

Direct Methods for Incommensurately Modulated Structures. On the Applicability of Normalized Structure Factors

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Abstract

The recently defined normalized structure factors for incommensurately modulated structures [Lam, Beurskens & van Smaalen (1993). *Acta Cryst.* A49, 709–721] have been subjected to extensive tests regarding their applicability in direct methods for phase determination. It is shown that the probability distribution associated with the structure invariants $E(-\mathbf{H})E(\mathbf{H})E(\mathbf{H} - \mathbf{H}')$, where \mathbf{H} and \mathbf{H}' are reciprocal vectors of main and/or satellite reflections, approximately has the same functional form as the Cochran distribution but triplet phase relations are relatively less reliable when satellites are involved. The use of the multidimensional Sayre equation for the determination of phases of satellite reflections [Hao, Liu & Fan (1987). *Acta Cryst.* A43, 820–824; Fu & Fan (1994). *J. Appl. Cryst.* 27, 124–127] is not improved by using normalized structure factors instead of ordinary structure factors.

1. Introduction

Direct methods for solving the phase problem in X-ray crystallography have been extended to incommensurately modulated structures by Fan and co-workers (Hao, Liu & Fan, 1987; Fu & Fan, 1994). The method was successfully used in solving modulated structures of ankangite (Xiang, Fan, Wu, Li & Pan, 1990), $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y$ (Mo, Cheng, Fan, Li, Sha, Zheng, Li & Zhao, 1992) and (perylene)- $[\text{Co}(\text{mnt})_2](\text{CH}_2\text{Cl}_2)_{0.5}$ (mnt = maleonitriledithiolate)§ (Lam, Beurskens, Smits, van Smaalen, de Boer & Fan, 1995), employing structure factors (F) for estimating the relative importance of the terms in the Sayre equation. The method was further extended to

incommensurate composite crystals (Fan, van Smaalen, Lam & Beurskens, 1993; Beurskens, Beurskens, Lam, van Smaalen & Fan, 1994; Sha, Fan, van Smaalen, Lam & Beurskens, 1994).

Recently, normalized structure factors (E) were defined for main reflections and satellite reflections of incommensurately modulated structures (Lam, Beurskens & van Smaalen, 1992, 1993, 1994). The conventional definition of normalized structure factors is

$$E(\mathbf{H}) = F(\mathbf{H})/g(\mathbf{H}),$$

where $g(\mathbf{H})$ is a real function that compensates for the fall-off of the scattering power of the atoms with increasing $\sin(\theta)$, including the effect of the overall temperature factor. This definition was extended to modulated structures by the introduction of a modified expression for the function $g(\mathbf{H})$, which includes overall modulation effects. Different expressions for $g(\mathbf{H})$ were required for main reflections and satellites. It was shown that the statistical distributions of the magnitudes of the newly defined E values obey similar distributions to those known for non-modulated crystals. It is not at all trivial or obvious, however, that phase relationships employing normalized structure factors of main and satellite reflections have the same statistical properties as for conventional (non-modulated) structures.

In the present paper, we explore in two ways the meaning of the normalized structure factors for modulated structures. Firstly, the probability distributions for triplet phases are calculated for a series of structures and compared with the Cochran distribution (Cochran & Woolfson, 1955; Cochran, 1955). Secondly, normalized structure factors instead of F values are used in the direct-methods procedure for phase determination as developed by Fan *et al.* (1993). Although it is expected that both approaches (F and E values) will generally provide a good solution of the phase problem, we investigated the possible advantage of using normalized structure factors.

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1.1. Formulae and definitions

The most frequently used phase relation in direct methods for solving (non-modulated) crystal structures is the three-phase structure invariant, *i.e.* the phase of the triple product $E(-\mathbf{H})E(\mathbf{H}')E(\mathbf{H}-\mathbf{H}')$ or $F(-\mathbf{H})F(\mathbf{H}')F(\mathbf{H}-\mathbf{H}')$. The phase sum Φ of the triplet,

$$\Phi(\mathbf{H}, \mathbf{H}') = \varphi(-\mathbf{H}) + \varphi(\mathbf{H}') + \varphi(\mathbf{H}-\mathbf{H}') \quad (1)$$

is independent of the choice of the space-group origin and is likely to be close to zero for large magnitudes of $|E(-\mathbf{H})|$, $|E(\mathbf{H}')|$ and $|E(\mathbf{H}-\mathbf{H}')|$. In other words, the so-called Σ_2 relationship,

$$\varphi(\mathbf{H}) \simeq \varphi(\mathbf{H}') + \varphi(\mathbf{H}-\mathbf{H}'), \quad (2)$$

is more reliable if all three corresponding $|E|$ values are large.

