*Acta Cryst.* (1996). A**52**, 385–390

# On Integrating the Techniques of Direct Methods with Anomalous Dispersion: the One-Phase Structure Seminvariants in the Tetragonal System

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(*Received 8 May 1995; accepted 13 December 1995*)

## Abstract

Conditional probability distributions are derived for the one-phase structure seminvariants in the presence of anomalous scattering for the tetragonal space group *P*4.

## 1. Introduction

The results of Hauptman (1982*b*) clearly imply that the fusion of the traditional techniques of direct methods with anomalous dispersion will facilitate the solution of those crystal structures that contain one or more anomalous scatterers. The method has already been extended to the probabilistic theory of one-phase structure seminvariants for the monoclinic and orthorhombic systems (Velmurugan & Hauptman, 1989) and applications of the new theory have also been described (Velmurugan, Hauptman & Potter, 1989). The present paper extends the above work to the tetragonal system (Velmurugan & Hauptman, 1988).

In the presence of anomalous scatterers, the normalized structure factor

$$E_{\mathbf{H}} = |E_{\mathbf{H}}| \exp(i\varphi_{\mathbf{H}}) \tag{1}$$

is defined by

$$E_{\mathbf{H}} = \alpha_{\mathbf{H}}^{-1/2} \sum_{j=1}^{N} f_{j\mathbf{H}} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) \tag{2}$$

$$= \alpha_{\mathbf{H}}^{-1/2} \sum_{j=1}^{N} |f_{j\mathbf{H}}| \exp[i(\delta_{j\mathbf{H}} + 2\pi \mathbf{H} \cdot \mathbf{r}_j)], \tag{3}$$

where

$$f_{j\mathbf{H}} = |f_{j\mathbf{H}}| \exp(i\delta_{j\mathbf{H}}) \tag{4}$$

is the (in general complex) atomic scattering factor (a function of $|\mathbf{H}|$ as well as of $j$) of the atom labeled $j$, $\mathbf{r}_j$ is its position vector, $N$ is the number of atoms in the unit cell and

$$\alpha_{\mathbf{H}} = \sum_{j=1}^{N} |f_{j\mathbf{H}}|^2. \tag{5}$$

For a normal scatterer, $\delta_{j\mathbf{H}} = 0$; for an atom that scatters anomalously, $\delta_{j\mathbf{H}} \neq 0$. Owing to the presence of the anomalous scatterers, the atomic scattering factors $f_{j\mathbf{H}}$, as functions of $(\sin\theta)/\lambda$, do not have the same shape for different atoms even approximately. Hence, the dependence of the $f_{j\mathbf{H}}$ on $|\mathbf{H}|$ cannot be ignored, in contrast to the usual practice when anomalous scatterers are not present. For this reason, the subscript $\mathbf{H}$ is not suppressed in the symbols $f_{j\mathbf{H}}$ and $\alpha_{\mathbf{H}}$ [see (5)].

† DCB contribution no. 868.

### 1.1. *Tetragonal system, space group P4*

In the space group *P*4, the single phases that are structure seminvariants are of the form $S = \varphi_{hk0}$ ($h + k$ even). Thus we have two cases, namely,

(i) when $h$ and $k$ are both odd;

(ii) when $h$ and $k$ are both even.

(i) *h and k both odd.* One embeds the one-phase structure seminvariants $S$ in the three-phase structure invariant $T$, an extension of the seminvariant $S$.

$$T = \varphi_{hk0} + \varphi_{-(h+k)/2,(h-k)/2,l} + \varphi_{-(h-k)/2,-(h+k)/2,\bar{l}}, \tag{6}$$

where $l$ is an arbitrary integer. The first neighborhood of $T$ consists of the three magnitudes $|E_{hk0}|$, $|E_{-(h+k)/2,(h-k)/2,l}|$ and $|E_{-(h-k)/2,-(h+k)/2,\bar{l}}|$. In the event that $h$ and $k$ are both odd, the first neighborhood of $S$ is defined to consist of the same three magnitudes $|E_{hk0}|$, $|E_{-(h+k)/2,(h-k)/2,l}|$ and $|E_{-(h-k)/2,-(h+k)/2,\bar{l}}|$. It should be noted that in (6) $l$ is arbitrary; hence, there are many extensions of $S$ and therefore many first neighborhoods of $S$.

In the present paper, the joint probability distribution of the three structure factors whose magnitudes constitute a neighborhood of $S$ is first derived, for the space group *P*4, when anomalous scatterers are present (see Appendix *A*). This distribution leads directly to the major result of this paper, equation (34), the conditional probability distribution of the one-phase structure seminvariant $\varphi_{hk0}$ (when $h$ and $k$ are both odd), assuming as known the three magnitudes in any of its first neighborhoods. Owing to their extreme length, details of the derivations are omitted altogether.

(ii) *h and k are both even.* When $h$ and $k$ are both even, we have, in addition to $T$ [equation (6)], another extension $T'$, namely,

$$T' = \varphi_{hk0} + \varphi_{\bar{h}/2,\bar{k}/2,l'} + \varphi_{\bar{h}/2,\bar{k}/2,\bar{l}'}, \tag{7}$$

where $l'$ is an arbitrary integer.

