

relaxation is of appreciable importance to the point where one may expect a modification of certain physical quantities. It is thus indispensable to calculate such quantities, using relaxed model configurations rather than unrelaxed ones.

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#### References

ALLEN, R. E. & DE WETTE, F. W. (1969). *Phys. Rev.* **179**, 873–892.

ALLPRESS, J. G. & SANDERS, J. V. (1967). *Surf. Sci.* **7**, 1–25.

FARGES, J., DE FERAUDY, M. F., RAOULT, B. & TORCHET, G. (1977). *J. Phys. Colloq.* **38**, C2, 47–51.

GILLET, E. & GILLET, M. (1972). *J. Cryst. Growth*, **13/14**, 212–216.

GILLET, M. & GILLET, E. (1966). *Proc. 6th Int. Conf. Electron Microsc., Kyoto*, pp. 633–634.

INO, S. (1966). *J. Phys. Soc. Jpn*, **21**, 346–362.

LENNARD-JONES, J. E. & INGHAM, A. E. (1925). *Proc. R. Soc. London Ser. A*, **107**, 636–653.

MACKAY, A. (1962). *Acta Cryst.* **15**, 916–918.

YANG, C. Y. (1979). *J. Cryst. Growth*, **47**, 274–282.

*Acta Cryst.* (1982). **A38**, 663–670

## The SIR Program.

### II. The Evaluation and Use of Two-Phase Seminvariants

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#### Abstract

New faster and more accurate procedures for the evaluation of two-phase seminvariants by means of the representation theory are described. Some special relationships are also considered and specific methods for their estimation are proposed. The use of the generalized first representation is discussed and detailed examples are given. These ideas for the evaluation of two-phase seminvariants have been introduced in the SIR program and examples of actual applications are given.

#### 1. Introduction\*

Two-phase s.s.'s are those linear combinations of two phases,

$$\Phi = \varphi_u + \varphi_v, \quad (1)$$

\* Symbols and abbreviations are defined in the Appendix.

whose indices satisfy the condition  $\mathbf{h}_u + \mathbf{h}_v \equiv 0 \pmod{\omega_s}$  where  $\mathbf{h}_u$  and  $\mathbf{h}_v$  are the vectors seminvariantly associated with  $\mathbf{u}$  and  $\mathbf{v}$ , and  $\omega_s$  is the seminvariant modulus of the given space group.

The first representation (Giacovazzo, 1977) of a two-phase seminvariant of first rank is given by the set of quartet invariants of the form

$$\varphi_v + \varphi_{uR_p} + \varphi_{h_1R_p} - \varphi_{h_2R_p}, \quad (2a)$$

$$\varphi_v + \varphi_{uR_q} + \varphi_{h_1R_q} - \varphi_{h_2R_q}, \quad (2b)$$

where  $\mathbf{h}_1$  and  $\mathbf{h}_2$  are appropriate vectors which can vary over lines or planes of the reciprocal lattice; we will say that they belong to the sets  $\{\mathbf{h}_1\}$  and  $\{\mathbf{h}_2\}$ . The collection of diffraction magnitudes which are basis or cross terms of the quartets (2) constitutes the first phasing shell  $\{B\}_1$  of  $\Phi$ .

Two kinds of conditional probability distributions for  $\Phi$ , given all the magnitudes in  $\{B\}_1$ , were obtained by

Giacovazzo (1979). The first type (exponential-Bessel type) was directly calculated *via* the Fourier transform of the characteristic function. The second type (Von Mises type) was obtained *via* the Fourier transform of a series expansion of the characteristic function.

An algorithm suitable for the automatic estimation of the s.s.'s in all the space groups up to the orthorhombic system was described by Giacovazzo, Spagna, Vicković & Viterbo (1979) (hereafter GSVV-IV). The algorithm requires a six-variate distribution of the type

$$P(|E_{h_1}|, |E_{h_2}|, |E_u|, |E_v|, |E_{h_1(\mathbf{R}_q - \mathbf{R}_p)}|, |E_{h_2(\mathbf{R}_q - \mathbf{R}_p)}|) \quad (3)$$

with  $\mathbf{h}_1$  and  $\mathbf{h}_2$  appropriately varying within the sets  $\{\mathbf{h}_1\}$  and  $\{\mathbf{h}_2\}$ . The estimation of the two-phase s.s.'s is done by means of the formula

$$\langle \cos \Phi \rangle = I_1(G)/I_0(G), \quad (4)$$

where

$$G = 2 \sum_{(p,q)} A_{pq} \left/ \left[ 1 + \sum_{(p,q)} C_{pq} \right] \right., \quad (5)$$

$$A_{pq} = \frac{1}{2N} R_u R_v \sum_j' a_j \Delta_j \quad (6)$$

$$C_{pq} = \frac{1}{2N} \left\{ \varepsilon_u \varepsilon_v (\varepsilon_5 + \varepsilon_6) + (\varepsilon_u + \varepsilon_v) \sum_j' b_j + \sum_j' r_j \right\} \quad (7)$$

with

$$a = \varepsilon_1 + \varepsilon_2 + \varepsilon_1 \varepsilon_5 + \varepsilon_2 \varepsilon_6 + 2\varepsilon_1 \varepsilon_2 \quad (8)$$

$$\Delta = \cos\{2\pi(\mathbf{h}_1 \mathbf{T}_p - \mathbf{h}_2 \mathbf{T}_q)\}, \quad (9)$$

$$b = \varepsilon_1 \varepsilon_2 \quad (9)$$

$$r = \frac{1}{4}\{L_4(E_1) \varepsilon_5 + L_4(E_2) \varepsilon_6\}. \quad (10)$$

The numerical indices of the terms  $\varepsilon$  and  $E$  refer to the order of the terms in (3). The summation in (5) is over all matrices  $(\mathbf{R}_q - \mathbf{R}_p)$  contributing to the first representation of  $\Phi$ . The summations over  $j$  in (6) and (7) are over all pairs  $(\mathbf{h}_1, \mathbf{h}_2)$ , and the primes indicate that duplicated contributors have not been included.

