Laplace transform [the unity on the right-hand side of the first equation of (14)] cannot be derived straightforwardly. Nevertheless, because their equation (14) is correct for some reason, the author believes that the rest of their calculation is useful. In fact, their equation (15) is the same as the present result [(16*a*) and (16*b*)] if one replaces $\{\tau/(1+\tau p_{o,h})\}$ with the general expression $g(p_{o,h})$ after putting $p_o = p$ and $p_h = q$.

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The Joint Probability Distribution of Any Set of Phases Given Any Set of Diffraction Magnitudes. III. A Function to Maximize

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Abstract

The joint probability distribution method described in paper I [Giacovazzo, Burla & Cascarano (1992). *Acta Cryst.* A**48**, 901–906] and paper II [Burla, Cascarano & Giacovazzo (1992). *Acta Cryst.* A**48**, 906–912] of this series has been considered in order to obtain a function that is maximized by the true crystal structure. The phasing process is carried out by maximizing such a function *via* a modified tangent refinement: this implies the active use of negative triplet and quartet relationships. The major effects provoked in a direct procedure by the use of numerous phase relationships with expected negative cosines are analysed. Practical applications are also described.

Symbols and notation

We adopt the symbols and notation used in papers I and II of the series (Giacovazzo, Burla & Cascarano, 1992; Burla, Cascarano & Giacovazzo, 1992).

Introduction

In papers I and II, the conditional joint probability distribution of n phases given p ($p \geq n$) moduli was studied. The calculations were performed in order to allow for large values of n and p: *i.e.* n should be the number of strong reflections to be phased by a standard direct procedure and p may be the number of measured reflections. Two expressions were derived, both including triplet and quartet invariant contributions: the first formula [see equation (1) of paper II] may be considered as a development of Hauptman's mathematical approach, the second [see equation (2) of paper II] of Giacovazzo's approach. Both expressions were checked to assess their theoretical soundness and practical usefulness for phase solution. The first one was found to present unacceptable features for a well behaved distribution (in agreement with some recent results obtained by Altomare, Burla, Cascarano, Giacovazzo & Guagliardi, 1993). The second distribution function, even though better designed, is not maximized by the correct set of phases (as one would expect for sufficiently large values of n and p). Accordingly, the combined use of triplet and quartet invariants in the tangent procedure proved to be of limited usefulness. This was ascribed to the limited accuracy of the probabilistic estimates of quartet invariants and, therefore, to some insufficiency in the mathematics used by Hauptman and by Giacovazzo. We show in this paper that a modified expression for the distribution (2) of paper II is frequently maximized by the correct solution. As a practical consequence, the

active use of negative estimated triplet and quartet invariants in the phasing procedures is suggested. However, the massive use of negative invariants in a tangent routine creates non-negligible problems that are here analysed. Applications are also presented.

A distribution function to maximize

To aid the reader, we reproduce equation (2) of paper II.

$$P(\varphi_1,\ldots,\varphi_n|R_1,\ldots,R_p) \simeq \frac{1}{L}\exp\left(\sum_{\text{triplets}} T_{ijl}\cos t_{ijl} + \sum_{\text{quartets}} Q''_{ijlm}\cos q_{ijlm}\right), \quad (1)$$

where L is a normalization constant,

$$t_{ijl} = \varphi_i + \varphi_j + \varphi_l,$$
$$q_{ijlm} = \varphi_i + \varphi_j + \varphi_l + \varphi_m,$$
$$T_{ijl} = 2R_iR_jR_l/N^{1/2},$$
$$Q''_{ijlm} = B_{ijlm}(w + w_5\varepsilon_5 + w_6\varepsilon_6 + w_7\varepsilon_7)/(1 + Z_{ijlm}),*$$
$$B_{ijlm} = 2R_iR_jR_lR_m/N$$

and

$$Z_{ijlm} = [(\varepsilon_1\varepsilon_2 + \varepsilon_3\varepsilon_4)w_5\varepsilon_5 + (\varepsilon_1\varepsilon_3 + \varepsilon_2\varepsilon_4)w_6\varepsilon_6 + (\varepsilon_1\varepsilon_4 + \varepsilon_2\varepsilon_3)w_7\varepsilon_7]/2N.$$