Thus, we find that, when $h$ and $k$ are both even, the first neighborhood of $S$ and its extension consist of the five magnitudes $|E_{hk0}|$, $|E_{-(h+k)/2,(h-k)/2,l}|$, $|E_{-(h-k)/2,-(h+k)/2,\bar{l}}|$, $|E_{\bar{h}/2,\bar{k}/2,l'}|$ and $|E_{\bar{h}/2,\bar{k}/2,\bar{l}'}|$.

## 2. The joint probability distribution of the three structure factors $|E_{hk0}|$, $|E_{-(h+k)/2,(h-k)/2,l}|$ and $|E_{-(h-k)/2,-(h+k)/2,\bar{l}}|$

The first neighborhood of the one-phase structure seminvariant $\varphi_{hk0}$ (when $h$ and $k$ are both odd) is defined to consist of the three magnitudes:

$$R = |E_{hk0}|, \quad R_L = |E_{-(h+k)/2,(h-k)/2,l}|, \quad \bar{R}_L = |E_{-(h-k)/2,-(h+k)/2,\bar{l}}|. \tag{8}$$

The atomic position vectors $r_j$ and the integer $l$ are fixed; the ordered pair of integers $(h,k)$ is assumed to be the primitive random variables. The phases of the associated structure factors are denoted by

$$\Phi = \varphi_{hk0}, \quad \Phi_L = \varphi_{-(h+k)/2,(h-k)/2,l}, \quad \bar{\Phi}_L = \varphi_{-(h-k)/2,-(h+k)/2,\bar{l}}. \tag{9}$$

For space group $P4$, introduce the abbreviations

$$f_{j\,hk0} = f_j, \quad \delta_j = \delta_{j\,hk0}, \quad f_{jL} = f_{j\,-(h+k)/2,(h-k)/2,l}, \quad f_{j\bar{L}} = f_{j\,-(h-k)/2,-(h+k)/2,\bar{l}}, \quad \delta_{jL} = \delta_{j\bar{L}} \tag{10}$$

$$\alpha = \sum_{j=1}^{N} |f_j|^2, \quad \alpha_L = \sum_{j=1}^{N} |f_{jL}|^2. \tag{11}$$

Our major goal is to determine the conditional probability distribution of the one-phase structure seminvariant $\varphi_{hk0}$, given the three magnitudes (8) in its first neighborhood, which, in the favorable case that the variance of the distribution happens to be small, yields a reliable estimate of the seminvariant (the neighborhood principle).

### 2.1. *Notation and definitions*

Define $C$, $S$, $C_2$ and $S_2$ by

$$C = (1/\alpha)\sum_{j=1}^{N} |f_j|^2 \cos 2\delta_j \tag{12}$$

$$S = (1/\alpha)\sum_{j=1}^{N} |f_j|^2 \sin 2\delta_j \tag{13}$$

$$C_2 = (1/\alpha_L)\sum_{j=1}^{N} |f_{jL}|^2 \cos 2\delta_{jL} \tag{14}$$

$$S_2 = (1/\alpha_L)\sum_{j=1}^{N} |f_{jL}|^2 \sin 2\delta_{jL}, \tag{15}$$

where $f_j$, $\delta_j$, $f_{j\bar{L}}$, $f_{jL}$, $\alpha$ and $\alpha_L$ are defined in (10) and (11).

Define $X$ and $\varepsilon$ by means of

$$X\cos\varepsilon = C, \quad X\sin\varepsilon = -S, \tag{16}$$

$$X = (C^2 + S^2)^{1/2}, \quad \tan\varepsilon = -S/C. \tag{17}$$

In a similar way, $X_2$ and $\varepsilon_2$ are defined by

$$X_2\cos\varepsilon_2 = C_2, \quad X_2\sin\varepsilon_2 = -S_2, \tag{18}$$

$$\tan\varepsilon_2 = -S_2/C_2, \quad X_2 = (C_2^2 + S_2^2), \tag{19}$$

$$C_1 = (1/\alpha^{1/2}\alpha_L)\sum_{j=1}^{N} |f_j f_{j\bar{L}}^2| \cos\delta_j, \tag{20}$$

$$S_1 = (1/\alpha^{1/2}\alpha_L)\sum_{j=1}^{N} |f_j f_{j\bar{L}}^2| \sin\delta_j, \tag{21}$$

$$C_{12} = (1/\alpha^{1/2}\alpha_L)\sum_{j=1}^{N} |f_j f_{j\bar{L}}^2| \cos(\delta_j + 2\delta_{jL}) \tag{22}$$

$$S_{12} = (1/\alpha^{1/2}\alpha_L)\sum_{j=1}^{N} |f_j f_{j\bar{L}}^2| \sin(\delta_j + 2\delta_{jL}) \tag{23}$$

$$C_{\bar{1}2} = (1/\alpha^{1/2}\alpha_L)\sum_{j=1}^{N} |f_j f_{j\bar{L}}^2| \cos(-\delta_j + 2\delta_{jL}) \tag{24}$$

$$S_{\bar{1}2} = (1/\alpha^{1/2}\alpha_L)\sum_{j=1}^{N} |f_j f_{j\bar{L}}^2| \sin(-\delta_j + 2\delta_{jL}). \tag{25}$$

