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A Statistical Study on the Measurability of Bijvoet Differences in Crystals with Type-I and Type-II Degree of Centrosymmetry

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The probability distributions of the normalized Bijvoet differences x and Δ are derived for non-centrosymmetric crystals with type-I and type-II degree of centrosymmetry assuming that there is a single anomalous scatterer in the unit cell besides a sufficiently large number of similar normal scatterers. The theoretical results are used to study the influence of degree of centrosymmetry on the measurability of Bijvoet differences. It is found that, for given values of k and σ_2^2, the measurability is in general poorer in the type-I case than in the type-II case.

1. Introduction

Two possible types of degree of centrosymmetry that a non-centrosymmetric crystal could exhibit have been defined (Parthasarathy & Parthasarathi, 1976; hereafter PP, 1976) and the probability distributions of intensities and phases of reflexions in such crystals have also been derived (Parthasarathy & Parthasarathi, 1974*a*; Parthasarathi & Parthasarathy, 1974; PP, 1976). In this paper we shall derive the probability distributions of the normalized Bijvoet differences $x(=|\Delta I|/4\sigma_Q\sigma'_P)$ and $\Delta(=|\Delta I|/\sigma_N'^2)$ in such crystals with a single anomalous scatterer in the unit cell besides the light atoms. The theoretical distributions are used to study how the measurability of Bijvoet differences is influenced by the two types of degree of centrosymmetry. Such a study is useful owing to the sensitiveness of the anomalous scattering method in resolving space-group ambiguities (Srinivasan & Vijayalakshmi, 1972). In this paper we shall follow the notation in PP (1976) and Parthasarathy (1967).

2. Derivation of the theoretical distributions of x and Δ

The normalized Bijvoet differences x and Δ have been shown to be (Parthasarathy, 1967)

$$x=y'_Py_Q|\sin(\alpha_Q-\alpha'_P)| \tag{1}$$

$$\Delta=4k\sigma_1\sigma_2x\,. \tag{2}$$

From (1) and (2) it is clear that the probability density function (hereafter PDF) of Δ could be readily obtained if that of x is known. We shall therefore first derive the PDF of x and then deduce that of Δ for each case.

We shall make the following assumptions: (i) The normal scatterers are sufficiently large in number and are of similar scattering power. (ii) The single anomalous scatterer in the unit cell is situated at the position of the approximate centre of symmetry in the case of the crystal with type-I and at the position of the exact centre of symmetry in the case of the crystal with type-II degree of centrosymmetry. It is convenient to take the origin on the single anomalous scatterer in the unit cell, so that $y'_P\equiv 1$ and $\alpha'_P\equiv 0$ for every reflexion. (1) can then be rewritten, $x=y_Q|\sin\alpha_Q|$. Since by definition x is positive

$$x=y_Q\sin\alpha_Q\,,\quad 0\le y_Q<\infty\,,\quad 0\le\alpha_Q<\pi\,. \tag{3}$$

From (3) it is clear that the PDF of x could be obtained from the joint distribution function $P(y_Q,\alpha_Q)$, which is available for each of the cases considered here. The quantity α_Q in (3) is not a convenient one for this purpose, since $\sin\alpha_Q$ is not monotonic in the range 0 to π. However, since $\sin\alpha_Q$ is symmetrical about $\alpha_Q=\pi/2$, x has the same value for $\alpha_Q=\alpha$ and $\alpha_Q=\pi-\alpha$ where α is defined to be an acute angle. We can therefore restrict the range of the argument of the sine function to 0 to $\pi/2$, provided we take into account the actual probabilities of occurrence for the two events, namely, $\alpha_Q=\alpha$ and $\alpha_Q=\pi-\alpha$. In this context it is found to be convenient to define a new variable α as

$$\alpha=\begin{cases}\alpha_Q & \text{if } \alpha_Q\le\pi/2\\ \pi-\alpha_Q & \text{if } \alpha_Q>\pi/2\end{cases} \tag{4}$$

so that

$$x=y_Q\sin\alpha\,,\quad 0\le y_Q<\infty\,,\quad 0\le\alpha\le\pi/2\,. \tag{5}$$

We shall derive the distribution of x by first obtaining the joint distribution $P(y_Q,\alpha)$.