The probability density for Φ is given by the Cochran distribution (Cochran, 1955):

$$P(\Phi) = [2\pi I_0(\kappa)]^{-1} \exp[\kappa \cos(\Phi)], \quad (3)$$

where I_n is a modified Bessel function of the first kind and

$$\kappa(\mathbf{H}, \mathbf{H}') = 2C|E(-\mathbf{H})E(\mathbf{H}')E(\mathbf{H}-\mathbf{H}')|. \quad (4)$$

with

$$C = \sum_{j=1}^{N_0} Z_j^3 \left[\sum_{j=1}^{N_0} Z_j^2 \right]^{-3/2}. \quad (5)$$

N_0 is the number of atoms in the unit cell. Note that, for equal-atom structures, $C = N_0^{-1/2}$. The variance of Φ is given by (Karle & Karle, 1966)

$$\sigma^2(\kappa) = (\pi^2/3) + [4/I_0(\kappa)] \left\{ \sum_{n=1}^{\infty} [I_{2n}(\kappa)/(2n)^2] - \sum_{n=0}^{\infty} [I_{2n+1}(\kappa)/(2n+1)^2] \right\}.$$

In the case of centrosymmetric structures, where the phases φ are restricted to 0 and π , the probability that the sign relationship

$$s(\mathbf{H}) \simeq s(\mathbf{H}')s(\mathbf{H}-\mathbf{H}') \quad (6)$$

is true is given by (Cochran & Woolfson, 1955)

$$P^+(x) = \frac{1}{2} + \frac{1}{2} \tanh(x) \quad (7)$$

with

$$x(\mathbf{H}, \mathbf{H}') = C|E(-\mathbf{H})E(\mathbf{H}')E(\mathbf{H}-\mathbf{H}')| = \kappa(\mathbf{H}, \mathbf{H}')/2. \quad (8)$$

For modulated structures, the phase sum

$$\Phi = \varphi(-\mathbf{H}_{\text{sat}}) + \varphi(\mathbf{H}'_{\text{main}}) + \varphi(\mathbf{H}_{\text{sat}} - \mathbf{H}'_{\text{main}}),$$

where $\mathbf{H}'_{\text{main}}(h', k', l', 0)$ is a main reflection and $\mathbf{H}_{\text{sat}}(h, k, l, m)$ and $\mathbf{H}_{\text{sat}} - \mathbf{H}'_{\text{main}}$ are satellite reflections,

Table 1. Test structures, with space group of the average structure and references; limitations for $s [= \sin(\theta)/\lambda]$ are given

Compound	Space group	s (\AA^{-1})	Reference
Na_2CO_3	$C2/m$	1.00	van Aalst, den Hollander, Peterse & de Wolff (1976)
K_2SeO_4	$Pnam$	1.00	Yamada & Ikeda (1984)
NbTe_4	$P4/mcc$	1.00	van Smaalen, Bronsema & Mahy (1986)
$\text{K}_{0.3}\text{MoO}_3$	$C2/m$	0.80	Schutte & de Boer (1993)
Mo_8O_{23}	$P2/c$	0.80	Komdeur, de Boer & van Smaalen (1990)
PECO*	$P\bar{1}$	0.66	Lam, Beurskens, Smits, van Smaalen, de Boer & Fan (1995)
A1-A4	$P\bar{1}$	0.80	Artificial C_{50} structures, see Table 2
C1-C4	$P\bar{1}$	0.80	Artificial C_{50} structures, see Table 2

*PECO is short notation for the compound (perylene)- $[\text{Co}(\text{mnt})_2](\text{CH}_2\text{Cl}_2)_{0.5}$, mnt is maleonitridithiolate.

is also a structure invariant. The following triplet relations can be distinguished:

$$mmm : \varphi(\mathbf{H}_{\text{main}}) \approx \varphi(\mathbf{H}'_{\text{main}}) + \varphi(\mathbf{H}_{\text{main}} - \mathbf{H}'_{\text{main}}); \quad (9)$$

$$sms : \varphi(\mathbf{H}_{\text{sat}}) \approx \varphi(\mathbf{H}'_{\text{main}}) + \varphi(\mathbf{H}_{\text{sat}} - \mathbf{H}'_{\text{main}}); \quad (10)$$

$$sss : \varphi(\mathbf{H}_{\text{sat}}) \approx \varphi(\mathbf{H}'_{\text{sat}}) + \varphi(\mathbf{H}_{\text{sat}} - \mathbf{H}'_{\text{sat}}); \quad (11)$$

with similar expressions for centrosymmetric *mmm*, *sms* and *sss* triplets for the sign relation (6).

