

## On the Application of Phase Relationships to Complex Structures. IV. The Coincidence Method Applied to General Phases

BY T. DEBAERDEMAEKER\* & M. M. WOOLFSON

*Physics Department, University of York, England*

(Received 18 January 1972)

For space groups with translational elements of symmetry it is possible to find relationships between the phases of pairs of reflexions which are of the same parity group. When the reflexions have one index in common then many indications for a given relationship may appear. A rigorous theory is described which enables the variance of the relationships to be derived although, in practice, a less rigorous approach is preferred which is more amenable to numerical work. The phase-coincidence procedure is being incorporated as an option in the MULTAN computer package for solving non-centrosymmetric structures.

### Introduction

The idea of a coincidence was first introduced by Grant, Howells & Rogers (1957) to relate the signs of structure factors of the same parity group for centrosymmetric structures. In those cases where there are translational elements of symmetry it is found possible to get negative, as well as positive, relationships between signs and also to get several indications for one particular relationship. Thus for the two-dimensional space group  $pgg$  we have the following relationships:

$$s(h, k', 0)s(h', k + k', 0) \approx s(h' - h, k, 0)$$

and

$$s(\bar{h}, k', 0)s(h', k + k', 0) = (-1)^{h+k'} s(h, k', 0)s(h', k + k', 0) \\ \approx s(h' + h, k, 0)$$

which lead to the conclusion

$$s(h' + h, k, 0) \approx (-1)^{h+k'} s(h' - h, k, 0) \quad (1)$$

with a probability which depends on the magnitude of the involved structure factors.

Since the indices in relationship (1) are independent of  $k'$  several indications can be found giving a positive or negative relationship between the signs of the two structure factors depending on the parity of  $k'$ . If one relationship between signs is much more strongly indicated than the other then the overall probability may be high enough for the relationship to be accepted with confidence.

In the present paper these ideas are extended to the determination of probable relationships between the phases of reflexions for non-centrosymmetric space groups in which there are translational elements of symmetry.

### The basis of the method

In the usual procedures for structure solving by direct methods one normally generates at an early stage a  $\sum_2$

listing as described by Karle & Karle (1966). This tabulates for each  $E_h$  in the basic data set the pairs of terms  $E_{h'}$  and  $E_{h-h'}$  which contribute to the right-hand side of the tangent formula. From such a listing one can readily deduce the existence of pairs of phase relationships of the general form

$$\phi_p + C_{prs}(\phi_r + \phi_s) + b_{prs} \approx 0 \text{ (modulo } 2\pi)$$

and

$$\phi_q + C_{qrs}(\phi_r + \phi_s) + b_{qrs} \approx 0 \text{ (modulo } 2\pi) \quad (2)$$

where the  $C$ 's can be  $\pm 1$  and the  $b$ 's are constant angles which arise because of the translational symmetry. For  $P2_12_12_1$  for example, depending on the values of the  $C$ 's and  $b$ 's, this can lead to a relationship between  $\phi_p$  and  $\phi_q$  of one of the forms

$$\phi_p = \phi_q \quad (3a)$$

$$\phi_p = \phi_q + \pi \quad (3b)$$

$$\phi_p = -\phi_q \quad (3c)$$

$$\phi_p = -\phi_q + \pi. \quad (3d)$$

Where several indications of a sign relationship, such as (1), are found the reflexions have one index in common and we can illustrate for  $P2_12_12_1$  how this also arises for relationships of form (3).

Consider the following phase relationships:

$$\phi(h_1, k_1, l_1) \approx \phi[h, \frac{1}{2}(k_1 + k_2), \frac{1}{2}(l_1 + l_2)] \\ + \phi[h_1 - h, \frac{1}{2}(k_1 - k_2), \frac{1}{2}(l_1 - l_2)] \quad (4a)$$

$$\phi(h_1, k_2, l_2) \approx \phi[h, \frac{1}{2}(k_1 + k_2), \frac{1}{2}(l_1 + l_2)] \\ + \phi[h_1 - h, \frac{1}{2}(k_2 - k_1), \frac{1}{2}(l_2 - l_1)]. \quad (4b)$$

From these it follows that

$$\phi(h_1, k_1, l_1) - \phi(h_1, k_2, l_2) \approx \phi[h_1 - h, \frac{1}{2}(k_1 - k_2), \frac{1}{2}(l_1 - l_2)] \\ - \phi[h_1 - h, \frac{1}{2}(k_2 - k_1), \frac{1}{2}(l_2 - l_1)]. \quad (5)$$

However, for the space group  $P2_12_12_1$  the right-hand side of relationship (5) has a precise value and so we find

$$\phi(h_1, k_1, l_1) \approx \phi(h_1, k_2, l_2) + \{h_1 - h + \frac{1}{2}(k_1 - k_2)\}\pi. \quad (6)$$

\* Present address: Mineralogisches Institut der Universität, Deutschhausstr. 10, 355 Marburg/Lahn, Germany (BRD).

