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The RED Extinction Model. II. Refinement of Extinction and Thermal Vibration Parameters for SrF_2 Crystals

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Abstract

The RED extinction model reported previously [Kulda (1987). *Acta Cryst.* A**43**, 167–173] was applied to several neutron diffraction data sets, some of them already used in the design of the Cooper & Rouse [*Acta Cryst.* (1971), A**27**, 622–628] empirical extinction formula and in the tests of the Becker & Coppens [*Acta Cryst.* (1974), A**30**, 129–147] formalism. The results of least-squares refinements fully confirm the expected gain in agreement due to an improved description of the coherent part of the wave interaction by the RED model, whose adequacy is further supported by the realistic values of the refined effective deformation gradient and mean free path between subsequent reflections. The RED-based harmonic thermal vibration parameters are systematically somewhat larger than those obtained within the Becker & Coppens formalism and follow more closely the expected quasi-harmonic temperature dependence. Significant differences are also found between the two models in terms of the derived room-temperature Debye–Waller parameters. The RED values $B_{Sr} = 0{\cdot}557\,(10) \times 10^{-2}$ and $B_F = 0{\cdot}830\,(10) \times 10^{-2}$ nm^2 agree better with the results of shell model calculations based on experimental phonon dispersion curves.

1. Introduction

In two recent articles (Kulda, 1987, 1988), hereafter papers *A* and *B*, respectively, we reported a new extinction formalism based on the RED (random elastic deformation) model of a real imperfect crystal. It was concluded that its main advantage should arise from direct application of the dynamical diffraction theory to the description of the coherent part of the wave interaction responsible for primary extinction and broadening of the reflection curve due to particle-size effects. Secondary extinction is treated by solving the energy transport equations for crystals of isotropic shape given by Becker & Coppens (1974*a*, 1975) – hereafter B&C.

The present paper deals with a demonstration of the practical use of the RED formalism in the least-squares refinement of extinction and thermal vibration parameters. For comparison of the performance of several extinction models we chose the neutron diffraction data on SrF_2 collected by Cooper & Rouse (1970, 1971). To these data the Cooper & Rouse (1970) extinction formula was tailored and, later on, they were employed by Becker & Coppens (1974*b*) and Cooper & Rouse (1976) for tests of the B&C formalism. For the following discussion of the influence of the extinction model on the refined thermal vibration parameter values we have added further data on SrF_2 published by Mair, Barnea, Cooper & Rouse (1974) which include results of measurement at elevated temperatures. For all these data the traditional mosaic models can be claimed to work satisfactorily. Best agreement is usually attained within the B&C formalism which will therefore be used in what follows for comparison with RED.

2. Method of data analysis

The refinement on all of the data sets was performed with the help of a purpose-written computer code, *THERM*, based on a Levenberg–Marquardt-type nonlinear least-squares algorithm [*e.g.* procedure *CURFIT* in the book by Bevington (1976)] using numerical calculation of derivatives. The quantity minimized was $\sum w_i(F_{oi}^2 - F_{ci}^2)^2$, F_o and F_c representing the observed and calculated structure factors, respectively. Individual data points were weighted by squared reciprocals of the estimated standard deviations published together with the data. Values of the thermal diffuse scattering correction were taken from the same source. The effects of thermal motion on the structure factors were represented by the Willis (1969) formalism employed in the paper of Mair *et al.* (1974) and both harmonic vibration parameters α_{Sr}, α_F and the anharmonic parameter β_F were refined. For evaluation of the extinction correction $y = y_s(x_{RED})$ within the RED approach we employed the analytical approximation (*A*16) [equation (16) of paper *A*] to the B&C solution for secondary extinction with a Gaussian angular distribution. Equation (*B*11) was used to calculate x_{RED} depending on the free parameters $\bar{t}$, R and c. In order to eliminate the influence of possible differences in the efficiency of various least-squares minimization algorithms in all cases we also used a refinement based on the B&C

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Table 1. *Results of refinement of data* (I)