Then, $X_1$, $\varepsilon_1$, $X_{12}$, $\varepsilon_{12}$, $X_{\bar{1}2}$ and $\varepsilon_{\bar{1}2}$ are defined by the following equations:

$$X_1\cos\varepsilon_1 = C_1, \quad X_1\sin\varepsilon_1 = -S_1, \tag{26}$$

$$\tan\varepsilon_1 = -S_1/C_1, \quad X_1 = (C_1^2 + S_1^2)^{1/2}, \tag{27}$$

$$X_{12}\cos\varepsilon_{12} = C_{12}, \quad X_{12}\sin\varepsilon_{12} = -S_{12} \tag{28}$$

$$\tan\varepsilon_{12} = -S_{12}/C_{12}, \quad X_{12} = (C_{12}^2 + S_{12}^2)^{1/2}, \tag{29}$$

$$X_{\bar{1}2}\cos\varepsilon_{\bar{1}2} = C_{\bar{1}2}, \quad X_{\bar{1}2}\sin\varepsilon_{\bar{1}2} = -S_{\bar{1}2}, \tag{30}$$

$$\tan\varepsilon_{\bar{1}2} = -S_{\bar{1}2}/C_{\bar{1}2}, \quad X_{\bar{1}2} = (C_{\bar{1}2}^2 + S_{\bar{1}2}^2)^{1/2}. \tag{31}$$

Following the procedure described in Appendix $A$, we finally arrive at the joint probability distribution [see (66)] of the three structure factors $E_{hk0}$, $E_{-(h+k)/2,(h-k)/2,l}$, $E_{-(h-k)/2,-(h+k)/2,\bar{l}}$ as

$$\begin{aligned} P \simeq\ & (RR_L\bar{R}_L/\pi^3)\exp[-(R^2 + R_L^2 + \bar{R}_L^2)] \\ & \times \exp[XR^2\cos(2\Phi + \varepsilon) + 4X_1R(R_L^2 + \bar{R}_L^2 - 2) \\ & \times \cos(\Phi + \varepsilon_1)]\exp[2X_2R_L\bar{R}_L\cos(\Phi_L + \bar{\Phi}_L + \varepsilon_2) \\ & + 4X_{12}RR_L\bar{R}_L\cos(\Phi + \Phi_L + \bar{\Phi}_L + \varepsilon_{12}) \\ & + 4X_{\bar{1}2}RR_L\bar{R}_L\cos(-\Phi + \Phi_L + \bar{\Phi}_L + \varepsilon_{\bar{1}2})]. \end{aligned} \tag{32}$$

### 3. Conditional probability distribution of the one-phase structure seminvariants $\varphi_{hk0}(=S)$ given the three magnitudes $|E_{hk0}|$, $|E_{-(h+k)/2,(h-k)/2,l}|$, $|E_{-(h-k)/2,-(h+k)/2,\bar{l}}|$ in its first neighborhood: space group $P4$

Refer to §2 for the probabilistic background. The conditional probability distribution of $S$, assuming as known the three magnitudes (8) in its first neighborhood, is denoted by

$$P(\Phi|R, R_L, \bar{R}_L). \tag{33}$$

Then, $P(\Phi|R, R_L, \bar{R}_L)$ is obtained from (66) of Appendix $A$ by fixing $R$, $R_L$ and $\bar{R}_L$ in accordance with (8) and integrating $P$ [(66)] with respect to $\Phi_L$ and $\bar{\Phi}_L$ between the limits 0 and $2\pi$ and multiplying by a suitable normalizing parameter.

The final formula, the first major result of this paper, is simply

$$\begin{aligned} P(\Phi|R, R_L, \bar{R}_L) = (1/M)\exp[&a\cos\Phi + b\cos 2\Phi \\ &+ c'\sin\Phi + d\sin 2\Phi] \\ \times I_0[&e + A\cos\Phi + B\cos 2\Phi \\ &+ C'\sin\Phi + D\sin 2\Phi]^{1/2}, \end{aligned} \tag{34}$$

where $M$ is a suitable normalizing constant, $I_0$ is the modified Bessel function and

$$\begin{aligned} a &= 4R(R_L^2 + \bar{R}_L^2 - 2)C_1, \\ b &= R^2 C, \\ c' &= 4R(R_L^2 + \bar{R}_L^2 - 2)S_1, \\ d &= R^2 S, \\ e &= 4R_L^2\bar{R}_L^2[(C_2^2 + S_2^2) + 4R^2(C_{12}^2 + C_{\bar{1}2}^2 + S_{12}^2 + S_{\bar{1}2}^2)], \\ A &= 16RR_L^2\bar{R}_L^2[C_2(C_{12} + C_{\bar{1}2}) + S_2(S_{12} + S_{\bar{1}2})], \\ B &= 32R^2R_L^2\bar{R}_L^2[C_{12}C_{\bar{1}2} + S_{12}S_{\bar{1}2}], \\ C' &= 16RR_L^2\bar{R}_L^2[C_2(S_{12} - S_{\bar{1}2}) - S_2(C_{12} - C_{\bar{1}2})], \\ D &= 32R^2R_L^2\bar{R}_L^2[S_{12}C_{\bar{1}2} - C_{12}S_{\bar{1}2}]. \end{aligned} \tag{35}$$

