.

In the expressions that follow all functions for the $\bar{h}\bar{k}\bar{l}$ reflection are evaluated in terms of the functions for the hkl reflection by using the fact that in going from \mathbf{S} to $-\mathbf{S}$ all centrosymmetric functions are unchanged while all antisymmetric functions are changed in sign alone.

For a general structure the Bijvoet intensity difference is

$$\begin{aligned} \Delta I = & 4 \sum_p G_p^2 f_{a,p} f_p'' [T_{c,p}^2 + T_{a,p}^2] \\ & + 4 \sum_p \sum_{q \neq p} G_p G_q \{ f_{a,p} f_q'' [(T_{c,p} T_{c,q} + T_{a,p} T_{a,q}) c_{pq} \\ & + (T_{c,p} T_{a,q} - T_{a,p} T_{c,q}) s_{pq}] \\ & + f_{c,p}' f_q'' [-(T_{c,p} T_{a,q} - T_{a,p} T_{c,q}) c_{pq} \\ & + (T_{c,p} T_{c,q} + T_{a,p} T_{a,q}) s_{pq}] \}. \end{aligned} \quad (7)$$

Although the introduction of the antisymmetric atomic functions f_a and T_a has greatly expanded the expression for ΔI , it can be seen that a nonzero anomalous dispersion correction f_p'' is still a necessary condition for Friedel's law to break down. The average intensity of the Friedel pair is

$$\begin{aligned} I_{av} = & \sum_p G_p^2 [f_{c,p}'^2 + f_{a,p}^2 + f_p''^2] [T_{c,p}^2 + T_{a,p}^2] \\ & + \sum_p \sum_{q \neq p} G_p G_q \{ [f_{c,p}' f_{c,q}' + f_{a,p} f_{a,q} + f_p'' f_q''] \\ & \times [(T_{c,p} T_{c,q} + T_{a,p} T_{a,q}) c_{pq} \\ & + (T_{c,p} T_{a,q} - T_{a,p} T_{c,q}) s_{pq}] \\ & + 2 f_{c,p}' f_{a,q}' [-(T_{c,p} T_{a,q} - T_{a,p} T_{c,p}) c_{pq} \\ & + (T_{c,p} T_{c,q} + T_{a,p} T_{a,q}) s_{pq}] \}. \end{aligned} \quad (8)$$

The effect of bonding on the Bijvoet ratios ($T_a = 0$)

If we consider low-angle reflections where T_a may be neglected, equations (7) and (8) reduce to

$$\begin{aligned} \Delta I(T_a = 0) = & 4 \sum_p G_p^2 f_{a,p} f_p'' T_{c,p}^2 \\ & + 4 \sum_p \sum_{q \neq p} G_p G_q \{ f_{a,p} f_q'' c_{pq} \\ & + f_{c,p}' f_q'' s_{pq} \} T_{c,p} T_{c,q} \end{aligned} \quad (9)$$

and

$$\begin{aligned} I_{av}(T_a = 0) = & \sum_p G_p^2 [f_{c,p}'^2 + f_{a,p}^2 + f_p''^2] T_{c,p}^2 \\ & + \sum_p \sum_{q \neq p} G_p G_q \{ [f_{c,p}' f_{c,q}' \\ & + f_{a,p} f_{a,q} + f_p'' f_q''] c_{pq} \\ & + 2 f_{c,p}' f_{a,q}' \} T_{c,p} T_{c,q}. \end{aligned} \quad (10)$$

In the approximation of a spherical charge distribution, a single atom appears identical regardless of the direction from which it is viewed. When a redistribution of charge occurs due to bonding, the atom is no longer spherically symmetric and, in particular, it may no longer appear identical when viewed from opposite directions. Thus, we obtain a contribution given by the first term in equation (9).

In the analysis of most cubic structures $f_{c,j}$ and $T_{c,j}$ are assumed to be isotropic. If f_a is neglected all reflections at the same value of $(\sin \theta)/\lambda$ will have the same absolute value of the Bijvoet ratio. However, since f_a is direction dependent, different values of the intensity ratio will be obtained for these reflections when f_a is included. Unfortunately, for most cubic structures the contribution due to f_a is only significant in the region where it is rare for more than one reflection to occur at the same Bragg angle. We know of no instance in which such a difference between Bijvoet ratios has been reliably observed.