Formalism	Becker & Coppens (1974*a*, 1975) Primary + type I Lorentzian secondary				RED			
λ (nm)	0·0746	0·0865	0·1077	All	0·0746	0·0865	0·1077	All
α_{Sr} (10^{-17} J nm^{-2})	5·34 (13)	5·60 (6)	5·60 (6)	5·66 (4)	5·85 (15)	5·50 (8)	5·92 (8)	5·61 (3)
α_F (10^{-17} J nm^{-2})	3·99 (6)	3·88 (3)	3·90 (2)	3·87 (2)	4·39 (7)	3·86 (5)	4·05 (4)	3·92 (2)
$-\beta_F$ (10^{-16} J nm^{-3})	6 (2)	4·3 (3)	4·7 (7)	4·6 (5)	7 (2)	4·4 (10)	4·5 (8)	4·5 (5)
r (μm)	18 (1)	12·3 (7)	13·0 (4)	13·3 (3)	-	-	-	-
$g \times 10^{-3}$	17·6 (4)	22·8 (3)	23·0 (2)	21·8 (2)	-	-	-	-
$\bar{t}$ (mm)	-	-	-	-	0·326 (7)	0·310 (10)	0·251 (4)	0·255 (2)
R (m)	-	-	-	-	5·04 (12)	3·43 (13)	3·03 (6)	2·94 (2)
c	-	-	-	-	0·5	0·633	0·549	0·576
y^{min}	0·253	0·206	0·146	0·150	0·279	0·225	0·176	0·178
y_P^{min}	0·750	0·824	0·736	0·728	0·753	0·669	0·612	0·615
R_1 (%)	1·28	1·41	0·77	1·40	1·21	0·98	0·62	1·19
R_{2w} (%)	3·25	3·46	1·97	2·81	3·15	3·04	1·50	2·56
S	4·7	13·5	13·0	12·2	4·5	12·0	10·0	11·2

Table 2. *Results of refinement of data* (II)

Formalism	Becker & Coppens (1974*a*, 1975) Primary + type I Lorentzian secondary				RED			
T (K)	293	401	443	773	293	401	443	773
α_{Sr} (10^{-17} J nm^{-2})	4·94 (5)	5·44 (4)	5·65 (3)	5·10 (2)	5·71 (6)	5·82 (7)	5·75 (3)	5·21 (2)
α_F (10^{-17} J nm^{-2})	3·93 (3)	3·80 (2)	3·94 (2)	3·57 (1)	3·81 (2)	4·07 (3)	4·04 (2)	3·62 (1)
$-\beta_F$ (10^{-16} J nm^{-3})	4 (1)	3·1 (6)	3·7 (4)	3·6 (2)	3·4 (10)	3·8 (7)	3·7 (3)	3·7 (1)
r (μm)	12·6 (8)	17·4 (6)	18·2 (4)	15·1(6)	-	-	-	-
$g \times 10^{-3}$	18·4 (3)	20·5 (3)	19·2 (2)	17·6 (2)	-	-	-	-
$\bar{t}$ (mm)	-	-	-	-	0·299 (6)	0·232 (5)	0·226 (2)	0·293 (3)
R (m)	-	-	-	-	2·63 (5)	2·90 (7)	2·77 (2)	3·21 (3)
c	-	-	-	-	0·5	0·425	0·504	0·472
y^{min}	0·246	0·233	0·241	0·328	0·285	0·271	0·272	0·362
y_P^{min}	0·857	0·684	0·671	0·753	0·701	0·658	0·682	0·760
R_1 (%)	0·90	0·69	0·64	1·16	0·85	0·60	0·55	0·86
R_{2w} (%)	2·38	2·06	1·74	1·91	2·18	1·45	1·35	1·25
S	4·7	15·1	12·6	11·11	4·3	11·0	10·0	7·4

formalism. The general formula $y = y_p(x_p)y_s(y_p x_s)$ of Becker & Coppens (1975) with Lorentzian angular distribution and y_s corresponding to either type I or mixed-type secondary extinction appeared most suitable in all cases. In most of the measurements samples of isotropic shape - spheres, cylinders with the axis perpendicular to the plane of incidence - were used, the only exception being the data (III) (*cf.* next section). Here again a constant beam path in the sample was assumed, corresponding to a cylinder of equal volume and height, which proved a reasonable approximation. For the assessment of the goodness of fit the S value was calculated,

