

the possible insufficiency of model approximations. In this respect, too, the results obtained seem to be encouraging; much work is needed to improve the potentials, if very accurate computations of elastic constants are wanted.

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Least-Squares Absolute-Structure Refinement. Practical Experience and Ancillary Calculations

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Abstract

The least-squares refinement of non-centrosymmetric crystal structures as inversion twins is presented. It is shown that the absolute-structure (twin) parameter x may be used to define the chirality or polarity of untwinned crystals. The method has been applied to 20 compounds. The least-squares refinement of the absolute-structure parameter is rapid and stable. The value of x generally falls within three e.s.d.'s of the physically meaningful range $0 \leq x \leq 1$ and the e.s.d.'s increase as f'' becomes smaller. New residual and goodness-of-fit values are defined to judge the efficiency of the method. The estimated standard deviation of x , taken with a pseudo Durbin-Watson d statistic, provides an excellent criterion for the reliability of the absolute-structure determination. Refinements on data sets including very accurately measured Friedel pairs of reflections have also been tested. The

determination of the free direction(s) of origin-free space groups and an efficient algorithm for the inversion of a crystal structure that refines to $x \approx 1$ are given in detail. The data and procedural structures necessary for an efficient computer implementation of absolute-structure refinement are also considered. The formulae giving the correction for the effects of anomalous dispersion on $|F_{\text{obs}}|$ from an inversion-twinned crystal are given. These corrected $|F_{\text{obs}}|$ are the ones to be used in an electron-density calculation. The correlation of residuals following least-squares refinement is quantified by using a pseudo Durbin-Watson d statistic. The causes of the correlation, its effect on the value of x and its e.s.d., and ways of avoiding the correlation are considered. It is shown that in using x it is more suitable to refine on $|F|^2$ than $|F|$. A weighting scheme is presented and tested that increases the sensitivity of a refinement to absolute structure.

Introduction

The technique of determining chirality or polarity of non-centrosymmetric crystal structures during least-squares refinement was suggested by Rogers (1981) as an alternative to practical and theoretical difficulties arising in the use of Hamilton's *R*-factor ratio test (Hamilton, 1965). In the Rogers technique a parameter η is defined that multiplies all of the imaginary anomalous dispersion factors f'' to give $\eta f''$. η is refined in the normal way by least squares. Jones (1984a) has presented some results of the practical application of the Rogers η refinement on real crystals. For a wide range of medium-to-strong anomalous scatterers, Jones shows that η refinement is an effective and robust method. However, his results are mostly limited to 'complete' data sets where all reflections and their antireflections have been measured, and to medium-to-strong anomalous scattering effects. Jones did not attempt the application to a limited set of very-high-accuracy intensity data of selected Friedel pairs, especially where the anomalous scattering is weak (Rabinovich & Hope, 1980).

From theoretical considerations and computer simulations, Flack (1983b) has shown some shortcomings in the Rogers η parameter, which might lead to a false least-squares minimum and unreliable estimated standard deviations. It is possible to overcome these deficiencies by refining an alternative parameter x , which describes the crystal as an inversion twin. $1-x$ and x are then respectively the fractions of the structure and its inverse in the macroscopic sample. The necessary structure-factor equation is given by

$$|F(h, k, l, x)|^2 = (1-x)|F(h, k, l)|^2 + x|F(-h, -k, -l)|^2. \quad (1)$$

The computer simulations showed that x both converges more rapidly than η and does not fall into false minima. Further, x , unlike η , is defined in terms of a physically realizable state of a macroscopic sample (*i.e.* an inversion twin) and any value $0 \leq x \leq 1$ has a ready interpretation.

The current work is arranged in the following way. Firstly, the practical application of the refinement of x to real-crystal data is presented. The first section uses routine data measurements, in most of which all Friedel pairs have been measured. Following this comes refinements using a routine data set coupled with high-accuracy measurements on selected Friedel-pair measurements taken from the literature. Afterwards, the algorithms of some ancillary calculations necessary when treating non-centrosymmetric crystal structures by means of the refinement of x are presented. These algorithms concern the generation of constraints in origin-free space groups, the inversion of a structure solution to make the chirality or polarity of the structure model correspond to that of

the crystal, the data structures and calculation techniques useful for an efficient implementation of absolute-structure refinement and the necessary correction to apply to $|F_{\text{obs}}|$ from an inversion-twinned crystal for the purposes of calculating electron density values. With these algorithms incorporated into a program system, the possibility of user error or oversight can be greatly reduced. The paper concludes with three sections concerning the incidence of correlated residuals, the choice of whether to refine on $|F|$ or $|F|^2$, and the derivation and testing of a weighting scheme to make refinement more sensitive to the absolute structure of a crystal. These three sections have consciously been grouped together as our current understanding of these problems is less well advanced than for the preceding sections. However, it is considered vital to draw attention to these issues so that further experimentation may take place.

It cannot be overemphasized at this point that the determination of absolute structure must be an integral part of the determination of any non-centrosymmetric crystal structure if one is to avoid biased atomic parameters (Cruickshank & McDonald, 1967). Some of the fundamental problems involved in dealing with physical properties and the chirality and polarity of crystals, such as the choice and sense of axes, have been very clearly exposed by Rogers (1975).

Jones (1984a) has suggested the use of the term 'absolute structure' to distinguish between the correct structure and its inverse. This term, which will be widely used in this paper, encompasses both chirality and polarity. x of (1) will be called the absolute-structure parameter. A further difficulty in terminology arises in the use of the words polar and polarity as applied to crystal structures. In this work, the definitions of polar direction, polar axes and polar point group are those given in *International Tables for Crystallography* (1983). The polarity of a crystal is determined by finding the sense of the polar directions by some means. There is a subset of polar point/space groups where the position of the origin may be freely chosen in at least one direction. These will be referred to as origin-free point/space groups. Note especially that this use is contrary to that of Waser (1974), Cruickshank & McDonald (1967) and Templeton (1982).

Refinements with routine data sets

In Tables 1 and 2 are presented the results of least-squares refinements using the parameter x for the non-centrosymmetric crystal structures measured in this laboratory over a period of approximately 18 months. The intensity measurements are from routine data collections made with Mo $K\alpha$ radiation at room temperature on a Philips PW1100 four-circle diffractometer. Parameters refined were the scale factor,

Table 1. *Least-squares absolute-structure refinement on some compounds*

Compounds are arranged in descending order of the largest f'' . Intensity measurements were performed with Mo $K\alpha$ at room temperature. If no restriction is indicated on an index for the hkl range it means that the index varied over the whole range of positive and negative values as limited by $\sin(\theta)/\lambda$. * means that antireflections were measured. $N\chi_o$ is calculated for Friedel pairs having $\chi_o > 2.0$ or when marked with ** for $\chi_o > 4.0$. The definition of the parameters is given in the text. The e.s.d. of x is given in parentheses.

References: CENZ, Cenizal & Parthé (1985); DEPDM, Depmeier (1985); BEDU, Bernardinelli, Dunand, Flack, Yvon, Giersch & Ohloff (1984); BEWG, Bernardinelli & Giersch (1985); HIJE and HIBO, Jefford, Bernardinelli, Boukouvalas & Higa (1985); BEDE, Berset, Depmeier, Boutellier & Schmid (1985); BEGE, Gérard, Lucken & Bernardinelli (1985); MEDE, Mendoza-Alvarez, Depmeier, Schmid & Yvon (1985b); MEAL, Mendoza-Alvarez, Depmeier, Schmid & Yvon (1985a); BEKU, Kündig, Perret & Bernardinelli (1985); DUFL, Dunand & Flack (1983); BERN, Bernardinelli & Flack (1985); BECH, Oppolzer, Chapuis & Bernardinelli (1984a); BEKE, Oppolzer, Kelly & Bernardinelli (1984); BEOP, Oppolzer, Chapuis & Bernardinelli (1984b); BEFL, Oppolzer, Dudfield & Bernardinelli (1985); HOVE, Hovestreydt (1984); BEGI, Bernardinelli & Giersch (1985).