Actual contributions could provide good estimates of some tens of two-phase s.s.'s by means of the Von-Mises-type probability distributions. In the first applications of this rather effective algorithm, however, we could not avoid relatively high computing times in those cases of higher symmetry in which the estimation of a two-phase s.s. may use a large set of diffraction magnitudes. The need of a faster procedure led us to a new approach which is able to reduce the computing time only by discarding the less useful (in the statistical sense) information contained in the first phasing shell. The procedure is described in § 2. In § 3 some special two-phase s.s.'s are discussed and a more effective procedure for their estimation is described,

while in § 4 some special quartets and their use in the procedure are considered.

The concept of a *generalized first representation* of a s.s. was introduced by Giacovazzo (1980a,c). The usefulness of the additional information contained in the first generalized phasing shell when  $\varphi_u$  and  $\varphi_v$  are restricted phases were described by Burla, Nunzi, Giacovazzo & Polidori (1981). In § 5 we show that such information can also improve the estimate of general two-phase s.s.'s.

We have also tested the use of the exponential-Bessel-type probability distributions according to the procedure described by Giacovazzo (1980b). The resulting estimates are slightly better than those obtained with the Von-Mises-type formulae but the computing time is almost trebled. This convinced us not to pursue any further this attempt unless we can find a faster algorithm.

Finally, in § 6 the use of two-phase s.s.'s in the SIR program is described along with some actual applications.

## 2. The new fast procedure

Among the quartets forming the first representation of  $\Phi$  those with the highest values of the basis magnitudes will give rise to the most efficient contributions to (5). Since: (a)  $|E_{h_1}|$  is a basis magnitude of the quartet (2b) and a cross magnitude of the quartet (2a); (b)  $|E_{h_2}|$  is a basis magnitude of (2a) and a cross of (2b); we have used the following simple criterion in order to select the contributions from the most reliable quartets: the terms involving  $E_1$  or  $E_2$  in (8), (9) and (10) are introduced into the calculations only if  $\varepsilon_1$  or  $\varepsilon_2$  is larger than a given threshold (TRSH1).

The selection procedure not only on average halves the computing time but in most cases gives a better ranging of the estimates by increasing the signal-to-noise ratio in the statistical contribution to the formulae of the different magnitudes in the first phasing shell. An example is given in Table 1, where the results for the test structure 3-chloro-1,3,4-triphenyl-2-azetidinone (AZET,  $Pca2_1$ ,  $C_{12}H_{16}ClNO$ ,  $Z = 8$ ) (Colens, Declercq, Germain, Putzeys & Van Meerse, 1974) are reported. The comparison of the results obtained with and without the selection procedure shows that in the first case the % of correct indications (*cf.* legend of Table 1) among the relations with higher  $|G|$  is increased.

## 3. The estimation of some special two-phase seminvariants

Some special two-phase s.s.'s may be estimated by exploiting additional information not used in the

Table 1. Comparison of the results obtained for AZET (a) with and (b) without the selection procedure described in §2

In column 1 are the different limits of the argument of the Bessel functions in equation (3); in column 2 the cumulative average phase differences in degrees between the estimated [ $\Phi_e = \cos^{-1}(\cos \Phi_e)$ ] and the true ( $\Phi_e$ ) values of the relationships; in column 3 the mean differences of the corresponding cosines; in column 4 the mean differences between the nearest +1.0 or -1.0 value of the estimated cosine and the true cosine; columns 5, 6, 7, 8 indicate the cumulative numbers of total, correct and incorrect and the percent of correct relationships (correct means that the estimated and true cosine have the same sign; this distinction between correct and incorrect estimates for non-centrosymmetric space groups is purely indicative). The total number of relationships in (a) and (b) is different (119 and 128) because the s.s.'s for which there are no contributors are not counted.

G	$\langle  \Phi_e - \Phi_l  \rangle$	$\langle  \cos \Phi_e - \cos \Phi_l  \rangle$	$\langle   \pm 1.0 - \cos \Phi_l   \rangle$	Number of relationships			% Correct
				Total	Correct	Incorrect	
(a) Contributors included if $\varepsilon_1$ or $\varepsilon_2$ greater than 2.0							
0.0	47.90	0.5768	0.5040	119	92	27	77.31
0.40	43.70	0.4772	0.2567	76	69	7	90.79
0.60	39.13	0.4063	0.1590	64	62	2	96.88
0.80	36.69	0.3707	0.1448	51	50	1	98.04
1.00	32.41	0.3219	0.1506	39	38	1	97.44
1.20	27.96	0.2735	0.1672	24	23	1	95.83
1.40	26.25	0.2305	0.1065	16	16	0	100.00
1.60	24.69	0.2075	0.1150	13	13	0	100.00
1.80	21.67	0.1754	0.1304	9	9	0	100.00
2.00	22.86	0.1710	0.1294	7	7	0	100.00
2.20	21.50	0.1553	0.1453	6	6	0	100.00
2.40	25.25	0.1397	0.0258	4	4	0	100.00
(b) All contributors included							
0.0	47.62	0.5731	0.4532	128	101	27	78.91
0.40	45.20	0.4976	0.2487	83	76	7	91.57
0.60	39.98	0.4151	0.1287	65	64	1	98.46
0.80	37.85	0.3825	0.1279	52	51	1	98.08
1.00	33.51	0.3288	0.1303	37	36	1	97.30
1.20	31.20	0.2880	0.1452	25	24	1	96.00
1.40	28.29	0.2569	0.1669	17	16	1	94.12
1.60	24.38	0.2225	0.2079	13	12	1	92.31
1.80	21.64	0.1576	0.1206	11	11	0	100.00
2.00	18.11	0.1286	0.1435	9	9	0	100.00
2.20	19.88	0.1375	0.1185	8	8	0	100.00
2.40	19.88	0.1375	0.1185	8	8	0	100.00

calculations described in paper GSVV-IV. We emphasized there the fact that, for a given s.s.  $\Phi = \varphi_u + \varphi_v$ , more than one pair ( $\mathbf{R}_p, \mathbf{R}_q$ ) of rotation matrices can contribute to its first representation.

