MATTHEWS, B. W., GRUTTER, M. G., ANDERSON, W. F. & REMINGTON, S. J. (1981). *Nature (London)*, **290**, 334–335.

MATTHEWS, B. W. & REMINGTON, S. J. (1974). *Proc. Natl. Acad. Sci. USA*, **71**, 4178–4182.

MOEWSE, P. C. & KRETSINGER, R. H. (1975). *J. Mol. Biol.* **91**, 201–228.

RAMACHANDRAN, G. N., RAMAKRISHNAN, C. & SESISAKHARAN, V. (1963). *J. Mol. Biol.* **7**, 95–99.

REMANE, A. (1952). *Die Grundlagen des Natürlichen Systems, der vergleichenden Anatomie und der Phylogenetik.* Leipzig: Akademische Verlagsgesellschaft.

REMINGTON, S. J. & MATTHEWS, B. W. (1978). *Proc. Natl. Acad. Sci. USA*, **75**, 2180–2184.

ROSSMANN, M. G. (1974). *New Sci.* **61**, 266–268.

ROSSMANN, M. G. & ARGOS, P. (1975). *J. Biol. Chem.* **250**, 7525–7532.

ROSSMANN, M. G. & ARGOS, P. (1976). *J. Mol. Biol.* **105**, 75–95.

ROSSMANN, M. G. & ARGOS, P. (1977). *J. Mol. Biol.* **109**, 99–129.

SALEMME, F. R., FREER. S. T., XUONG, N. H., ALDEN, R. A. & KROUT, J. (1973). *J. Biol. Chem.* **248**, 3910–3921.

STERNBERG, M. J. E. & THORNTON, J. M. (1977). *J. Mol. Biol.* **110**, 285–296.

STUART, D. (1979). PhD thesis. Univ. of Bristol.

TAKANO, T., KALLAI, O. B., SWANSON, R. & DICKERSON, R. E. (1973). *J. Biol. Chem.* **248**, 5234–5255.

The Influence of Rational Dependence on the Probability Distribution of Structure Factors

BY V. GRAMLICH

Institut für Kristallographie und Petrographie der ETH, CH-8092 Zürich, Switzerland

Dedicated to Professor J. D. Dunitz on the occasion of his 60th birthday

Abstract

An index subgroup of strong main reflexions and cosets of weak reflexions are typical features of crystal structures with systematic rational dependence of the atom coordinates exhibiting a pseudotranslational symmetry. The mean squares of these normalized structure-factor sets which deviate significantly from unity are interpreted in terms of correlation coefficients of the atom coordinates. An asymptotic form of the von Mises distribution of a structure factor phase is derived which allows for rational dependence and makes explicit use of the $|E|^2$ values of the different structure-factor sets. The formula provides a basis for the use of phase relationships of the type 'weak–strong–weak' proposed in the recent literature. The limits of the method are estimated. In particular, symmetry and homometry problems in superstructures are more complex than in usual cases and their careful consideration is essential for the success of procedures intending an automatic solution.

Introduction

The concept of rational dependence of atom coordinates in connexion with the statistics of normalized structure factors was introduced by Hauptman & Karle (1953). Renormalization was proposed in order to remove problems imposed by systematically strong and weak reflexion classes occurring in this context (Hauptman & Karle, 1959). No general statistical basis for this procedure was available. Despite some successful attempts at direct phase determination for superstructures, the method was not much further developed. Combined trial-and-error, Patterson and Fourier methods turned out to be a powerful tool (*cf.* Schulz, 1976, and references cited therein).

The application of direct methods to structures containing heavy atoms (Beurskens & Noordik, 1971) was successful even if the heavy atoms exhibited some subperiodicity (*cf. DIRDIF*: Beurskens, Bosman, Doesburg, Gould, van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981, and references cited therein). In this context procedures using partial information (Main, 1976; Heinerman, Krabbendam & Kroon, 1977) may be mentioned. Giacovazzo (1983) developed a new theory for the use of *a priori* known partial structure information and compared his method with the difference structure factor (*DIRDIF*) approach. *DIRDIF* will fail if the input model consists of nearly all atoms in idealized positions (Beurskens & Bosman, 1982).

The main difference in the approach of this paper compared with others is the explicit use of the information $|E(\mathbf{h}_n)|^2{}^{\mathbf{h}_n}$ (different numbers for different classes $n = 1, \ldots p$, if rational dependence is prominent). This is particularly interesting for those superstructures where a known 'average' model may explain the strong reflexions quite satisfactorily but

does not contribute to the classes of the weak reflexions at all.