Chemical formula	Space group	Reference	Max. $\sin \theta/\lambda$ \AA^{-1}	hkl range	$R(\%)$	N_{obs}	$N\chi_o$	Max χ_c	x
Zr ₃ Ir	I42m	CENZ	0.70	$0 \leq k \leq h, l^*$	6.0	451	40	4.7	0.05 (7)
Sr ₈ (Al ₁₂ O ₂₄)(WO ₄) ₂	I42m	DEPM	0.64	h, k, l^*	2.0	441	159**	16.8	0.54 (9)
C ₂₅ H ₃₅ O ₄ Br	P2 ₁ 2 ₁ 2 ₁	BEDU	0.53	$0 \leq h, k, l^*$	4.6	2519	321	21.6	0.012 (21)
C ₂₅ H ₃₅ O ₄ Br	P2 ₁ 2 ₁ 2 ₁	BEWG	0.53	$0 \leq h, k, l^*$	8.5	1828	137	36.4	-0.02 (3)
(C ₁₅ H ₂₀ O ₂ BrCl) ₂	P2 ₁ 2 ₁ 2 ₁	HIJE	0.53	$0 \leq h, k, l^*$	7.4	2460	239	18.7	0.06 (2)
C ₁₅ H ₂₀ OBrCl	P2 ₁	HIBO	0.62	$h; 0 \leq k, l^*$	3.8	1389	312	48.0	-0.01 (2)
Cu ₃ B ₇ O ₁₃ I	F43c	BEDE	0.57	$h, k; 0 \leq l$	1.4	110	16**	9.9	-0.03 (9)
C ₅ H ₇ O ₂ SbCl ₄	P2 ₁	BEGE	0.60	$h; 0 \leq k, l^*$	5.3	1700	296	31.2	-0.01 (8)
Zn ₃ B ₇ O ₁₃ Cl	R3c	MEDE	1.08	$0 \leq h, h+k, l$	5.1	1425	17**	13.2	0.09 (5)
Fe ₃ B ₇ O ₁₃ Cl	R3c	MEAL	1.08	$0 \leq h, h+k, l$	3.8	1432	17**	12.8	-0.01 (6)
C ₁₃ H ₁₂ O ₄ Cr	P2 ₁ 2 ₁ 2 ₁	BEKU	0.64	$0 \leq h, k, l^*$	3.3	2002	53	0.7	0.51 (4)
C ₇ B ₇ O ₁₃ Cl	F43c	DUFL	1.00	h, k, l^*	4.3	828	47	5.8	-0.01 (4)
C ₄ H ₅ O ₄ K	P2 ₁ 2 ₁ 2 ₁	BERN	0.70	$0 \leq h, k, l^*$	2.2	1392	157	11.0	-0.03 (6)
C ₂₅ H ₄₁ NO ₄ S	P2 ₁ 2 ₁ 2 ₁	BECH	0.51	$0 \leq h, k, l^*$	5.7	1732	55	4.0	0.05 (26)
C ₁₉ H ₂₄ O ₄ S	P2 ₁ 2 ₁ 2 ₁	BEKE	0.55	$0 \leq h, k, l^*$	5.5	1300	52	3.3	-0.39 (32)
C ₁₄ H ₂₁ NO ₃ S	P2 ₁ 2 ₁ 2 ₁	BEOP	0.55	$0 \leq h, k, l^*$	4.7	1131	66	5.2	0.10 (17)
C ₂₄ H ₄₅ NO ₂ S	P2 ₁ 2 ₁ 2 ₁	BEFL	0.51	$0 \leq h, k, l^*$	4.9	1957	61	1.5	0.13 (20)
MgNH ₄ PO ₄ ·6H ₂ O	Pmn2 ₁	HOVE	0.64	$0 \leq h, k; l^*$	2.9	1052	41	1.3	0.11 (17)
C ₁₆ H ₃₀ O ₂	P2 ₁ 2 ₁ 2 ₁	BEGI	0.55	$0 \leq h, k, l^*$	4.2	2030	23	0.3	-0.6 (2.0)

absolute-structure parameter x , atomic positional and displacement parameters, which usually were anisotropic for most atoms. Full-matrix least-squares refinement on $|F|$ undertaken by a local version of the XRAY76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used for almost all of the refinements. The x parameter converges in two cycles with one large step followed by a small adjustment even when $x \approx 0.5$. However, when the anomalous dispersion contribution is very small three or four cycles are required. It was never necessary to damp the refinement of x . The conventional R factor on $|F|$ is unweighted and calculated from the N_{obs} reflections. Tables 1 and 2 are arranged in descending order of the largest value of f'' and the quantities whose values are given therein are defined as follows:

$$\Delta_o = |F_{\text{obs}}(h, k, l)|^2 - |F_{\text{obs}}(-h, -k, -l)|^2,$$

$$\Delta_c = |F_{\text{calc}}(h, k, l)|^2 - |F_{\text{calc}}(-h, -k, -l)|^2,$$

$$\chi_o = |\Delta_o|/\sigma(\Delta_o), \quad \chi_a = |\Delta_o - \Delta_c|/\sigma(\Delta_o),$$

$$\chi_c = |\Delta_c|/\sigma(\Delta_o),$$

$$R\Delta = \sum |\Delta_o - \Delta_c|/\sum |\Delta_o|, \quad wR\Delta = \{\sum \chi_a^2/\sum \chi_o^2\}^{1/2}$$

$$S_o = \{\sum \chi_o^2/(N\chi_o - 1)\}^{1/2}, \quad S_a = \{\sum \chi_a^2/(N\chi_o - 1)\}^{1/2},$$

$$d'' = 2 \sum (\Delta_o - \Delta_c)^2 / \sum (|F_{\text{obs}}|^2 - |F_{\text{calc}}|^2)^2. \quad (2)$$

$N\chi_o$ is the number of Friedel pairs with $\chi_o > 2.0$ (or 4.0 when marked by **) that contribute to the sums

used to calculate the values in Table 2. All sums are taken over the $N\chi_o$ terms apart from the denominator of d'' , which has twice this number of terms. $R\Delta$ and $wR\Delta$ are unweighted and weighted R factors that apply to differences between Friedel opposites of the difference between observed and calculated squared structure amplitudes. S_o and S_a are goodness-of-fit values that apply to differences between Friedel opposites as-observed and observed-minus-calculated. $R\Delta$, $wR\Delta$, S_o , S_a and d'' (discussed below), taken with x and its e.s.d., are intended as sounder indicators of the fit of the refinement compared to the conventional R factors of the 'correct' and 'inverted' structures so convincingly criticized by Rogers (1981). As a further aid to understanding, histograms of Friedel-pair differences of three of the compounds of Tables 1 and 2 are presented in Fig. 1.