The constant term in relationship (6), taken modulo  $2\pi$ , is either 0 or  $\pi$  and will vary with the parity of  $h$  so that the two reflexions will be related as in (3a) or (3b) for different values of  $h$ . A pair of relationships such as (3a) and (3b) may be considered as giving 'opposite' indications since the phase relationship differs by  $\pi$  in going from one to the other. The same applies to the pair (3c) and (3d). When opposite indications occur it is clearly desirable to combine them in some way to determine the dominant relationship and to find some measure of its reliability.

It should be noted that a pair of relationships such as (3a) and (3c) need not be 'opposite' and indeed could be consistent. This would be true for  $\phi_p = \phi_q = 0$  or  $\phi_p = \phi_q = \pi$ . Similarly (3a) and (3d) would be consistent with  $\phi_p = \phi_q = \pm \frac{1}{2}\pi$ .

The actual form of the phase relationships which can be found will depend on the space group. However, as has already been indicated, in practice the relationships are readily accessible to anyone with a  $\Sigma_2$  computer program.

### The formal theory of coincidence phase relationships

A single relationship of type (3) is derived from a pair of relationships such as (4a) and (4b). Let us write these in a general way:

$$\phi_p \approx \eta \quad (7a)$$

and

$$\zeta_q = c\phi_q - m\pi \approx \eta \quad (7b)$$

where  $c = \pm 1$  and  $m = 0$  or 1.

With each of these relationships there will be associated a value of

$$\kappa = 2\sigma_3\sigma_2^{-3/2}|E_1E_2E_3| \quad (\text{Karle \& Karle, 1966})$$

where  $\sigma_n = \sum_{j=1}^N Z_j^n$ ,  $Z_j$  is the atomic number of the  $j$ th

atom in the unit cell and the  $E$ 's are the three normalized structure factors for the reflexions involved in the relationship.

We shall indicate the values of  $\kappa$  for (7a) and (7b) as  $\kappa_1$  and  $\kappa_2$  respectively.

From a theory given by Cochran (1955) the probability distributions for  $\phi_p$  and  $\zeta_q$  are given by

$$P_1(\phi_p) = [2\pi I_0(\kappa_1)]^{-1} \exp[\kappa_1 \cos(\phi_p - \eta)] \quad (8a)$$

and

$$P_2(\zeta_q) = [2\pi I_0(\kappa_2)]^{-1} \exp[\kappa_2 \cos(\zeta_q - \eta)] \quad (8b)$$

where  $I_0$  is a modified Bessel function (Watson, 1966, p. 77).

The form of these two distributions is illustrated in Fig. 1. The variances,  $V_1$  and  $V_2$ , of the distributions may be obtained from the values of  $\kappa_1$  and  $\kappa_2$  from a formula given by Karle & Karle (1966).

If we now consider a quantity

$$\theta = \phi_p - \zeta_q \quad (9)$$

then this has a probability distribution

$$\begin{aligned} P_{\kappa_1, \kappa_2}(\theta) &= \int_{-\pi}^{\pi} P_1(x)P_2(x+\theta)dx \\ &= [4\pi^2 I_0(\kappa_2)]^{-1} \int_{-\pi}^{\pi} \exp[\kappa_1 \cos(x-\eta) \\ &\quad + \kappa_2 \cos(x+\theta-\eta)]dx. \end{aligned}$$

Since the integrand is periodic and the integral covers one complete period one may replace  $x - \eta$  by  $y$  so that

$$P_{\kappa_1, \kappa_2}(\theta) = [4\pi^2 I_0(\kappa_1)I_0(\kappa_2)]^{-1} \int_{-\pi}^{\pi} \exp[\kappa_1 \cos y + \kappa_2 \cos(y+\theta)]dy. \quad (10)$$

The term in square brackets is now

$$(\kappa_1 + \kappa_2 \cos \theta) \cos y - \kappa_2 \sin \theta \sin y$$

which equals  $R \cos(y + \alpha)$ , where

$$R = (\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos \theta)^{1/2} \quad (11)$$

and

$$\tan \alpha = \kappa_2 \sin \theta / (\kappa_1 + \kappa_2 \cos \theta).$$

Hence

$$P_{\kappa_1, \kappa_2}(\theta) = [4\pi^2 I_0(\kappa_1)I_0(\kappa_2)]^{-1} \int_{-\pi}^{\pi} \exp[R \cos(y + \alpha)]dy.$$

Once again, in view of the periodic nature of the integrand,  $\alpha$  may be ignored and, from a result given in Watson (1966, p. 181), we find

$$P_{\kappa_1, \kappa_2}(\theta) = [2\pi I_0(\kappa_1)I_0(\kappa_2)]^{-1} \times I_0\{(\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos \theta)^{1/2}\}. \quad (12)$$

However we may write

$$\begin{aligned} I_0\{(\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos \theta)^{1/2}\} &= I_0(\kappa_1)I_0(\kappa_2) \\ &\quad + 2 \sum_{n=1}^{\infty} I_n(\kappa_1)I_n(\kappa_2) \cos(n\theta) \end{aligned} \quad (13)$$