(i) *The case of a crystal with type*-I *degree of centrosymmetry*

From (13) of Parthasarathy & Parthasarathi (1974*a*) we have

$$P(y_Q,\alpha_Q)=\frac{2y_Q}{\pi\sqrt{1-D_Q^2}}\times\exp\left[-y_Q^2\left(\frac{\cos^2\alpha_Q}{1+D_Q}+\frac{\sin^2\alpha_Q}{1-D_Q}\right)\right] \tag{6}$$

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where the factor 2 arises since α_Q is now restricted to the range 0 to π [see (3)]. By definition (Luzzati, 1952)

$$D_Q=\langle\cos 2\pi H\,.\,\Delta\mathbf{r}\rangle_Q=\exp\left(-\frac{\pi^3}{4}H^2\langle|\Delta\mathbf{r}|\rangle_Q^2\right). \quad (7)$$

From (4) and (6) the joint PDF of y_Q and α is

$$\begin{aligned}P(y_Q,\alpha)&=P(y_Q,\alpha_Q=\alpha)+P(y_Q,\alpha_Q=\pi-\alpha)\\&=\frac{4y_Q}{\pi\sqrt{1-D_Q^2}}\exp\left[-y_Q^2\left(\frac{\cos^2\alpha}{1+D_Q}+\frac{\sin^2\alpha}{1-D_Q}\right)\right]\end{aligned} \quad (8)$$

which leads to the joint distribution of x and α

$$P(x,\alpha)=\frac{4x\operatorname{cosec}^2\alpha}{\pi\sqrt{1-D_Q^2}}\times\exp\left[-\frac{x^2}{1-D_Q}-\frac{x^2\cot^2\alpha}{1+D_Q}\right]. \quad (9)$$

The PDF of x is therefore given by

$$P(x)=\frac{4x}{\pi\sqrt{1-D_Q^2}}\exp\left(-\frac{x^2}{1-D_Q}\right)\times\int_0^{\pi/2}\exp\left[-\frac{x^2\cot^2\alpha}{1+D_Q}\right]\operatorname{cosec}^2\alpha\,\mathrm{d}\alpha\,. \quad (10)$$

The integral in (10) can be evaluated by changing the variable to $w=(x\cot\alpha)/\sqrt{1+D_Q}$. Thus we have

$$P(x)=\frac{2}{\sqrt{\pi(1-D_Q)}}\exp\left[-x^2/(1-D_Q)\right]. \quad (11)$$

The cumulative function and expectation value of x can be readily obtained from (11) as

$$N(x)=\operatorname{erf}\left(x/\sqrt{1-D_Q}\right) \quad (12)$$

$$\langle x\rangle=[(1-D_Q)/\pi]^{1/2}\,. \quad (13)$$

Since $\Delta=4k\sigma_1\sigma_2x$ it readily follows from (12) and (13) that

$$N(\Delta)=\operatorname{erf}\left(\Delta/4k\sigma_1\sigma_2\sqrt{1-D_Q}\right) \quad (14)$$

$$\langle\Delta\rangle=4k\sigma_1\sigma_2[(1-D_Q)/\pi]^{1/2}\,. \quad (15)$$

The quantity that is relevant for the measurability of Bijvoet differences is the fractional number of reflexions for which Δ is greater than any specific value Δ_0, say. We shall refer to this as the complementary cumulative function and denote it by $N_c(\Delta_0)$. Since $N_c(\Delta)=1-N(\Delta)$, we have from (14)

$$N_c(\Delta)=1-\operatorname{erf}\left(\Delta/4k\sigma_1\sigma_2\sqrt{1-D_Q}\right). \quad (16)$$

(ii) *The case of a crystal with type*-II *degree of centrosymmetry*

We can rewrite (10) of PP (1976) as

$$P(y_Q,\alpha_Q)=\frac{2y_Q}{\pi\sqrt{1-r^2}}\times\exp\left[-y_Q^2\left(\frac{\cos^2\alpha_Q}{1+r}+\frac{\sin^2\alpha_Q}{1-r}\right)\right]. \quad (17)$$