The function (1) will be maximum when

$$S'' = \sum_{\text{triplets}} T_{ijl}\cos t_{ijl} + \sum_{\text{quartets}} Q''_{ijlm}\cos q_{ijlm} = \text{maximum}. \quad (2)$$

If (2) is truncated to $N^{-1/2}$-order terms, it reduces to

$$S = \sum_{\text{triplets}} T_{ijl}\cos t_{ijl} = \text{maximum}, \quad (3)$$

which coincides with Cochran's (1952) relationship

$$S = \int_V \rho^3(\mathbf{r})\mathrm{d}\mathbf{r} = \text{maximum}.$$

It was shown in paper II that neither (2) nor (3) is usually satisfied by the correct set of phases. In general, things get worse if the quartet contribution is considered. That was ascribed (see paper II) to the lower accuracy of the quartet estimates. We note now that the quartet contribution to S'', say

$$SQ'' = \sum_{\text{quartets}} Q_{ijlm}\cos q_{ijlm},$$

behaves quite similarly to S; in particular, it is always maximum for the Patterson solution and increases when n increases. Such behaviour may also be associated with the *objective* correlation between the positive estimated quartets and the triplets (each positive estimated quartet is the sum of two triplets in S). If this hypothesis holds, any formula that is unable to destroy such a correlation will also be unable to improve the behaviour of S by the additional quartet contribution. It was emphasized in paper II that both the Hauptman and Giacovazzo quartet theories frequently require the use of mathematical approximations (normally series expansions). While negligible for single-quartet estimation, their effects are quite remarkable when a large number of triplet and quartet relationships are simultaneously handled. This makes it difficult to correct for triplet and quartet correlation. In the framework of Giacovazzo's theory, a useful practical choice would be to eliminate from the set of quartets in (2) the subset of positive estimated quartets. Then, no pair of triplets can be found in S that by addition generates a negative estimated (neg. est.) quartet. Let us denote by SQN'' the contribution to S'' arising from the negative quartets. Then, it is interesting to study the behaviour of

$$S''' = \sum_{\text{triplets}} T_{ijl}\cos t_{ijl} + \sum_{\substack{\text{neg. est.}\\ \text{quartets}}} Q''_{ijlm}\cos q_{ijlm} = S + SQN'', \quad (4)$$

to see if the relation

$$S''' = \text{maximum} \quad (5)$$

is satisfied by the correct set of phases. We use the test structures quoted in Table 1. We first pay attention to the structures BED, CEPHAL, GRA4, MBH2, NEWQB, PGE2, QUINOL and SCHWARZ, which crystallize in symmorphic space groups, where the so-called 'Patterson solution' is frequently encountered among the trials produced by a multisolution process. In particular, we want to see if the value of S''' calculated for the correct structure is larger than the corresponding value for the 'Patterson solution'. While (5) is an asymptotical property (it is expected to be satisfied for sufficiently large values of n and p), it is important to check its behaviour when n is the number of reflections usually phased in a standard direct procedure. The results are shown in Table 2: n is the number of large-modulus reflections chosen by *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) for the phasing process and NTRIP and NQUAR are the numbers of calculated triplets and negative quartets, respectively. The quartets are obtained by the standard *SIR*88 program as differences of pairs of psi-0 triplets. The triplet contribution S to S''' for the correct solution and for the 'Patterson solution' is calculated using Cochran's traditional T_{ijl} coefficients. We note that, while S is never maximum for the true solution, S''' is a maximum for

* In paper II, the expression for Q''_{ijlm} was reproduced incorrectly. The form given here is correct.

Table 1. *Code name, space group and crystallochemical data for the test structures*