In Table 1 of that paper such different pairs ( $\mathbf{R}_p, \mathbf{R}_q$ ) were shown for each type of s.s. in the eight symmetry classes up to the orthorhombic system, and from now on we will refer to the rotation matrices by the same notation introduced there. An example will clarify the purpose of this section. Let the point group be  $mmm$  and  $\Phi = \varphi_{357} + \varphi_{\bar{3}\bar{1}\bar{7}}$ , then  $(\mathbf{u} + \mathbf{v}) \equiv 0 \pmod{(0,2,0)}$  and the pair ( $\mathbf{R}_1, \mathbf{R}_7$ ) will give rise to the following quartets (for each quartet we give the cross vectors after the vertical bar):

$$(\mathbf{R}_1, \mathbf{R}_7) \begin{cases} \varphi_{\bar{3}\bar{1}\bar{7}} + \varphi_{357} + \varphi_{h\bar{2}l} - \varphi_{h2l} | (040), \\ (\bar{3} + h \bar{3} \bar{7} + l), (3 + h 3 7 + l) \\ \varphi_{\bar{3}\bar{1}\bar{7}} + \varphi_{357} + \varphi_{3+h37+l} - \varphi_{3+h\bar{3}\bar{7}+l} | (0\bar{6}0), \\ (h2l), (6 + h 2 14 + l), \end{cases} \quad (11)$$

where  $h$  and  $l$  are free indices. This is not the only pair of matrices contributing to the first representation of  $\Phi$ .

In fact, the conditions (i)  $(\mathbf{u} + \mathbf{v}) \equiv 0 \pmod{(2,2,0)}$ , (ii)  $(\mathbf{u} + \mathbf{v}) \equiv 0 \pmod{(0,2,2)}$ , and (iii)  $(\mathbf{u} + \mathbf{v}) \equiv 0 \pmod{(2,2,2)}$  are also satisfied and the pairs of matrices (i) ( $\mathbf{R}_1, \mathbf{R}_4$ ), ( $\mathbf{R}_6, \mathbf{R}_7$ ), (ii) ( $\mathbf{R}_1, \mathbf{R}_2$ ), ( $\mathbf{R}_7, \mathbf{R}_8$ ), and (iii) ( $\mathbf{R}_1, \mathbf{R}_5$ ), ( $\mathbf{R}_2, \mathbf{R}_6$ ), ( $\mathbf{R}_3, \mathbf{R}_7$ ), ( $\mathbf{R}_4, \mathbf{R}_8$ ) will give rise to quartets of type (2).

With the help of equations (19) of GSVV-IV, the reader can verify that the basis vectors of the new quartets are subsets of the set of basis vectors of the quartets (11). However, some cross terms of these quartets, in our example

$$(6 \ 6 \ 14), (6 \ 4 \ 14), (660), (0 \ 4 \ 14), (0 \ 6 \ 14), (640), (12)$$

do not coincide with any basis or cross term of the quartets (11). The new cross vectors refer to quartets which are symmetry equivalent to quartets (11) and are nothing but the extra cross terms which can be obtained for some quartets when using the full first phasing shell (Giacovazzo, 1976; Busetta, Giacovazzo, Burla, Nunzi, Polidori & Viterbo, 1980).

The procedure used in paper GSVV-IV exploits all the quartets arising from a pair ( $\mathbf{R}_p, \mathbf{R}_q$ ) provided that the corresponding sets  $\{\mathbf{h}_1\}$  and  $\{\mathbf{h}_2\}$  are symmetry

independent of other sets  $\{\mathbf{h}_1\}$  and  $\{\mathbf{h}_2\}$  arising from other pairs of matrices; in the example given above only the quartets (11) would be considered. The additional contributors, such as those indicated in (12), appear in the probabilistic formulae (4)–(10) as  $\varepsilon_5$  or  $\varepsilon_6$  and in particular they will contribute as terms  $\varepsilon_u \varepsilon_v \varepsilon_5$  or  $\varepsilon_u \varepsilon_v \varepsilon_6$  to (7), as terms  $\varepsilon_1 \varepsilon_5$  or  $\varepsilon_2 \varepsilon_6$  to (8) and as terms  $L_4(E_1) \varepsilon_5$  or  $L_4(E_2) \varepsilon_6$  to (10). They had been previously neglected as we did not intend to increase further the computing time, which, as we mentioned before, becomes rather large when there are two free indices as in (11). With the new faster procedure we can now afford to use all the magnitudes belonging to the first phasing shell, provided they satisfy the selection criterion. We have noticed that the introduction of the new terms in most cases improves the estimate of the two-phase s.s.'s; in some cases, where their contribution is predominant, they can have a stronger positive effect.

#### 4. Special quartets in the first representation

Because of special algebraic relations among  $\mathbf{u}$ ,  $\mathbf{v}$ ,  $\mathbf{h}_1$ , and  $\mathbf{h}_2$ , quartets (2) may be of special type. In these cases the estimation of their contributions to (5) requires some caution. We give here an example.