Here r is a measure of the type-II degree of centrosymmetry. It is clear that (6) and (17) have the same functional form with D_Q or r, as the case may be, as a parameter of the distribution. It follows that the results derived in (11)–(16) hold for the present case provided we replace D_Q by r. We thus have

$$P(x)=\frac{2}{\sqrt{\pi(1-r)}}\exp\left[-x^2/(1-r)\right] \quad (18)$$

$$N(x)=\operatorname{erf}\left(x/\sqrt{1-r}\right) \quad (19)$$

$$\langle x\rangle=[(1-r)/\pi]^{1/2} \quad (20)$$

$$N(\Delta)=\operatorname{erf}\left(\Delta/4k\sigma_1\sigma_2\sqrt{1-r}\right) \quad (21)$$

$$\langle\Delta\rangle=4k\sigma_1\sigma_2[(1-r)/\pi]^{1/2} \quad (22)$$

$$N_c(\Delta)=1-\operatorname{erf}\left(\Delta/4k\sigma_1\sigma_2\sqrt{1-r}\right). \quad (23)$$

3. Discussion of the theoretical results

(i) *Type*-I *case*. From (16) it is clear that $N_c(\Delta)$ depends on the parameters $k,\sigma_2^2(=1-\sigma_1^2)$ and D_Q which in turn is a function of $\langle|\Delta\mathbf{r}|\rangle_Q$ and $(\sin\theta)/\lambda$ [see (7)]. The average value of $N_c(\Delta)$ over the various values of $(\sin\theta)/\lambda$ can be obtained (Parthasarathy & Parthasarathi, 1974*b*) as

$$\langle N_c(\Delta)\rangle_H=\frac{3}{H_{\max}^3}\int_0^{H_{\max}}N_c(\Delta)H^2\mathrm{d}H \quad (24)$$

where $H=2(\sin\theta)/\lambda$ and $H_{\max}=2/\lambda$. The value of $\langle N_c(\Delta=0{\cdot}05)\rangle_H$ is shown in Fig. 1(*a*)–(*c*) as a function of $\langle|\Delta\mathbf{r}|\rangle_Q$ for the typical values of $k=0{\cdot}05$, 0·1 and 0·2. It is clear from these figures that when the degree of centrosymmetry is high, say $\langle|\Delta\mathbf{r}|\rangle_Q<0{\cdot}1$ Å the measurability of Bijvoet differences is too low to be useful for structure determination *via* the quasi-anomalous method. Further even the breakdown of Friedel's law could not be easily detected when $\langle|\Delta\mathbf{r}|\rangle_Q$ and k are both too small [*e.g.* if $\langle|\Delta\mathbf{r}|\rangle_Q=0{\cdot}06$ and $k=0{\cdot}05$ then $N_c(\Delta=0{\cdot}05)<1\%$]. This point is relevant in connexion with space-group determination in such crystals by the anomalous scattering method.

(ii) *Type*-II *case*. From (23) it is clear that $N_c(\Delta)$ depends on the parameters k, σ_2^2 and r which (unlike the D_Q of the type-I case) is practically independent of $(\sin\theta)/\lambda$ in structures with similar light atoms. The variation of $N_c(\Delta=0{\cdot}05)$ as a function of r is shown in Fig. 1(*d*)–(*f*) for the typical values of $k=0{\cdot}05$, 0·1, 0·2. It is seen that while for small values of k (*e.g.* $k=0{\cdot}05$) the measurability systematically decreases as r increases, for large values (*e.g.* $k=0{\cdot}2$) the measurability (though slightly decreasing with increasing value of r) does not seem to be affected adversely so long as $r\le0{\cdot}6$. Thus even if 50% of the atoms form a centrosymmetric group, there will be a sufficient number of reflexions with measurable Bijvoet differences provided k has moderate values.