In all cases shown in Table 1, the value of x lies in the physically valid region $0 \leq x \leq 1$ within three e.s.d.'s. No constraint has been applied on x during the least-squares refinement. This observation confirms both the excellent behaviour of x refinement obtained in the computer simulations (Flack, 1983b) and the essential correctness of the imaginary anomalous dispersion factors used (*International Tables for X-ray Crystallography*, 1974). Apart from the compounds DEPM and BEKU all values of x lie within two or three e.s.d.'s of 0.0 since, where necessary, the atomic coordinate sets have been

inverted to make the crystal and model polarities identical. Where the absolute configuration of a molecule is known by chemical or other means, this agrees in all cases with that determined by absolute-structure refinement (BEDU, BEWG, BERN, BECH, BEKE, BEOP, BEFL). No attempt has been made to correlate either physical, chemical or morphological properties of the samples used in the diffraction studies of the achiral (but polar) crystals (*i.e.* CENZ, DEPM, BEDE, MEDE, MEAL, DUFL, HOVE). For DEPM and BEKU the value of x clearly indicates that the samples are inversion twins with approximately 50% of each component. The final compound BEGI contains only two oxygen for 16 carbon atoms. Measured as a routine data set with Mo $K\alpha$ radiation one would hardly expect to be able to distinguish the absolute structure. The results of the refinement, which did not diverge, amply confirm this suspicion.

As a general trend the e.s.d.'s on x increase as the f'' 's become smaller. The Friedel-pair $R\Delta$ factors and goodness-of-fit statistics given in Table 2 also show that the agreement becomes less good as the values of f'' diminish. Under these conditions one sees that the $R\Delta$ factors become large and that the reduction in the goodness-of-fit in going from S_o to S_d becomes smaller. Especially interesting is the case of the compounds DEPM and BEKU, which x refinement showed to be 50% inversion twins. The statistics contained in Table 2 measure differences between Friedel pairs and the extent to which these are taken into account by the structure model. Although the f'' 's are considerable for these compounds, the twinning will remove differences between Friedel pairs. One hence obtains high $R\Delta$ factors and no difference between S_o and S_d .

Similar conclusions can be drawn from the histograms shown in Fig. 1. The absolute structure of

crystal BERN has clearly been determined by x refinement and, as expected, the histogram of the observed-minus-calculated Friedel differences (χ_d) is narrower about the origin than that of the as-observed differences (χ_o). For the twinned crystal BEKU the two histograms overlap completely whereas for BEOP, with $x = 0.10$ (17), one sees only a slight thinning of the histogram compatible with the high e.s.d. of x . The histogram of the as-observed differences (χ_o) provides a valuable method of assessing the absence of a centre of symmetry in a crystal of unknown structure.

Refinements with selected Friedel-pair measurements

These refinements were carried out on the published data* of the compound 4,4'-dimethylchalcone ($C_{17}H_{16}O$) - hereafter DMC - whose crystal structure was determined by Rabinovich & Shakked (1974) and refined to an R value of 0.045. The molecule of DMC is achiral and crystallizes in the space group $P2_12_12_1$. Rabinovich & Hope (1980) have determined the

* Data generation of DMC.

The list of structure factors (Supplementary Publication No. SUP 30554) of DMC produced by Rabinovich & Shakked (1974) was kindly provided by the Executive Secretary of the International Union of Crystallography. The list includes three measured reflections (774, 775 and 776) outside the limiting $Cu K\alpha$ sphere. The e.s.d.'s or the weights of $|F_{obs}|$ are not given. E.s.d.'s were generated from a model consisting of a constant background and a stability contribution to the variance proportional to the square of the intensity. With weights equal to the inverse of the variance, the e.s.d.'s were adjusted to give an approximately flat distribution of weighted squared differences when analysed in terms of $\sin(\theta)/\lambda$ and $|F_{obs}|$. The generated e.s.d.'s are too large as judged by a goodness-of-fit of approximately 0.5.

The three sets of very accurate selected Friedel-pair measurements marked (a), (b) and (c) were taken from Rabinovich & Hope (1980). As the authors report only mean intensities, Bijvoet ratios and their e.s.d.'s, these had to be converted back to net intensity measurements (and their e.s.d.'s) by assuming that the e.s.d. of reflection and antireflection were identical. These three sets, each of 14 measurements, were combined separately with the (P) data set to give sets (Pa), (Pb) and (Pc). The assignment of scale factors was carried out as follows. In all cases the (P) reflections were assigned to one scale factor. For (a) and (b) in (Pa) and (Pb) the reflections 114 and $\bar{1}\bar{1}4$ were given a separate scale factor as were 122 and $\bar{1}\bar{2}2$ whilst the remaining ten measurements were put together in a fourth scale-factor group. For (c) in (Pc) each Friedel pair was assigned to a separate scale factor giving eight scales in all. This curious assignment of scale factors is necessary owing to the measurement conditions used by Rabinovich & Hope (1980) and the detailed information available in their paper. One further adjustment of the intensity data was necessary. The chirality of the crystal used to measure (P) need not be the same as those of (a), (b) and (c). In a refinement on (Pa), (Pb) or (Pc) one absolute-structure parameter should be assigned to the (P) set and another to the (a), (b) or (c) set. However, our program only allows for the refinement of one absolute-structure parameter. Under these conditions we inverted the Friedel measurements in (b) and (c), according to the absolute structure determined by Rabinovich & Hope (1980), so that the absolute structure of the (P), (a), (b) and (c) sets are all identical.

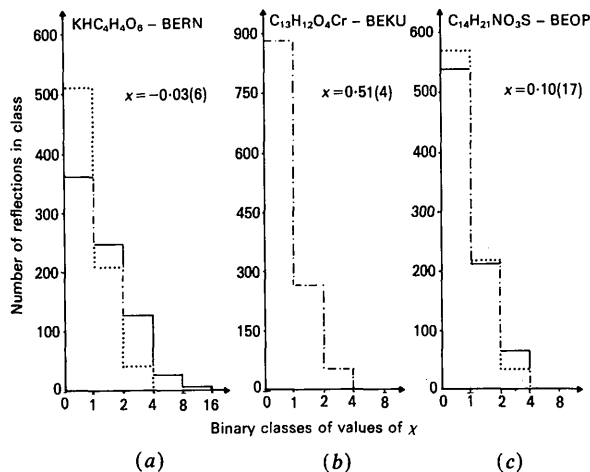


Fig. 1. Histograms from three compounds of Friedel-pair differences. Each histogram shows the number of reflections in the range of value of χ . Continuous line, $N\chi_o$; dotted line, $N\chi_d$; chain dotted line, overlapping lines.

Table 2. *Friedel-pair agreement factors for the compounds in Table 1*

Definition of the parameters is given in the text. The calculation of d'' of equation (2) was added into the program at a late stage and the value is not available for all compounds.

Reference	$R\Delta(\%)$	$wR\Delta(\%)$	S_o	S_d	d''
CENZ	36.1	41.1	2.95	1.21	0.46
DEPM	97.8	99.8	19.3	19.2	
BEDU	21.7	21.7	6.44	1.40	
BEWG	40.3	30.6	4.91	1.50	1.61
HIJE	47.2	42.4	4.35	1.85	0.15
HIBO	25.3	26.2	8.83	2.31	0.02
BEDE	27.4	49.1	6.22	3.05	0.26
BEGE	63.4	99.1	37.2	36.8	0.12
MEDE	56.5	58.1	16.2	9.45	
MEAL	45.8	42.4	10.5	4.43	0.05
BEKU	99.7	100	3.02	3.03	
DUFL	48.3	51.4	3.62	1.86	
BERN	35.2	42.1	3.51	1.48	
BECH	84.7	87.4	2.52	2.20	
BEKE	90.8	93.4	2.42	2.26	
BEOP	73.4	72.3	2.92	2.12	0.01
BEFL	93.0	93.0	2.60	2.42	0.12
HOVE	91.3	93.1	2.56	2.38	
BEGI	100	100	2.36	2.36	

absolute conformation of two samples of DMC from very careful intensity measurements of seven selected Friedel pairs on each by comparing observed and calculated Bijvoet ratios. Even using Cu $K\alpha$ radiation the imaginary anomalous dispersion contribution is tiny. Rabinovich & Hope (1980) have undertaken a careful statistical analysis of their data in order to show that their measured Friedel-pair differences are significant and that these correspond significantly to those calculated from the structure solution of Rabinovich & Shakked (1974).