Renormalization implies that triplets involving reflexions from weak cosets are as reliable as if the $|E|^2$ values of the weak cosets were near unity. It was argued later that this conclusion is in fact true for triplets involving two reflexions of the weak cosets (Gramlich, 1975). This was confirmed by adequate discussions of the Sayre equation in terms of the Fourier transforms of the strong and weak reflexion classes (Fan & Zheng, 1981, and references cited therein) or in terms of the reflexion classes directly (Gramlich, 1978):

Let the reflexion indices of the subgroup of systematically strong reflexions be abbreviated by $\mathbf{h}_0$, those of the $(p-1)$ corresponding cosets by $\mathbf{h}_n$, $n = 1 \ldots p - 1$ (p is the number of subcells in the unit cell). Sayre's equation may then be written

$$F(\mathbf{h}_n) = (\Phi/V)\left\{\sum_{\mathbf{h}_0'} F(\mathbf{h}_0')F(\mathbf{h}_n - \mathbf{h}_0')\right.$$

$$\left. + \sum_{\mathbf{h}_m'} F(\mathbf{h}_m')F(\mathbf{h}_n - \mathbf{h}_m')\right\}. \qquad (1)$$

The ratio of the averaged scattering factors to the squared ones is abbreviated by Φ. If $\mathbf{h}_n$ and $\mathbf{h}_m'$ belong to the same coset, $\mathbf{h}_n - \mathbf{h}_m' = \mathbf{h}_0''$ is an element of the subgroup of the strong main reflexions. Therefore, the first sum occurs twice:

$$F(\mathbf{h}_n) = (2\Phi/V)\sum_{\mathbf{h}_0'} F(\mathbf{h}_0')F(\mathbf{h}_n - \mathbf{h}_0')$$

$$+ (\Phi/V)\sum_{\mathbf{h}_m'}^{(m \neq n)} F(\mathbf{h}_m')F(\mathbf{h}_n - \mathbf{h}_m'). \qquad (2)$$

This equation is identical with the approximate formula given by Fan [equation (8) in Fan, Yao, Main & Woolfson, 1983] if the last sum is omitted. The latter provides an estimate of the error due to the approximation in the theory of Fan et al. (1983). In particular, for the frequent case $p = 2$ (two subcells in the true cell) the last sum in (2) is void so that the equation is independent of the approximation in Fan et al. (1983) for this special case. Since $\mathbf{h}_n - \mathbf{h}_0'$ in (2) belongs to the same coset as $\mathbf{h}_n$, the relationship between systematically weak and strong reflexions does not provide any direct connexion between reflexions of different cosets. Finally, it may be seen from (2) that straightforward renormalization is in conflict with Sayre's equation.

Phase triplets involving three reflexions from the weak cosets were considered by Boehme (1982). Depending on the chosen hypothetical examples, normal, aberrant or undefined triplet distributions were found. Therefore, if nothing is known about the superstructure, the omission of these triplets from the phase determination seems to be a wise precaution.

Correlation coefficients

The normalized structure factor of an equal-atom structure with N atoms in the unit cell is given by

$$E(\mathbf{h}_n) = (1/N^{1/2})\sum_{j=1}^{N} \xi_j(\mathbf{h}_n)$$

with

$$\xi_j(\mathbf{h}_n) = \exp(2\pi i \mathbf{h}_n \mathbf{x}_j).$$

The mean-squared structure factors of the reflexion classes

$$\overline{|E(\mathbf{h}_n)|^2}^{\mathbf{h}_n} = (1/N)\sum_{jj'}\overline{\xi_j(\mathbf{h}_n)\xi_{j'}(\mathbf{h}_n)}^{\mathbf{h}_n} = v_n \qquad (3)$$

are known numbers with small deviations from unity. Superstructures are characterized by rather large values for the strong main reflexions ($v_0 \lesssim p$, p being the number of subcells) and small ones for the cosets. Let us now interpret $\xi_j(\mathbf{h}_n)$ as complex variables (cf. Wooding, 1956), with zero mean; unit variances

$$\mathrm{var}\{\xi_j(\mathbf{h}_n)\} = \overline{\xi_j(\mathbf{h}_n)\xi_j^*(\mathbf{h}_n)}^{\mathbf{h}_n} = 1$$

and covariances

$$\mathrm{cov}\{\xi_j(\mathbf{h}_n), \xi_{j'}(\mathbf{h}_n)\} = \overline{\xi_j(\mathbf{h}_n)\xi_{j'}^*(\mathbf{h}_n)}^{\mathbf{h}_n}, j \neq j'.$$

The deviation of the $|E|^2$ averages in (3) from unity depends on the average covariances:

$$\overline{|E(\mathbf{h}_n)|^2}^{\mathbf{h}_n} = 1 + (1/N)\sum_{j \neq j'} \mathrm{cov}\{\xi_j(\mathbf{h}_n), \xi_{j'}(\mathbf{h}_n)\}.$$