A comparison of the measurability in typical type-I and type-II cases could be interesting. We shall take the following situations: type-I case with $\langle|\Delta \mathbf{r}|\rangle_Q=$ 0·1 Å *vs* type-II case with $r=0·5$. We shall set $k=0·1$ and $\sigma_2^2=0·5$. It is seen from Fig. 1 that while the number of reflexions having a $\Delta>0·05$ is only 8% in the type-I case, it is as high as 60% for the type-II case. Thus the measurability of Bijvoet differences is very much poorer in the type-I case than in the type-II case.

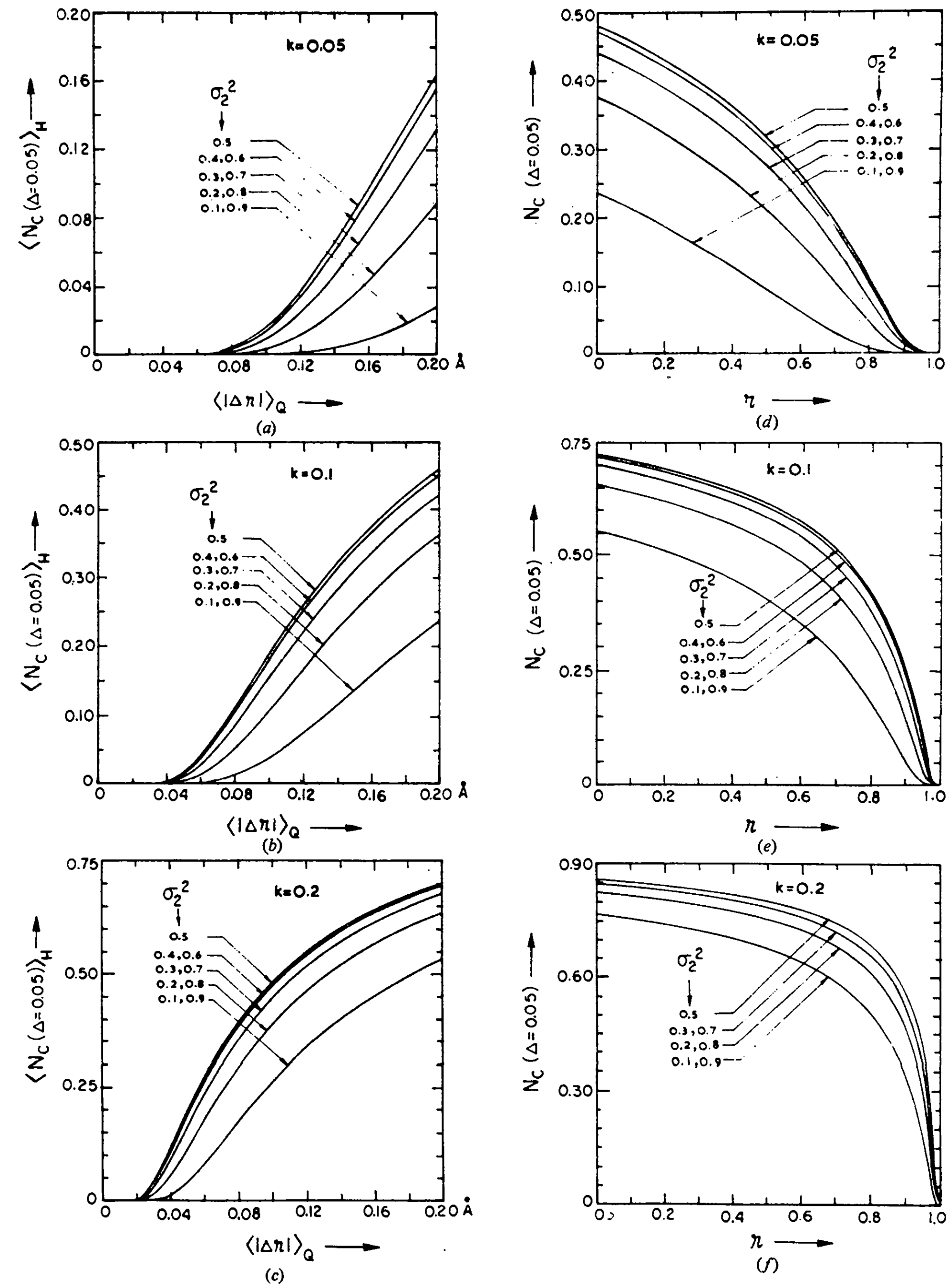

Fig. 1. The fractional number of reflexions for which the normalized Bijvoet difference $\Delta>0·05$ as a function of the degree of centrosymmetry for different values of k and σ_2^2 (which is the fractional contribution to the local mean intensity from the normal scatterers). (*a*)–(*c*) are for the type-I case and (*d*)–(*f*) are for the type-II case.

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X-ray Determination of Thermal Expansion of Olivines

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Precise measurement of the thermal expansion of natural olivines at elevated temperatures by X-ray diffraction yields the following equations for the cell volume (V) with temperature (t): $Fo_{92\cdot5}$: $V_t = 291{\cdot}13 + 83{\cdot}6 \times 10^{-4}t + 6{\cdot}5 \times 10^{-7}t^2$, $25 < t < 973\,°C$; $Fo_{90\cdot4}$: $V_t = 291{\cdot}45 + 80{\cdot}4 \times 10^{-4}t + 11{\cdot}3 \times 10^{-7}t^2$, $25 < t < 963\,°C$; $Fo_{53\cdot8}$: $V_t = 298{\cdot}58 + 76{\cdot}4 \times 10^{-4}t + 17{\cdot}2 \times 10^{-7}t^2$, $25 < t < 432\,°C$, where the units are Å^3 and °C. Similar expressions are reported for the individual lattice parameters. Expressions for thermal expansions are derived. Volume thermal expansion varies linearly with temperature. A decrease in the Mg/Fe ratio in olivine decreases the thermal expansion in the observed temperature range.

Introduction

