and (*A*.4*a*) and (*A*.6*a*) by

$$\frac{\sum_q}{\sum_N}+\frac{\alpha_M}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}=\frac{\langle|E_{\mathbf{h}}|^2\rangle-\alpha_{\mathbf{h}}}{1-\alpha_{\mathbf{h}}}. \qquad (A.8b)$$

The average $\langle|E_{\mathbf{h}}|^2\rangle$ are made over subsets of reflexions with fixed α.

Equations (*A*.8) may be interpreted by observing that, while

$$\int_V \rho_p(\mathbf{r})\,d\mathbf{r}=\int_V \hat{\rho}_p(\mathbf{r})\,d\mathbf{r},$$

it holds that

$$\int_V \hat{\rho}_p^2(\mathbf{r})\,d\mathbf{r}\leq\int_V \rho_p^2(\mathbf{r})\,d\mathbf{r}.$$

The excess of scattering power of ρ_p with respect to $\hat{\rho}_p$ is completely transferred to the set of superstructure reflexions. Thus the averages $\langle|E'_{\mathbf{h}}|^2\rangle_{\text{sub}}$ and $\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}$ will lead, through (*A*.4) and (*A*.6), to

$$\left(\frac{\sum_{\hat{p}}}{\sum_N}-\frac{1}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)$$

and to

$$\left(\frac{\sum_{\hat{p}}}{\sum_N}+\frac{\alpha_M}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)$$

rather than to the identification of $\sum_{\hat{p}}/\sum_N$, $\sum_{p-\hat{p}}/\sum_N$, $\sum_q/\sum_N$. Thus, even if the various subsets of reflexions may be renormalized by using the corresponding experimental values of $\langle|F_{\mathbf{h}}|^2\rangle$, the information (so useful for estimating triplet reliability) on $\sum_{\hat{p}}$, $\sum_{p-\hat{p}}$ and $\sum_q$ is not accessible.

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Direct Methods and Structures Showing Superstructure Effects. IV. A New Approach for Phase Solution

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Abstract

The mathematical model proposed in paper III of this series [Cascarano, Giacovazzo & Luić (1988). *Acta Cryst.* A**44**, 176-183] for describing structures with superstructure effects has been used to derive probabilistic formulas for estimating triplet invariants. The formulas obtained proved sufficiently robust to be applied successfully to a wide range of structures with superstructure effects, in which deviations both of replacive and of displacive type from ideal pseudotranslational symmetry occur.

Symbols and abbreviations

Symbols and abbreviations are as in paper III (Cascarano, Giacovazzo & Luić, 1988) of this series. Reference will also be made to papers I (Cascarano, Giacovazzo & Luić, 1985) and II (Cascarano, Giacovazzo & Luić, 1987).

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1. Introduction

In paper III a general mathematical model was proposed which is able to describe a large variety of pseudotranslational symmetries. According to this model, the electron density distribution $\rho(\mathbf{r})$ was divided into two components, $\rho_p(\mathbf{r})$ and $\rho_q(\mathbf{r})$, the first of which approximately satisfies pseudotranslational symmetry. Statistical analysis of diffraction data gives in favourable cases approximate information on the scattering power of the average structure $\hat{\rho}_p(\mathbf{r})$, so that it seems more useful to study triplet invariants in terms of the electron distribution

$$\rho(\mathbf{r}) = \rho_{\hat{p}}(\mathbf{r}) + \rho_{p-\hat{p}}(\mathbf{r}) + \rho_q(\mathbf{r}) \qquad (1)$$

where $\rho_{\hat{p}}(\mathbf{r}) = \hat{\rho}_p(\mathbf{r})$ and $\rho_{p-\hat{p}}(\mathbf{r}) = \rho_p(\mathbf{r}) - \hat{\rho}_p(\mathbf{r})$.

It will be seen that probabilistic estimation of triplet invariants benefits from the Fourier transform of the pseudotranslational symmetry just as other methods (Main, 1976; Beurskens, Prick, Doesburg & Gould, 1979; Giacovazzo, 1983; Camalli, Giacovazzo & Spagna, 1985) take advantage of the Fourier transform of a molecular fragment when its orientation or position is known *a priori*. Though the Fourier transform of the pseudotranslational symmetry does not give information on single triplets but only on classes of triplets, its use as prior information in probabilistic approaches will prove quite useful.