In  $P2_12_1$  we can estimate  $\Phi = \varphi_{2129} + \varphi_{2329}$  via the following quartets:

(1) pair  $(\mathbf{R}_2, \mathbf{R}_3)$

$$\left\{ \begin{array}{l} \varphi_{2329} + \varphi_{2\bar{1}\bar{2}9} + \varphi_{2\bar{1}\bar{1}} - \varphi_{21l} | (420), (0\ 2\ 29 - l), \\ (0\ \bar{2}\ \bar{2}9 + l) \end{array} \right. \quad (13a)$$

$$\left\{ \begin{array}{l} \varphi_{2329} + \varphi_{\bar{2}\bar{1}\bar{2}9} + \varphi_{0\bar{2}\bar{2}9+l} - \varphi_{0\bar{2}\bar{2}9+l} | (040), (21l), \\ (\bar{2}\ \bar{1}\ \bar{5}8 + l), \end{array} \right. \quad (13b)$$

where  $l$  is a free index;

(2) pair  $(\mathbf{R}_3, \mathbf{R}_4)$

$$\left\{ \begin{array}{l} \varphi_{2329} + \varphi_{\bar{2}\bar{1}\bar{2}9} + \varphi_{\bar{h}\bar{1}\bar{2}9} - \varphi_{\bar{h}129} | (0\ 2\ 58), \\ (2 - h\ 2\ 0), (2 + h\ \bar{2}\ 0), \end{array} \right. \quad (14a)$$

$$\left\{ \begin{array}{l} \varphi_{2329} + \varphi_{\bar{2}\bar{1}\bar{2}9} + \varphi_{\bar{2}+\bar{h}\bar{2}0} - \varphi_{\bar{2}+\bar{h}20} | (040), (\bar{h}\ 1\ 29), \\ (\bar{4} + \bar{h}\ \bar{1}\ \bar{2}9), \end{array} \right. \quad (14b)$$

where  $h$  is a free index. When in case (1)  $l = 29$  and in case (2)  $h = 2$ , both quartets (13a) and (14a) become of the type:

$$\varphi_v + \varphi_{u\mathbf{R}_2} - \varphi_u + \varphi_{u\mathbf{R}_4} \quad (15)$$

with the same vector  $\mathbf{u}$  appearing three times; furthermore  $\mathbf{u}$  appears two times as cross vector of (13b) and (14b).

The contribution to (5) of these very special quartets must be evaluated by special formulae. This is particularly important considering that  $|E_u|$  belongs to the set of the largest normalized amplitudes used to

form two-phase s.s.'s. Probability considerations suggest under these conditions replacement of  $\varepsilon_{\mathbf{h}_2 = \mathbf{u}}$  by  $(E_u^2 - 3)/3$  in (8)–(10). Since quartets (13) and (14), for  $l = 29$  and  $h = 2$  respectively, contribute with the same terms, only the unique contributors will be considered.

#### 5. The estimation of $\Phi$ via its generalized first representation

Let  $\Phi = \varphi_u + \varphi_v$  be a two-phase seminvariant of first rank. Then for a pair of rotation matrices  $(\mathbf{R}_p, \mathbf{R}_q)$  we have

$$\mathbf{u} = \mathbf{h}_1 - \mathbf{h}_2 \quad (16)$$

$$\mathbf{v} = -\mathbf{h}_1 \mathbf{R}_p + \mathbf{h}_2 \mathbf{R}_q.$$

We show now that under certain conditions we can construct, besides (2), an additional quartet of the type

$$\psi = \varphi_{u\mathbf{R}_p} + \varphi_{u\mathbf{R}_q} + \varphi_{v\mathbf{R}_p} + \varphi_{v\mathbf{R}_q}. \quad (17)$$

Because of (16), the invariance condition for (17) to be a quartet can be written as

$$\begin{aligned} (\mathbf{u} + \mathbf{v})(\mathbf{R}_p + \mathbf{R}_q) &= (\mathbf{h}_1 - \mathbf{h}_2)(\mathbf{R}_p + \mathbf{R}_q) - (\mathbf{h}_1 \mathbf{R}_p \\ &\quad - \mathbf{h}_2 \mathbf{R}_q)(\mathbf{R}_p + \mathbf{R}_q) = 0. \end{aligned} \quad (18)$$

If  $\mathbf{R}_p$  and  $\mathbf{R}_q$  are the rotational components of symmetry operators of order two, as in all space groups up to the orthorhombic system, then (18) reduces to

$$(\mathbf{h}_1 - \mathbf{h}_2)(\mathbf{I} - \mathbf{R}_p)(\mathbf{I} - \mathbf{R}_q) = 0,$$

which is certainly satisfied when  $\mathbf{R}_p = \mathbf{I}$  or  $\mathbf{R}_q = \mathbf{I}$ . The quartet (17) can then be written in the simpler form

$$\psi = \varphi_u + \varphi_{u\mathbf{R}_q} + \varphi_v + \varphi_{v\mathbf{R}_q}. \quad (19)$$

Since  $\psi = 2\Phi - 2\pi(\mathbf{u} + \mathbf{v})\mathbf{T}_q$ , then the estimation of  $\psi$  estimates  $2\Phi$  too. All the magnitudes which are basis or cross terms of the quartet (17) constitute the first phasing shell of  $2\Phi$ . In space groups of class  $P222$  there are cases with both  $\mathbf{R}_p$  and  $\mathbf{R}_q$  different from  $\mathbf{I}$ , in which the more general condition (18) is satisfied and the relation (17),  $\psi = 2\Phi - 2\pi(\mathbf{u} + \mathbf{v})(\mathbf{T}_p + \mathbf{T}_q)$  is used. It can be easily seen that in fact these cases can always be reconducted to the condition leading to the quartet (19).