Least-squares refinements on $|F|$ were carried out separately on the data sets (P) (that used in the structure determination of DMC by Rabinovich & Shakked, 1974) and (Pa), (Pb) and (Pc) obtained by combining (P) with the three sets of accurate measurements (a), (b) and (c) of Rabinovich & Hope (1980). Atomic parameters were taken from Rabinovich & Shakked (1974) corrected for typographic errors as indicated in the Cambridge Structural Database. Scale factors, absolute-structure parameter, atomic positional and anisotropic displacement parameters for the O and C atoms were refined. Hydrogen atoms were included but not refined. An isotropic secondary extinction correction (Becker & Coppens, 1974) was refined with set (P) and subsequently applied but not refined with sets (Pa), (Pb) and (Pc). Weights were equal to the inverse of the variance of an observation. The atomic parameters and residuals obtained from refinement of (P) gave essentially the same values as those obtained by Rabinovich & Shakked (1974). In Table 3, reading only those entries with $\varphi = 0$, one finds the results of the refinements. These were stable and converged in three or four cycles. All R factors are in the range 4.7 to 5.7%. One can see that the results of

Table 3. *Results of refinements on DMC*

φ is a parameter of the weighting scheme and x is the value of the absolute-structure parameter. E.s.d. of x is given in parentheses.

Dataset	φ	x
(P)	0	-0.96 (82)
(Pa)	0	-0.133 (20)
(Pa)	100	-0.124 (15)
(Pa)	1000	-0.120 (11)
(Pb)	0	-0.102 (15)
(Pb)	10	-0.100 (14)
(Pb)	10000	-0.109 (8)
(Pc)	0	0.052 (20)
(Pc)	10	0.056 (18)
(Pc)	100000	0.054 (8)

Rabinovich & Hope (1980) are confirmed by x refinement although the values of x are sometimes more than three e.s.d.'s away from the ideal value of 0.0. Without further data it is not possible to identify the cause of this discrepancy.

Constraints for origin-free space groups

In an origin-free space group the origin may be freely placed in at least one direction. If suitable action is not taken the presence of the floating origin leads to the least-squares normal-equations matrix becoming singular. The most common approach to this problem is to constrain the atomic coordinates along the origin-free direction(s) by fixing the value of one atom or linear combination of atoms either by reduction of variables or Lagrangian multipliers. Other solutions are to use a block-diagonal refinement, to analyse the eigenvalues and eigenvectors of the normal-equations matrix or to use a generalized inverse.

For the constraining of atomic coordinates, it is first necessary to identify the origin-free direction(s) from the symmetry operations of the space group. The details of this calculation are given in Appendix A. As yet it has not been possible to select an unequivocal criterion leading to a unique constraint (Templeton, 1960; Waser, 1974; Flack, 1983a).

Inverting a structure

Refinement of x may lead to a value of $x \approx 1.0$ for an untwinned sample. The absolute structure of the crystal is thus inverted with respect to the structure model. In many cases one will wish to invert the atomic coordinate set so that the absolute structures correspond. The calculation of this inversion is not without its pitfalls. Depending on the space group and its description, the point of inversion may not be at the origin and, in the case of the 11 enantiomorphic pairs of space groups, inversion implies a change of space group. The details of an efficient algorithm for dealing with these problems are given in Appendix A.

Computer implementation

At first sight it might appear that the evaluation of the inversion-twinned structure factor and its derivatives as defined by (1) would lead to a doubling of calculation time since one has to evaluate two untwinned structure factors to obtain one twinned one. However, by a suitable structuring of both the intensity data and the structure-factor calculation algorithm it is possible to accomplish the refinement of x with very little overhead.

Firstly it is very efficient to arrange the intensity data so that information on the reflection and anti-reflection either form part of the same logical record or one follows the other in sequence. Now as both $|F(h, k, l, x)|^2$ and $|F(-h, -k, -l, x)|^2$ depend on $|F(h, k, l)|^2$ and $|F(-h, -k, -l)|^2$, the latter two quantities need only be calculated once and saved temporarily for the evaluation of the two inversion-twinned structure factors. The same arguments apply for the calculation of the derivatives. In this way the ratio of the number of twinned-to-untwinned structure factors is one for complete data sets including both reflections and antireflections.

Secondly, in the evaluation of $|F(h, k, l)|$ one forms algebraic sums of terms that are the products of sine or cosines with atomic-scattering-factor values. Exactly the same terms occur in the calculation of $|F(-h, -k, -l)|$ but with some of the signs reversed. Hence by simultaneously calculating $|F(h, k, l)|$ and $|F(-h, -k, -l)|$, and their derivatives, or by saving some intermediate results, a considerable economy of calculation may be achieved. This economy would offset the extra calculation time brought about by the use of the absolute-structure parameter.

Electron density calculation

For the calculation of electron density values, an estimate of the anomalous dispersion contribution needs to be subtracted from each of the $|F_{\text{obs}}|$ before performing the Fourier inversion. In the method due to Larson (1976), it is assumed that the observed structure amplitude is a good measure of the calculated structure amplitude with dispersion and that the corrected observed structure amplitude is a good measure of the dispersion-free calculated structure amplitude. In essence this method allows the anomalous dispersion contribution to each structure factor to be scaled giving a different contribution to the observed and calculated structure factors. On the other hand Schwarzenbach & Flack (undated) have preferred to assume that the dispersion contributions to the observed and calculated structure factors are identical. Either calculation supposes the sample not to be inversion-twinned. In Appendix C the generalization of the Schwarzenbach & Flack (undated) analysis to inversion-twinned crystals is presented.

We have extensively tested the use of the formulae of Appendix C on the data from compound BERN (Bernardinelli & Flack, 1985) of Tables 1 and 2. For example, difference electron density maps calculated after refinements from both the correct and inverted coordinate sets produce identical results.

Correlated residuals

Of the utmost importance in absolute-structure determination through refinement of the parameter x is the reliability that one can place on its estimated standard deviation. In this respect the problems that have been encountered in the evaluation of the e.s.d.'s obtained from the Rietveld profile refinement of powder diffraction data (e.g. Shirley, 1984; Sparks, 1985; Rollett, 1984; Prince, 1984) are very instructive. Claim and counter-claim have succeeded one another as to whether the e.s.d.'s are 'correct'. One of us (Flack, 1984, 1985) has suggested that the value of the Durbin-Watson d statistic (Durbin & Watson, 1950, 1951, 1971) is of the greatest help in evaluating these contested e.s.d.'s. Recall that for uncorrelated residuals one expects a value of d of 2.0, while for positive or negative correlation, where adjacent residuals tend to have the same or opposite sign, d becomes less or greater than 2.0 respectively, the limiting values being 0.0 and 4.0. For time series measurements with autocorrelated errors (see Flack, Vincent & Vincent, 1980) it is known that values of d away from 2.0 indicate unbiased parameter estimates but e.s.d.'s that may be wildly in error. In the realm of diffraction physics this situation has long been known to exist for gas electron diffraction measurements (Morino, Kuchitsu & Murata, 1965; Murata & Morino, 1966). However, it will be supposed here that the major perturbations for crystal diffraction measurements are due to the so-called systematic errors such as absorption, extinction, thermal diffuse scattering, multiple scattering and shape of profile function. Clearly these can lead to biased parameter estimates. They may also produce incorrect e.s.d.'s.

d'' , defined in (2), is a pseudo Durbin-Watson d statistic, which considers only the correlation between the members of Friedel pairs. As such it is intended as a pointer to the effect of systematic errors in producing correlated residuals in a least-squares refinement and perturbing the estimate of x and its e.s.d.