An algebraic analysis of the information contained in the various classes of triplets is undertaken in § 2. Use is made there of the Cochran (1955) relationship relating triplets to the integral value of $\rho^3(\mathbf{r})$ [for a related analysis see Gramlich (1984)]. In § 3 the main probabilistic formulae for triplet invariants are given. Experimental data are given in § 4.

2. Algebraic considerations

From (1)

$$F_{\mathbf{h}} = (F_{\mathbf{h}})_{\hat{p}} + (F_{\mathbf{h}})_{p-\hat{p}} + (F_{\mathbf{h}})_q. \qquad (2)$$

If $\mathbf{h}$ corresponds to a substructure reflexion then (see the appendix of paper III)

$$F_{\mathbf{h}} = (F_{\mathbf{h}})_{\hat{p}} + (F_{\mathbf{h}})_q; \qquad (3)$$

if $\mathbf{h}$ corresponds to a superstructure reflexion then

$$F_{\mathbf{h}} = (F_{\mathbf{h}})_{p-\hat{p}} + (F_{\mathbf{h}})_q. \qquad (4)$$

A triplet of type 'sub-sub-sub' may be written

$$\begin{aligned} F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}} &= [(F_{\mathbf{h}})_{\hat{p}} + (F_{\mathbf{h}})_q][(F_{\mathbf{k}})_{\hat{p}} + (F_{\mathbf{k}})_q] \\ &\quad \times [(F_{\overline{\mathbf{h}+\mathbf{k}}})_{\hat{p}} + (F_{\overline{\mathbf{h}+\mathbf{k}}})_q] \\ &= (F_{\mathbf{h}})_{\hat{p}}(F_{\mathbf{k}})_{\hat{p}}(F_{\overline{\mathbf{h}+\mathbf{k}}})_{\hat{p}} + (F_{\mathbf{h}})_q(F_{\mathbf{k}})_q(F_{\overline{\mathbf{h}+\mathbf{k}}})_q \\ &\quad + \ldots + \text{mixed terms}. \end{aligned}$$

The average value of $F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}}$ may be obtained by observing that mixed terms are all expected to be dispersed around zero: this is due to the basic assumption that ρ_p (and therefore $\rho_{\hat{p}}$ and $\rho_{p-\hat{p}}$) is uncorrelated with ρ_q, so that

$$\int_V \rho_p^m(\mathbf{r})\rho_q^n(\mathbf{r})\,d\mathbf{r} = 0.$$

Then

$$\begin{aligned} \langle F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}}\rangle &= \langle (F_{\mathbf{h}})_{\hat{p}}(F_{\mathbf{k}})_{\hat{p}}(F_{\overline{\mathbf{h}+\mathbf{k}}})_{\hat{p}}\rangle \\ &\quad + \langle (F_{\mathbf{h}})_q(F_{\mathbf{k}})_q(F_{\overline{\mathbf{h}+\mathbf{k}}})_q\rangle. \end{aligned} \qquad (5)$$

The mean values on the right-hand side of (5) are both expected to be positive in accordance with Cochran's (1955) relationship

$$\langle F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}}\rangle = L\int_V \rho^3(\mathbf{r})\,d\mathbf{r},$$

where L is a suitable constant. Accordingly

$$\langle F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}}\rangle = L_{\hat{p}}\int_V \rho_{\hat{p}}^3(\mathbf{r})\,d\mathbf{r} + L_q\int_V \rho_q^3(\mathbf{r})\,d\mathbf{r}. \qquad (6)$$

No negative term occurs on the right-hand side of (6): it may be concluded that the presence of eventual non-ideal pseudotranslational symmetry does not affect the positivity of triplet relationships of type 'sub-sub-sub'.

Let us now look at a 'super-super-super' triplet: according to (4) and because of the same considerations invoked for 'sub-sub-sub' triplets we now obtain

$$\langle F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}}\rangle = L_q\left[\int_V \rho_{p-\hat{p}}^3(\mathbf{r})\,d\mathbf{r} + \int_V \rho_q^3(\mathbf{r})\,d\mathbf{r}\right]. \qquad (7)$$

While the second integral on the right-hand side of (7) is always positive, the first one may vanish (ideal pseudotranslation), or may be positive or negative according to circumstances.