Structure code*	Space group	Molecular formula	Z
AMIDE[1]	$Pbc2$	$C_7H_9N_3O_2$	8
APAPA	$P4_12_12$	$C_{30}H_{37}N_{15}O_{16}P_2.6H_2O$	8
AZET	$Pca2_1$	$C_{21}H_{16}ClNO$	8
BED	$I4$	$C_{26}H_{26}N_4O_4$	8
BOBBY	$P2_13$	$Na^+.Ca^{2+}.N(CH_2CO_2)_3^{3-}$	4
CEPHAL	$C2$	$C_{18}H_{21}NO_4$	8
CIME[2]	Cc	$C_{10}H_{18}N_6SO$	4
CUIMID	$P3_221$	$C_6H_8ClCuN_4$	6
DIAM	$P4_2/n$	$C_{14}H_{20}O$	8
DIOLE	$I\bar{4}2d$	$C_{10}H_{18}O_2$	16
ERGO	$P2_12_12_1$	$C_{28}H_{44}O$	8
ERICA[3]	$P2_1$	$C_{37}H_{43}FeO_4P$	2
FEGAS[4]	$P6_3/mmc$	$Fe_2Ga_2S_5$	2
GIAC[5]	$P2_1/c$	$C_{17}H_{17}NO_2S$	4
GOLDMAN2	Cc	$C_{28}H_{16}$	8
GRA4[6]	$P\bar{1}$	$C_{30}H_{22}N_2O_4$	2
HOV1	$C2/m$	$Pr_{14}Ni_{16}Si_{11}$	4
INOS	$P2_1/n$	$C_6H_{12}O_6.H_2O$	8
LOGANIN	$P2_12_12_1$	$C_{17}H_{26}O_{10}$	4
MBH2	$P1$	$C_{15}H_{24}O_3$	3
MGHEX	$P3_1$	$C_{48}H_{68}N_{12}MgO_{12}.2ClO_4.4CH_3CN$	3
MUNICH1	$C2$	$C_{20}H_{16}$	8
NEWQB	$P\bar{1}$	$C_{24}H_{20}N_2O_5$	4
NO55	$Fdd2$	$C_{20}H_{24}N_4$	16
PGE2	$P1$	$C_{20}H_{32}O_5$	1
POCRO[7]	$B112/m$	$K_2Se_{16}Cr_{10}$	1
QUINOL	$R\bar{3}$	$C_6H_6O_2$	54
RIFOLO[8]	$P2_1$	$C_{39}H_{49}NO_{13}.CH_3OH.H_2O$	2
SALEX[9]	$P\bar{3}$	$K_{3.86}Na_{5.30}H_3O^+_{0.84}Fe^{3+}_6.$-$O_2(SO_4)_{12}.17.08H_2O$	1
SCHWARZ	$P1$	$C_{46}H_{70}O_{27}$	1
SELENID	$P2_1$	$C_{22}H_{28}O_2Se$	2
SKN1[10]	$P3_1$	$C_7H_{16}ClNO_4$	3
SUOA	$P2_12_12_1$	$C_{28}H_{38}O_{19}$	4
TPH	$C222_1$	$C_{24}N_2H_{20}$	12
TUR10	$P6_322$	$C_{15}H_{24}O_2$	12
WINTER2	$P2_1$	$C_{52}H_{83}N_{11}O_{16}.3CH_2Cl_2$	2

*Complete references for most of the structures are not given for the sake of brevity. The reader is referred to magnetic tapes distributed by the crystallographic group in Göttingen.

References: (1) Viterbo (unpublished); (2) Kojić-Prodić, Ružić-Toroš, Bresciani-Pahor & Randaccio (1980); (3) Bromley, Collingwood, Davies, Othen & Watkin (1990); (4) Cascarano, Douggy-Smiri & Nguyen-Huy Dung (1987); (5) Babudri, Florio, Zuccaro, Cascarano & Stasi (1985); (6) crystallographic group of York (private communication); (7) Nguyen-Huy Dung, Vo-Van Tien, Behm & Beurskens (1987); (8) Cerrini, Lamba, Burla, Polidori & Nunzi (1988); (9) Scordari & Stasi (1990); (10) distributed by the crystallographic group in Oxford (unpublished).

Table 2. *Results for structures crystallizing in a symmorphic space group with the triplet contribution to S and S‴ calculated using the Cochran parameters*

n is the number of strong reflections chosen by *SIR*88; NTRIP and NQUAR are the numbers of triplets and quartets found among the n reflections; values of S, SQN'' and S''' are given for the correct structure and, in parentheses, for the 'Patterson solution'.