When the model used in a least-squares refinement parameterizes completely the non-random variations of the observed data, unbiased estimates of both parameters and their e.s.d.'s are obtained (Prince, 1984). We have confirmed this theoretical result by refinements on 100 simulated data sets of KH tartrate where each reflection was given an independent Gaussian error. Normal probability plots for scale, atomic positional and displacement parameters, and absolute-structure parameter were produced. No sub-

stantial deviations from the ideal plot of unit slope and zero intercept were found. These refinements produced values of d'' of approximately 2.25. Further experiments were performed in which the variance-covariance matrix of the observations became block diagonal rather than diagonal. The 2×2 blocks were for Friedel-pair measurements, the off-diagonal terms of which were given the value $\rho\sigma^2$, where σ^2 is the observed variance of both reflection and anti-reflection and ρ is a correlation coefficient assumed to be constant over the whole data set. Performing refinements with different values of ρ , it was found that the parameter estimates and d'' were independent of ρ whilst the e.s.d. of x depended strongly on the value of ρ . The only source of systematic error in these refinements on $|F|$ was the setting to zero of reflections whose calculated or observed $|F|^2$ was negative.

On studying Table 2, one sees that all of the data sets for which d'' is available suffer from positive correlated residuals. Recall that all these data sets were measured on a routine basis with the primary objective of determining atomic positions. Absorption and extinction corrections were either not carried out or carried out to a low degree of accuracy. Effects such as thermal diffuse scattering and multiple scattering were never treated. Such systematic effects are certainly the cause of the correlated residuals. Nevertheless it is clear from Table 1 that there is little or no bias in the value of x arising even with correlated residuals. Owing to the limited data available to us, it is not possible at present to state to what extent the e.s.d.'s of x are affected by the correlation of the residuals. However, the closer d'' approaches 2.0 the smaller becomes the bias in the e.s.d.'s of x . We interpret the simulations described above as indicating that it is the analysis and correction of the systematic errors rather than the use of off-diagonal weighting schemes that will produce reliable parameter values and e.s.d.'s.

Refinement on $|F|$ or $|F|^2$?

The form of $|F(h, k, l, x)|^2$ given in (1) for the inversion-twinned crystal is such that $|F|^2$ will be non-negative for $0 \leq x \leq 1$ but it may become negative outside this range. For untwinned crystals the theoretical value of x is either 0 or 1 whereas the least-squares estimator of x will take values in the neighbourhood of 0 or 1. As can be seen in Table 1 the estimator of x can thus frequently take values of $x < 0$ (or $x > 1$) and these can produce some negative values of the calculated value of $|F|^2$. The corresponding problem of negative values for the observed $|F|^2$ is well known (see for example French & Wilson, 1978) and it is interesting to see which of the proposed solutions for observed $|F|^2$ might be applied to calculated values.

A most commonly applied approach when carrying out refinement on $|F|$ is to set negative $|F|^2$ values to zero. This is the one currently used in our program system (Stewart *et al.*, 1976). It seems to have little or no justification (Hirshfeld & Rabinovich, 1973). French & Wilson (1978) use Bayesian statistics to generate a non-negative from a negative $|F|^2$. The basis for such a technique as applied to negative calculated values seems dubious. One might argue in favour of including in the least squares penalty functions designed to keep x in the range $0 \leq x \leq 1$ so that negative calculated $|F|^2$ do not occur. We are convinced that this method would be disastrous. The expected values of x (0 and 1) for untwinned crystals occur at the boundaries of the physically acceptable region. The penalty functions would necessarily have large derivatives in the neighbourhood of 0 and 1 leading to unstable refinements and worthless e.s.d.'s on x . The only method that seems to circumvent naturally and efficiently the problem is to carry out the least-squares refinement on $|F|^2$ and to include as such both the negative values of the observed and calculated $|F|^2$. To our great regret we have not taken sufficiently seriously the conclusions of Hirshfeld & Rabinovich (1973) as most refinements described in this paper are based on $|F|$.

Weighting scheme

Parsifal's theorem shows that minimization of

$$Q = \sum w(\mathbf{h}) [F_o(\mathbf{h}) - F_c(\mathbf{h})]^2$$

with reciprocal-space unit weights [$w(\mathbf{h}) = 1$] is equivalent to minimizing

$$U = \int W(\mathbf{x}) [\rho_o(\mathbf{x}) - \rho_c(\mathbf{x})]^2 d\mathbf{x},$$

the integral of the difference density squared over the unit-cell volume, with direct-space unit weights [$W(\mathbf{x}) = 1$]. For any direct-space weighting scheme $W(\mathbf{x})$ there exists in principle the corresponding reciprocal-space one $w(\mathbf{h})$. Dunitz & Seiler (1973) have been able to produce the reciprocal-space weighting scheme corresponding to increasing the direct-space weight of the atomic centres and decreasing the weight of the interatomic regions. This scheme attempts to fit more accurately the electron density of the atomic sites.

Appendix B gives the derivation, based on the above approach, of a reciprocal-space weighting factor capable of adjusting the sensitivity of a refinement to the centrosymmetric or the antisymmetric part of the electron density and also to the absolute structure. In the derivation the electron density is first decomposed into a centrosymmetric and an antisymmetric contribution. These contributions can then be given different weights in the minimization of U . In order to allow for the absolute structure it is the complex effective electron scattering density that has to be

decomposed into centro- and antisymmetric contributions of both the real and imaginary parts. The weighting factor for refinement on $|F|$ is given by

$$w(\mathbf{h}) = [(1 - \mu)A^2 + (1 + \mu)B^2 + \varphi|F(\mathbf{h})|^2 - |F(-\mathbf{h})|^2] / (1 + \mu^2)(A^2 + B^2). \quad (3)$$

Any system of weights ω for refinement on $|F|$ may be transformed into a system u for refinement on $|F|^2$ by

$$u(\mathbf{h}) = \omega(\mathbf{h}) / (2|F| + \omega^{-1/2})^2.$$

μ may take any value between -1 and $+1$. With $\mu = 0$, the centrosymmetric and the antisymmetric parts of the electron density contribute equally. When μ is given a positive value, it will progressively make the fitting of the non-centrosymmetric part of the model more important than the centrosymmetric part. φ may take any positive value. Its effect is to increase the weight of those reflections that show the largest differences between the calculated structure factors for the reflection and anti-reflection. In passing it should be pointed out that the form of this weighting factor corresponds exactly to the conclusions of Dunitz & Shearer (1960) and Marsh (1981) concerning the capital importance of weak reflections in resolving ambiguities between centro- and non-centrosymmetric structures.