If deviation from ideality is due only to small shifts of atoms from exact positions then $\int_V \rho_{p-\hat{p}}^3(\mathbf{r})\,d\mathbf{r}$ may in general be neglected with respect to $\int_V \rho_q^3(\mathbf{r})\,d\mathbf{r}$ [in which case $\rho_{p-\hat{p}}(\mathbf{r})$ is mostly constituted of pairs of nearly equivalent alternately positive and negative peaks: see Fig. 2 of paper III]: in this case 'super-super-super' triplets are always expected to have positive cosines. If $\int_V \rho_{p-\hat{p}}^3(\mathbf{r})\,d\mathbf{r}$ is negative and larger than $\int_V \rho_q^3(\mathbf{r})\,d\mathbf{r}$ (see Fig. 1 of paper III), then the expected value of a 'super-super-super' triplet is negative. Thus, in the absence of any prior information on the nature of $\rho_{p-\hat{p}}$, the use of 'super-super-super' triplets in direct procedures for solving crystal structures is sometimes contra-indicated.

For a 'super-super-sub' triplet one obtains

$$\begin{aligned} \langle F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}}\rangle &= \langle (F_{\mathbf{h}})_{p-\hat{p}}(F_{\mathbf{k}})_{p-\hat{p}}(F_{\overline{\mathbf{h}+\mathbf{k}}})_{\hat{p}}\rangle \\ &\quad + \langle (F_{\mathbf{h}})_q(F_{\mathbf{k}})_q(F_{\overline{\mathbf{h}+\mathbf{k}}})_q\rangle \\ &= L_m\int_V \rho_{p-\hat{p}}^2(\mathbf{r})\rho_{\hat{p}}(\mathbf{r})\,d\mathbf{r} + \int_V \rho_q^3(\mathbf{r})\,d\mathbf{r}. \end{aligned} \qquad (8)$$

For structures with ideal pseudotranslational symmetry the average positivity of the triplet is only secured by ρ_q, while a supplementary non-vanishing term arises in structures with non-ideal

pseudotranslational symmetry. Both the integrals on the right-hand side are never negative: thus the positivity of 'super-super-sub' triplets is not affected by non-ideal pseudotranslational symmetry.

For a 'sub-sub-super' triplet, the existence of which was first suggested in paper I, the mean value

$$\begin{aligned}\langle F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}}\rangle &= \langle (F_{\mathbf{h}})_q (F_{\mathbf{k}})_q (F_{\mathbf{h}+\mathbf{k}})_q\rangle \\ &\quad + \langle (F_{\mathbf{h}})_{\hat{p}} (F_{\mathbf{k}})_{\hat{p}} (F_{\overline{\mathbf{h}+\mathbf{k}}})_{p-\hat{p}}\rangle \\ &= L_q \int_V \rho_q^3(\mathbf{r})\,d\mathbf{r} \\ &\quad + L_n \int_V \rho_{\hat{p}}^2(\mathbf{r})\rho_{p-\hat{p}}(\mathbf{r})\,d\mathbf{r} \end{aligned} \tag{9}$$

is obtained. Even if $\rho_{\hat{p}}$ and $\rho_{p-\hat{p}}$ overlap significantly, the integral

$$\int_V \rho_{\hat{p}}^2(\mathbf{r})\rho_{p-\hat{p}}(\mathbf{r})\,d\mathbf{r}$$

is always expected to vanish, owing to the relation

$$\int_V \rho_{p-\hat{p}}(\mathbf{r})\,d\mathbf{r} = 0.$$

Thus

$$\langle F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}}\rangle = L_q \int_V \rho_q^3(\mathbf{r})\,d\mathbf{r}. \tag{10}$$

In conclusion, triplets of type 'sub-sub-super' are never expected to be negative.

3. Probabilistic estimation of triplet invariants

The method of joint probability distribution functions may be usefully applied to the electron density distribution (1) even if negative peaks occur in the component $\rho_{p-\hat{p}}(\mathbf{r})$. The mathematical model described in paper III will be used. For the sake of brevity only the final formulas are given here: the reader may justify them *via* the algebraic conclusions of § 2.

The conditional probability distribution of $\Phi = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}}$ given $|E_{\mathbf{h}}|$, $|E_{\mathbf{k}}|$, $|E_{\mathbf{h}-\mathbf{k}}|$ is a von Mises distribution of type

$$\begin{aligned} P(\Phi) &\simeq \{2\pi I_0[G(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})]\}^{-1} \\ &\quad \times \exp[G(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})\cos\Phi] \end{aligned} \tag{11}$$

where

$$G(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k}) \simeq \frac{2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|}{[N(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})]^{1/2}}. \tag{12}$$

The value of $N(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})$ for a given triplet is defined in the following way.