$$S = \left[\sum_j w_j(F_{oj} - F_{cj})^2/(N_o - N_v)\right]^{1/2}, \qquad (1)$$

where N_o and N_v are the numbers of data points and free parameters, respectively, as well as the agreement factors

$$R_i = \sum_j |F_{oj}^i - |F_{cj}|^i \Big/ \sum_j F_{oj}^i, \qquad (2)$$

$$R_{iw} = \left[\sum_j w_j(F_{oj}^i - |F_{cj}|^i)^2 \Big/ \sum_j w_j F_{oj}^{2i}\right]^{1/2}, \quad i = 1, 2. \qquad (3)$$

R_{2w} is pertinent to eventual significance tests (Hamilton, 1965) of the refined parameter values.

3. Results of refinement

Eleven data sets originating from three neutron diffraction experiments were reanalysed: (I) data obtained by Cooper & Rouse (1970, 1971) at room temperature, 293 K, on a spherical crystal of diameter 3 mm with three different wavelengths in the range 0·0746–0·1077 nm; (II) room-temperature data of Cooper & Rouse (1971) and data of Mair, Barnea, Cooper & Rouse (1974) collected at three elevated temperatures, 401–773 K, on a cylinder ∅3 × 8 mm with neutron wavelength 1·071 nm; (III) data obtained by Mair *et al.* (1974) at four temperatures in the range 295–893 K on a cube-shaped crystal of side 4 mm with neutron wavelength 0·0979 nm. For all calculations the previous value of the lattice parameter $a_{SrF_2} = 5{\cdot}794$ Å and the actual scattering lengths $b_{Sr} = 7{\cdot}02$ and $b_F = 5{\cdot}654$ fm (Koester, Rauch, Herkens & Schroeder, 1981) were employed. The results of refinements are displayed in Tables 1–3, which contain the resulting thermal and extinction parameters, the minimum primary (y_P^{min}) and total (y^{min}) extinction factors and the agreement factors R_1 and R_{2w} for each data set.

Table 3. *Results of refinement of data* (III)

Formalism	Becker & Coppens (1974*a*, 1975) Type I Lorentzian secondary				RED $C(c,\theta)=\cos\theta$			
T (K)	295	493	693	893	295	493	693	893
α_{Sr} (10^{-17} J nm^{-2})	4·82 (11)	5·52 (8)	5·54 (6)	5·14 (7)	5·88 (11)	5·77 (8)	5·53 (6)	5·25 (8)
α_F (10^{-17} J nm^{-2})	3·30 (6)	3·62 (5)	3·55 (3)	3·43 (4)	3·92 (6)	3·92 (4)	3·64 (3)	3·50 (5)
$-\beta_F$ (10^{-16} J nm^{-3})	1 (2)	2·9 (5)	3·9 (5)	4·3 (4)	2 (2)	3·6 (9)	4·1 (5)	4·5 (5)
$g\times10^{-3}$	3·45 (7)	2·83 (6)	2·26 (5)	2·51 (7)	-	-	-	-
$\bar{t}$ (mm)	-	-	-	-	1·02 (1)	1·12 (2)	1·27 (2)	0·62 (2)
R (m)	-	-	-	-	4·53 (7)	4·64 (9)	4·58 (11)	1·66 (6)
y^{min}	0·317	0·361	0·416	0·411	0·346	0·370	0·413	0·427
y_P^{min}	1	1	1	1	0·648	0·684	0·767	0·931
R_1 (%)	2·08	2·24	2·06	3·29	1·42	1·99	2·11	3·38
R_{2w} (%)	4·30	4·06	3·50	4·90	3·05	3·40	3·07	4·93
S	10·9	9·1	7·2	9·3	7·8	7·7	6·4	9·5

Our reanalyses of data (I) within the B&C formalism using the type I secondary extinction model with Lorentzian angular distribution reproduced quite closely the original results of Becker & Coppens (1974*b*) and Cooper & Rouse (1976), yet the primary extinction already proved significant at shorter wavelengths and was therefore allowed for in the final results. As far as data (II) and (III) are concerned, application of the B&C formalism noticeably improved the R factors in comparison with the original treatments based on the Cooper & Rouse (data II) and Zachariasen (1967) (data III) models. The agreement between observed and calculated structure factors within the RED formalism is in all but one case better than achieved with the B&C models. Because of the presence of primary extinction the RED free parameters $\bar{t}$ and R were jointly significant at a 1% confidence level or better for all data sets, while c could be omitted from the refinement for complete data (III) and for two other data sets.