The weighting factor has been tested by refinements on DMC and the results are presented in Table 3. The value of μ was fixed at 0.0 . Weights were equal to the product of the inverse of the variance of an observation and $w(\mathbf{h})$, given in (3). Increasing the value of the parameter φ in the weighting factor does not alter significantly the value of x but does reduce, as expected, its e.s.d.

Concluding remarks

The use of the x parameter in the least-squares refinement of non-centrosymmetric crystal structures has been shown to be of very general application, of rapid convergence and to provide parameter values with estimated standard deviations that are quantitatively justifiable. In particular it should be clear that with x refinement and the ancillary calculations detailed in this paper incorporated into a program system one has a simple and fairly foolproof method of dealing in a perfectly general way with non-centrosymmetric crystal structures. The user is hence relieved of some of the technical difficulties associated with the space-group symmetry of the crystal. Moreover, the form of the results of the absolute-structure determination as a value with an estimated standard deviation seems more readily comprehended by many of those using crystal-structure determination over the alternative significance points associated with Hamilton's R -factor ratio test. Of the different statistical descriptors that have been used to assess the reliability of

absolute-structure determination, we have found the value of x , its estimated standard deviation and the pseudo Durbin-Watson statistic d'' to be particularly useful.

Jones (1984*b*), in his analysis of structures recorded in the Cambridge Structural Database for 1982, poses several questions arising from absolute-configuration determinations. Is an R value of 0.113 adequate? Do four reflections constitute a large enough set of Friedel-pair measurements? Is it acceptable to use Friedel pairs from only the $hk0$ reflections? We are also concerned that in very many cases, where calculated and observed Bijvoet ratios have been compared in order to determine absolute structure, no error estimates, either variances or covariances, are reported for the calculated Bijvoet ratios. In such cases, no allowance is made for the possible variation of these calculated ratios owing to errors in the estimated parameters of the structure solution. It should, however, be clear that by using the absolute-structure parameter x and simultaneously refining on both the 'complete' data set and the selected Friedel-pair intensity measurements a quantitative answer to this type of question can be obtained through the e.s.d. of x as we have shown for the case of DMC. Clearly, as the atomic structural parameters (both positional and displacement) are varied with the absolute-structure parameter x the difficulties in using error-ignored calculated Bijvoet ratios can be completely avoided.

It is our firm opinion that all structure refinements of non-centrosymmetric crystals should include the absolute-structure parameter. It is clear that those wishing to determine absolute configuration will be drawn to this technique but we wish once again to emphasize that in non-centrosymmetric space groups biased atomic parameters, both positional and displacement, can result from incorrectly allowing for the effects of absolute structure. If a value of the absolute-structure parameter and its e.s.d. are quoted as part of structure determination on a non-centrosymmetric crystal, one can be confident that the necessary precautions to avoid bias have been taken. Hence, the publication of absolute-structure parameters for all non-centrosymmetric crystal-structure determinations whether the constituent entities are chiral or not is always justified.

Certain points need further study and more experimental data. Firstly, we have been able to demonstrate that the weighting scheme to render a refinement more sensitive to absolute structure does produce a decrease in the e.s.d. of x . However, this scheme includes contributions from the calculated structure factors and some bias may be introduced in this way. It would be useful also to see the influence on the other parameters of using this weighting scheme and its sensitivity to the threshold value frequently used to exclude weak reflections. Secondly, none of our data has been corrected for absorption. Nevertheless,

the values of x seem to be entirely reasonable. The bias in the value of x brought about by the neglect of absorption would thus seem to be very small for these data sets. We are actively considering this matter at present. Thirdly, we have also been able to show the presence of correlated residuals in many of our refinements through the use of the pseudo Durbin-Watson parameter d'' . What the precise effect of this correlation is on the e.s.d. of x in any particular case is an open question.

The stable nature of x refinement has led us to revise our previous opinion (Flack, 1983*b*) on the moment at which this parameter should be introduced in the least squares. In our program system (Stewart *et al.*, 1976) we now automatically start the refinement of x at the outset and no longer wait for the stage of refining anisotropic atomic displacement parameters.

It is intended to extend the ideas presented in this paper to the more general problems of pseudomeroheredral twinning and to the testing of the space-group symmetry of crystal structures.

The cooperation of our colleagues who so willingly put the results of their structure refinements at our disposition for inclusion in this paper is warmly appreciated. The authors are very grateful to the two referees for their very helpful comments on this paper. Professors H.-B. Bürgi, D. Schwarzenbach and Drs J. J. Daly and A. F. Williams are thanked for their attentive reading and critical remarks on the manuscript.

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APPENDIX A

Two related derivations are given in this Appendix. The first shows the equations necessary for finding the origin-free direction(s) in a given space group. The second shows how the coordinates of a structure may be changed in order to switch from one chirality or polarity to another.

Let the symmetry operations of the space group be represented by matrices S_m , t_m , b_n and L_j for $m = 1, 2, \dots, M$, $n = 1, 2, \dots, N$, $j = 1, 2, \dots, \infty$, where S_m is a 3×3 rotation matrix being a representation of one of the symmetry operations of the crystal point group, t_m a 3×1 translation vector associated with S_m , b_n a 3×1 Bravais-lattice centring translation vector and L_j one of the set of primitive lattice translation vectors. M and N are the number of symmetry operations and centring translations respectively. From one arbitrary point x , the infinite set $\{x\}$ of symmetry-related points is composed of

$$x_{mnj} = S_m x + t_m + b_n + L_j \quad (A1)$$

Free choice of origin. We seek those cases where an arbitrary displacement of x by an amount δ produces the same arbitrary shift in all the elements of $\{x\}$. From (A1), on displacement by δ , a set of points $\{x'\}$ composed of

$$x'_{mnj} = S_m(x + \delta) + t_m + b_n + L_j \quad (A2)$$

is obtained and each individual point will be displaced by

$$\Delta_m = \Delta_{mnj} = x'_{mnj} - x_{mnj} = S_m \delta. \quad (A3)$$

For the set of points to be displaced without deformation, i.e. that δ corresponds to an isometry, all the Δ must be equal to δ since one of the S_m is 1. Thus,

$$\delta = \Delta_m = S_m \delta \quad \text{for } m = 1, 2, \dots, M. \quad (A4)$$

It may be shown that the M equations in (A4) are solved by the single equation

$$\Omega \delta = \delta \quad (A5)$$

making use of the idempotent projector

$$\Omega = 1/M \sum S_m \quad (A6)$$

Clearly, in the general case, (A5) may be solved by finding the eigenvectors of Ω associated with an eigenvalue of +1. If Ω has no eigenvalue of +1, only the trivial solution, $\delta = 0$, is possible. As the only possible eigenvalues of Ω are 0 or +1, trace (Ω) will give the number of eigenvalues of value +1 and this is the number of free dimensions in the choice of origin of the space group.

With the space group described in an axial system defined by its principal symmetry elements, as is done in *International Tables for Crystallography* (1983), the matrix Ω is diagonal in all cases except point groups 3 and $3m$ referred to rhombohedral axes. (In the latter cases Ω has elements of $\frac{1}{3}$ everywhere, giving one eigenvalue of +1 with eigenvector parallel to $[1, 1, 1]$.) In practice then it is unnecessary to analyse Ω with an eigenvalue/eigenvector routine as the origin-free directions may be found by inspection of the diagonal elements of Ω .