3(*a*) '*Sub-sub-sub*' *triplets*

Equation (III.4) may be replaced [see (6)] by

$$\begin{aligned}[N(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})]^{-1/2} &\simeq \frac{1}{S(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})} \\ &\quad \times \left\{\left(\frac{\beta}{m} n_1^2 n_2^2 n_3^2 \ldots\right)\frac{[\sum_3]_{\hat{p}}}{\sum_N^{3/2}} + \frac{[\sum_3]_q}{\sum_N^{3/2}}\right\}\end{aligned}$$

where

$$S(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k}) = [\langle|E'_{\mathbf{h}}|^2\rangle\langle|E'_{\mathbf{k}}|^2\rangle\langle|E'_{\mathbf{h}-\mathbf{k}}|^2\rangle]^{1/2},$$

$$[\sum_3]_{\hat{p}} = \sum_{j=1}^{\hat{p}} \hat{f}_j(\mathbf{h})\hat{f}_j(\mathbf{k})\hat{f}_j(\mathbf{h}-\mathbf{k}),$$

$$[\sum_3]_q = \sum_{j=p+1}^{N} f_j(\mathbf{h}) f_j(\mathbf{k}) f_j(\mathbf{h}-\mathbf{k})$$

where $\hat{p}$ is the number of peaks in $\rho_{\hat{p}}(\mathbf{r})$.

3(*b*) '*Super-super-super*' *triplets*

From (7),

$$\begin{aligned}[N(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})]^{-1/2} &\simeq \frac{1}{S(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})}\left\{\frac{[\sum_3]_{p-\hat{p}}}{\sum_N^{3/2}} + \frac{[\sum_3]_q}{\sum_N^{3/2}}\right\}\end{aligned}$$

where

$$[\sum_3]_{p-\hat{p}} = \sum_{j=1}^{p-\hat{p}} \delta f_j(\mathbf{h})\,\delta f_j(\mathbf{k})\,\delta f_j(\mathbf{h}-\mathbf{k}),$$

and summation goes over the $(p-\hat{p})$ peaks in $\rho_{p-\hat{p}}(\mathbf{r})$.

3(*c*) '*Super-super-sub*' *triplets*

From (8),

$$\begin{aligned}[N(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})]^{-1/2} &= \frac{1}{S(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})}\left\{\frac{[\sum_3]_{p-\hat{p},\hat{p}}}{\sum_N^{3/2}} + \frac{[\sum_3]_q}{\sum_N^{3/2}}\right\}\end{aligned}$$

where

$$[\sum_3]_{p-\hat{p},\hat{p}} = \sum_j |\Delta f_j(\mathbf{h})\,\Delta f_j(\mathbf{k})\,\Delta f_j(\mathbf{h}-\mathbf{k})|.$$

The summation goes over those peaks in $\rho_{p-\hat{p}}(\mathbf{r})$ whose squares at least partially overlap with peaks in $\rho_{\hat{p}}(\mathbf{r})$ [see (8)]. Δf_j is the scattering factor of the electron peak in common between $|\rho_{p-\hat{p}}(\mathbf{r})|$ and $\rho_{\hat{p}}(\mathbf{r})$.

3(*d*) '*Sub-sub-super*' *peaks*

From (10),

$$[N(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})]^{-1/2} \simeq \frac{1}{S(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})}\left\{\frac{[\sum_3]_q}{\sum_N^{3/2}}\right\}.$$

3(*e*) *The general formula*

The various results above may be described *via* the unique general expression:

$$\begin{aligned}[N(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})]^{-1/2} &\simeq \frac{1}{S(\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k})}\left\{\left(\frac{\beta}{m} n_1^2 n_2^2 n_3^2 \ldots\right)\frac{[\sum_3]_{\hat{p}}}{\sum_N^{3/2}}\right. \\ &\quad \left. + \frac{[\sum_3]_q}{\sum_N^{3/2}} + g_1\frac{[\sum_3]_{p-\hat{p}}}{\sum_N^{3/2}} + g_2\frac{[\sum_3]_{p-\hat{p},\hat{p}}}{\sum_N^{3/2}}\right\}\end{aligned} \tag{13}$$

where: (1) $g_1 = 0$, unless the triplet is of 'super-super-

super' type, in which case $g_1 = 1$; (2) $g_2 = 0$, unless the triplet is of 'super-super-sub' type, when $g_2 = 1$.