Early studies on linear thermal expansion of olivines were made by Kozu, Uyeda & Tsurumi (1934) and Rigby, Lowell & Green (1946) using dilatometers for their measurements. Recently, Soga & Anderson (1967) measured the average thermal expansion of forsterite with a fused-silica dilatometer using a linear displacement transducer. The only previous X-ray studies on forsterite were done by Skinner (1962). He used an X-ray diffractometer and reported the mean thermal expansion of synthetic forsterite (Mg_2SiO_4) from 20 to 1000 °C. No systematic work has been done to determine the instantaneous thermal expansion in different axes and to see the effect of the Mg/Fe ratio on thermal expansion of olivines. This report presents the detailed measurements of the lattice parameters at elevated temperatures on natural olivines having three different compositions.

Experimental

The experimental details were the same as in our previous work (Singh, Simmons & McFarlin, 1975). The Norelco wide-range goniometer with an MRC high-temperature diffractometer attachment were used. Thin-film sample mounts were found to be most suitable for this work and they were scanned between 16 and 87° 2θ. The temperature of the heating stage was read with a Pt, Pt+13%Rh thermocouple and controlled within ± 2 °C. High-purity platinum powder mixed with the sample was used in determining the exact temperature of the sample.

A determinative curve based on analysed natural olivines by Jambor & Smith (1964) was used to determine the compositions of natural olivines. The value of d_{130} for each mineral was measured and the compositions were calculated. We also calculated lattice parameters at 25 °C from our analytical expressions and used them to evaluate d_{130} and d_{174} and to calculate the Fo percentage. The compositions determined by all these methods agreed to within ± 1% for each mineral and the mean values are given in Table 1 with some other physical properties.

Table 1. *Characterization of the experimental materials*

Fo percentage	92·5	90·4	53·8
Location	Day Book North Carolina	San Carlos Arizona	Bushveldt S. Africa
Bulk density (g/cm^3)	3·266	3·469	3·765
Refractive indices	$\alpha = 1{\cdot}642$ $\gamma = 1{\cdot}678$	$\alpha = 1{\cdot}653$ $\gamma = 1{\cdot}691$	$\alpha = 1{\cdot}729$ $\gamma = 1{\cdot}771$