4. Discussion on extinction in SrF_2

First let us test the validity of the initial assumptions of the RED model for the refined parameters $\bar{t}$, R, c given in Tables 1-3. The primary extinction correction within RED rests on the validity of the asymptotic formula for reflection probability [equations (*A*4), (*A*5)] when the variation range of the dimensionless Bragg-angle deviation Y exceeds the interval $\langle -1, 1\rangle$. The angular widths $w_G=(F_G/\Omega)d_G^2\tan\theta$ corresponding to $\Delta Y=2$ for some selected reflections and temperatures, displayed in Table 4, range from 0·005″ arc for the weakest reflections to approximately 1″ for the strongest one, 220. Here we obtain from (*B*6) for typical values $R=2$ m and $c=0{\cdot}5$ a maximum distance

$$\Delta s_0=\Delta s_G=w_G R/C(c,\theta)=15\ \mu\text{m},$$

which has to be smaller than the mean beam path in a single domain $\bar{l}$. The latter is not directly represented by the refined parameters, we only know that its magnitude is unimportant, as long as it is much smaller than $\bar{t}$, so that the original binomial distribution can be replaced by the Gaussian approximation (*A*9). For our data the refined magnitude of $\bar{t}$ always exceeds 0·1 mm and is therefore consistent with domain diameters of the order of 10 μm which satisfy the above questioned assumption for the strongest reflections. An equally important fact is that the $\bar{t}$ is in all cases about one order of magnitude smaller than the sample dimensions so that the application of the energy transport equations, assuming many rescattering events along the beam path, is justified – at least approximately.

Table 4. *Dynamical reflection widths w_G and extinction distances Δ_G [equation (B7)] of selected* SrF_2 *reflections for neutron wavelength* 0·0979 nm

T (K)	293	493	693	893
w_{220} (″)	0·98	0·95	0·92	0·88
w_{355} (″)	0·14	0·12	0·10	0·08
w_{046} (″)	0·07	0·05	0·02	0·005
Δ_{220} (μm)	32	33	34	35
Δ_{355} (μm)	165	197	237	296
Δ_{046} (μm)	342	507	1090	4400

Another question concerns the extent to which the RED model may correspond to physical reality. The parameter c falls mostly into the range 0–0·5, indicating, according to the definition of $C(c,\theta)$ [equation (*B*1)], that misorientation predominates in the deformation as expected. A pure $\cos\theta$ dependence of the deformation gradient is, however, observed only for the data (III); for the rest the more general definition of $C(c,\theta)$ is necessary. The refined R values of 2–4 m imply, as we have deduced, Bragg-angle variation of approximately 1″ arc on distances about 10–20 μm. The presence of such distortions is frequently subject to X-ray topography studies and is quite typical for crystals of medium quality. Similarly, the values of the mean free path $\bar{t}$, if understood as a correlation distance between equally oriented parts of a deformed lattice in the vicinity of crystal defects, appear acceptable. For these reasons we may consider our $\bar{t}$, R, c values as realistic; nevertheless, a more detailed study of the correlation between the RED parameters and the particular defect structure remains desirable.

As far as the comparison of the behaviour of both models is concerned, mere inspection of Tables 1-3 reveals that the minimum extinction factors are somewhat larger for RED than for B&C and that for all but one data set better agreement (characterized by R_{2w}) is achieved within RED. The former effect is due to the new form of the primary extinction correction responsible for the saturation of the y^{-1} curves in Fig. *A*3. As expected there exist two sources of improvement of the R factors. For data (I) the ratio R_{2w}^{BC}/R_{2w}^{RED} rises monotonically with wavelength as the role of primary extinction increases. A similar situation is met for data (III) where $R = 4$ m and $\bar{t} = 1$ mm indicate the presence of large domains of pure misorientation ($c = 0$) and primary extinction is very pronounced within RED. For the B&C model no meaningful value of the domain radius could be refined and the extinction was interpreted as pure type I secondary. The gain in agreement obtained with RED is highest at 295 K and drops with temperature as the structure factors decrease because of thermal motion. At 893 K, where primary extinction remains important for the 220 reflection only, both models yield about equal results.