The use of (13) in direct procedures requires some supplementary observations:

(1) According to the model proposed in papers I and II, a fixed value of $N(\mathbf{h}, \mathbf{k}, \mathbf{h}-\mathbf{k})$ may be associated with a given type of triplet. The present model partially destroys this correspondence since $N(\mathbf{h}, \mathbf{k}, \mathbf{h}-\mathbf{k})$ is also a soft function of $(\sin\theta)/\lambda$.

(2) While $[\sum_3]_N/\sum_N^{3/2}$ may be statistically estimated from the chemical formula, this is in general impossible for $[\sum_3]_{\hat{p}}/\sum_N^{3/2}$, $[\sum_3]_{p-\hat{p}}/\sum_N^{3/2}, \ldots$, which therefore will be approximated in terms of the fractional scattering power.

(3) The term $[\sum_3]_{\hat{p}}/\sum_N^{3/2}$ will thus be replaced by

$$\left(\frac{\sum_{\hat{p}}}{\sum_N}\right)\frac{[\sigma_3]_N}{[\sigma_2]_N^{3/2}}$$

where $\sum_{\hat{p}}/\sum_N$ is estimated at $(\sin\theta)/\lambda = 0$ *via* the least-squares straight line representing $\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}$ as a function of $(\sin\theta)/\lambda$ [see § 3(*c*) of paper III]:

$$\frac{[\sum_3]_{\hat{p}}}{\sum_N^{3/2}} = (1 - \langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}})|_{\text{at } (\sin\theta)/\lambda = 0}\frac{[\sigma_3]_N}{[\sigma_2]_N^{3/2}}.$$

Correspondingly

$$\frac{[\sum_3]_q}{\sum_N^{3/2}} = (\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}})|_{\text{at } (\sin\theta)/\lambda = 0}\frac{[\sigma_3]_N}{[\sigma_2]_N^{3/2}}.$$

(4) $[\sum_3]_{p-\hat{p},\hat{p}}/\sum_N^{3/2}$ is always non-negative. Its value is expected to increase with $(\sin\theta)/\lambda$ if [see equation (*A*.6*a*) and § 3(*c*) of paper III]

$$\sum_{p-\hat{p}}/\sum_N = \frac{\alpha_M - 1}{\alpha_M}[\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}} - \langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}|_{\text{at } (\sin\theta)/\lambda = 0}]$$

is an increasing function of $(\sin\theta)/\lambda$. In the absence of supplementary information the following approximation will be used:

$$[\sum_3]_{p-\hat{p},\hat{p}}/\sum_N^{3/2} = \frac{\alpha_M - 1}{\alpha_M}[\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}} - \langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}|_{\text{at } (\sin\theta)/\lambda = 0}]\frac{[\sigma_3]_N}{[\sigma_2]_N^{3/2}}$$

and $\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}$ is calculated at the $(\sin\theta)/\lambda$ which is maximum among those corresponding to $\mathbf{h}$, $\mathbf{k}$ and $\mathbf{h}-\mathbf{k}$ vectors.

(5) $[\sum_3]_{p-\hat{p}}/\sum_N^{3/2}$ may be positive, zero or negative according to circumstances. Its absolute value is expected to increase with $(\sin\theta)/\lambda$ if $\sum_{p-\hat{p}}/\sum_N$ is an increasing function of $(\sin\theta)/\lambda$, and may be approximated by

$$\text{SPP} = \pm\left\{\frac{\alpha_M - 1}{\alpha_M}[\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}} - \langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}|_{\text{at } (\sin\theta)/\lambda = 0}]\right\}\frac{[\sigma_3]_N}{[\sigma_2]_N^{3/2}} \quad (14)$$

Table 1. *For the random structures S*1, *S*1*M and S*4 *the three types of triplets are ranked according to the reliability parameter G*

n is the number of triplets lying between G_i and G_{i+1}, % is the percentage of triplets with positive cosine.

	*S*1		*S*1*M*		*S*4	
'Super-super-super' reflexions						
G	*n*	%	*n*	%	*n*	%
2·0	42	100	364	93·4		
2·4	344	97·7	251	97·6	70	0·09
3·0	559	99·6	142	98·6	356	0·12
3·6	289	100	54	98·1	216	0·06
4·2	130	100	21	100	91	0·04
4·8	65	100	2	100	30	0·03
5·5	22	100	1	100	16	0·05
6·5	8	100	1	100	4	0·00
'Super-super-sub' reflexions						
G	*n*	%	*n*	%	*n*	%
1·2	999	81·4	1283	88	4	100
1·6	1342	87·2	1267	90·8	1185	99·7
2·0	410	94·4	397	95·5	1393	99·9
2·4	82	97·6	106	98·1	587	100
3·0	10	100	30	100	273	100
3·6			3	100	57	100
4·2			3	100	9	100
4·8					7	100
'Sub-sub-sub' reflexions						
G	*n*	%	*n*	%	*n*	%
2·4	5	100	1	100		
3·0	242	100	38	97·4	24	100
3·6	259	100	176	99·4	157	100
4·2	136	100	211	100	168	100
4·8	50	100	153	100	132	100
5·5	15	100	103	100	86	100
6·5	8	100	82	100	52	100
9·0	1	100	30	100	21	100