Structure code	n	NTRIP	S	NQUAR	SQN''	S'''
BED	286	4585	3079	8192	339	3418
			(6490)		(−2999)	(3491)
CEPHAL	334	3751	2768	4464	224	2991
			(4754)		(−1256)	(3498)
GRA4	394	5898	23225	10023	2810	26034
			(25694)		(−4682)	(21011)
MBH2	416	3494	3911	5220	341	4252
			(5894)		(−1840)	(4054)
NEWQB	473	5365	5252	36007	793	6045
			(7868)		(−4672)	(3196)
PGE2	300	3736	5007	12564	795	5803
			(7695)		(−5702)	(1992)
QUINOL	296	6025	8763	70136	1734	10497
			(11657)		(−8637)	(3020)
SCHWARZ	470	4556	6002	6852	404	6407
			(8551)		(−2540)	(6012)

Table 3. *Results for structures crystallizing in a symmorphic space group with the triplet contribution to S and S‴ calculated using the P10 formula*

See caption of Table 2 for explanation.

Structure code	S	S'''
BED	3801	4140
	(5827)	(2828)
CEPHAL	3095	3319
	(4478)	(3222)
GRA4	24234	27043
	(24923)	(20241)
MBH2	4364	4705
	(5604)	(3764)
NEWQB	5828	6621
	(6130)	(1459)
PGE2	5578	6373
	(6639)	(937)
QUINOL	10052	11786
	(10014)	(1377)
SCHWARZ	6585	6989
	(8199)	(5660)

GRA4, MBH2, NEWQB, PGE2, QUINOL and SCHWARZ. This remarkable result may be further improved if we replace Cochran's T_{ijl} parameters by the corresponding parameters provided by the *P*10 formula (Cascarano, Giacovazzo, Camalli, Spagna, Burla, Nunzi & Polidori, 1984). The results are shown in Table 3. Now S''' is a maximum for the correct solution in all cases. The general effect of the *P*10 formula (compare Table 3 with Table 2) is that S''' increases for the correct solution and decreases for the Patterson solution.

An important additional test, of remarkable practical interest (see next section), is the assessment of whether S''' is more efficient than S as a figure of merit; *i.e.* if S''' is (or is close to) a maximum for the correct structure, even with respect to the various trial solutions produced by a multisolution approach. In Table 4, we show for SCHWARZ the values of S (Cochran's parameters) and S''' for the best ten solutions stored by a default run of *SIR*88 (for each set, the value of the standard combined figure of merit CFOM is also given). Set 1, selected for its highest value of CFOM, is the true solution, with which the largest value of S''' is associated. However, S is a minimum for set 1. Analogous calculations for BED and CEPHAL show that S''' is again a maximum for the correct solution while the

Table 4. *SCHWARZ results*

For each of the ten trial solutions stored by a default run of *SIR*88, the combined figure of merit CFOM and the values of S and S''' are given.

Set	CFOM	S	S'''
1	0.919	5994	7428
2	0.628	6347	6900
3	0.607	6373	6846
4	0.607	6418	6871
5	0.607	6349	6753
6	0.605	6432	6897
7	0.605	6346	6797
8	0.604	6454	6886
9	0.596	6393	6800
10	0.596	6448	6867

maximum of S is attained for an incorrect solution. Our conclusion is that the maximum of S''' tends to characterize the correct solution with much higher frequency than the maximum of S.

Practical use of the term S''' in tangent procedures

In *SIR*88, phases are determined using the classical tangent formula (Karle & Hauptman, 1956)

$$\tan\varphi_{\mathbf{h}} \simeq \sum_{\mathbf{k}} T_{\mathbf{h},\mathbf{k}} \sin(\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}) / \sum_{\mathbf{k}} T_{\mathbf{h},\mathbf{k}} \cos(\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}),$$

with the following modifications: (*a*) the $T_{\mathbf{h},\mathbf{k}}$ are the reliability parameters provided by the *P*10 formula; (*b*) the negative estimated triplets are excluded from the phasing process. The negative estimated triplets are combined with the negative estimated quartets to give rise to a powerful figure of merit (Cascarano, Giacovazzo & Viterbo, 1987; Cascarano, Giacovazzo & Guagliardi, 1992).