For data (II), unlike the preceding case, the ratio R_{2w}^{BC}/R_{2w}^{RED} rises with temperature. Here, however, the RED results with $\bar{t}$ about 0·2 mm, a value comparable to those given for the extinction distance Δ_G in Table 4, signal the presence of the broadening of the reflection curve for a large number of reflections. This effect becomes even more important at elevated temperatures, where the Δ_G also rise. In this situation the efficiency of the B&C formalism is limited because the simultaneous refinement of the primary and mixed-type secondary extinction model is usually not feasible, as noted already by Becker & Coppens (1975). Moreover, the contribution of the particle size r enters the angular profile width as $\lambda/(r \sin 2\theta)$, which reaches maximum at low scattering angles. This result, derived on the basis of geometrical optics, is true only in the kinematical case. In practical situations the problem is usually posed in another way: to distinguish on the whole scale between weak reflections (often at large θ) behaving kinematically and having a broadened profile and the strong extinguished ones (often at small θ) with the angular profile dominated by mosaic spread (domain misorientation). For this purpose within RED, in analogy to the dynamical theory, the effective dimension of a diffracting crystal region is determined by comparison with the extinction distance Δ_G. The results obtained with RED for data (II) fully confirm the adequacy of this approach.

5. Discussion on temperature factors in SrF_2

An equally important criterion of adequacy as the goodness of fit considered in the preceding section is the quality of the physical information obtained from the least-squares refinement. The aim of the investigations from which the neutron diffraction data on SrF_2 originated was the determination of the thermal vibration parameters.

Table 5. *Comparison of the refined Debye-Waller parameters with the theoretical results of Elcombe* (1972); *all values correspond to room temperature* $T = 293$ K

	Theory	Experiment I	II	III	
B_{Sr} (10^{-2} nm^2)	0·538	0·566 (3)	0·559 (6)	0·543 (11)	RED
		0·564 (4)	0·647 (6)	0·663 (15)	B&C
B_F (10^{-2} nm^2)	0·808	0·826 (4)	0·845 (7)	0·820 (12)	RED
		0·837 (4)	0·822 (6)	0·927 (17)	B&C

As can be seen in Fig. 1, the choice of the extinction model affects the resulting values of the harmonic parameters α_{Sr}, α_F; obviously those derived with the help of RED, besides having less spread, are systematically higher than results based on the B&C formalism. The latter feature may be explained by a qualitative argument: in the course of refinement the Debye-Waller (DW) factors embedded in the theoretical structure factors increase the differences in intensity between strong (low *hkl*) and weak (high *hkl*) reflections; the extinction correction applied afterwards has an opposite tendency. Whenever within a certain model extinction is overestimated, larger values of the DW parameter B are required for compensation. As discussed in § 4 of paper *A* the introduction of the primary extinction factor in RED reduces somewhat the overall differences between the y values (*cf.* curves for $A = 0{\cdot}33$ in Fig. *A*3) so that lower DW parameters (higher α) may be refined for a given data set.

In Table 5 the experimentally determined room-temperature DW parameters may be compared with

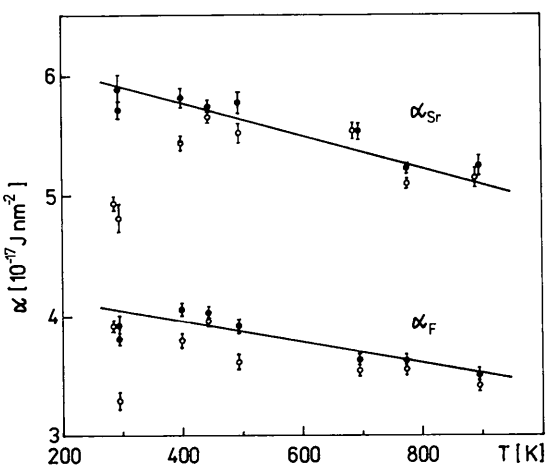

Fig. 1. Temperature dependence of the harmonic thermal vibration parameters α_{Sr} and α_F derived with the help of the RED (●) and B&C (○) extinction formalisms.