Conditional probability distributions of  $2\Phi$  given its first phasing shell were given by Giacobozzo & Vicković (1980). If  $\Phi$  is estimated via its first phasing shell, then the additional estimation of  $2\Phi$  via its first phasing shell may bring further information about  $\Phi$ . For instance, if the cross magnitudes of  $2\Phi$  are all large then  $\Phi$  is expected to be around zero or  $\pi$ , if the cross magnitudes are small then  $\Phi$  is expected to be around  $\pm\pi/2$ . This therefore justifies the introduction of the concept of the generalized first representation (Giacobozzo, 1980a,c), which for noncentrosymmetric

Table 2. Comparison of the results obtained for LITHO when (a) the generalized first representation is used and (b) the first representation only is used

G	$\langle  \Phi_e - \Phi_l  \rangle$	$\langle  \cos \Phi_e - \cos \Phi_l  \rangle$	$\langle   \pm 1.0 - \cos \Phi_l   \rangle$	Number of relations			% Correct
				Total	Correct	Incorrect	
(a) Generalized first phasing shell							
0.0	38.79	0.5438	0.8484	221	131	90	59.28
0.40	38.45	0.5050	0.6270	71	51	20	71.83
0.60	34.60	0.4369	0.4932	47	37	10	78.72
0.80	39.39	0.4726	0.4426	23	18	5	78.26
1.00	37.50	0.4143	0.2635	14	12	2	85.71
1.20	36.50	0.3946	0.2615	8	7	1	87.50
1.40	27.00	0.2603	0.1189	5	5	0	100.00
1.60	27.00	0.2533	0.0695	2	2	0	100.00
1.80	31.00	0.2494	0.0219	1	1	0	100.00
2.00	31.00	0.2494	0.0219	1	1	0	100.00
2.20	31.00	0.2494	0.0219	1	1	0	100.00
(b) First phasing shell only							
0.0	38.85	0.5447	0.8484	221	131	90	59.28
0.40	38.65	0.5078	0.6270	71	51	20	71.83
0.60	35.87	0.4565	0.5227	48	37	11	77.08
0.80	39.85	0.4831	0.4903	27	21	6	77.78
1.00	39.85	0.4395	0.2649	13	11	2	84.62
1.20	37.29	0.4240	0.2978	7	6	1	85.71
1.40	30.50	0.2952	0.0695	2	2	0	100.00
1.60	34.00	0.2865	0.0219	1	1	0	100.00
1.80	34.00	0.2865	0.0219	1	1	0	100.00

space groups is the collection of quartets (2) and (19). The set of magnitudes which are basis or cross terms of these quartets constitutes the generalized first phasing shell  $\{B\}_q^*$ .

We have not tried to obtain a theoretical expression for the conditional distribution of  $\Phi$  given  $\{B\}_q^*$ , because we foresee that the practical application of the formula would be computer-time consuming. We have preferred to introduce a fast empirical procedure which estimates  $\Phi$  by exploiting some basic feature of the exponential probabilistic formulae developed by Giacovazzo & Vicković (1980) for the estimation of  $2\Phi$ . The procedure is as follows: (a) the value of  $G$  as defined in § 2 is calculated; (b) each cross magnitude  $R_{\text{cross}}$  of  $2\Phi$  modifies  $G$  according to the following formula:

$$|G_{\text{new}}| = |G_{\text{old}}| + \frac{R_u^2 R_v^2}{4N} (R_{\text{cross}}^2 - 1), \quad (20)$$

which provides higher values of  $|G|$  when  $R_{\text{cross}}$  is large and smaller values of  $|G|$  if  $R_{\text{cross}}$  is small. This is in agreement with the rule which states that if the cross magnitudes of  $2\Phi$  are large or small then  $\Phi$  is closer to 0,  $\pi$  or to  $\pm\pi/2$  respectively. In accordance with § 2 the contribution from large  $R_{\text{cross}}$  values is accepted only if  $R_{\text{cross}} > \text{TRSH1}$ : contributions from  $R_{\text{cross}} < 1$  are always accepted. Furthermore, if  $|G|$  as calculated by (4) is smaller than a given threshold (TRSH2), no further contribution from the cross magnitudes of  $2\Phi$  is accepted.

In Table 2 a comparison is made of the results obtained on the test structure of lithocholic acid (LITHO,  $P2_12_12_1$ ,  $C_{24}H_{40}O_3$ ,  $Z = 4$ ) (Arora, Germain & Declercq, 1976) when the  $2\Phi$  estimating terms are included with those obtained without these terms. From this and other examples it can be seen that, as expected, the influence on the estimates of the few additional contributors is not very large, but, in most cases, the correction goes in the right direction, while the increase in computing time is almost irrelevant. With reference to the computer output shown in Table 3 (cf. § 6) we can, for instance, point out that the first incorrect relationship has  $G = 1.20$ , whereas without the generalization it appears higher up in the list with  $G = 1.31$  (the computing time in the latter case is 4.87 s). We can therefore conclude that the inclusion of the  $2\Phi$  estimating terms is in general worth while.

## 6. Use of two-phase seminvariants in the SIR program

The procedures described in the previous sections have been included in the SIR program, whose general purpose has been illustrated in paper I of this series (Busetta, Giacovazzo, Burla, Nunzi, Polidori & Viterbo, 1980).

Two-phase s.s.'s are usually evaluated at two separate stages. The first is the estimation of the special two-phase s.s.'s formed by the combination of two one-phase s.s.'s. These are used in an optimization

procedure to improve the estimates of one-phase s.s.'s (Burla, Nunzi, Giacobuzzo & Polidori, 1981). These special two-phase s.s.'s are not included in the set of relations used by the program as their full information content is passed to the one-phase s.s.'s, which are actively employed in the phase determination process.