The results described in the preceding section suggest the active use in the phasing process of the negative estimated triplets and quartets *via* the modified tangent formula:

$$\begin{aligned}\tan\varphi_{\mathbf{h}} \simeq & \left[\sum_{\mathbf{k}} T_{\mathbf{h},\mathbf{k}} \sin(\varphi_k + \varphi_{\mathbf{h}-\mathbf{k}}) \right.\\ & \left. + \sum_{\mathbf{k},\mathbf{l}} Q''_{\mathbf{h},\mathbf{k},\mathbf{l}} \sin(\varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{h}-\mathbf{k}-\mathbf{l}})\right]\\ & \times \left[\sum_{\mathbf{k}} T_{\mathbf{h},\mathbf{k}} \cos(\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}) \right.\\ & \left. + \sum_{\mathbf{k},\mathbf{l}} Q''_{\mathbf{h},\mathbf{k},\mathbf{l}} \cos(\varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{h}-\mathbf{k}-\mathbf{l}})\right]^{-1}\\ = & A_{\mathbf{h}}/B_{\mathbf{h}}. \end{aligned} \tag{6}$$

This choice may be justified in the following way. The traditional tangent formula tries to maximize S starting from any initial set of phases. The trials produced by a multisolution procedure correspond to relative maxima of S: the various solutions are prevented from resulting in the same absolute maximum (usually corresponding to a wrong solution) by the prior information contained in the starting set of phases and in the space-group symmetry. The correct solution is eventually found by suitable figures of merit amongst the trials corresponding to relative maxima of S. If negative estimated triplets and quartets are introduced into (6), the phasing process tries to maximize S''' rather than S. Since the maxima of S''' will result in a correct solution with higher frequency than the maxima of S (see the previous section), a direct procedure using (6) is expected to succeed with higher frequency than a procedure using (5).

It is worthwhile to stress the innovative aspect of such a practice: the tangent formula directly tends to maximize a figure of merit rather than satisfy (3).

Applications

The active use of numerous negative phase relationships requires some non-negligible modifications in the tangent procedures. These mainly concern the tangent weighting scheme and the calculation of the figure of merit.

The tangent weighting scheme

The weight $w_{\mathbf{h}}$ associated with $\varphi_{\mathbf{h}}$ (Hull & Irwin, 1978; Burla, Cascarano, Giacovazzo, Nunzi & Polidori, 1987) is often assumed to depend on the ratio $\alpha_{\mathbf{h}}/\langle\alpha_{\mathbf{h}}\rangle$ or $(\alpha_{\mathbf{h}} - \langle\alpha_{\mathbf{h}}\rangle)/\sigma_{\alpha_{\mathbf{h}}}$, where $\alpha_{\mathbf{h}} = (A_{\mathbf{h}}^2 + B_{\mathbf{h}}^2)^{1/2}$. If only positive triplet relationships are used, $\alpha_{\mathbf{h}}$ may be considered as the modulus of the resultant of complex vectors $T_{ijl}\exp(it_{ijl})$ under the hypothesis that the t_{ijl} are distributed around zero according to von Mises distributions. Then,

$$\langle\alpha_{\mathbf{h}}\rangle = \sum_{\mathbf{k}} T_{\mathbf{h},\mathbf{k}} D_1(T_{\mathbf{h},\mathbf{k}}), \tag{7}$$

$$\sigma^2_{\alpha_{\mathbf{h}}} = (1/2)\sum_{\mathbf{k}} T^2_{\mathbf{h},\mathbf{k}}[1 + D_2(T_{\mathbf{h},\mathbf{k}}) - 2D_1^2(T_{\mathbf{h},\mathbf{k}})]. \tag{8}$$

$D_i(x) = I_i(x)/I_0(x)$ is the ratio of two modified Bessel functions, of orders i and zero.

Now, the additional use of negative triplets and quartet invariants breaks this assumption (*i.e.* negative phase invariants are now distributed around π). Calculations that are, for brevity, not shown here [see Cascarano, Giacovazzo, Burla, Nunzi & Polidori (1984) for the theoretical background] give the following result:

$$\langle\alpha_{\mathbf{h}}\rangle = \left|\sum_{\mathbf{k}} |T_{\mathbf{h},\mathbf{k}}| D_1(T_{\mathbf{h},\mathbf{k}}) + \sum_{\mathbf{k},\mathbf{l}} |Q_{\mathbf{h},\mathbf{k},\mathbf{l}}| D_1(Q_{\mathbf{h},\mathbf{k},\mathbf{l}})\right| \tag{9}$$