### 4. The joint probability distribution of the five structure factors $|E_{hk0}|$, $|E_{-(h+k)/2,(h-k)/2,l}|$, $|E_{-(h-k)/2,-(h+k)/2,\bar{l}}|$, $|E_{\bar{h}/2,\bar{k}/2,l'}|$ and $|E_{\bar{h}/2,\bar{k}/2,\bar{l}'}|$

The first neighborhood of the one-phase structure seminvariant $\varphi_{hk0}$ (when $h$ and $k$ are both even) has been defined to consist of the five magnitudes

$$\begin{gathered} R = |E_{hk0}|, \quad R_L = |E_{-(h+k)/2,(h-k)/2,l}|, \\ \bar{R}_L = |E_{-(h-k)/2,-(h+k)/2,\bar{l}}|, \quad R'_L = |E_{\bar{h}/2,\bar{k}/2,l'}|, \\ \bar{R}'_L = |E_{\bar{h}/2,\bar{k}/2,\bar{l}'}|. \end{gathered} \tag{36}$$

Since the method of deriving the joint probability distribution in this case closely resembles the one discussed in §2, we will give here only those steps where major changes occur.

The phases of the associated structure factors [of (36)] are denoted by

$$\begin{gathered} \Phi = \Phi_{hk0}, \quad \Phi_L = \varphi_{-(h+k)/2,(h-k)/2,l}, \\ \bar{\Phi}_L = \varphi_{-(h-k)/2,-(h+k)/2,\bar{l}}, \quad \Phi'_L = \varphi_{\bar{h}/2,\bar{k}/2,l'}, \\ \Phi'_{\bar{L}} = \varphi_{\bar{h}/2,\bar{k}/2,\bar{l}'}. \end{gathered} \tag{37}$$

We introduce the abbreviations

$$f_{j\,\bar{h}/2,\bar{k}/2,l'} = f'_{jL} \quad (= f_{j\,\bar{h}/2,\bar{k}/2,\bar{l}'}), \tag{38}$$

$$\delta'_{jL} = \delta_{j\,\bar{h}/2,\bar{k}/2,l'}, \tag{39}$$

$$\alpha'_L = \sum_{j=1}^{N} |f'_{jL}|^2. \tag{40}$$

#### 4.1. *Notation and definitions*

In addition to the notation and definitions in §2.1 (when $h$ and $k$ are both even), we now have the following additional definitions:

$$C'_2 = (1/\alpha'_L)\sum_{j=1}^{N} |f'_{jL}|\cos 2\delta'_{jL}, \tag{41}$$

$$S'_2 = (1/\alpha'_L)\sum_{j=1}^{N} |f'_{jL}|\sin 2\delta'_{jL}, \tag{42}$$

where $f'_{jL}$, $\delta'_{jL}$ and $\alpha'_L$ are defined in (38), (39) and (40), respectively.

Define $X'_2$ and $\varepsilon_{45}$ by means of

$$X'_2\cos\varepsilon_{45} = C'_2, \quad X'_2\sin\varepsilon_{45} = -S'_2, \tag{43}$$

$$X'_2 = (C'^2_2 + S'^2_2)^{1/2}, \quad \tan\varepsilon_{45} = -S'_2/C'_2. \tag{44}$$

Next, make the definitions

$$C'_1 = (1/\alpha^{1/2}\alpha'_L)\sum_{j=1}^{N} |f_j f'^2_{jL}|\cos\delta_j, \tag{45}$$

$$S'_1 = (1/\alpha^{1/2}\alpha'_L)\sum_{j=1}^{N} |f_j f'^2_{jL}|\sin\delta_j, \tag{46}$$

$$C'_{12} = (1/\alpha^{1/2}\alpha'_L)\sum_{j=1}^{N} |f_j f'^2_{jL}|\cos(\delta_j + 2\delta'_{jL}), \tag{47}$$

$$S'_{12} = (1/\alpha^{1/2}\alpha'_L)\sum_{j=1}^{N} |f_j f'^2_{jL}|\sin(\delta_j + 2\delta'_{jL}), \tag{48}$$

$$C'_{\bar{1}2} = (1/\alpha^{1/2}\alpha'_L)\sum_{j=1}^{N} |f_j f'^2_{jL}|\cos(-\delta_j + 2\delta'_{jL}), \tag{49}$$

$$S'_{\bar{1}2} = (1/\alpha^{1/2}\alpha'_L)\sum_{j=1}^{N} |f_j f'^2_{jL}|\sin(-\delta_j + 2\delta'_{jL}). \tag{50}$$