Inverting the structure. We seek those cases where the inversion of x in some point produces the complete inverted structure represented by the set $\{x\}$, (A1), inverted in some point. Let us invert the set of points $\{x\}$, (A1), through a point at c to obtain the set $\{x'\}$ of the inverted structure, of which the elements are given by

$$x'_{mnj} = 2c - x_{mnj} \quad (A7)$$

and which on substituting (A1) leads to

$$x'_{mnj} = S_m(-x) - t_m + b_n + L_j + 2c. \quad (A8)$$

Let the original point x be inverted through a point at k whilst remaining in the original space group and setting. The new point x'' generated from x is given by

$$x'' = 2k - x \quad (A9)$$

and leads to a set of points $\{\mathbf{x}''\}$ with components

$$\mathbf{x}_{m'n'y}'' = \mathbf{S}_m(-\mathbf{x}) + \mathbf{t}_m + \mathbf{b}_n + \mathbf{L}_j + 2\mathbf{S}_m\mathbf{k}, \quad (\text{A10})$$

which should be compared to the components of the correct set of points for the inverted structure given in (A8). The objective is to produce the set $\{\mathbf{x}'\}$ in (A8) from $\{\mathbf{x}''\}$ in (A10) by a suitable choice of \mathbf{k} and \mathbf{c} . These sets can be made identical only when $m = m'$ since \mathbf{x} takes arbitrary values and equating (A8) and (A10) under these conditions leads to

$$(\mathbf{t}_m + \mathbf{b}_n + 2\mathbf{S}_m\mathbf{k}) \bmod \mathbf{1} = (-\mathbf{t}_m + \mathbf{b}_n + 2\mathbf{c}) \bmod \mathbf{1} \quad (\text{A11})$$

since $(\mathbf{L}_j - \mathbf{L}_j) \bmod \mathbf{1} = \mathbf{0}$. Further, as $(\mathbf{b}_n - \mathbf{b}_n) \bmod \mathbf{1} = \mathbf{b}_i$ one finds

$$(2\mathbf{t}_m + \mathbf{b}_n + 2\mathbf{S}_m\mathbf{k} - 2\mathbf{c}) \bmod \mathbf{1} = \mathbf{0}. \quad (\text{A12})$$

The existence of an identity operator $(\mathbf{1}, \mathbf{0})$ amongst the $\{\mathbf{S}, \mathbf{t}\}$ and a Bravais-lattice translation of $\mathbf{0}$ amongst the \mathbf{b}_n leads to $2(\mathbf{k} - \mathbf{c}) \bmod \mathbf{1} = \mathbf{0}$, which on substitution in (A12) gives

$$(2\mathbf{t}_m + \mathbf{b}_n + 2\mathbf{S}_m\mathbf{c} - 2\mathbf{c}) \bmod \mathbf{1} = \mathbf{0}. \quad (\text{A13})$$

Thus, for some \mathbf{c} to be a valid inversion point to change from one polarity to another by substituting $2\mathbf{c} - \mathbf{x}$ for \mathbf{x} for all atoms in the asymmetric unit whilst remaining in the space group and *description*, (A13) has to be obeyed by all symmetry operators $(\mathbf{S}_m, \mathbf{t}_m)$ for at least one of the Bravais-lattice translations \mathbf{b}_n . For the 22 space groups forming the 11 enantiomorphic pairs, there will be no solution of (A13) and the structure can be inverted by changing all \mathbf{x} into $-\mathbf{x}$ and $(\mathbf{S}_m, \mathbf{t}_m)$ into $(\mathbf{S}_m, -\mathbf{t}_m)$.

A concise numerical solution of (A13) is achieved by trial and error. As many cases have a solution of $\mathbf{c} = \mathbf{0}$, one may vary each component of $2\mathbf{c}$ in steps of $\frac{1}{2}$ starting from 0 and going to a maximum value of $\frac{1}{2}$. The value of \mathbf{c} is not unique. There are seven cases where for the standard setting of the space group as given in *International Tables for Crystallography* (1983) $\mathbf{c} \neq \mathbf{0}$. These are: *Fdd2* $\frac{1}{8}\frac{1}{8}\mathbf{0}$; *I4₁* $0\frac{1}{4}\mathbf{0}$; *I4₁22* $0\frac{1}{4}\frac{1}{8}$; *I4₁md* $0\frac{1}{4}\mathbf{0}$; *I4₁cd* $0\frac{1}{4}\mathbf{0}$; *I42d* $0\frac{1}{4}\frac{1}{8}$; *F4₁32* $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ (see also Parthé & Gelato, 1984).

APPENDIX B

Derivation of weighting scheme

Let the complex difference effective electron scattering density be denoted by $\Delta\rho(\mathbf{x})$ so that

$$\Delta\rho(\mathbf{x}) = \Delta\rho^0(\mathbf{x}) + i\Delta\rho''(\mathbf{x}). \quad (\text{B1})$$

Decomposing the components of $\Delta\rho(\mathbf{x})$ into centro- and antisymmetric contributions one obtains

$$\Delta\rho(\mathbf{x}) = \Delta\rho_c^0(\mathbf{x}) + \Delta\rho_a^0(\mathbf{x}) + i[\Delta\rho_c''(\mathbf{x}) + \Delta\rho_a''(\mathbf{x})], \quad (\text{B2})$$

where

$$\Delta\rho_c^0(\mathbf{x}) = \frac{1}{2}[\Delta\rho^0(\mathbf{x}) + \Delta\rho^0(-\mathbf{x})] \quad (\text{B3})$$

$$\Delta\rho_a^0(\mathbf{x}) = \frac{1}{2}[\Delta\rho^0(\mathbf{x}) - \Delta\rho^0(-\mathbf{x})] \quad (\text{B4})$$

$$\Delta\rho_c''(\mathbf{x}) = \frac{1}{2}[\Delta\rho''(\mathbf{x}) + \Delta\rho''(-\mathbf{x})] \quad (\text{B5})$$

$$\Delta\rho_a''(\mathbf{x}) = \frac{1}{2}[\Delta\rho''(\mathbf{x}) - \Delta\rho''(-\mathbf{x})]. \quad (\text{B6})$$

Write T^{-1} for the inverse Fourier transform and thus

$$T^{-1}[\Delta\rho(\mathbf{x})] = \Delta F(\mathbf{h}). \quad (\text{B7})$$

Now define

$$\Delta\varepsilon(\mathbf{x}) = a_1\Delta\rho_c^0 + a_2\Delta\rho_a^0 + ia_3\Delta\rho_c'' + ia_4\Delta\rho_a''. \quad (\text{B8})$$

Notice that different weights have been given to the centro- and antisymmetric components of the real and imaginary parts of $\Delta\rho(\mathbf{x})$ as represented by the coefficients a_1, a_2, a_3 and a_4 .

$$T^{-1}[\Delta\varepsilon(\mathbf{x})] = \Delta E(\mathbf{h}), \quad (\text{B9})$$

$$\Delta E(\mathbf{h}) = T^{-1}[\Delta\varepsilon(\mathbf{x})]$$

$$= a_1\Delta A^0 + ia_2\Delta B^0 + ia_3\Delta B'' - a_4\Delta A'', \quad (\text{B10})$$

and the minimization of $\sum |\Delta E(\mathbf{h})|^2$, which minimizes $\int \Delta\varepsilon(\mathbf{x})^2 d\mathbf{x}$, may be written in terms of the desired weighting scheme $w(\mathbf{h})$ through

$$|\Delta E(\mathbf{h})|^2 = w(\mathbf{h})|\Delta F(\mathbf{h})|^2. \quad (\text{B11})$$