In analogy with ordinary direct methods and in view of the validity of the Sayre equation for modulated structures [proved by Hao *et al.* (1987)], it may be expected that the reliability of the triplet relations (2) and (6) increases with increasing values of $|E(-\mathbf{H})|$, $|E(\mathbf{H}')|$ and $|E(\mathbf{H}-\mathbf{H}')|$ for all triplet structure invariants. In this paper, we present numerical tests for this hypothesis. In addition, it may be expected that the probability distribution associated with the structure invariants $E(-\mathbf{H})$, $E(\mathbf{H}')$ and $E(\mathbf{H}-\mathbf{H}')$ closely resembles the Cochran distribution (3) for the *mmm* triplets but the nature of the distribution for *sms* triplets is in principle unknown. In this paper, we also investigate the resemblance of the *sms* triplet distribution with the Cochran distribution.

2. Numerical test procedures and results

Numerical tests have been performed with structure factors from several compounds with a one-dimensional displacive modulation. In all cases, main reflections and first-order satellites were used. Several data sets were obtained for experimentally determined centrosymmetric structures (Table 1) but, instead of the measured intensities, calculated structure factors were employed,

Table 2. Characteristics of artificial C_{50} structures with displacive modulations (see Table 1) (Lam, Beurskens & van Smaalen, 1993)

Compound	Atomic modulation function
A1	Random amplitudes and directions
A2	Random amplitudes and directions
A3	Identical amplitudes and random directions
A4	Rigid-body displacement
C1	Random amplitudes and directions
C2	Random amplitudes and directions
C3	Identical amplitudes and random directions
C4	Rigid-body displacement

thus avoiding complications due to incomplete data sets as published in the literature. Further tests were done for artificial non-centrosymmetric and centrosymmetric test structures (Tables 1 and 2), with randomly generated atomic coordinates and various modulation characteristics (Lam *et al.*, 1993). For each structure except (perylene)[Co(mnt)₂](CH₂Cl₂)_{0.5}, all reflections within the $\sin(\theta)/\lambda$ range as given in Table 1 were calculated in order to be able to use the normalization procedure and to perform the calculations given in §2.1. For (perylene)[Co(mnt)₂](CH₂Cl₂)_{0.5}, we used the same set of reflections as used in the structure refinement (Lam *et al.*, 1995). Only the reflections with largest F and largest E values were used for the tests given in §2.2.

2.1. Test results regarding the three-phase structure invariant

To investigate the meaning and usefulness of $|E|$ values for modulated structures, a number of tests were done on structures given in Tables 1 and 2. Of the three types of triplet relations given by (9)–(11), the *sms* triplets (10) are of prime interest because they play a key role in the expansion from phases of main reflections to those of the satellites. Almost all incommensurately modulated structures determined up to now were solved after finding the average structure. Good starting phases of the main reflections therefore can be assumed to be available for generating phases of the satellites. For most of the strong reflections, the phases will not differ much from the phases calculated for the average structure, therefore *mmm* triplets should follow the Cochran distribution reasonably well. Nevertheless, for comparison, we have included the *mmm* triplets (9) in our test calculations. The *sss* triplets (11) have not been included because they involve second- or higher-order satellites, which are usually few and weak. Moreover, if all phases of first-order satellites have been determined, straightforward tangent expansion would lead to the phases of the higher-order satellites.*

* The program *DIMS* (see §2.2) does use higher-order satellites when available.

For all test structures, all possible *mmm* and *sms* triplets were generated and the phase sums Φ (1) were obtained from the contributing calculated structure factors. Triplets involving special reflections were omitted because they may show different statistical behaviour. Nevertheless, preliminary test runs for Na₂CO₃, NbTe₄ and K₂SeO₄ show that the inclusion of special reflections does not make any significant difference in the probability distributions.

For the non-centrosymmetric case, the variance was calculated by determining the average squared phase sums found for the *mmm* and *sms* triplets in intervals of