Then, $X'_1$, $\varepsilon'_1$, $X'_{12}$, $\varepsilon'_{14}$, $X'_{\bar{1}2}$ and $\varepsilon'_{\bar{1}4}$ are defined by the following equations:

$$X'_1\cos\varepsilon'_1 = C'_1, \quad X'_1\sin\varepsilon'_1 = -S'_1, \tag{51}$$

$$\tan\varepsilon'_1 = -S'_1/C'_1, \quad X'_1 = (C'^2_1 + S'^2_1)^{1/2}, \tag{52}$$

$$X'_{12}\cos\varepsilon'_{14} = C'_{12}, \quad X'_{12}\sin\varepsilon'_{14} = -S'_{12} \tag{53}$$

$$\tan\varepsilon'_{14} = -S'_{12}/C'_{12}, \quad X'_{12} = (C'^2_{12} + S'^2_{12})^{1/2}, \tag{54}$$

$$X'_{\bar{1}2}\cos\varepsilon'_{\bar{1}4} = C'_{\bar{1}2}, \quad X'_{\bar{1}2}\sin\varepsilon'_{\bar{1}4} = -S'_{\bar{1}2}, \tag{55}$$

$$\tan\varepsilon'_{\bar{1}4} = -S'_{\bar{1}2}/C'_{\bar{1}2}, \quad X'_{\bar{1}2} = (C'^2_{\bar{1}2} + S'^2_{\bar{1}2})^{1/2} \tag{56}$$

The procedure described in Appendix *A* has to be slightly modified to arrive at the joint probability distribution of the *five structure-factor* magnitudes $R\ (=|E_{hk0}|)$, $R_L\ (=|E_{-(h+k)/2,(h-k)/2,l}|)$, $\bar{R}_L\ (=|E_{-(h-k)/2,-(h+k)/2,\bar{l}}|)$, $R'_L\ (=|E_{\bar{h}/2,\bar{k}/2,l'}|)$ and $\bar{R}'_L\ (=|E_{\bar{h}/2,\bar{k}/2,\bar{l}'}|)$ and the corresponding phases when $h$ and $k$ are both even. This distribution function finally turns out to be

$$\begin{aligned}
&P(R, R_L, \bar{R}_L, R'_L, \bar{R}'_L; \Phi, \Phi_L, \bar{\Phi}_L, \Phi'_L, \bar{\Phi}'_L)\\
&\quad\simeq (RR_L\bar{R}_LR'_L\bar{R}'_L/\pi^5)\\
&\qquad\times\exp[-(R^2 + R^2_L + \bar{R}^2_L + R'^2_L + \bar{R}'^2_L)]\\
&\qquad\times\exp[XR^2\cos(2\Phi+\varepsilon)\\
&\qquad+4X_1R(R^2_L + \bar{R}^2_L - 2)\cos(\Phi+\varepsilon_1)\\
&\qquad+2X'_1R(R'^2_L + \bar{R}'^2_L - 2)\cos(\Phi+\varepsilon'_1)]\\
&\qquad\times\exp[2X_2R_L\bar{R}_L\cos(\Phi_L+\bar{\Phi}_L+\varepsilon_2)\\
&\qquad+4X_{12}RR_L\bar{R}_L\cos(\Phi+\Phi_L+\bar{\Phi}_L+\varepsilon_{12})\\
&\qquad+4X_{\bar{1}2}RR_L\bar{R}_L\cos(-\Phi+\Phi_L+\bar{\Phi}_L+\varepsilon_{\bar{1}2})\\
&\qquad+2X'_2R'_L\bar{R}'_L\cos(\Phi'_L+\bar{\Phi}'_L+\varepsilon_{45})\\
&\qquad+2X'_{12}RR'_L\bar{R}'_L\cos(\Phi+\Phi'_L+\bar{\Phi}'_L+\varepsilon'_{14})\\
&\qquad+2X'_{\bar{1}2}RR'_L\bar{R}'_L\cos(-\Phi+\Phi'_L+\bar{\Phi}'_L+\varepsilon'_{\bar{1}4})].
\end{aligned}\tag{57}$$

## 5. The conditional probability distribution of the one-phase structure seminvariant $\varphi_{hk0} = S$ ($h$ and $k$ both even) given the five magnitudes $|E_{hk0}|$, $|E_{-(h+k)/2,(h-k)/2,l}|$, $|E_{-(h-k)/2,-(h+k)/2,\bar{l}}|$, $|E_{\bar{h}/2,\bar{k}/2,l'}|$ and $|E_{\bar{h}/2,\bar{k}/2,\bar{l}'}|$ in its first neighborhood

Refer to §4 for the probabilistic background. The conditional probability distribution of $S$ assuming as known the five magnitudes (36) in its first neighborhood is denoted by

$$P(\Phi|R, R_L, \bar{R}_L, R'_L, \bar{R}'_L). \tag{58}$$

Then, $P(\Phi|R, R_L, \bar{R}_L, R'_L, \bar{R}'_L)$ is obtained from (57) by fixing $R, \bar{R}_L, R_L, \bar{R}'_L$ and $R'_L$ in accordance with (36) and integrating $P$ [(57)] with respect to $\Phi_L$, $\Phi'_L$, $\bar{\Phi}_L$ and $\bar{\Phi}'_L$ between the limits 0 and $2\pi$ and multiplying by a suitable normalizing parameter.