The most significant bonding contribution to ΔI and I_{av} is from the terms containing $f_{a,p} f_q'' c_{pq}$ and $f_{c,p}' f_{a,q}' s_{pq}$ respectively. By comparing these with the generally dominant terms in each expression, $f_{c,p}' f_q'' s_{pq}$ in equation (9) and $f_{c,p}' f_{c,q}' c_{pq}$ in equation (10), we obtain an estimate of the mean effect of the redistributed charge on ΔI and I_{av} . This, of course, assumes that all substructures contribute similarly. The proportional contribution to the Bijvoet ratio due to bonding, $[B(f_a \neq 0) - B(f_a = 0)]/B(f_a = 0)$, is then given approximately by the ratio $f_{a,p}/f_{c,p}$. No single general expression is available for $f_{a,p}$; however, we will assume from the studies of diamond (Dawson, 1967b) and zinc blende (Moss, 1977) that the value of $f_{a,p}$ is about the same for all atoms at the peak of the bonding charge redistribution and take $f_{a,p} = 0.15$ (e.u.). At low Bragg angles, in the region of the maximum of $f_{a,p}$, we can take $f_{c,p} \approx Z_p$, the atomic number. Thus,

$$f_{a,p}/f_{c,p} \approx 0.15/Z_p, \quad (11)$$

a very small contribution indeed. This approximation is only a guide to the mean effect on the intensity difference. For particular reflections the effect of f_a may be much more significant, especially if the reflections are weak.

The effect of anharmonicity on the Bijvoet ratios ($f_a = 0$)

For high-angle reflections, where f_a may be neglected, equations (7) and (8) become:

$$\begin{aligned} \Delta I(f_a = 0) = & 4 \sum_p \sum_{q \neq p} G_p G_q f_{c,p}' f_q'' [-(T_{c,p} T_{a,q} \\ & - T_{a,p} T_{c,q}) c_{pq} \\ & + (T_{c,p} T_{c,q} + T_{a,p} T_{a,q}) s_{pq}] \end{aligned} \quad (12)$$

and

$$I_{av}(f_a = 0) = \sum_p G_p^2 [f'_{c,p}{}^2 + f''_{c,p}{}^2] [T_{c,p}^2 + T_{a,p}^2] \\ + \sum_p \sum_{q \neq p} G_p G_q \{ [f'_{c,p} f'_{c,q} + f''_{c,p} f''_{c,q}] \\ \times [(T_{c,p} T_{c,q} + T_{a,p} T_{a,q}) c_{pq} \\ + (T_{c,p} T_{a,q} - T_{a,p} T_{c,q}) s_{pq}] \}. \quad (13)$$

Unlike in equation (9), there is now no contribution to the Bijvoet intensity difference due to each substructure alone. For a single substructure consisting of atoms with spherically symmetric charge distributions, undergoing anharmonic vibration, the instantaneous scattering is the same for both Friedel reflections. The noncentrosymmetric nature of the motion is only reflected in the Bijvoet intensity difference when the motion of the surrounding substructures is also considered.

As for f_a in equations (9) and (10), the directional dependence of T_a can lead to different absolute values of the Bijvoet ratios for harmonically equivalent reflections at the same $(\sin \theta)/\lambda$ value. Such differences have been observed experimentally in cubic zinc sulphide (McIntyre, Moss, Boehm & Barnea, 1975); similar differences would be expected in wurtzite structures (Whiteley, Moss & Barnea, 1978).

In general, the dominant anharmonic contributions to ΔI and I_{av} arise from the terms $(T_{c,p} T_{a,q} - T_{a,p} T_{c,q})$. The usual harmonic contributions are due to terms containing $T_{c,p} T_{c,q}$. We can estimate the average relative effect of anharmonicity on the Bijvoet ratio by comparing these two contributions. Assuming all atoms undergo similar anharmonic vibrations within a particular lattice, an estimate of the average proportional contribution of anharmonicity to the ratio can be found from $T_{a,p}/T_{c,p}$.

Most noncentrosymmetric sites can be considered to have tetrahedral or near-tetrahedral arrangements of at least the nearest atoms. As a guide we can assume for $T_{a,p}$ the form appropriate to a purely tetrahedral site oriented along a [111] direction (Dawson, Hurley & Maslen, 1967). Thus

$$T_{a,p}/T_{c,p} = 8hkl(k_B T)^2 (\pi/a_0)^3 \beta_p / \alpha_p^3 \quad (14)$$

where k_B is Boltzmann's constant, T is the absolute temperature, α_p and β_p are the quadratic and cubic coefficients of the one-particle potential for a tetrahedral site:

$$V_p(\mathbf{u}) = V_{0,p} + \frac{1}{2} \alpha_p (x^2 + y^2 + z^2) + \beta_p xyz. \quad (15)$$

In equation (15), x , y and z are the coordinates of the instantaneous displacement \mathbf{u} of an atom in the p th substructure from its equilibrium position and α_p is related to the usual isotropic Debye-Waller factor B_p by $\alpha_p = 8\pi^2 k_B T / B_p$. In several simple inorganic compounds $|\beta_p|$ has been observed to be approxi-

mately 2×10^{-12} erg \AA^{-3} , a value that may be useful for estimating the influence of anharmonicity in other compounds and structures.