where the sign remains uncertain. The assumption $[\sum_3]_{p-\hat{p}}/\sum_N^{3/2} = 0$ may be maximally non-committal in the absence of any supplementary information.

In order to check the above conclusions under well established conditions the random structures *S*1 (perfect pseudotranslational symmetry), *S*1*M* (displacive deviations from ideal pseudotranslational symmetry) and *S*4 (replacive deviations) described in paper III have been used. In Table 1 triplets of type 'super-super-super', 'super-super-sub' and 'sub-sub-sub' are ranked in order of the reliability parameter *G* for each structure. It may be observed that 'sub-sub-sub' are always well estimable.

Also 'super-super-sub' triplets are always expected to be positive, no matter whether displacive or replacive deviations from ideal pseudotranslational symmetry occur. By contrast, and in agreement with the theoretical conclusions in § 2, 'super-super-super' triplets are expected to be positive if ideal pseudotranslational symmetry or displacive deviations from it occur, while, in the case of replacive deviations, this kind of triplet is on the average negative rather than positive [in accordance with the large negative value of $\int_V \rho^3_{p-\hat{p}}(\mathbf{r})\,\mathbf{dr}$ for *S*4].

Table 2. *Freieslebenite: triplets of type 'super-super-super' are ranked according to G*

n is the number of triplets with reliability parameter larger than the corresponding *G*, % is the percentage of positive ones.

	Old procedure		New procedure	
G	*n*	%	*n*	%
0·4	1148	49·7	1328	55·2
0·6	1148	49·7	857	58·5
0·8	1145	49·6	456	60·5
1·0	1071	48·7	222	65·3
1·4	705	45·2	36	83·3
2·0	267	43·1	1	100
2·4	104	46·2	1	100
2·8	29	48·3		

4. Practical applications

The normalization procedure described in paper III and the probabilistic formulas described in § 3 of this paper have been implemented in the *SIR* program (Cascarano, Giacovazzo, Burla, Nunzi, Polidori, Camalli, Spagna & Viterbo, 1985). The procedure has been applied to the six test structures quoted in Table 2 of paper III: some references to results obtained by application of the procedure described in papers I and II is also made.

Freieslebenite

Remarkable displacive deviations from ideal pseudotranslation $\mathbf{u}=(\mathbf{a}/2+\mathbf{b}/3)$ occur in this interesting structure. Since **u** approximately relates Pb, Ag and Sb, replacive deviations are also relevant. There are non-negligible negative peaks in $\rho_{p-\hat{p}}$, while $\int_V \rho^3_{p-\hat{p}}(\mathbf{r})\,d\mathbf{r}$ is a small positive number. Thus 'super-super-super' triplets are expected to be positive on the average, but rather dispersed around 2π. This is confirmed in Table 2, where it is also shown that the new procedure ranks 'super-super-super' triplets markedly better than the old one. Triplets of type 'sub-sub-sub' and 'super-super-sub' are efficiently estimated both by the present and by the old procedure. Even if both procedures routinely solve the structure, the new one provides more precise structural parameters.

Mesolite

Both displacive and replacive deviations from ideality are associated with the vecor $\mathbf{u}=\mathbf{a}/3$. Replacive deviations are rather small: accordingly both the old and the new procedures easily solve the structure.

Ferri

Displacive deviations from $\mathbf{u}=(\mathbf{a}+\mathbf{b})/2$ are negligible, as well as replacive deviations (**u** mostly relates Fe atoms). All types of triplets are reliable: the structure is easily solved by both procedures.

Table 3. *Pocro: triplets of type 'super-super-super' are ranked according to G*

n is the number of triplets with reliability parameter larger than the corresponding *G*, % is the percentage of positive ones.