the theoretical results of Elcombe (1972) based on measured phonon dispersion curves and shell model calculations. The mean of the RED-based values deduced from data (I), (II) and (III) amounts to $0{\cdot}557\,(10)\times10^{2}$ and $0{\cdot}830\,(10)\times10^{2}$ nm^{2} for the strontium and fluorine atoms, respectively.

With increasing temperature the harmonic vibration parameters α_{Sr}, α_F are expected to fall approximately linearly (Mair *et al.*, 1974, and references therein). The values based on the B&C formalism displayed in Fig. 1 are scattered so much that the slope of the temperature dependence cannot be determined with sufficient accuracy. This obstacle was circumvented by Mair *et al.* (1974) by the application of a special weighting scheme giving less importance to severely extinguished reflections and the quasi-harmonic variation

$$\alpha_j = \alpha_{0j}[1-2(\chi\gamma_G - 10k_B\gamma_j/\alpha_j^2)(T-T_0)] \quad (4)$$

was inferred to fit their results reasonably. The value of $\chi\gamma_G = 1{\cdot}54\times10^{-4}$ K^{-1} (χ and γ_G represent the volume coefficient of expansion and the Grüneisen parameter, respectively) obtained by linear regression was, however, about twice as large as that obtained by Bailey & Yates (1967) from thermal expansion measurements. A weighted linear regression applied to the RED results for α_{Sr} and α_F displayed in Fig. 1 yields

$$\alpha_{Sr} = 6{\cdot}31\,(5) - 1{\cdot}37\,(7)\times10^{-3}T,$$
$$\alpha_F = 4{\cdot}31\,(3) - 0{\cdot}89\,(4)\times10^{-3}T.$$

When interpreted in terms of (4) these dependences lead to $(\chi\gamma_G - 10k_B\gamma_j/\alpha_j^2)$ equal to $1{\cdot}09\,(7)\times10^{-4}$ and $1{\cdot}03\,(5)\times10^{-4}$ K^{-1} for the Sr and F atoms, respectively. These new results lie much nearer to that of Bailey & Yates (1967), leaving less space for the eventual anharmonic contribution.

6. Concluding remarks

The RED extinction formalism reported in papers *A* and *B* was applied to 11 neutron diffraction data sets collected on various SrF_2 crystals. In comparison with the B&C results improved agreement between the observed and the calculated intensities was achieved whenever primary extinction or particle-size effects became important. In the remaining limiting case – pure type I secondary extinction – the two models are equivalent. The RED was found to yield systematically somewhat larger values of the harmonic thermal vibration parameters, following more closely the expected linear quasi-harmonic temperature dependence.

The results obtained support the adequacy of the RED approach with its emphasis on the deformed lattice domains and their stochastic interdependence. The principal advantage of the RED model consists of the realistic representation of the coherent part of the wave interaction in the crystal. This makes its application especially promising in neutron diffraction studies including time-of-flight experiments where extinction effects often become severe. Further extensions of this formalism towards anisotropic extinction and anomalous absorption are planned.

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A Centrosymmetrical Formula for Triplet Invariants in Dispersive Structures

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Abstract

While probabilistic formulae estimating triplet invariants in non-centrosymmetric dispersive structures are available, equivalent distributions in centrosymmetric dispersive structures are completely unknown. Filling this gap is the main aim of this paper. Some recipes for the use of centrosymmetrical triplets in phasing procedures are also given.

Notation

N number of atoms in the cell.

$f = f' + if''$ general expression for the atomic scattering factor.

$F_{\mathbf{h}} = A_{\mathbf{h}} + iB_{\mathbf{h}} = |F_{\mathbf{h}}| e^{i\varphi_{\mathbf{h}}}$ structure factor with index $\mathbf{h}$: $|F_{\mathbf{h}}|$ is its modulus, $\varphi_{\mathbf{h}}$ its phase.