For normal structures it is usually assumed that the variables are independent with vanishing mean covariances. In our case of systematic rational dependence in superstructures not all covariances are equally important. Only atom pairs correlated by the pseudo-translations, i.e. the translations corresponding to the subcells, will provide a relevant contribution to the mean covariances. If we postulate that the variables corresponding to the atoms in the subcell are independent, only $N(p-1)$ relevant correlation terms occur (cf. Fig. 1). If c_n is their mean, then

$$c_n = \{\overline{|E(\mathbf{h}_n)|^2}^{\mathbf{h}_n} - 1\}/(p-1) = (v_n - 1)/(p-1). \qquad (4)$$
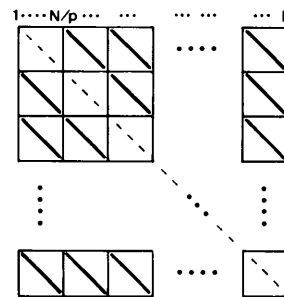

Fig. 1. Schematic drawing of the variance–covariance matrix of the variables $\xi_j(\mathbf{h}_n)$. The variables are ordered in p sets corresponding to the subcells. The heavy diagonals represent covariances of variables related by pseudotranslations. If the number of variables per subcell is not constant for all subcells equation (4) is only approximately valid.

Since the mean variances are unity, c_n is the mean correlation coefficient of the variables $\xi_j(\mathbf{h}_n)$ correlated by the pseudo translations. The coefficient c_0 of the subset of strong main reflexions $(n = 0)$ varies between 0 for normal structures without correlations and 1 for the limiting case of exactly fulfilled pseudotranslation symmetry. Similarly, c_n of the cosets is zero for normal structures and negative in case of correlations.

Probabilistic theory

In order to estimate the distribution of products

$$E(\mathbf{h}')E(\mathbf{h}_n - \mathbf{h}')$$

$$= (1/N) \sum_{j1,j2} \exp\{2\pi i[\mathbf{h}'(\mathbf{x}_{j1} - \mathbf{x}_{j2}) + \mathbf{h}_n\mathbf{x}_{j2}]\} \quad (5)$$

for fixed $\mathbf{h}_n$ with independent variable $\mathbf{h}'$, mean and variance are calculated first. Averaging is performed separately for the subgroup $m = 0$ and the cosets $m = 1, \ldots, (p - 1)$:

$$(1/p) \sum_{m=0}^{p-1} \overline{E(\mathbf{h}'_m)E(\mathbf{h}_n - \mathbf{h}'_m)}^{\mathbf{h}'_m}$$

$$= (1/N^{1/2})E(\mathbf{h}_n) + (1/Np)$$

$$\times \sum_{m=0}^{p-1} \sum_{j1 \neq j2} \overline{\exp\{2\pi i[\mathbf{h}'_m(\mathbf{x}_{j1} - \mathbf{x}_{j2}) + \mathbf{h}_n\mathbf{x}_j]\}}^{\mathbf{h}'_m}.$$

The special case $j1 = j2$ has been separated. Although the random contributions of the exponentials in the second term of the right hand side cancel for structures with postulated rational independence, we must consider here the systematic contributions caused by the rational dependence. However, the sum over all classes

$$\sum_{m=0}^{p-1} \exp\{2\pi i\mathbf{h}'_m(\mathbf{x}_{j1} - \mathbf{x}_{j2})\}$$

becomes systematically small or zero if the difference $\mathbf{x}_{j1} - \mathbf{x}_{j2}$ is nearly or exactly a pseudo translation. Hence

$$\overline{E(\mathbf{h}')E(\mathbf{h}_n - \mathbf{h}')}^{\mathbf{h}'} \simeq (1/N^{1/2})E(\mathbf{h}_n) \quad (6)$$

in accordance with the formulae mentioned in the introduction.

The second moment is given by

$$\overline{|E(\mathbf{h}')E(\mathbf{h}_n - \mathbf{h}')|^2}^{\mathbf{h}'} = (1/p) \sum_{m=0}^{p-1} \overline{|E(\mathbf{h}'_m)E(\mathbf{h}_n - \mathbf{h}'_m)|^2}^{\mathbf{h}'_m}.$$

If $E(\mathbf{h}'_m)$ and $E(\mathbf{h}_n - \mathbf{h}'_m)$ are considered as random variables and assumed to be independent, the averages of the products on the right hand side can be approximated by the products of the averages $v_m v_{n-m}$. An appropriate vector numbering of the cosets is required here; e.g. each coset will be uniquely characterized by the index of its representative reflexion in a cell reciprocal to the subcell. In order

to maintain a one-to-one correspondence of the number n and the characteristic vector $\mathbf{n}$ of any coset, the vector $\mathbf{n} - \mathbf{m}$ is again to be replaced by the representative one of the coset to which it belongs. Neglecting terms containing $1/N$, the variance becomes

$$(1/p) \sum_{m=0}^{p-1} v_m v_{n-m} = 1 + \{(p-1)^2/p\} \sum_{m=0}^{p-1} c_m c_{n-m}. \quad (7)$$