The predictions of equation (14) and the full calculations for the zinc blende structure from equations (12) and (13) compare well. Also noteworthy is the dependence of $T_{a,p}/T_{c,p}$ on α_p . Clearly, a small value of α_p is far more influential on the possibility of observing the effects of anharmonicity on the Bijvoet intensity difference and ratio than the anharmonic parameter β_p itself. Equation (14) also indicates that, as with the effects on the structure amplitude, we may expect far more significant changes in the Bijvoet differences and ratios due to anharmonicity at either higher temperatures or larger values of $(\sin \theta)/\lambda$.

Validity of Friedel's law in noncentrosymmetric structures

If we take all f_a and T_a to be zero, equation (7) simplifies to:

$$\Delta I(T_a, f_a = 0) = 4 \sum_p \sum_{q \neq p} G_p G_q f'_{c,p} f''_{c,q} s_{pq} T_{c,p} T_{c,q}. \quad (16)$$

This expression is equivalent to equation (4) of Iwasaki (1974). Consequently, $\Delta I(T_a, f_a = 0)$ vanishes if either

$$G_p = 0 \quad \text{for all but one } p \quad (17a)$$

or

$$\gamma_p - \gamma_q + 2\pi \mathbf{S} \cdot (\mathbf{u}_p - \mathbf{u}_q) = n\pi \quad (n: \text{integer}) \quad (17b)$$

for any combination of p and q and any \mathbf{S} .

From these conditions and equation (16) it is immediately obvious that $\Delta I(T_a, f_a = 0)$ vanishes for any of the three following cases: (i) a centrosymmetric crystal [equation (17b)], (ii) a crystal consisting of only one type of atom [equation (17a)] or (iii) a crystal containing no anomalous scatterers [equation (16)]. Iwasaki proposes several specific noncentrosymmetric structures, other than these three cases, for which Friedel's law is always valid. In every such case condition (17b) must be satisfied, although it may also be necessary for (17a) to be satisfied for a subset of the complete set of reflections. In some structures in which the positional parameters of all atoms and the three components of \mathbf{u} are rational fractions of the cell edges, (17b) may also be satisfied for reflections with special indices. The best known of these is the zinc blende structure, for which (17b) becomes

$$h + k + l = 2n.$$

Since by choice of a face-centred unit cell h , k and l are also constrained to be all odd or all even, $\Delta I(T_a, f_a = 0)$ will be zero when h , k and l are even. In diffraction experiments on such structures, this partial fulfilment of

Friedel's law is frequently exploited to increase the number of equivalent reflections that can be measured.

If we include the antisymmetric atomic functions, the conditions for Friedel's law holding become even more restrictive. For convenience, we will consider their influence on ΔI separately.

The effect of bonding ($T_a = 0$)

For antisymmetric charge distributions alone, from equation (9) $\Delta I(T_a = 0)$ vanishes and Friedel's law holds if

$$G_p = 0 \quad \text{for all } p \text{ and any } \mathbf{S} \quad (18a)$$

or,

the structure consists of a pair of substructures that are identical except for f_a having opposite sign. (18b)

Condition (18a) is trivial. A structure satisfying (18b) has a centre of inversion located on the midpoint of the line between any two atoms in the different substructures and hence is centrosymmetric. Thus, when $f_a \neq 0$ Friedel's law breaks down for all noncentrosymmetric structures.

Another way of viewing the implications of equation (9) is that the first term in equation (9) renders condition (17a) invalid; the second term invalidates condition (17b).

From the fact that (17a) is no longer valid, it now also follows that *Friedel's law generally does not hold for noncentrosymmetric structures of elements.*

Since condition (17b) is invalid, the noncentrosymmetric structures suggested by Iwasaki will only give centrosymmetric X-ray diffraction patterns when $f_a = 0$. Also, the partial validity of Friedel's law, such as is observed in zinc blende, will in general break down when $f_a \neq 0$. This is confirmed by several reported measurements of differences between the 222 and $\bar{2}\bar{2}\bar{2}$ reflections in zinc blende structures: GaAs (Colella, 1971), InSb (Bilderback & Colella, 1976), and ZnSe (McIntyre, Moss, Boehm & Barnea, 1975).

The effect of anharmonicity ($f_a = 0$)

If we include only the effects of anharmonic thermal vibration, the conditions for $\Delta I(f_a = 0)$ vanishing are from equation (12)

$$G_p = 0, \quad \text{for all but one } p \text{ and for any } \mathbf{S} \quad (19a)$$

or,

the structure consists of any number of substructures all of which have the same f'_c and f'' but may have different expressions for T_c and T_a . (19b)

Condition (19a) can from our earlier discussion only be satisfied for a centrosymmetric structure. The only

noncentrosymmetric structures that can satisfy (19b) are those of elements.