$$\begin{aligned}\sigma^2_{\alpha_{\mathbf{h}}} = & (1/2)\sum_{\mathbf{k}} T^2_{\mathbf{h},\mathbf{k}}[1 + D_2(T_{\mathbf{h},\mathbf{k}}) - 2D_1^2(T_{\mathbf{h},\mathbf{k}})]\\ & + (1/2)\sum_{\mathbf{k},\mathbf{l}} Q^2_{\mathbf{h},\mathbf{k},\mathbf{l}}[1 + D_2(Q_{\mathbf{h},\mathbf{k},\mathbf{l}}) - 2D_1^2(T_{\mathbf{h},\mathbf{k},\mathbf{l}})].\end{aligned} \tag{10}$$

Relations (9) and (10) show that the value of $\sigma^2_{\alpha_{\mathbf{h}}}$ is not affected by the signs of T and Q, while the value

of $\langle\alpha_{\mathbf{h}}\rangle$ is very sensitive to them. In general, the additional existence of negative phase relationships lowers $\langle\alpha_{\mathbf{h}}\rangle$ and, therefore, the expected phase reliability of $\varphi_{\mathbf{h}}$.

Figures of merit

The ratios $\alpha_{\mathbf{h}}/\langle\alpha_{\mathbf{h}}\rangle$ and $(\alpha_{\mathbf{h}}-\langle\alpha_{\mathbf{h}}\rangle)/\sigma_{\alpha_{\mathbf{h}}}$ are crucial for some time-honoured figures of merit such as MABS, ABSFORM and R_α (Declercq, Germain & Woolfson, 1979; Karle & Karle, 1966) and some new ones like NALF (Cascarano, Giacovazzo & Viterbo, 1987; Cascarano, Giacovazzo & Guagliardi, 1992). Use of (9) and (10) rather than (7) and (8) allows a more correct calculation of the parameters $\langle\alpha_{\mathbf{h}}\rangle$ and $\sigma_{\alpha_{\mathbf{h}}}$.

A modified version of *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993) has been used to check the efficiency of (6). The results are shown in Table 5. The following points should be noted:

(*a*) The structure solution is always attempted by a default run of *SIR*92. The starting set of phases includes only the origin- (and eventually the enantiomorph-) fixing reflections plus five symbolic phases to permute according to the magic-integers approach (Main, 1977).

(*b*) The relative efficiency of (6) is checked according to different protocols. (i) Equation (5) is first used where $T_{\mathbf{h},\mathbf{k}}$ are Cochran's parameters (protocol 1). (ii) Equation (5) is again used where the $T_{\mathbf{h},\mathbf{k}}$ are the *P*10 parameters (protocol 2). As in *SIR*88, only positive estimated triplets are actively used. (iii) Equation (6) is applied (protocol 3), which involves the active use of negative triplet and negative quartet invariants.

Table (5) shows that:

(i) 17 structures (BED, CEPHAL, ERGO, GOLDMAN2, GRA4, NOV1, MBH2, MGHEX, MUNICH1, NEWQB, NO55, PGE2, QUINOL, SCHWARZ, SUOA, TPH and WINTER2) are not solved by a default run according to protocol 1.

(ii) Only 10 structures (CEPHAL, ERGO, HOV1, MGHEX, MUNICH1, NEWQB, PGE2, SCHWARZ, SUOA and WINTER2) remain unsolved after a default run according to protocol 2, indicating the greatest efficiency of the *P*10 estimates.

(iii) Only five structures (MGHEX, MUNICH1, SCHWARZ, SUOA and WINTER2) remain unsolved after a default run according to protocol 3. The results prove the greater efficiency of the tangent formula that maximizes S''' with respect to the traditional tangent formula. As a last note, MGHEX, MUNICH1, SCHWARZ, SUOA and WINTER2 are solved by nondefault runs of the program (*e.g.* by increasing the number of symbolic phases in the starting set).

Table 5. *Success and failure for the phasing process according to various protocols*

Protocol 1: only triplets estimated by the Cochran formula are used. Protocol 2: only triplets estimated positive by the *P*10 formula are actively used. Protocol 3: positive and negative estimated (by the *P*10 formula) and negative quartets are actively used. *Y* denotes success in the phasing process, *N* denotes failure.