If (6) is interpreted as an estimate of $E(\mathbf{h}_n)$ through a large sum of, say, s terms

$$E(\mathbf{h}_n) = \sum_{\mathbf{h}'}^{(s)} \{(N^{1/2}/s)E(\mathbf{h}')E(\mathbf{h}_n - \mathbf{h}')\},$$

its probability distribution is approximately a Gaussian normal distribution with mean

$$\mu = \sum_{\mathbf{h}'}^{(s)} \{(N^{1/2}/s)E(\mathbf{h}')E(\mathbf{h}_n - \mathbf{h}')\}$$

and variance

$$\sigma^2 = \sum_{\mathbf{h}'}^{(s)} (N/s^2)\left\{\sum_{m=0}^{p-1} v_m v_{n-m}\right\} = (N/s) \sum_{m=0}^{p-1} v_m v_{n-m}.$$

The conditional probability distribution of the phase φ of E, given its magnitude, is a von Mises distribution (Heinerman, Krabbendam & Kroon, 1977):

$$P\{\varphi(\mathbf{h}_n)\} = \{1/[2\pi I_0(\alpha_n)]\} \exp\{\alpha_n \cos[\varphi(\mathbf{h}_n) - \beta]\} \quad (8)$$

with

$$\alpha_n \exp(i\beta) = \sum_{\mathbf{h}'}^{(s)} K(\mathbf{h}_n\mathbf{h}') \exp\{i[\varphi(\mathbf{h}') + \varphi(\mathbf{h}_n - \mathbf{h}')]\}$$

and

$$K(\mathbf{h}_n\mathbf{h}') = \{2p/(N^{1/2} \sum_{m=0}^{p-1} v_m v_{n-m})\}$$

$$\times E(\mathbf{h}_n)E(\mathbf{h}')E(\mathbf{h}_n - \mathbf{h}').$$

The formula given here is an asymptotic one for a large number of contributors. Therefore, an extrapolation of (8) to triplet relationships $(s = 1)$ is not justified. However, triplet relationships compatible with (8) may be considered; if the compatible probability distribution of triplets is denoted by P_c it follows that

$$P_c\{\varphi(\mathbf{h}_n)\} = \frac{1}{2\pi I_0[K(\mathbf{h}_n\mathbf{h}')]} \exp\{K(\mathbf{h}_n\mathbf{h}')$$

$$\times \cos[\varphi(\mathbf{h}_n) - \varphi(\mathbf{h}') - \varphi(\mathbf{h}_n - \mathbf{h}')]\}, \quad (9)$$

with the value of $K(\mathbf{h}_n\mathbf{h}')$ given by (8). This formula may be compared with that given by Cochran (1955) for the estimate of a phase through a triplet relationship. The only difference is (7) occurring in the denominator of $K(\mathbf{h}_n\mathbf{h}')$ which now becomes dependent on the coset n.

For $n = 0$, the subset of strong main reflexions, triplets of the type 'strong–strong–strong' and 'strong–weak–weak' occur, and are governed by the parameter $K(\mathbf{h}_0\mathbf{h}')$. For $n > 0$ 'weak–strong–weak' and 'weak–weak–weak' type triplets appear with the stronger parameter $K(\mathbf{h}_n\mathbf{h}')$. Thus the distribution of the triplets is apparently no longer uniquely defined (except for the 'strong–strong–strong' ones). The distribution

(a)

(b)

(c)

Fig. 2. Dependence of the cosine invariants

$$\cos \Psi = \cos [\varphi(-\mathbf{h}) + \varphi(\mathbf{h}') + \varphi(\mathbf{h} - \mathbf{h}')]$$

on

$$K(\mathbf{h}\mathbf{h}') \simeq (2/N^{1/2})|E(\mathbf{h})E(\mathbf{h}')E(\mathbf{h} - \mathbf{h}')|$$

for the test example mesolite. (a) Conventional normalization. (b) Separate normalization (renormalization) for sets $k \equiv 0 (\text{mod } 3)$ and $k \equiv 1 (\text{mod } 3)$. (c) Dependence on $K(\mathbf{h}_n\mathbf{h}')$. Conventional normalization. $K(\mathbf{h}_0\mathbf{h}')$ is used for 'strong–strong–strong' triplets and $K(\mathbf{h}_1\mathbf{h}')$ for the remaining ones. The calculation of $K(\mathbf{h}_n\mathbf{h}')$ according to equation (8) is based on $v_0 = \overline{|E(\mathbf{h}_0)|^{2}}^{\mathbf{h}_0} = 2 \cdot 33$ and $v_1 = v_2 = \overline{\|E(\mathbf{h}_1)|^{2}}^{\mathbf{h}_1} = 0 \cdot 32$.

seems to depend on the coset type of the phase to be determined by the triplet. A possible way out of this dilemma is to assume that the observed probability distribution of the triplets of a given type may be estimated through the strongest value of K: e.g. $K(\mathbf{h}_n\mathbf{h}')$ for triplets 'weak–strong–weak' connecting reflexions of the coset n. The value $K(\mathbf{h}_0\mathbf{h}')$ of (8) for triplets of the same type 'strong–weak–weak' contributing to a strong main reflexion would correspond to the low weight for this case.