G	*n*	%
0·6	504	34·5
1·0	446	33·2
1·4	282	28·7
2·0	102	32·4
2·4	49	30·6
2·8	20	30·0
3·2	9	11·1

Fega

Small displacive deviations from $\mathbf{u}=\mathbf{c}/3$ occur. Since **u** approximately relates Ga-Ga-S atoms, some few negative peaks can be found in $\rho_{p-\hat{p}}$ which can however be neglected when compared with larger and numerous positive peaks in $\rho_{\hat{p}}$ and ρ_q. Thus 'super-super-super' triplets (377 triplets up to $G\simeq 8{\cdot}5$, all correct) and 'super-super-sub' triplets (811 triplets up to $G\simeq 4{\cdot}6$, the most reliable 650 correct) play an important role: by contrast only 166 'sub-sub-sub' triplets (up to $G\simeq 8{\cdot}5$, all correct) are available, which therefore play a secondary role in the phasing process. Trials by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) were unsuccessful. The structure was solved by the procedure described in papers I and II; the solution is also easily found by the present method.

Cimetidine

Pseudotranslational vector $\mathbf{u}=(\mathbf{a}+\mathbf{c})/2$ ideally relates S atoms. According to Kojić-Prodić, Ružić-Toroš, Bresciani-Pahor & Randaccio (1980), *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) gave only chicken-wire *E* maps. The structure was solved by using, as known phases, 13 reflexions phased on the basis of the S-atom coordinates.

The routine application of the present procedure easily provides solutions with all 18 non-hydrogen atoms of the molecule.

Pocro

In this remarkable structure the pseudotranslational vector $\mathbf{u}=(\mathbf{a}/6+\mathbf{c}/2)$ approximately relates three sequences of six atoms: Cr-Cr-Cr-Cr-Cr-Cr, Se-Se-Se-Se-Se-Se and Se-Se-nul-Se-Se-nul, where nul stands for 'absent atom'. Thus remarkable deviations from ideality both of displacive and of replacive type are present. Accordingly 'sub-sub-sub' and 'super-super-sub' triplets are accurately estimated by our formulas, while 'super-super-super' triplets are mostly negative (see Table 3). In spite of this unfavourable situation, seven of the eight symmetry-independent atoms are in the first ten peaks of

the E map with the highest figure of merit. Unexpectedly, the largest maximum corresponds to the K atom, which is shifted from the correct position by about 0·3 Å, and peaks 3, 8 and 9 are false.

Even if all the test structures are routinely solved by our program, the above results suggest a further modification. According to paper III deviations of replacive type cannot be foreseen by means of the statistical analysis of diffraction data (but forecasts can sometimes be made on the basis of the cell contents). Thus the default choice SPP = 0 for (14) may be adequate or inadequate according to circumstances. In order to allow the user to modify the default assumptions the term

$$\frac{[\sum_3]_q}{\sum_N^{3/2}} + g_1 \frac{[\sum_3]_{p-\hat{p}}}{\sum_N^{3/2}}$$

in (13) has been replaced by

$$\frac{[\sum_3]_q}{\sum_N^{3/2}} (1 + \text{coeff.}\ g_1).$$

In default conditions coeff. = 0: then assumption SPP = 0 is confirmed; coeff. = −1 eliminates 'super-super-super' triplets from the phasing procedure, coeff. = +1 corresponds to the largest confidence in 'super-super-super' triplets. Which choice is best is unpredictable: for example, the program is not able to fix the origin for Freieslebenite if coeff. = −1, while the same choice for Pocro leads to a very good E map (that with largest figure of merit) whose first seven peaks correspond to correct Se and Cr atomic positions, and whose peak number 11 provides K atomic positions.

5. Concluding remarks

The probabilistic theory described in this paper and in paper III seems to be sufficiently robust to be applied successfully to direct solution of a large variety of structures showing superstructure effects. Even if it is not always possible, from the statistical analysis of diffraction data, accurately to estimate the various parameters of real pseudotranslational symmetries, the information content to be exploited is so large as to make very easy the solution of crystal structures which would otherwise be rather difficult by traditional methods. The implementation of the theory in *SIR* has been made in such a way that a solution may be obtained quite automatically without user intervention (the only directive strictly needed is PSEUDO, which starts the procedure).