The second stage consists of the estimation of all other two-phase s.s.'s: centrosymmetric pairs when both phases have restricted values and general relations when one or both phases have general values. The most reliable estimates are then included in the phase determination process. In Tables 3 and 4 are reproduced the relevant parts of the computer outputs obtained for LITHO and for a reduction derivative of a sesquiterpene from *Clavularia Koellikeri* (TURS11, P2<sub>1</sub>, C<sub>15</sub>H<sub>24</sub>O<sub>4</sub>, Z = 4) (Braekman, Daloz, Dupont, Tursch, Declercq, Germain & Van Meerse, 1981). In the top part of these tables are shown the results for the centrosymmetric pairs. The most reliably estimated relationships are listed first and then a statistical analysis of all these special two-phase s.s.'s is given as

the cumulative numbers of total, correct and incorrect [NR(TOT), NR(C), NR(W)] and the percent of correct relations.  $P(+)$  is given by

$$P(+) = \frac{1}{2} + \frac{1}{2} \tanh(\text{ARG}), \quad (21)$$

where  $\text{ARG} = G/2$ , with  $G$  computed as in (5). In the bottom part of Tables 3 and 4 the best estimates of the general two-phase s.s.'s are listed. To the right of the column with the values of  $G$  the estimated and the true values of  $\cos \Phi$  are given, followed by their absolute difference. The last three columns show the estimated [ $\cos^{-1}(\cos \Phi_e)$ ] and the true value of  $\Phi$  and their absolute difference.

The computer times given in the legends of Tables 3 and 4 refer to an Olivetti-Hitachi 5560 computer. The results obtained confirm the validity of the concluding remarks of paper GSVV-IV, and also show the improvement, both in terms of better estimates and in terms of reducing the computing time, obtained by the application of the procedures described in this paper.

Table 3. Two-phase s.s. results obtained with the SIR program on LITHO

The 100 largest  $|E|$ 's have been used to form the relationships with TRSH1 = 2.0 and TRSH2 = 0.8. The computer time is 4.91 s.

CENTROSYMMETRIC PAIRS (2)														
	U	E(U)	$\Phi(U)$	V	E(V)	$\Phi(V)$	ARG	P(+)	$\Phi(U) - \Phi(V)$					
									EST TRUE					
1)	9(3 3 0)	2.63	270	23(7 3 0)	2.34	90	-1.375	0.060	180 180					
2)	12(3 5 0)	2.53	90	23(7 3 0)	2.34	90	0.922	0.863	0 0					
STATISTICS														
	ABS(G).GT.	NR(TOT)	NR(C)	NR(W)	PERCENT CORRECT									
	0.0	25	21	4	84.00									
	0.400	8	8	0	100.00									
	0.600	3	3	0	100.00									
	0.800	2	2	0	100.00									
	1.000	1	1	0	100.00									
	1.200	1	1	0	100.00									
GENERAL TWO-PHASE SEMINVARIANTS (21)														
	U	E(U)	$\Phi(U)$	V	E(V)	$\Phi(V)$	TYPE	G	COS [ $\Phi(U) \pm \Phi(V)$ ]		DEL (COS)	E	T	DEL  E - T
									EST	TRUE				
1)	1(1 1 12)	3.06	340	88(3 7 12)	1.84	172	U - V	-2.23	-0.7288	-0.9781	0.2494	137	168	31
							U + V	-1.61	-0.6258	-0.8829	0.2572	129	152	23
2)	34(3 5 11)	2.16	355	64(1 1 11)	1.99	219	U - V	-1.41	-0.5798	-0.7193	0.1396	125	136	11
							U + V	-1.45	-0.5894	-0.8290	0.2387	126	146	20
3)	11(0 2 23)	2.55	180	57(2 4 23)	2.02	187	U - V	1.37	0.5699	0.9925	0.4227	55	7	48
4)	2(2 4 1)	2.97	206	69(2 4 15)	1.92	87	U - V	1.20	0.5221	-0.4848	1.0069	59	119	60
5)	17(1 12 4)	2.43	222	72(1 6 4)	1.91	41	U - V	-1.03	-0.4636	-0.9998	0.5362	118	179	61
6)	38(4 5 14)	2.13	131	89(0 11 14)	1.83	270	U - V	-1.03	-0.4636	-0.7547	0.2912	118	139	21
7)	7(2 0 11)	2.64	90	32(2 2 13)	2.19	77	U - V	1.00	0.4546	0.9744	0.5197	63	13	50
8)	56(4 2 17)	2.02	255	71(2 4 17)	1.91	147	U - V	-0.88	-0.4095	-0.3090	0.1005	114	108	6
9)	37(2 6 24)	2.13	326	40(4 6 0)	2.11	180	U - V	-0.86	-0.4009	-0.8290	0.4281	114	146	32
10)	3(0 0 18)	2.87	180	25(2 4 18)	2.30	242	U - V	-0.86	-0.4000	0.4695	0.8695	114	62	52
11)	69(2 4 15)	1.92	87	74(4 6 15)	1.90	85	U - V	-0.84	-0.3939	0.9994	1.3933	113	2	111
12)	5(0 3 23)	2.80	270	6(2 3 17)	2.77	81	U - V	-0.83	-0.3370	-0.9877	0.6007	113	171	58
13)	46(0 11 15)	2.09	90	86(2 11 7)	1.86	19	U - V	0.82	0.3838	0.3256	0.0582	67	71	4
14)	13(4 6 12)	2.51	99	78(4 4 12)	1.88	304	U + V	1.09	0.4863	0.7314	0.2451	61	43	18
15)	2(2 4 1)	2.97	206	57(2 4 23)	2.02	187	U + V	0.81	0.3810	0.8387	0.4577	68	33	35
16)	36(1 2 28)	2.14	277	42(1 2 18)	2.10	95	U + V	1.06	0.4749	0.9781	0.5032	62	12	50
17)	63(3 6 2)	1.99	300	72(1 6 4)	1.91	41	U + V	0.92	0.4248	0.9455	0.5207	65	19	46
18)	38(4 5 14)	2.13	131	52(4 7 14)	2.04	224	U + V	1.41	0.5806	0.9962	0.4155	55	5	50
19)	59(2 2 8)	2.01	116	96(6 4 8)	1.80	70	U + V	-1.37	-0.5689	-0.9945	0.4256	125	174	49
20)	28(2 4 11)	2.27	358	32(2 2 13)	2.19	77	U + V	-0.81	-0.3821	0.2588	0.6409	112	75	37
21)	50(1 7 19)	2.06	224	61(1 9 19)	2.00	44	U + V	1.17	0.5129	-0.0349	0.5478	59	92	33

Table 4. Two-phase s.s. results obtained with the SIR program on TURS11

The 96 largest |E|'s have been used with TRSH1 = 2.0 and TRSH2 = 0.8. The computer time is 2.25 s.