One thus has

$$|\Delta E(\mathbf{h})|^2 = (a_1\Delta A^0 - a_4\Delta A'')^2 + (a_2\Delta B^0 + a_3\Delta B'')^2 \quad (\text{B12})$$

$$|\Delta F(\mathbf{h})|^2 = (\Delta A^0 - \Delta A'')^2 + (\Delta B^0 + \Delta B'')^2, \quad (\text{B13})$$

$$w(\mathbf{h}) = [(a_1\Delta A^0 - a_4\Delta A'')^2 + (a_2\Delta B^0 + a_3\Delta B'')^2] \times [(\Delta A^0 - \Delta A'')^2 + (\Delta B^0 + \Delta B'')^2]^{-1}. \quad (\text{B14})$$

Assuming that $\Delta A^0 = sA^0$, $\Delta B^0 = sB^0$, $\Delta A'' = sA''$ and $\Delta B'' = sB''$, and writing $a_1^2 = (1 - \mu)/(1 + \mu^2)$, $a_2^2 = (1 + \mu)/(1 + \mu^2)$, $a_3^2 = 4\varphi^2/[(1 + \mu)(1 + \mu^2)]$ and $a_4^2 = 4\varphi^2/[(1 - \mu)(1 + \mu^2)]$, one obtains the weighting scheme given in the main text.

APPENDIX C

Correction of $|F_{\text{obs}}|$ for anomalous dispersion

Calculated structure factors without anomalous dispersion for reflection and antireflection are given by

$$F_+ = A^0 + iB^0 = |F|\cos\alpha_0 + i|F|\sin\alpha_0 \quad (\text{C1})$$

$$F_- = A^0 - iB^0 = |F|\cos\alpha_0 - i|F|\sin\alpha_0. \quad (\text{C2})$$

The calculated structure factors due to anomalous dispersion alone are

$$F_+'' = A_+'' + iB_+''; \quad F_-'' = A_-'' + iB_-'' \quad (\text{C3})$$

and the complete dispersion-included calculated structure factors are

$$F_{D+} = F_+ + F''_+ = (A^0 + A''_+) + i(B^0 + B''_+) \quad (C4)$$

$$F_{D-} = F_- + F''_- = (A^0 + A''_-) + i(-B^0 + B''_-). \quad (C5)$$

Let the dispersion-included observed structure factors be called F_{o+} and F_{o-} and the dispersion-free observed structure factors are given by

$$F_{on+} = A_{on} + iB_{on} = |F_{on}| \cos \alpha_0 + i|F_{on}| \sin \alpha_0 \quad (C6)$$

$$F_{on-} = A_{on} - iB_{on} = |F_{on}| \cos \alpha_0 - i|F_{on}| \sin \alpha_0. \quad (C7)$$

The structure amplitude squared observed from an inversion-twinned crystal is given by

$$|G_o|^2 = (1-x)|F_{o+}|^2 + x|F_{o-}|^2, \quad (C8)$$

in which, according to the Schwarzenbach & Flack (undated) hypothesis, one may substitute

$$F_{o+} = F_{on+} + F''_+; \quad F_{o-} = F_{on-} + F''_- \quad (C9)$$

to give

$$|F_{on}|^2 + 2[A_x \cos \alpha_0 + B_x \sin \alpha_0]|F_{on}| + A_x^2 + B_x^2 + E - |G_o|^2 = 0, \quad (C10)$$

where

$$A_x = (1-x)A''_+ + xA''_- \quad (C11)$$

$$B_x = (1-x)B''_+ - xB''_-$$

$$E = (1-x)(A''_+^2 + B''_+^2) + x(A''_-^2 + B''_-^2) - A_x^2 - B_x^2. \quad (C12)$$

Solution of (C10) leads to

$$|F_{on}| = -[A_x \cos \alpha_0 + B_x \sin \alpha_0] \pm \{ |G_o|^2 - [A_x \sin \alpha_0 - B_x \cos \alpha_0]^2 - E \}^{1/2}, \quad (C13)$$

which is the expression for the observed structure amplitude corrected for anomalous dispersion to be used in electron density calculations. We have chosen to accept that solution in (C13) for which $|F_{on}|$ has its value closest to that of $|F|$, the calculated anomalous-dispersion-free structure amplitude. In a program system it may be convenient to conserve A_x and B_x , anomalous contributions to the pseudo structure factor G of the inversion twin, in place of A''_{\pm} and B''_{\pm} . The expression under the square root in (C13) is set to zero if it becomes negative. For centrosymmetric structures $A'' = A''_{\pm}$ and $B'' = B''_{\pm}$ are used in place of A_x and B_x and E is set to zero in order to make (C13) independent of the physically meaningless x .

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Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.

Acta Cryst. (1985). A41, 511

Crystal optics with spatial dispersion and excitons. By V. M. AGRANOVICH and V. L. GINSBURG. Pp. xi + 441. Berlin: Springer-Verlag, 1984. Price US \$49.00.

This is a densely packed monograph, written for specialists. It is a detailed, sophisticated presentation of the mathematical physics of optical phenomena in crystalline materials, treated with considerable rigour in terms of the electromagnetic-field equations and the complex dielectric-constant tensor. It concentrates on the phenomenon of dispersion (the effect of the change of wavelength) and on the application of the concepts of the exciton (quantized, local, but mobile electronic or magnetic excitation) and the polariton (effectively the photon, considered in the context of the crystalline medium in which it travels). It should be added that this volume is the English translation of the Russian-language publication of 1979, itself an updated expanded version of an original Russian text.

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Acta Cryst. (1985). A41, 511

Properties of crystalline silicon carbide. Diodes; molecular species in the gas phase; amorphous silicon-carbon alloys. (*The silicon supplement*, Vol. B2 of the *Gmelin handbook of inorganic chemistry*, 8th ed.) By J. SCHLICHTING, G. CZACK, E. KOCHBIENEMANN, P. KUHN and F. SCHRÖDER. Pp. xvi + 314. Berlin: Springer Verlag, 1984. Price DM 1080.

Silicon carbide has been investigated extensively by physicists, chemists, ceramic engineers, electronic engineers, crystallographers, materials scientists and others, on account of its very special structural characteristics and multifarious applications. The scientific literature on this

material is therefore spread over a very diverse range of journals covering different disciplines of science. This handbook is an excellent attempt to compile all the data available up to the middle of 1983 on different aspects of the material and its uses.

The first chapter, which comprises 80% of the book (245 pages), deals with the properties of crystalline SiC. It gives an account of the various polytype structures in which the material crystallizes, the notations used to describe them, the theories of their formation, polytype transformations, structural defects, radiation damage, electronic band structure, lattice dynamics, bonding, mechanical, thermal, electrical, magnetic, optical and surface properties of the material.

The second chapter (23 pages) deals with the diodes prepared from α - and β -SiC, their electrical characteristics, luminescence behaviour, stability and breakdown. The third chapter (3 pages) describes the occurrence and detection of the different molecular species in the silicon-carbon system in the gaseous phase. The fourth and last chapter (36 pages) gives an extensive review of the structure and properties of amorphous silicon-carbon alloys, which frequently contain hydrogen and sometimes fluorine or oxygen. The optical properties of these amorphous alloys are compared with those of hydrogenated amorphous silicon material.

A separate volume covering the phase diagram, formation, preparation, manufacture and chemical reactions of SiC is planned to appear in the near future. These aspects are therefore not covered in the present volume. The authors are to be congratulated on the very thorough review of the literature that they have performed. For anyone working on the silicon-carbon system this volume provides an invaluable storehouse of information and data. While strongly recommending this volume as a standard work of reference, I must warn prospective buyers of its fantastically high price.

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