Test example

Mesolite, $Na_2Ca_2Al_6Si_9O_{30}.8H_2O$, is a zeolite of the natrolite group with an interesting superstructure caused by cation ordering in the zeolite cavities. The structure was solved by Adiwidjaja (1972) with trial and error and later, independently, by Gramlich (1975) using *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Crystal data are $a = 18 \cdot 41$ (1), $b = 56 \cdot 67$ (1), $c = 6 \cdot 547$ (2) Å; space group $Fdd2$. The crystal structure is strongly related to natrolite and scolezite with a threefold b axis (Adiwidjaja, 1972).

Cosine invariants of all three types 'strong–strong–strong', 'weak–strong–weak' and 'weak–weak–weak' are analysed as a function of $K(\mathbf{h}_n\mathbf{h}')$. Fig. 2(a) shows the distribution for conventional normalized structure factors. Triplets of strong reflexions only and those with reflexions from the weak cosets clearly belong to two different populations. Separate normalization of the subset of strong reflexions and the weak coset does not provide a well defined dependence of the invariants on $K(\mathbf{h}_n\mathbf{h}')$, cf. Fig. 2(b). In principle, the coset $n = 1$ of reflexions with $k \equiv 1 \pmod 3$ is sufficient for the description of the systematically weak reflexions since the coset $k \equiv 2 \pmod 3$ is Friedel conjugate with respect to the latter. If the cosine invariants are plotted against $K(\mathbf{h}_n\mathbf{h}')$ with values of the index n chosen as described in the previous section, a satisfactorily smooth curve is obtained (Fig. 2c). The distribution of the triplet phases for a given value of $K(\mathbf{h}_n\mathbf{h}')$ is compared with the theoretical curve $P_c(\Psi)$ in Fig. 3.

Limits of the method

Although the theory presented here is quantitatively different from the method of Fan *et al.* (1983) it confirms the essential features: if nothing is known about the superstructure 'weak–strong–weak' triplets may be very useful, whereas triplets involving three reflexions of the weak cosets may be much less reliable. The theory is based on the assumption of an equal-atom structure, and the method will, in fact, fail for certain heavy-atom structures.

Cochran (1955) has shown that the integral over the cubed electron density is a powerful overall esti-
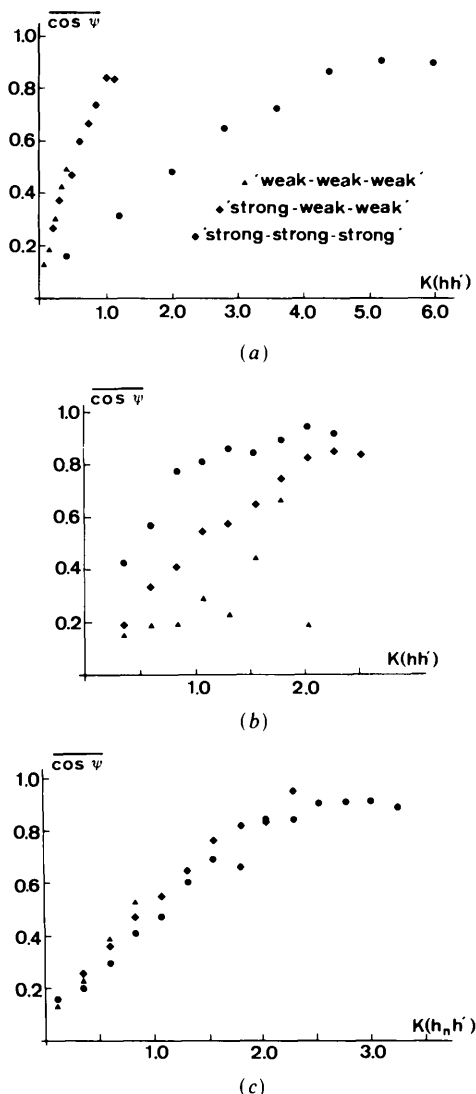
mate of the triplets:

$$V \int_0^1\!\!\int\!\!\int (\rho - \bar{\rho})^3 \, dx = (1/V^2) \sum_{h,k}{}' F(h)F(-k)F(k-h).$$