CENTROSYMMETRIC PAIRS (3)

	U	E(U)	Φ(U)	V	E(V)	Φ(V)	ARG	P(+)	Φ(U) - Φ(V)	
									EST	TRUE
1)	2(1 0 -7)	3.19	360	4(1 0 -1)	3.00	180	-1.161	0.089	180	180
2)	2(1 0 -7)	3.19	360	3(2 0 3)	3.00	360	0.935	0.866	0	0
3)	3(3 0 3)	3.00	360	45(3 0 9)	2.02	180	-0.857	0.153	180	180

STATISTICS

ABS(G).GT.	NR(TOT)	NR(C)	NR(W)	PERCENT CORRECT
0.0	24	17	7	70.83
0.400	5	4	1	80.00
0.600	3	3	0	100.00
0.800	3	3	0	100.00
1.000	1	1	0	100.00

GENERAL TWO-PHASE SEMINVARIANTS (9)

	U	E(U)	Φ(U)	V	E(V)	Φ(V)	G	COS  Φ(U) ± Φ(V)		DEL (COS)	PHI		DEL  E - T
								EST	TRUE		E	T	
1)	15(1 10 -1)	2.37	343	17(1 10 5)	2.34	183	-1.55	-0.6134	-0.9397	0.3263	128	160	32
2)	64(1 11 -4)	1.94	15	69(1 11 2)	1.91	162	-1.44	-0.5566	-0.8387	0.2521	126	147	21
3)	11(2 5 11)	2.47	358	82(4 5 5)	1.84	170	-1.30	-0.5501	-0.9903	0.4401	123	172	49
4)	10(5 9 -6)	2.48	28	57(5 9 0)	1.98	244	-1.26	-0.5375	-0.8090	0.2716	123	144	21
5)	34(2 6 9)	2.12	98	36(4 6 3)	2.10	276	-1.22	-0.5280	-0.9994	0.4714	122	178	56
6)	53(4 4 7)	1.99	40	89(0 4 11)	1.82	126	1.17	0.5108	0.0693	0.4411	59	86	27
7)	21(2 9 -2)	2.29	345	65(4 9 -8)	1.92	195	-1.13	-0.4995	-0.8660	0.3666	120	150	30
8)	63(4 8 -4)	1.95	190	85(6 8 -10)	1.82	311	-1.02	-0.4616	-0.5150	0.0534	117	121	4
9)	39(3 5 12)	2.07	154	78(3 5 6)	1.85	332	-1.00	-0.4535	-0.9994	0.5459	117	178	61

Table 5. Figures of merit given by the SIR program for LITHO, CORT and PHOTO

	SET	ABSFOM	RESID	SS1FOM	SS2FOM	NQUEST	CFOM	
LITHO	1	0.903	23.76	0.732	0.254	0.000	0.496	
	2	0.887	20.92	0.851	0.363	0.006	2.076	
	3	1.025	23.48	0.772	0.318	-0.064	1.735	
	4	0.994	22.91	0.779	0.242	-0.042	1.212	
	5	1.016	22.94	0.717	0.310	-0.099	1.688	
	6	0.951	21.84	0.646	0.302	0.016	0.960	
	7	0.918	21.81	0.924	0.402	0.009	2.505	
	8	1.027	23.41	0.772	0.316	-0.051	1.696	
	9*	1.184	18.57	0.820	0.399	-0.260	4.602	
	10	1.184	18.56	0.820	0.398	-0.261	4.601	
	Min	0.887	18.56	0.646	0.242	-0.261	0.496	
	Max	1.184	23.76	0.924	0.402	0.016	4.602	
CORT	1	1.103	23.73	0.604	0.024	0.083	2.632	
	2	0.975	22.93	0.400	0.093	0.031	2.661	
	3	1.099	22.40	0.501	0.128	0.005	3.651	
	4	1.056	25.71	0.162	0.138	-0.069	2.712	
	5	0.894	26.86	0.097	0.013	0.018	0.927	
	6	1.075	21.04	0.516	0.054	-0.114	3.750	
	7	0.906	26.67	-0.462	-0.021	0.018	0.304	
	8*	1.135	21.10	0.661	0.142	-0.213	4.989	
		Min	0.894	21.04	-0.462	-0.021	-0.213	0.304
		Max	1.135	26.86	0.661	0.142	0.083	4.989
PHOTO	1	1.073	31.29	-0.925	0.166	0.106	1.317	
	2	1.174	31.72	-0.082	0.221	0.091	2.419	
	3	1.062	27.80	0.522	0.226	-0.019	3.659	
	4	0.809	26.09	-0.811	0.123	0.017	1.671	
	5*	1.350	35.19	0.579	0.294	-0.024	3.962	
	6	1.195	33.68	0.308	0.282	0.059	3.070	
	7	0.941	24.32	0.446	0.249	0.012	3.636	
	8	1.224	30.25	0.308	0.304	-0.005	3.938	
	9	1.337	35.39	0.522	0.271	-0.005	3.640	
	10	1.179	32.46	-0.220	0.197	0.143	1.829	
		Min	0.809	24.32	-0.925	0.123	-0.024	1.317
		Max	1.350	35.39	0.579	0.304	0.143	3.962