The final formula, the second major result of this paper, is simply

$$\begin{aligned}
&P(\Phi|R, R_L, \bar{R}_L, R'_L, \bar{R}'_L)\\
&\quad=(1/M_1)\exp[a_1\cos\Phi + b_1\cos 2\Phi + c'_1\sin\Phi\\
&\qquad+d_1\sin 2\Phi]I_0[e + A\cos\Phi + B\cos 2\Phi + C'\sin\Phi\\
&\qquad+D\sin 2\Phi]^{1/2}I_0[e_1 + A_1\cos 2\Phi + B_1\cos 2\Phi\\
&\qquad+C''\sin\Phi + D_1\sin 2\Phi]^{1/2},
\end{aligned}\tag{59}$$

where $M_1$ is a suitable normalizing constant, $I_0$ is the modified Bessel function and

$$\begin{aligned}
a_1 &= a + 2R(R'^2_L + \bar{R}'^2_L - 2)C'_1,\\
b_1 &= b,\\
c'_1 &= c' + 2R(R'^2_L + \bar{R}'^2_L - 2)S'_1,\\
d_1 &= d,\\
e_1 &= 4R'^2_L\bar{R}'^2_L[(C'^2_2 + S'^2_2) + R^2(C'^2_{12} + S'^2_{12} + C'^2_{\bar{1}2} + S'^2_{\bar{1}2})],\\
A_1 &= 8RR'^2_L\bar{R}'^2_L[C'_2(C'_{12} + C'_{\bar{1}2}) + S'_2(S'_{12} + S'_{\bar{1}2})],\\
B_1 &= 8R^2R'^2_L\bar{R}'^2_L[C'_{12}C'_{\bar{1}2} + S'_{12}S'_{\bar{1}2}],\\
C'' &= 8RR'^2_L\bar{R}'^2_L[C'_2(S'_{12} - S'_{\bar{1}2}) - S'_2(C'_{12} - C'_{\bar{1}2})],\\
D_1 &= 8R^2R'^2_L\bar{R}'^2_L[S'_{12}C'_{\bar{1}2} - C'_{12}S'_{\bar{1}2}].
\end{aligned}\tag{60}$$

For the definition of $a$, $b$, $c'$, $d$, $e$, $A$, $B$, $C''$ and $D$, refer to (35) (remembering that $h$ and $k$ are now both even). The other symbols have already been defined in §§2 and 4.

## 6. The one-phase structure seminvariants in the tetragonal system for some primitive non-centrosymmetric space groups of type 2*P*20

As the theory for the one-phase structure seminvariants of the form $\varphi_{hk0}$ (when $h+k$ is even) for the tetragonal space group *P*4 was treated in detail in the earlier sections, only a brief summary of the results is given here for space groups like $P4_2$, *P*4*mm*, *P*4*bm*, *P*4*cc*, $P4_2cm$, $P4_2nm$, $P4_2bc$ in the tetragonal system.

### 6.1. *Summary of final results*

The conditional probability distribution function obtained for the one-phase structure seminvariants ($\varphi_{hk0}$ when $h+k$ is even) for some tetragonal space groups for the two cases (i) when $h$ and $k$ are both odd and (ii) when $h$ and $k$ are both even takes the general forms given by (61) and (62), respectively. The values of the parameter $P$ for difference space groups are given in Table 1 for the two cases, namely (i) when $h$ and $k$ are both odd and (ii) when $h$ and $k$ are both even.

Table 1. *Values of P for different space groups*

| Space groups | $P$ |  |
|---|---|---|
|  | $h$ and $k$ both odd | $h$ and $k$ both even |
| $P4$ | 1 | 1 |
| $P4mm$ | 1 | 1 |
| $P4bm$ | 1 | 1 |
| $P4cc$ | 1 | 1 |
| $P4_2$ | $(-1)^L$ | $(-1)^L$ |
| $P4_2cm$ | $(-1)^L$ | $(-1)^L$ |
| $P4_2nm$ | $-(-1)^L$ | $(-1)^L$ |
| $P4_2bc$ | $(-1)^L$ | $(-1)^L$ |

(i) *h and k are both odd.* The conditional probability distribution for the one-phase structure seminvariant $\varphi_{hk0}$ can now be written in a compact form as follows:

$$P(\Phi|R, R_L, \bar{R}_L) = (1/M)\exp\{a\cos\Phi + b\cos 2\Phi + c'\sin\Phi + d\sin 2\Phi\}I_0[e + A\cos\Phi + B\cos 2\Phi + C'\sin\Phi + D\sin 2\Phi]^{1/2}, \quad (61)$$

where $M$ is a suitable normalizing constant, $I_0$ is the modified Bessel function and

$$\begin{aligned}
a &= 4PR(R_L^2 + \bar{R}_L^2 - 2)C_1,\\
b &= R^2C,\\
c' &= 4PR(R_L^2 + \bar{R}_L^2 - 2)S_1,\\
d &= R^2S,\\
e &= 4R_L^2\bar{R}_L^2[(C_2^2 + S_2^2) + 4R^2(C_{12}^2 + S_{12}^2 + C_{\bar{1}2}^2 + S_{\bar{1}2}^2)],\\
A &= 16PR\bar{R}_L^2R_L^2[C_2(C_{12} + C_{\bar{1}2}) + S_2(S_{12} + S_{\bar{1}2})],\\
B &= 32R^2R_L^2\bar{R}_L^2[C_{12}C_{\bar{1}2} + S_{12}S_{\bar{1}2}],\\
C' &= 16PRR_L^2\bar{R}_L^2[C_2(S_{12} - S_{\bar{1}2}) - S_2(C_{12} - C_{\bar{1}2})],\\
D &= 32R^2R_L^2\bar{R}_L^2[S_{12}C_{\bar{1}2} - C_{12}S_{\bar{1}2}].
\end{aligned}$$