V is the unit-cell volume; ρ and $\bar{\rho}$ are the electron density and its average. Trivial triplets with $h = 0$, $k = 0$ or $h = k$ are excluded from the primed sum: $F(000)$ may be formally set equal to zero. $\rho(x)$ is decomposed into the subcell part ρ_p, the Fourier transform of the strong main reflections, and $\Delta\rho$, the difference or complement structure [the latter concept was proposed by Jeffery (1964) for the Fourier transform of the weak coset reflexions]:

$$\rho(x) = \rho_p(x) + \Delta\rho(x). \tag{10}$$

Using these terms in the integral above, the cases with squared and cubed complement structure are of special interest:

$$V \int_0^1\!\!\int\!\!\int (\rho_p - \bar{\rho}) \, \Delta\rho^2 \, dx$$
$$= (1/V^2) \sum_{h_0,h_n'} \mp (h_0)F(-h_n')F(h_n' - h_0). \tag{11}$$

The right hand side is the sum of the 'strong–weak–weak' triplets. The left hand side may be considered as a correlation coefficient between ρ_p and $\Delta\rho^2$: $\overline{\rho_p \Delta\rho^2} - \bar{\rho}\,\overline{\Delta\rho^2}$. It is generally positive but may be zero or negative if the maxima of $\Delta\rho^2$, the squared complement structure, coincide with values of the subcell structure which are less than or equal to the average electron density $\bar{\rho} = \bar{\rho}_p$. This may be possible if heavy atoms do not contribute significantly to $\Delta\rho$, whereas light atoms do. Hence, the typical conditions for successful application of *DIRDIF* (Beurskens *et al.*, 1981) describe the limits of the direct method of this paper and of Fan *et al.* (1983). The converse is also true, so that the methods are in fact complementary.
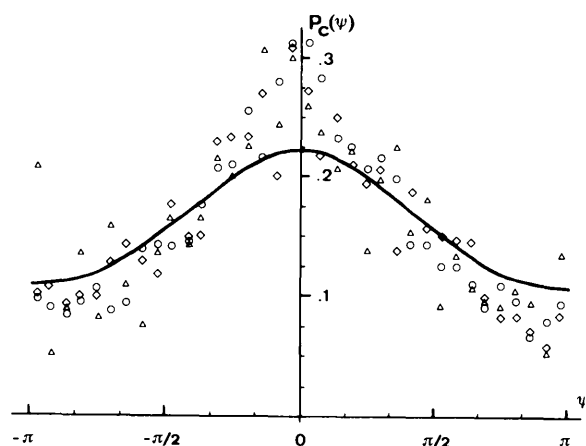

Fig. 3. Observed and calculated distribution $P_c(\Psi)$ for triplets with $K(h_n h') = 0.36$. The observed data are taken from the interval $K(h_n h') = 0.36$ (12).

The integral over the cubed complement structure,

$$V \int_0^1\!\!\int\!\!\int (\Delta\rho)^3 \, dx = (1/V^2) \sum_{h_n,h_m'} F(h_n)F(-h_m')F(h_m' - h_n) \tag{12}$$

with

$$n \neq 0, \qquad m \neq 0, \qquad n \neq m,$$

is given by the sum of the 'weak–weak–weak' triplets. The integral over $\Delta\rho$ is zero since the Fourier transform of $\Delta\rho$ is zero at the origin by definition. Therefore, the integral over $(\Delta\rho)^3$ is probably zero: normal and aberrant 'weak–weak–weak' triplets are equally probable. However, if a few large negative peaks in $\Delta\rho$ are compensated by a greater number of small positive ones, aberrant triplets are highly probable. Correspondingly, normal triplets may be expected in the opposite case. According to the examples given by Boehme (1982), 'weak–weak–weak' triplets with a high value of $K(hh')$ may be more reliably π than 0 under specific conditions. Equation (12) is a general criterion for these conditions.

Symmetry and origin definition

Solving superstructures by direct methods in two steps as proposed by Fan *et al.* (1983) requires the usual origin definition and a secondary one for the subcell structure. This may be seen most easily in the following example. Consider a centrosymmetric superstructure $(P\bar{1})$ where all three edges of the subcell (space group $P\bar{1}$ assumed for the subcell structure) are doubled ($p = 8$). Only one of the eight non-equivalent symmetry centres in the subcell can be maintained for the superstructure. In order to guarantee the occurrence of the correct solution in the multisolution set all possible non-equivalent origins of the subcell structure must be taken into account systematically. Therefore, it is not sufficient to select the seminvariant starting reflexions solely according to the criteria of optimal strategy as is done by the *CONVERGE* procedure of *MULTAN*. In the example above, the seminvariant reflexions must be carefully selected so that the origin of the subcell structure can be properly defined. If this is done, the multisolution procedure will of course provide the complete set of non-equivalent maximal subgroups of the superspace group automatically, and the correct solution can be found. For a discussion of non-equivalent subgroups see Billiet (1981).