1. Introduction

Probabilistic treatment of the anomalous-dispersion effect in phasing procedures [see Srinivasan & Parthasarathy (1976) and literature there quoted] is more important in non-centrosymmetric than in centrosymmetric space groups. Accordingly approaches estimating two-phase and three-phase structure invariants are always described in $P1$ (Heinerman, Krabbendam, Kroon & Spek, 1978; Hauptman, 1982; Giacovazzo, 1983).

While in $P1$

$$A_{\mathbf{h}} = \sum_{j=1}^{N} (f_j' \cos 2\pi\mathbf{hr}_j - f_j'' \sin 2\pi\mathbf{hr}_j)$$

$$B_{\mathbf{h}} = \sum_{j=1}^{N} (f_j' \sin 2\pi\mathbf{hr}_j + f_j'' \cos 2\pi\mathbf{hr}_j),$$

in $P\bar{1}$

$$A_{\mathbf{h}} = 2 \sum_{j=1}^{N/2} f_j' \cos 2\pi\mathbf{hr}_j$$

$$B_{\mathbf{h}} = 2 \sum_{j=1}^{N/2} f_j'' \cos 2\pi\mathbf{hr}_j,$$

so that $F_{\mathbf{h}} = F_{-\mathbf{h}}$ always. It may therefore be expected that probabilistic formulae for centrosymmetric space groups will be formally quite different from the corresponding non-centrosymmetric ones. Thus it is of non-negligible interest to derive probabilistic formulae for the estimation of the structure invariants in centrosymmetric space groups. Suitably generalized, these formulae may be used in non-centrosymmetric groups for the estimation of two-phase and three-phase structure invariants constituted by symmetry-restricted phases.

In centrosymmetric crystals the distribution $P(A_{\mathbf{h}}, B_{\mathbf{h}})$ when dispersive atoms are present has been determined by Wilson (1980); the conditional distribution $P(\Phi_{\mathbf{h}} | |F_{\mathbf{h}}|)$ for the two-phase invariant $\Phi_{\mathbf{h}} = \varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}}$ has been provided by Giacovazzo (1987). It is the aim of this paper to develop probabilistic formulae for triplet invariants in centrosymmetric space groups and suggest how they may be used in practical procedures for phase solution.

2. The joint probability distribution function $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h}+\mathbf{k}})$ in $P\bar{1}$

Since $F_{\mathbf{h}} = F_{-\mathbf{h}}$, probabilistic formulae for triplet invariants may be derived *via* the joint probability distribution $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h}+\mathbf{k}})$. Here we introduce the carrying variables u_i, v_i, $i = 1, 2, 3$ associated with A_i and B_i, $i = 1, 2, 3$ respectively, and calculate the characteristic function $C(u_1, u_2, u_3, v_1, v_2, v_3)$ retaining terms up to order $1/\sqrt{N}$. Its Fourier transform gives the required joint probability distribution function

$$\begin{aligned} P(A_1, A_2, A_3, B_1, B_2, B_3) &\simeq 1/(2\pi)^6 \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \exp[-i(u_1A_1 + u_2A_2 \\ &+ u_3A_3 + v_1B_1 + v_2B_2 + v_3B_3)] \\ &\times \exp\{-\tfrac{1}{2}[\alpha_{11}u_1^2 + \alpha_{22}u_2^2 + \alpha_{33}u_3^2 + \beta v_1^2 \\ &+ \beta v_2^2 + \beta v_3^2 + 2\alpha_{14}u_1v_1 + 2\alpha_{25}u_2v_2 + 2\alpha_{36}u_3v_3] \\ &- i[\alpha_{123}u_1u_2u_3 + \alpha_{126}u_1u_2v_3 + \alpha_{135}u_1v_2u_3 \\ &+ \alpha_{234}v_1u_2u_3 + \alpha_{156}u_1v_2v_3 + \alpha_{246}v_1u_2v_3 \\ &+ \alpha_{345}v_1v_2u_3 + \alpha_{456}v_1v_2v_3]\} \, du_1 \cdots dv_3, \end{aligned}$$

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