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Thermal Phonons in the Modified Two-Beam Description of Diffraction near a Three-Beam Point

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Abstract

The influence of thermal phonons on the dynamical diffraction **0H** near a third reciprocal-lattice point **L**, in an otherwise perfect crystal, is investigated theoretically. It is shown that in the first-order modified two-beam description [Juretschke (1984). *Acta Cryst.* A40, 379-389] all effects due to phonon transitions are governed by the usual Bessel functions, but only of arguments involving **H**. With this proviso, the first-order modified two-beam description of diffraction near **L** incorporates phonon coupling entirely in the standard manner of the strict two-beam case. Therefore typical phonon influences, such as the Debye-Waller factor or thermal diffuse scattering, can be discussed directly in the neighborhood of n-beam diffraction merely by using the modified parameters, *i.e.* structure factors, absorption coefficients *etc.* in a traditional two-beam formulation. Some additional implications of this result about the effect of other deviations from crystal perfection on the modified two-beam description are also pointed out.

Introduction

The first-order dynamical theory of the modified two-beam description of diffraction near a three-beam point, developed for perfect crystals (Juretschke, 1982, 1984; Høier & Marthinsen, 1983; Chang, 1984), has satisfactorily reproduced a variety of experimental data involving three-beam and higher interactions (Juretschke, 1984, 1986*a*; Juretschke & Wagenfeld, 1986). Such agreement suggests that the degree of crystal perfection does not crucially affect the main predictions of the theory, but it remains to be shown explicitly why this is so. In this paper we study the influence on the modified two-beam description of deviations from periodicity induced by thermal atomic motions. This mainly requires rederiving the basic equations of the modified two-beam approach in the presence of phonons, and then inspecting these equations for their predictions, specifically with respect to the dispersion surface, the Debye-Waller factor and thermal diffuse scattering.

It was originally expected that at finite temperature each structure factor entering into the theory would carry its own Debye-Waller factor. However, as shown below, this is not the case. Even though the modified two-beam formulation involves the structure factors of all coupled reciprocal-lattice points, temperature effects are governed entirely by the Debye-Waller factor of the primary interaction.

These results, correct in the asymptotic regime, of course also bear on the more general three-beam case at finite temperatures, a configuration for which the effect of phonon coupling apparently has not been worked out explicitly.

General formulation

In a three-beam interaction we describe propagation by the three propagation vectors $\mathbf{K}_0$, $\mathbf{K}_H$, and $\mathbf{K}_L$. If the primary diffraction is chosen to be *via* **H**, and the additional coupling occurs *via* **L**, then the usual two-beam phase matching now requires two conditions:

$$\mathbf{K}_H = \mathbf{K}_0 + \mathbf{H}; \quad \mathbf{K}_L = \mathbf{K}_0 + \mathbf{L}. \tag{1}$$

Maxwell's equations lead to six scalar equations for the field amplitudes, usually decomposed into the two principal polarizations σ and π with respect to the plane of incidence

$$(E_0^\sigma, E_H^\sigma; E_0^\pi, E_H^\pi; E_L^\sigma, E_L^\pi). \tag{2}$$

These equations involve the structure factors F_H, F_L and F_{L-H}, and the deviations ξ_i of the propagation vectors from their average value within the crystal

$$\xi_i = (\mathbf{K}_i \cdot \mathbf{K}_i)^{1/2} - k(1 - \tfrac{1}{2}\Gamma F_0), \quad i = \mathbf{0}, \mathbf{H}, \mathbf{L}, \tag{3}$$

where $k = \omega/c$, $\Gamma = e^2/(\varepsilon_0 m\omega^2 v_{\text{cell}})$.

The modified two-beam description applies when $\xi_L \gg \xi_0, \xi_H$, *i.e.* when **L** is still far from the Ewald sphere. In that case ξ_L is a known parameter (proportional to the distance of **L** from the Ewald sphere) and the two fields E_L^σ, E_L^π can be expressed in terms of the other four fields of (2), and ξ_L. The remaining four equations can then be recast into standard two-beam form, at least to terms including $1/\xi_L$ (Juretschke, 1984). In the notation of that paper, these equations are

$$\begin{aligned} 2\xi_0^\sigma E_0^\sigma + k\Gamma F_{H\bar{L}}^\sigma E_H^\sigma &= 0 \\ k\Gamma F_{HL}^\sigma E_0^\sigma + 2\xi_H^\sigma E_H^\sigma &= 0 \\ 2\xi_0^\pi E_0^\pi + k\Gamma F_{H\bar{L}}^\pi E_H^\pi &= 0 \\ k\Gamma F_{HL}^\pi E_0^\pi + 2\xi_H^\pi E_H^\pi &= 0, \end{aligned} \tag{4}$$

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