This behaviour can be explained by the relatively low weight $K(hh')$ allotted in (8) to any contribution of systematically weak reflexions to the strong ones. This compares well with the fact that the weak coset reflexions which are necessary for complete origin definition do not contribute to the first step in the

two-step procedure of Fan *et al.* (1983). Although an automatic solution of the secondary origin problem may be feasible without the knowledge of the space group of the subcell structure,* it would be much more efficient if this space group were known.

The weak link between different cosets

The probabilities (8) indicate that there is a weak link between different cosets through the phase relationships. This is accounted for in the two-step procedure of Fan *et al.* (1983) by disregarding relationships involving three systematically weak reflexions. Phase shifts of up to three cosets (or up to six if Friedel-connected pairs are counted separately) can be fixed by origin definition. In addition, at least one reflexion of any possibly remaining coset should appear in the starting set. In the $P\bar{1}$ example above, the seven cosets (in this case parity classes) must be present in the starting set. The multisolution procedure will then provide all possible phase shifts of the cosets.

However, if there are no phase restrictions for the reflexions of the cosets, troubles may arise. Fan *et al.*'s (1983) equation, *i.e.* equation (2) with the second sum neglected, is invariant under an overall phase shift of the considered coset *n*. Examples have been described by Boehme (1983). It cannot be expected that such a phase shift, introduced by the starting phases, will be refined in a tangent refinement procedure based on Fan *et al.*'s equation. The correct solution might be unrecognizable if the starting phases of the multisolution method are varied in the usual steps of about $\pi/2$. The use of all triplets, as indicated by (8), in the final stages of the tangent refinement could perhaps solve the problem. Furthermore, the inclusion of these triplets is necessary in order to make the procedure compatible with the Sayre equation if statistical weights are used as proposed by Hull & Irwin (1978).

It has been tacitly assumed that the phase problem has a unique solution (*cf.* the discussion in Hauptman & Karle, 1953). Practical experience has confirmed this assumption: sets of homometric structures fulfilling all criteria of reasonable interatomic distances and thermal parameters are extremely rare. Homometric sets of superstructure solutions with different phase shifts of the cosets may not be easily discernible by the usual figures of merit because of the inherent weak link between the cosets. Careful refinements and critical discussions of facts of crystal chemistry may be necessary in order to obtain a final unique solution of the superstructure problem (*cf.* Schulz & Tscherry: Appendix in Tscherry, Schulz & Laves, 1972).

---

* For example, by requiring that the greatest common divisor of all determinants formed by the starting reflexions from the strong subgroup of main reflexions should equal *p*, the number of subcells in the unit cell.

Conclusion

If pseudotranslation symmetry of a structure is caused by more or less exactly fulfilled rational dependence of heavy atoms, difference structure factor methods (van den Hark, Prick & Beurskens, 1976; Hull & Irwin, 1978) are superior to renormalization procedures. The latter will invariably fail in the limiting case of weak reflexion cosets caused exclusively by very light atoms accompanied by very heavy ones in rationally dependent positions.

Although renormalization has been a successful tool for the direct solution of superstructures it implies the disadvantage that phase relationships between three reflexions of the weak cosets should be removed (Fan *et al.*, 1983). Consistent contributions of all triplets are provided by a coset-dependent reliability parameter $K(\mathbf{h}_n\mathbf{h}')$ given in (8) of this paper. Renormalization is not necessary but the technical disadvantage of the selection of a representative number of reflexions for each coset is implied. This will of course be managed automatically if renormalized structure factors are used. However, renormalization implies a modified $K_m(\mathbf{h}_n\mathbf{h}'_m)$ dependent not only on coset *n* but also on coset *m* of any contributing reflexion $\mathbf{h}'_m$ in order to remain compatible with Sayre's equation.

The influence of rational dependence on higher-order invariants is not well known. One of the few available examples is the crystal structure of prostaglandin $E1$-9-sulfone (Fronckowiak, Fortier, DeTitta & Hauptman, 1977) which was solved using quinets only. Since two independent molecules in the cell are approximately related by $\frac{1}{2}c$, the *l*-odd data are systematically weak. The discriminants of 'strong–strong–strong–weak–weak' type quintets provided very reliable estimates of the quintets, even though the absolute values of the discriminants were small compared with those of the 'strong–strong–strong–strong–strong' quintets (Hauptman, 1983). Therefore, it might be expected that relationships for higher-order invariants exist which are similar to those described in this paper for triplets.

References

ADIWIDJAJA, G. (1972). *Strukturbeziehungen in der Natrolithgruppe und das Entwaesserungsverhalten des Skolezit.* Dissertation, Univ. Hamburg.
BEURSKENS, P. T. & BOSMAN, W. P. (1982). *Z. Kristallogr.* **159**, 139–140.

BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., GOULD, R. O., VAN DEN HARK, TH. E. M., PRICK, P. A. J., NOORDIK, J. H., BEURSKENS, G. & PARTHASARATHI, V. (1981). DIRDIF. Direct Methods for Difference Structures. Tech. Rep. 1981/2. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

BEURSKENS, P. T. & NOORDIK, J. H. (1971). Acta Cryst. A27, 187–198.

BILLIET, Y. (1981). Acta Cryst. A37, 649–652.

BOEHME, R. (1982). Acta Cryst. A38, 318–326.

BOEHME, R. (1983). Z. Naturforsch. Teil A, 38, 304–307.

COCHRAN, W. (1955). Acta Cryst. 8, 433–478.

FAN, H.-F., YAO, J.-X., MAIN, P. & WOOLFSON, M. M. (1983). Acta Cryst. A39, 566–569.

FAN, H.-F. & ZHENG, Q.-T. (1981). Acta Cryst. A37, C329.

FRONCKOWIAK, M., FORTIER, S., DeTITTA, G. & HAUPTMAN, H. (1977). Am. Crystallogr Assoc. Meet. 21–25 February 1977, Asilomar, California, USA. Abstr. KM3.

GIACOVAZZO, C. (1983). Acta Cryst. A39, 685–692.

GRAMLICH, V. (1975). Acta Cryst. A31, S90.

GRAMLICH, V. (1978). Acta Cryst. A34, S43.

HARK, TH. E. M. VAN DEN, PRICK, P. & BEURSKENS, P. T. (1976). Acta Cryst. A32, 816–821.

HAUPTMAN, H. (1983). Private communication.

HAUPTMAN, H. & KARLE, J. (1953). Solution of the Phase Problem. I. The Centrosymmetric Crystal. Am. Crystallogr. Soc. Monogr. No. 3. New York: Polycrystal Book Service.

HAUPTMAN, H. & KARLE, J. (1959). Acta Cryst. 12, 846–850.

HEINERMAN, J. J. L., KRABBENDAM, H. & KROON, J. (1977). Acta Cryst. A33, 873–878.

HULL, S. E. & IRWIN, M. J. (1978). Acta Cryst. A34, 863–870.

JEFFERY, J. W. (1964). Acta Cryst. 17, 776–777.

MAIN, P. (1976). In Crystallographic Computing Techniques, edited by F. R. AHMED, pp. 97–105. Copenhagen: Munksgaard.

MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J.-P. (1974). MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univ. of York.

SCHULZ, H. (1976). Z. Kristallogr. 144, 440–441.

TSCHERRY, V., SCHULZ, H. & LAVES, F. (1972). Z. Kristallogr. 135, 175–198.

WOODING, R. A. (1956). Biometrika, 43, 212–215.

Erratum

Acta Cryst. (1984). A40, 616

The standardization of inorganic crystal-structure data: erratum. By E. PARTHÉ and L. M. GELATO, Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24, quai Ernest Ansermet, CH-1211 Genève 4, Switzerland.

(Received 14 June 1984)

There is a printing error in Table 8 of Parthé & Gelato [Acta Cryst. (1984), A40, 169–183]. For PaBr$_3$ the published space group was Ccmm, while that for the standardized data is Cmcm.

All information is given in the Abstract.

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. (1984). A40, 616

Melting, localization, and chaos. Edited by R. K. KALIA and P. VASHISTA. Proceedings of the 9th Midwest Solid-State Theory Symposium, November 1981, Argonne National Laboratory, USA. Pp. xxiii + 301. Elsevier Science Publishing Co Inc, 1982. Price US $60.00, Dfl 160.00.

The book contains the reprints of 52 contributed and 16 invited papers, presented at the symposium mentioned above. It can be regarded as a review of the field of the melting process and of atomic arrangements in non-crystalline materials. Concerning the melting process, different models are discussed, both from the theoretical point of view and in the form of computer simulation. Also, the molecular dynamical treatment of phase transitions is described. The book includes a comprehensive theoretical and experimental treatment of metal–insulator transitions in disordered metals, thin films and amorphous semiconductors. Also treated are those phase transitions which are important in the theory of the mutual interaction of elementary particles, such as quarks and gluons. Throughout the whole volume there is scarcely one remark that has to do with crystallographic problems; however, for the amorphologist, the book may be of some interest. The main interest it will serve, however, will be for research workers concerned with the fields of percolation, critical phenomena etc. The book is of interest for the experimental as well as for the theoretical physicist – but, with experience, not so much for beginners. One has the impression that the frame for that conference, and therefore also for the ensuing conference proceedings, was a little bit too wide-spread.

S. STEEB

Max-Planck-Institut für Metallforschung
Seestrasse 92
7000 Stuttgart 1
Federal Republic of Germany