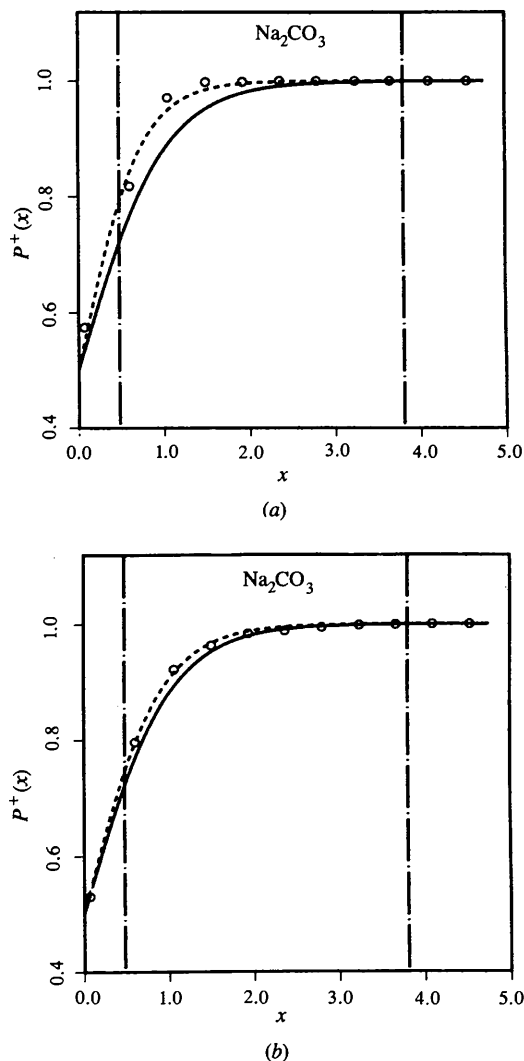


Fig. 1. Probability distribution $P^+(x)$ for structure Na₂CO₃. Circles represent experimental values. Solid curves represent the theoretical distribution for non-modulated structures according to Cochran. Dashed curves represent the q -fitted curve through the experimental points. Vertical lines are drawn at values of x where $|E(-\mathbf{H})E(\mathbf{H})E(\mathbf{H}-\mathbf{H}')|^{1/3}$ is equal to 1.3 or 2.6. (a) Probability distribution involving *mmm* triplets. (b) Probability distribution involving *sms* triplets.

κ . For the centrosymmetric case, the dependency of P^+ as a function of x was calculated by determining the ratio between the correct Σ_2 relations and the total number of Σ_2 relations in a given interval of x . A number of typical examples are given in Figs. 1 to 4. In all figures, the experimental points are presented together with the theoretical Cochran distributions [(3) and (7)] for non-modulated structures (solid line). The interval between the vertical lines given in Figs. 1–4 represents triplets that are of importance in direct-methods procedures. Triplets on the left are too weak to be used while triplets on the right are important but few in number. Although the test structures show distributions of $P(\Phi)$ or P^+ that roughly follow the general shape of the Cochran distributions, there are some differences, which will be discussed later.

The general trend in the results for the test structures shows that the triplet relationships involving satellite

reflections are less reliable than as given by the Cochran distribution for non-modulated structures. This is not surprising since the factor C (5) is smaller for larger structures, which suggests that C should also be smaller for modulated structures as they are 'larger' (*i.e.* more complicated) than the average structures. Note that for modulated structures we have taken N_0 as the number of atoms in the unit cell of the basic structure but it is clear that more 'atoms' are needed to describe the complete structure. In principle, we do not know how to define C for modulated structures. Therefore, we introduce an adjustable expression

$$C_{\text{mod}} = qC_{\text{aver}}$$

in which C_{aver} is the value of C calculated for the cell contents of the average structure (5), q is a 'correction' factor and C_{mod} is the redefined C for modulated structures. C_{mod} is used in the theoretical expressions

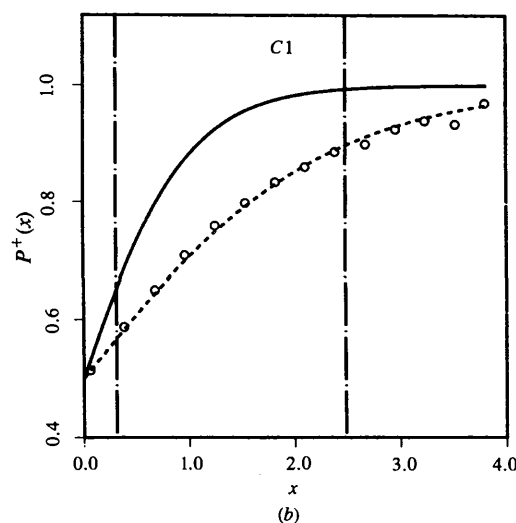
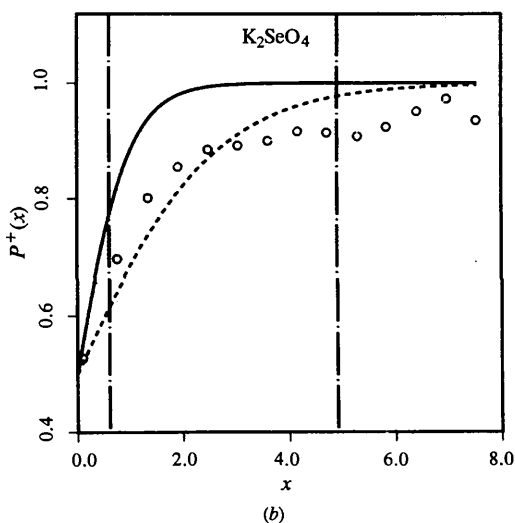
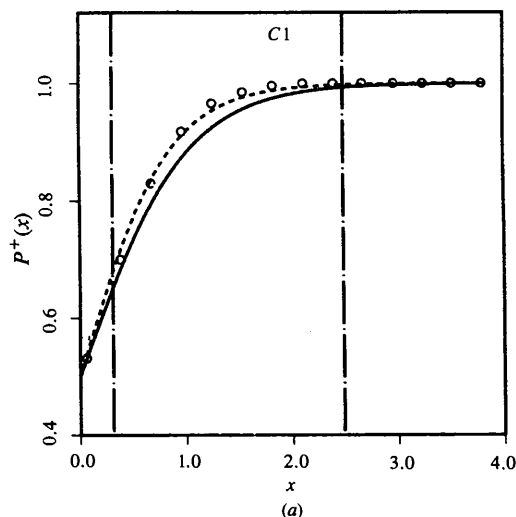
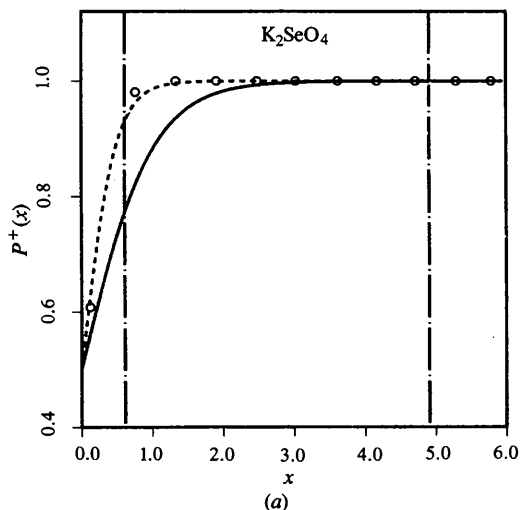