As in the previous section, since condition (17b) is no longer valid, the structures suggested by Iwasaki will not obey Friedel's law when $T_a \neq 0$. The partial validity of Friedel's law, such as observed in zinc blende, will also break down.

The general case ($T_a, f_a \neq 0$)

If we include both antisymmetric atomic functions, ΔI vanishes [equation (7)] when either

$$G_p = 0, \quad \text{for all } p \text{ and any } \mathbf{S} \quad (20a)$$

or,

the structure consists of a pair of substructures that are identical except for f_a and T_a having opposite signs. (20b)

As for condition (18b), a structure satisfying condition (20b) is centrosymmetric. The conclusions following on from (18a) for $\Delta I(T_a = 0)$ also apply here.

It must be noted that the validity of Friedel's law now depends on the symmetry properties of $f_{a,p}$ and $T_{a,p}$. If for a subset of the reflections satisfying condition (17b), both $f_{a,p}$ and $T_{a,p}$ are zero for all p , then ΔI will also vanish for this subset. For example, in the zinc blende structure, we will still have $\Delta I = 0$ for reflections of the type $hk0$ [the generalized zinc blende structure factor expressions have been considered by McIntyre, Moss & Barnea (1979)]. The conventional Cartesian axes used to describe the unit cell are the $\bar{4}$ axes of the point group of the atom at the origin. Since the symmetry element 2 is a subgroup of $\bar{4}$, both f_a and T_a are zero in all directions lying within the faces of the unit cell. The conditions for the applicability of Friedel's law now become even more restrictive than before: $h + k + l = 2n$, with one of the indices being zero. Similar reflection sets obeying Friedel's law may also exist in other noncentrosymmetric structures.

In general, if the point group for a site includes a twofold axis, f_a and T_a of the atoms at that site will vanish in directions perpendicular to that axis. Obviously, atoms lying on a mirror plane will not have antisymmetric components perpendicular to that plane.

Discussion

By introducing Dawson's generalized structure factor formalism into Iwasaki's substructure description, we have been able to obtain generalized expressions for the structure amplitudes and hence for the Bijvoet ratios of noncentrosymmetric crystals. Estimates for the mean effect of the antisymmetric components of bonding upon the Bijvoet ratios show that while it is in general quite small, specific reflections may be significantly

affected and thus provide a sensitive measure of these components. Since anharmonic effects are significant over a broader range of reciprocal space than the effects of bonding, the expression for the mean effect may be more useful for the former.

The inclusion of antisymmetric components has important implications for the validity of Friedel's law in noncentrosymmetric structures. In instances when in the conventional approximation ($f_a, T_a = 0$) sets of reflections in noncentrosymmetric structures obey Friedel's law, allowance for antisymmetric components imposes further restrictions upon such sets; they now generally no longer obey Friedel's law.

The effects of antisymmetric components on the intensities of reflections are often relatively greatest for weak reflections. Since these are also least sensitive to extinction, their measurement is of considerable value.

In noncentrosymmetric structures of elements we have shown that nonzero Bijvoet intensity differences are allowed if one recognizes antisymmetric components of the charge distribution due to bonding. In particular, such effects are to be expected in trigonal Se and Te structures (McIntyre, 1978) in which all of the constituent substructures are geometrically identical but the orientations of the atomic environments about each atom differ. 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 his postulates.

So far the consequences of the presence of antisymmetric components have only been observed in simple noncentrosymmetric structures: GaAs (Colella, 1971), ZnS (McIntyre, Moss, Boehm & Barnea, 1975), InSb (Bilderback & Colella, 1976), CdSe (Whiteley, Moss & Barnea, 1978), and ZnSe (McIntyre, Moss & Barnea, 1979). It is to be expected that such effects will be observable and even more varied in the more complex noncentrosymmetric organic and biologically important structures where their manifestations may be of particular interest and importance. Similarly, studies of the variation of some of these effects with temperature should prove of considerable value.

Neglect of antisymmetric components in accurate structure studies may lead to systematic errors. This will occur whenever a complete or partial satisfaction of Friedel's law for a noncentrosymmetric structure is unjustifiably assumed and exploited to increase the number of 'equivalent reflections' (in an attempt to improve the experimental accuracy) or to decrease the time required to obtain a complete reflection set. This

failure to recognize the influence of antisymmetric atomic features on the breakdown of Friedel's law may lead in the former case predominantly to an overestimate of errors and, more importantly, in the latter to incorrect refinement of the parameters.

Whereas the restrictions on Friedel's law require extended data collection in structural studies, they also provide a further qualitative and quantitative means of detecting a significant influence of antisymmetry in vibration and charge distribution on the diffraction experiment.

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