For the definition of $S$, $C$, $C_2$, $S_2$, $C_1$, $S_1$, $C_{12}$, $S_{12}$ $C_{\bar{1}2}$, $S_{\bar{1}2}$ refer to (12)–(15) and (20)–(25).

(ii) *h and k are both even.* The conditional probability distribution for the one-phase structure seminvariant $\varphi_{hk0}$ can be written in a compact form as follows.

$$\begin{aligned}
P(\Phi|R, R_L, \bar{R}_L, R'_L, \bar{R}'_L) = (1/M_1)&\exp\{a_1\cos\Phi + b_1\cos 2\Phi + c'_1\sin 2\Phi\\
&+ d_1\sin 2\Phi\}I_0[e + A\cos\Phi + B\cos 2\Phi + C'\sin\Phi\\
&+ D\sin 2\Phi]^{1/2}I_0[e_1 + A_1\cos\Phi + B_1\cos 2\Phi + C''\sin\Phi\\
&+ D_1\sin 2\Phi]^{1/2}, \qquad (62)
\end{aligned}$$

where $M_1$ is a suitable normalizing constant, $I_0$ is the modified Bessel function and

$$\begin{aligned}
a_1 &= 4PR(R_L^2 + \bar{R}_L^2 - 2)C_1 + 2R(R_L'^2 + \bar{R}_L'^2 - 2)C'_1,\\
b_1 &= R^2C,\\
c'_1 &= 4PR(R_L^2 + \bar{R}_L^2 - 2)S_1 + 2R(R_L'^2 + \bar{R}_L'^2 - 2)S'_1,\\
d_1 &= R^2S,\\
e &= 4R_L^2\bar{R}_L^2[(C_2^2 + S_2^2) + 4R^2(C_{12}^2 + S_{12}^2 + C_{\bar{1}2}^2 + S_{\bar{1}2}^2)],\\
A &= 16PRR_L^2\bar{R}_L^2[C_2(C_{12} + C_{\bar{1}2}) + S_2(S_{12} + S_{\bar{1}2})],\\
B &= 32R^2R_L^2\bar{R}_L^2[C_{12}C_{\bar{1}2} + S_{12}S_{\bar{1}2}],\\
C' &= 16PRR_L^2\bar{R}_L^2[C_2(S_{12} - S_{\bar{1}2}) - S_2(C_{12} - C_{\bar{1}2})],\\
D &= 32R^2R_L^2\bar{R}_L^2[S_{12}C_{\bar{1}2} - C_{12}S_{\bar{1}2}],\\
e_1 &= 4R_L'^2\bar{R}_L'^2[(C_2'^2 + S_2'^2) + R^2(C_{12}'^2 + S_{12}'^2 + C_{\bar{1}2}'^2 + S_{\bar{1}2}'^2)],\\
A_1 &= 8R^2R_L'^2\bar{R}_L'^2[C'_2(C'_{12} + C'_{\bar{1}2}) + S'_2(S'_{12} + S'_{\bar{1}2})],\\
B_1 &= 8R^2R_L'^2\bar{R}_L'^2[C'_{12}C'_{\bar{1}2} + S'_{12}S'_{\bar{1}2}],\\
C'' &= 8RR_L'^2\bar{R}_L'^2[C'_2(S'_{12} - S'_{\bar{1}2}) - S'_2(C'_{12} - C'_{\bar{1}2})],\\
D_1 &= 8R^2R_L'^2\bar{R}_L'^2[S'_{12}C'_{\bar{1}2} - C'_{12}S'_{\bar{1}2}].
\end{aligned}$$

For the definitions of $C'_2$, $S'_2$, $C'_1$, $S'_1$, $C'_{12}$, $S'_{12}$, $C'_{\bar{1}2}$ and $S'_{\bar{1}2}$, refer to (41), (42) and (45)–(50).

## APPENDIX *A*
## The joint probability distribution of the three structure factors $E_{hk0}$, $E_{-(h+k)/2,(h-k)/2,l}$ and $E_{-(h-k)/2,-(h+k)/2,\bar{l}}$ for the space group *P*4 when anomalous scatterers are present