Finally, two-phase s.s.'s are also used to compute a figure of merit at the end of the phase determination process when more than one solution has been obtained. The function employed is

$$SS2FOM = \sum_r G_r \cos(\varphi_u + \varphi_v)_r / \sum_r |G_r|, \quad (22)$$

where the summation is over all the relations for which an estimate has been obtained but have not been used during the phase determination process. SS2FOM is expected to be maximum for the correct set of phases. So far we have only a limited experience on the application of SS2FOM, but we have found that its discriminating ability is quite good. A summary of the results concerning the figures of merit obtained by means of the SIR program is shown in Table 5, for LITHO and for the test structures of cortisone (CORT,  $P_{21}2_12_1$ ,  $C_{21}H_{28}O_5$ ,  $Z = 4$ ) (Declercq, Germain & Van Meerssche, 1972) and of a photolysis product (PHOTO,  $P_{21}2_12_1$ ,  $C_{12}H_{13}NO_4$ ,  $Z = 4$ ) (Karle, Karle & Estlin, 1967). A detailed description of the use of all figures of merit in the program will be given elsewhere. We will just point out here that for the correct set of phases (indicated with an asterisk in Table 5) SS2FOM has either the highest or the second highest value and its selection power is comparable to that of the negative quartets figure of merit (NQUEST). SS1FOM is a function similar to (22) but the summation is over the estimated one-phase seminvariants.

## APPENDIX

- $N$  number of atoms in the unit cell  
 $E_h$  normalized structure factor  
 $R_h$  magnitude of the normalized structure factor  
 $\varepsilon_h$   $R_h^2 - 1$   
 $C_p$   $\{\mathbf{R}_p, \mathbf{T}_p\}$ ,  $p$ th symmetry operator  
 $\mathbf{R}_p$   $p$ th rotation matrix of the point group  
 $\mathbf{T}_p$  translation vector associated with the  $p$ th rotation matrix of the point group  
 $I$  identity  $3 \times 3$  matrix  
 $I_0(x), I_1(x)$  modified Bessel functions of order zero and one respectively  
 $L_4(x) = x^4 - 4x^2 + 2$   
 Laguerre polynomial of order 4  
 s.s. structure seminvariant.

## References

ARORA, S. K., GERMAIN, G. & DECLERCQ, J. P. (1976). *Acta Cryst.* B32, 415–419.

*Acta Cryst.* (1982). A38, 670–679

## Low-Resolution Neutron Diffractometry with a Position-Sensitive Multidetector

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## Abstract

A data reduction system for neutron crystallography using a two-dimensional planar multidetector is described. The method is based on an *a priori* calculation of the intensity distribution for each reflection for any crystal orientation. The orientation matrix of the crystal has to be known. From the calculated intensity distribution a mask is derived for each reflection. The detection elements of the detector which are inside the mask are summed to determine the intensity of that reflection and the cells outside are used to determine the background. The size of the mask is adapted to the relative height of the measured intensity of the reflector compared to the background. The

- BRAEKMAN, J. C., DALOZE, D., DUPONT, A., TURSCH, B., DECLERCQ, J. P., GERMAIN, G. & VAN MEERSSCHE, M. (1981). *Tetrahedron*, 37, 179–186.  
 BURLA, M. C., NUNZI, A., GIACOVAZZO, C. & POLIDORI, G. (1981). *Acta Cryst.* A37, 677–684.  
 Busetta, B., GIACOVAZZO, C., BURLA, M. C., NUNZI, A., POLIDORI, G. & VITERBO, D. (1980). *Acta Cryst.* A36, 68–74.  
 COLENS, A., DECLERCQ, J. P., GERMAIN, G., PUTZEYS, J. P. & VAN MEERSSCHE, M. (1974). *Cryst. Struct. Commun.* 3, 119–122.  
 DECLERCQ, J. P., GERMAIN, G. & VAN MEERSSCHE, M. (1972). *Cryst. Struct. Commun.* 1, 13–15.  
 GIACOVAZZO, C. (1976). *Acta Cryst.* A32, 958–967.  
 GIACOVAZZO, C. (1977). *Acta Cryst.* A33, 933–944.  
 GIACOVAZZO, C. (1979). *Acta Cryst.* A35, 296–305.  
 GIACOVAZZO, C. (1980a). *Acta Cryst.* A36, 362–372.  
 GIACOVAZZO, C. (1980b). *Direct Methods in Crystallography*. London: Academic Press.  
 GIACOVAZZO, C. (1980c). *Acta Cryst.* A36, 704–711.  
 GIACOVAZZO, C., SPAGNA, R., VICKOVIĆ, I. & VITERBO, D. (1979). *Acta Cryst.* A35, 401–412.  
 GIACOVAZZO, C. & VICKOVIĆ, I. (1980). *Acta Cryst.* A36, 1017–1025.  
 KARLE, I. L., KARLE, J. & ESTLIN, J. A. (1967). *Acta Cryst.* 23, 494–500.

theoretical intensity distribution for each reflection is calculated in reciprocal space from the primary-beam divergence and wavelength spread and the crystal mosaic spread, on the basis of the kinematic theory of diffraction. The derivation of the necessary equations, *i.e.* the determination of the resolution function of the instrument, is presented. Some typical results of data collection are also presented. The advantages of this data collection method are the safe determination of weak reflections, the easy discrimination of reflections which nearly overlap, the determination of crystal mosaic spread, and the discrimination of inelastic scattering in the proximity of intense reflections.

## 1. Introduction

Low-resolution neutron crystallography using  $H_2O/D_2O$  contrast variation is establishing itself as a useful

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