Fig. 2. Probability distribution $P^+(x)$ for structure K_2SeO_4 . See Fig. 1 for explanation.

Fig. 3. Probability distribution $P^+(x)$ for structure C1. See Fig. 1 for explanation.

(4) and (8). The parameter q is not known at the outset of the application of direct methods. It is expected that $q(mmm)$ for mmm triplets is about unity because the atomic positions of the average structure are usually well determined by the main reflections only. The $q(sms)$ values are expected to be smaller than unity because the main satellite reflections together define a 'larger' structure.

To describe the behaviour of the triplets, we have determined the q values for all test structures using the phases calculated from the known (modulated) structure. A fit* of the Cochran distribution to the experimental points, using q as the fitting parameter is also presented in the figures (dashed line).

The residual factor of the experimental points towards this modified Cochran distribution for centrosymmetric structures is defined as

$$R = \left\{ \frac{\sum_{i=1}^n (P_i^+ - P_{\text{mod},i}^+)^2}{\sum_{i=1}^n (P_{\text{mod},i}^+)^2} \right\}^{1/2},$$

in which P_i^+ is the experimental value, $P_{\text{mod},i}^+$ is the value belonging to the fitted curve of the modified Cochran distribution and n is the number of points used in the fitting procedure (n ranges from 6 to 14). A similar expression for non-centrosymmetric structures can be defined. [The least-squares estimated variance of q is given by $\sigma^2(q) = q^2 R^2 (n-1)^{-1}$.] Numerical values for the q values as well as the R values of mmm and sms triplets are given in Table 3 to describe the modified Cochran distribution. Some of the $q(mmm)$ values for experimentally determined structures deviate from $q = 1$, which is due to structural effects.† For randomly generated structures, the $q(mmm)$ values are around $q = 1$, showing that the Cochran distribution is valid for mmm triplets. For all structures, the $q(sms)$ values are much smaller, implying that the sms triplets are less reliable than the mmm triplets. A relatively small R value implies that the fitted curve follows the modified Cochran distribution rather well.

2.1.1. Individual results. Firstly, consider Na_2CO_3 (Fig. 1). Within the interval given by the two vertical lines, the Cochran distribution (solid line) rises rather quickly to its maximum at $P^+(x) = 1$. Consequently, the triplets within this interval are associated with large probabilities. (Of course, Na_2CO_3 is a small structure and its basic structure is easily solved by direct methods.) The experimental curve for the main reflections gives higher probabilities than the Cochran curve, which is related to the systematics in the structure (atoms at special positions, hypercentric $|E|$

distribution). Although the experimental curve, involving sms triplets, follows the Cochran curve rather precisely, it is lower than the corresponding mmm curve, which means that the sign relationship for sms triplets is slightly less reliable than for mmm triplets. The modified Cochran curves (dashed lines) follow the experimental points rather closely for Na_2CO_3 . Both $q(mmm)$ and $q(sms)$ values are larger than 1, showing that the direct methods for this modulated structure should work extremely well.