In order to derive the conditional probability distribution (66), it is necessary first to obtain the joint probability distribution

$$P = P(R, R_L, \bar{R}_L; \Phi, \Phi_L, \bar{\Phi}_L) \qquad (63)$$

of the three magnitudes $|E_{hk0}|$, $|E_{-(h+k)/2,(h-k)/2,l}|$ and $|E_{-(h-k)/2,-(h+k)/2,\bar{l}}|$ and the phases $\varphi_{hk0}$, $\varphi_{-(h+k)/2,(h-k)/2,l}$ and $\varphi_{-(h-k)/2,-(h+k)/2,\bar{l}}$ [refer to (8) and (9), respectively] of the three structure factors whose magnitudes constitute the first neighborhood of the one-phase structure seminvariant $\varphi_{hk0}$. The atomic position vectors $\mathbf{r}_j$ and the integers $l$ are fixed: the ordered pair of integers $(h, k)$ is assumed to be the primitive random variable. Then, following the early work of Karle & Hauptman (1958), $P$ is given by the sixfold integral

$$\begin{aligned}
P = [RR_L\bar{R}_L/(2\pi)^6] &\int_{\rho_1,\rho_2,\rho_3=0}^{\infty}\int_{\theta_1,\theta_2,\theta_3=0}^{2\pi} \rho_1\rho_2\rho_3\\
&\times \exp\{-i[R\rho_1\cos(\theta_1 - \Phi) + R_L\rho_2\cos(\theta_2 - \Phi_L)\\
&+ \bar{R}_L\rho_3\cos(\theta_3 - \bar{\Phi}_L)]\}\\
&\times \prod_{j=1}^{N/4} q_j\, \mathrm{d}\rho_1\mathrm{d}\rho_2\mathrm{d}\rho_3\mathrm{d}\theta_1\mathrm{d}\theta_2\mathrm{d}\theta_3, \qquad (64)
\end{aligned}$$

$$\begin{aligned} q_j = \big\langle \exp\{ i|f_j|/\alpha^{1/2} \{ &\rho_1 \cos[\delta_j + 2\pi(hx_j + ky_j) - \theta_1] \\ &+ \rho_1 \cos[\delta_j + 2\pi(-hx_j - ky_j) - \theta_1] \\ &+ \rho_1 \cos[\delta_j + 2\pi(kx_j - hy_j) - \theta_1] \\ &+ \rho_1 \cos[\delta_j + 2\pi(-kx_j + hy_j) - \theta_1]\} \\ &\times (i|f_{jL}|/\alpha_L^{1/2}) [\rho_2 \cos\{\delta_{jL} + 2\pi[-(h+k)x_j/2 \\ &+ (h-k)y_j/2 + lz_j] - \theta_2\} \\ &+ \rho_2 \cos\{\delta_{jL} + 2\pi[(h+k)x_j/2 - (h-k)y_j/2 \\ &+ lz_j] - \theta_2\} + \rho_2 \cos\{\delta_{jL} + 2\pi[(h-k)x_j/2 \\ &+ (h+k)y_j/2 + lz_j] - \theta_2\} \\ &+ \rho_2 \cos\{\delta_{jL} + 2\pi[-(h-k)x_j/2 - (h+k)y_j/2 \\ &+ lz_j] - \theta_2\} + \rho_3 \cos\{\delta_{jL} + 2\pi[-(h-k)x_j/2 \\ &- (h+k)y_j/2 - lz_j] - \theta_3\} \\ &+ \rho_3 \cos\{\delta_{jL} + 2\pi[(h-k)x_j/2 + (h+k)y_j/2 \\ &- lz_j] - \theta_3\} + \rho_3 \cos\{\delta_{jL} + 2\pi[-(h+k)x_j/2 \\ &+ (h-k)y_j/2 - lz_j] - \theta_3\} \\ &+ \rho_3 \cos\{\delta_{jL} + 2\pi[(h+k)x_j/2 - (h-k)y_j/2 \\ &- lz_j] - \theta_3\}] \}\big\rangle_{h,k}. \end{aligned} \quad (65)$$

The mathematical formalism derived and streamlined in recent years to evaluate $q_j$, $\prod_{j=1}^{N/4} q_j$ and the sixfold integral (64) has been described elsewhere (*e.g.* Hauptman, 1975, 1982*a*,*b*). This work suitably modified to incorporate the space-group symmetries and to accommodate the anomalous scatterers finally yields, after lengthy analysis, the remarkably simple formula

$$\begin{aligned} P \simeq (RR_L\bar{R}_L/\pi^3) &\exp[-(R^2 + R_L^2 + \bar{R}_L^2)] \\ &\times \exp[XR^2 \cos(2\Phi + \varepsilon) + 4X_1R(R_L^2 + \bar{R}_L^2 - 2) \\ &\times \cos(\Phi + \varepsilon_1)] \exp[2X_2R_L\bar{R}_L \cos(\Phi_L + \bar{\Phi}_L + \varepsilon_z) \\ &+ 4X_{12}RR_L\bar{R}_L \cos(\Phi + \Phi_L + \bar{\Phi}_L + \varepsilon_{12}) \\ &+ 4X_{\bar{1}2}RR_L\bar{R}_L \cos(-\Phi + \Phi_L + \bar{\Phi}_L + \varepsilon_{\bar{1}2})], \end{aligned} \quad (66)$$

where the parameters $X$, $X_2$, $X_1$, $X_{12}$, $X_{\bar{1}2}$, $\varepsilon$, $\varepsilon_2$, $\varepsilon_1$, $\varepsilon_{12}$ and $\varepsilon_{\bar{1}2}$ are defined in (16)–(31).

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