Structure code	Protocol 1	Protocol 2	Protocol 3
AMIDE	*Y*	*Y*	*Y*
APAPA	*Y*	*Y*	*Y*
AZET	*Y*	*Y*	*Y*
BED	*N*	*Y*	*Y*
BOBBY	*Y*	*Y*	*Y*
CEPHAL	*N*	*N*	*Y*
CIME	*Y*	*Y*	*Y*
CUIMID	*Y*	*Y*	*Y*
DIAM	*Y*	*Y*	*Y*
DIOLE	*Y*	*Y*	*Y*
ERGO	*N*	*N*	*Y*
ERICA	*Y*	*Y*	*Y*
FEGAS	*Y*	*Y*	*Y*
GIAC	*Y*	*Y*	*Y*
GOLDMAN2	*N*	*Y*	*Y*
GRA4	*N*	*Y*	*Y*
HOV1	*N*	*N*	*Y*
INOS	*Y*	*Y*	*Y*
LOGANIN	*Y*	*Y*	*Y*
MBH2	*N*	*Y*	*Y*
MGHEX	*N*	*N*	*N*
MUNICH1	*N*	*N*	*N*
NEWQB	*N*	*N*	*Y*
NO55	*N*	*Y*	*Y*
PGE2	*N*	*N*	*Y*
POCRO	*Y*	*Y*	*Y*
QUINOL	*N*	*Y*	*Y*
RIFOLO	*Y*	*Y*	*Y*
SALEX	*Y*	*Y*	*Y*
SCHWARZ	*N*	*N*	*N*
SELENID	*Y*	*Y*	*Y*
SKN1	*Y*	*Y*	*Y*
SUOA	*N*	*N*	*N*
TPH	*N*	*Y*	*Y*
TUR10	*Y*	*Y*	*Y*
WINTER2	*N*	*N*	*N*

Concluding remarks

The use of negative quartets in modified tangent procedures is not new [see their clever use in *SHELXS*86 (Sheldrick, 1991)]. However, the combined use of negative triplet and quartet relationships was never attempted, mostly because of their generally small reliability. This paper uses probabilistic considerations to give a theoretical justification for their active use in the phasing process. In particular, the innovative principle of maximizing a figure of merit *via* the tangent formula is introduced. The applications prove that the phasing process succeeds more frequently. In a subsequent paper, we will show that more powerful figures of merit can be identified that can be maximized by application of the tangent formula.

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Dynamical Treatment of the Splitting of Higher-Order-Laue-Zone Lines Induced by Dislocations in an Icosahedral Quasicrystal*

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Abstract

The dynamical theory of electron diffraction for quasicrystals (QCs) was used to treat the splitting behaviour of higher-order-Laue-zone (HOLZ) lines induced by dislocations in icosahedral quasicrystals (IQCs). The influences of some parameters on the splitting of HOLZ lines were calculated. On the basis of this calculation, several experimental convergent-beam electron diffraction patterns from the aluminium–copper–iron IQC were simulated. Good agreement between the experiment and the simulation confirms the correctness of the dynamical theory of electron diffraction for QCs.

1. Introduction

For crystals, the dynamical theory of electron diffraction (Hirsch, Howie, Nicholson, Pashley & Whelan, 1965) has been successfully used to explain almost all the experimental phenomena. Head, Humble, Clarebrogh, Mortoon & Forwood (1973) developed a matching program to identify defects such as dislocations and stacking faults by use of the two-beam approximation of the dynamical theory. Tanaka, Terauchi & Kanemaya (1988) discussed the defocus convergent-beam electron diffraction (CBED) patterns from defected crystals and determined the Burgers vectors of the dislocations and the displacement vectors of the faults. Lu, Wen, Zhang & Wang (1990), Zou, Yao & Wang (1991) and Kuo & Wang (1992) developed the many-beam method to simulate experimental CBED patterns and obtained good agreement. Dynamical calculation or simulation has become a powerful tool to analyse and study defects in crystals.

In this paper, we propose a method for treatment of the splitting of the higher-order-Laue-zone (HOLZ) lines in icosahedral quasicrystals (IQCs). This treatment is based on the dynamical theory of electron diffraction for QCs (see §2) proposed by

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