The second example is K_2SeO_4 . Compared with Na_2CO_3 , the experimental points for mmm triplets are much higher; $q(mmm) = 2.106$. The probability curve

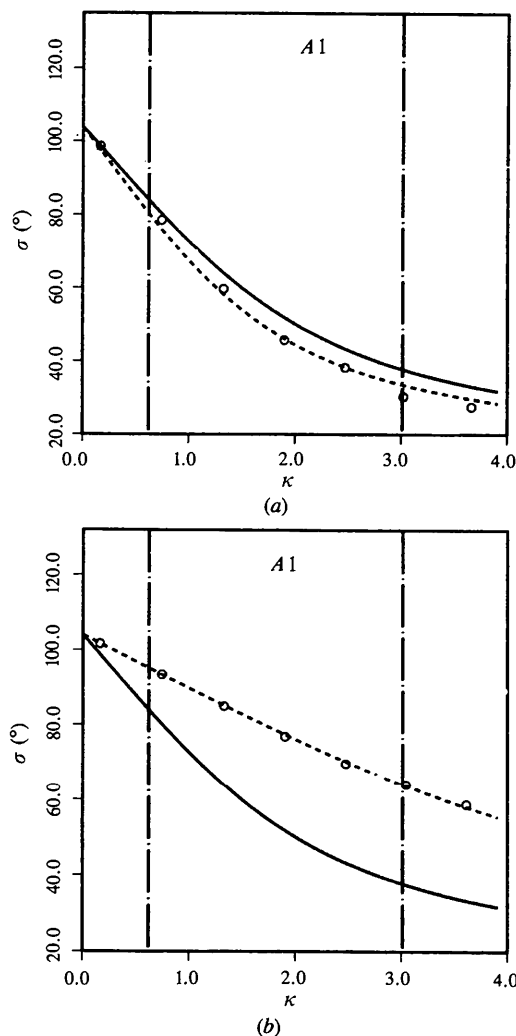


Fig. 4. Standard deviation $\sigma(\kappa)$ for structure A1. Circles represent experimental values. Solid curves represent the theoretical distribution for non-modulated structures according to Cochran. Dashed curves represent the q -fitted curve through the experimental points. Vertical lines are drawn at values of κ where $|E(-\mathbf{H})E(\mathbf{H})E(\mathbf{H}-\mathbf{H}')|^{1/3}$ is equal to 1.3 or 2.2. (a) Standard deviations involving mmm triplets. (b) Standard deviations involving sms triplets.

*Minimizing the squared differences of the experimental points and the Cochran function values. An experimental point is the observed $\sigma^2(\kappa)$ or $P^+(x)$ for a given interval in κ or x , respectively; the number of points is arbitrarily chosen. †*i.e.* non-random distribution of atoms, *e.g.* heavy atoms at special positions.

Table 3. Numerical results of the q -fitting procedure, together with the overall modulation amplitude U (Å) for several test structures

The residual factor R refers to the distribution of $\sigma(\kappa)$ or $P^+(x)$ for non-centrosymmetric (A1–A4) and centrosymmetric (C1–C4) structures, respectively.

	C_{aver}	U	$R(mmm)$	$q(mmm)$	$R(sms)$	$q(sms)$
Na ₂ CO ₃	0.217	0.386	0.014	1.400	0.005	1.113
K ₂ SeO ₄	0.279	0.096	0.008	2.106	0.054	0.381
NbTe ₄	0.226	0.169	0.012	2.699	0.007	0.824
K _{0.3} MoO ₃	0.131	0.033	0.006	3.526	0.046	0.469
Mo ₅ O ₂₃	0.155	0.046	0.007	2.642	0.057	0.203
PECO	0.183	0.421	0.013	0.770	0.020	0.718
A1	0.141	0.040	0.031	1.192	0.005	0.438
A2	0.141	0.200	0.032	1.133	0.018	0.537
A3	0.141	0.200	0.037	1.050	0.027	0.577
A4	0.141	0.200	0.016	0.834	0.023	0.504
C1	0.141	0.040	0.008	1.204	0.011	0.435
C2	0.141	0.200	0.006	1.117	0.006	0.529
C3	0.141	0.200	0.006	1.070	0.007	0.543
C4	0.141	0.200	0.004	0.953	0.014	0.513

for the mmm triplets rises very fast to its maximum, showing that no problems will be encountered when solving the basic structure by direct methods. In contrast with Na₂CO₃, however, the modified Cochran curve involving sms triplets does not follow the experimental points very well. Moreover, although the individual experimental points of the sms triplets show a similar trend compared with the theoretical Cochran distribution for non-modulated structures, the maximum probability of $P^+(x) = 1$ is not reached within the important interval between the vertical lines in Fig. 2. Consequently, the sms triplets are less reliable than predicted by the conventional Cochran distribution; $q(sms) = 0.381$.

Other experimentally determined structures given in Table 1 show a similar trend, hence their results need not be discussed individually.* However, corresponding fitting parameters $q(mmm)$ and $q(sms)$ are given in Table 3.

Results for the random centric test structure C1 are given in Fig. 3. For this test structure, which also reflects the general pattern of the other artificial centric structures, the mmm triplets show a distribution that approximately follows the Cochran distribution† but,

again, the distributions for the sms triplets are below the Cochran curve.

For the random non-centric structure A1, it is seen that the variances involving mmm triplets are approximately normal* and that the variances for sms triplets are much larger than normal, again showing that the sms triplets are less reliable than predicted by the Cochran distribution. Differences in results regarding the different types of modulation (comparing Tables 2 and 3) are significant but not dramatic.

Numerical results for the fitting parameter q , given in Table 3, are compared with the overall modulation amplitude U . No clear correlation can be seen between the q values involving mmm triplets and the overall modulation amplitudes. However, the q values for sms triplets seem to increase with increasing modulation effects, suggesting that the reliability of the sms triplets increases with increasing magnitude of the modulation.†

2.2. Test results using normalized structure factors in the Sayre relation

To examine the result of using normalized structure factors instead of ordinary structure factors, a number of tests were done using the program *DIMS* (Fu & Fan, 1994), which employs the full Sayre relation for modulated structures (Hao *et al.*, 1987) to refine the phases of the satellite reflections using calculated phases for the main reflections and random starting phases for the satellites. Because the procedure uses all reflections simultaneously, the reliabilities of the individual (sms) triplets are not relevant.‡

All tests were performed with known centrosymmetric incommensurately modulated structures (Table 1). The program *DIMS* was used to obtain the phases of the first-order satellites. Various program parameters were used as default values, limiting the number of participating reflections implied using the strongest E and F values. For each structure, the phases (signs) of the largest (normalized) structure factors were calculated by *DIMS* and compared with the true values. In Table 4, results are given for a number of test structures. Increasing the number of reflections (mains and satellites) causes reflections with lower E values to

* Figures representing the probability distribution $P^+(x)$ and standard deviation $\sigma(\kappa)$ for all centrosymmetric and non-centrosymmetric structures presented in Tables 1 and 2, except for those presented in Figs. 1–4, have been deposited with the IUCr (Reference: JS0032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. † Additional experiments on the mmm triplets, in which main reflections were normalized according to the conventional Wilson procedure, showed no significant difference to the mmm distribution given in Fig. 3. As a consequence, the small deviations of the experimental values for mmm distributions from the Cochran curves may be assigned to the not exactly randomness of the generated structures.

* Additional experiments on the mmm triplets, in which main reflections were normalized according to the conventional Wilson procedure, showed no significant difference to the mmm distribution given in Fig. 3. As a consequence, the small deviations of the experimental values for mmm distributions from the Cochran curves may be assigned to the not exactly randomness of the generated structures. † $|F|$ values of satellites increase with increasing modulation effects, which presumably enhances the information content of the E values. The magnitudes of the $|E|$ values have been normalized, but such enhancement can be present in the distributions of the E values. ‡ Note that C_{mod} (§2.1) is obtained *a posteriori* for the purpose of investigating the validity of the Cochran distribution for modulated structures. If $q(sms)$ was known *a priori*, it would have no effect on the *DIMS* procedure.

Table 4. Number of incorrect signs determined by program DIMS for several test structures

E : using normalized structure factors. F : using ordinary structure factors. Different numbers of main and satellite reflections are used; minimum E values for each set of reflections are given in parentheses.

	No. of main No. of satellite		500 E	500 F	1000 E	1000 F
	Na_2CO_3			(0.67)		(0.17)
	500	(1.02)	2	13	2	17
	1000	(0.56)	71	110	63	111
K_2SeO_4			(1.16)		(0.75)	
	500	(1.51)	2	1	2	31
	1000	(0.98)	16	29	27	38
NbTe_4^*			(0.34)		(0.00)	
	350	(1.11)	49	77	60	100
	500	(0.86)	101	114	126	138
PECO			(1.66)		(1.21)	
	500	(1.52)	6	8	12	9
	1000	(0.83)	96	52	129	81
Cl			(1.88)		(1.57)	
	500	(2.26)	4	1	1	1
	1000	(1.93)	4	1	1	2

* Only 642 main reflections are available for NbTe_4 .

participate in the Sayre tangent refinement. Increasing the number of main reflections generally leads to slightly more phase errors owing to the participation of more weak main reflections into the procedure (*i.e.* less reliable phase relationships). Increasing the number of satellites generally leads to many more phase errors. Although the weaker satellite reflections are less accurately phased, they are phased sufficiently well to be useful for the Fourier synthesis, in order to minimize truncation effects.

On comparison of the use of E values versus F values as input to the direct-methods procedure, no general trend is observed: the use of E values does not really reduce the number of wrongly determined phases. In all cases, the structures were easily solved by DIMS.

Note: after solving the phase problem, a four-dimensional electron-density map or an E map (see Appendix A) is to be constructed to extract the modulation amplitudes.

3. Concluding remarks

All test structures show distributions of P^+ or $P(\Phi)$ that more or less follow the shape of the Cochran distribution. Although no mathematical proof is given, the conclusion is reached that the meaning and behaviour of E values for incommensurately modulated structures, when considering the triplet relation, are similar to E values of non-modulated structures. In general, the probability for centric structures of a triplet relation involving satellites and main reflections is lower compared with one involving main reflections only; the standard deviation for the case of non-centrosymmetric structures is larger for the same

value of the triple product $|E(-H)E(H')E(H-H')|$. However, the phase problem for the satellite reflections may still be solved using procedures based on the triplet relation. Phase information may be extracted from the triplet relation by means of symbolic addition, multisolution methods *etc.* Further investigations regarding an adjustment of the constant C_{mod} are in progress. To obtain a more reliable estimation of the triplet probabilities, triplet probability distribution functions are being derived (Peschar, Israël & Beurskens, 1997).

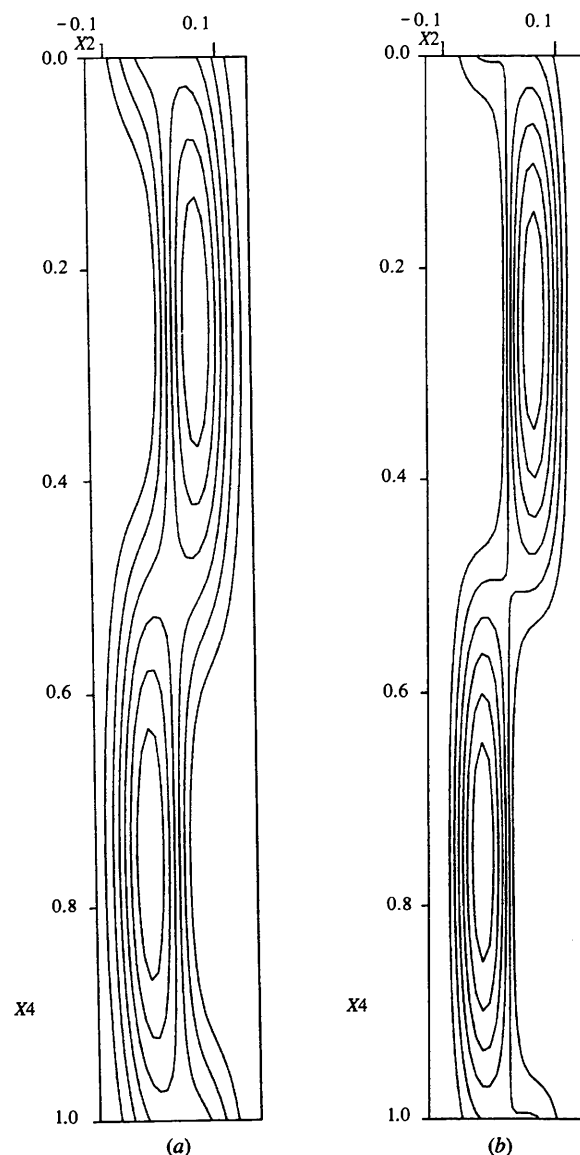


Fig. 5. Section of the four-dimensional Fourier synthesis of Na_2CO_3 through the position of a Na atom. Contours are plotted at arbitrary equally spaced intervals. (a) Using conventional F values. (b) Using E values.

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APPENDIX A

After the application of the direct-methods procedure, it is questionable whether a four-dimensional electron-density map or an E map is to be constructed. A comparison of one atom in an F map with the same atom in an E map is given in Fig. 5. The sharpening effect of using E values instead of F values on the electron-density shape of an Na atom of Na_2CO_3 is displayed on a two-dimensional section in four-dimensional space. The effect of sharpening is partly compensated for by truncation effects (a limited set of reflections is used, while only main reflections and first-order satellites were used in the calculation). The use of E maps in conventional direct-methods procedures suggest that E maps are suitable for automated determination of the modulation on amplitudes (see, for example, Oleksyn & Akselrud, 1995). Nevertheless, care should be taken especially for the higher harmonics of the modulation; it seems that the shape of the modulation of the Na atom in the F map is smoother than in the E map.

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