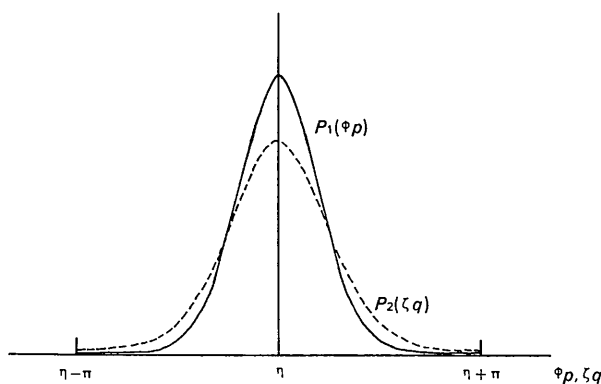


Fig. 1. A schematic representation of the functions  $P_1(\phi_p)$  and  $P_2(\zeta_q)$ .

(Watson, p. 365) where  $I_n$  is a modified Bessel function of order  $n$ . Substituting (13) into (12) gives  $P_{\kappa_1, \kappa_2}(\theta)$  as a series which will be found to converge quite rapidly for usual values of the  $\kappa$ 's.

If there are a number, say  $t$ , of consistent indications for a particular relationship then the resultant probability distribution of the values of  $\theta$  will be

$$\psi(\theta) = A \prod_{g=1}^t P_g(\theta) \quad (14)$$

where  $P_g(\theta)$  is  $P_{\kappa_1, \kappa_2}(\theta)$  for the  $g$ th pair of  $\kappa$ 's and  $A$  is a normalizing constant.

There may also be other indications, inconsistent with the previous set, which give probability distributions for  $\theta$  peaking at  $\theta = \pi$  rather than  $\theta = 0$  as does expression (12).

An analysis similar to that already carried out will show that the probability distribution of  $\theta$  for an 'inconsistent' indication is obtained from (12) by replacing  $\theta$  by  $(\pi - \theta)$ .

Expression (12) can now be written as

$$P_{\kappa_1, \kappa_2}(\theta) = [2\pi I_0(\kappa_1)I_0(\kappa_2)]^{-1} \{ I_0(\kappa_1)I_0(\kappa_2) + 2 \sum_{n=1}^{\infty} (-1)^{zn} I_n(\kappa_1)I_n(\kappa_2) \cos(n\theta) \} \quad (15)$$

where  $z=0$  if the relationship is consistent with equations (7) and  $z=1$  otherwise. These values of  $P_{\kappa_1, \kappa_2}(\theta)$ , substituted in equation (14), give the required resultant distribution of  $\theta$ .

The quantity of greatest interest is the variance of  $\theta$  which may be found as

$$\sigma_\theta^2 = \frac{\int_{-\pi}^{\pi} \theta^2 \psi(\theta) d\theta}{\int_{-\pi}^{\pi} \psi(\theta) d\theta} \quad (16)$$

This can be expressed in terms of series of products of Bessel functions but it will not be done here. In practice it has been found preferable to adopt a simpler, if less precise, approach in using coincidence phase relationships.

### An approximate theory

For a single indication, where the distribution function is found to be  $P_{\kappa_1, \kappa_2}(\theta)$  the variance is

$$V(\kappa_1, \kappa_2) = \int_{-\pi}^{\pi} \theta^2 P_{\kappa_1, \kappa_2}(\theta) d\theta \quad (17)$$

This is found to be

$$V(\kappa_1, \kappa_2) = \frac{\pi^2}{3} + 4 \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} D_n(\kappa_1) D_n(\kappa_2) \quad (18)$$

where

$$D_n(x) = I_n(x)/I_0(x).$$

In a computer program for any pair of  $\kappa$ 's the appropriate values of the  $D$ 's can be read from stored tables. However in our early work, before the formal theory had been fully developed, we actually used Gauss integration to evaluate the double integral obtained by substituting expression (10) in (17) and the results quoted in this paper were derived in that way.

Having a number of consistent indications one can then estimate a resultant variance by combining the consistent indications with inverse variance weighting. The resultant variance,  $V_0$ , is then given by

$$\frac{1}{V_0} = \sum_{\text{All indications}} \frac{1}{V(\kappa_1, \kappa_2)} \quad (19)$$

In similar fashion, by combining the indications which differ by  $\pi$  from the previous set we find the corresponding variance  $V_\pi$ . The overall variance,  $\sigma^2$ , is taken as that given by the expression

$$\frac{1}{\sigma^2} = \left| \frac{1}{V_0} - \frac{1}{V_\pi} \right| \quad (20)$$

where the variance is for  $\phi_p = \zeta_q$  or for  $\phi_p = \zeta_q + \pi$  depending on whether  $V_\pi > V_0$  or  $V_\pi < V_0$  respectively.

A large value of  $\sigma^2$  means that  $V_0$  approximately equals  $V_\pi$  and that there is no reliable relationship between  $\phi_p$  and  $\zeta_q$ .

This approach is intuitive and cannot be formally justified but we are confident that it gives a reasonable measure of the reliability of the coincidence phase relationships.

Sometimes the two reflexions whose phases are being related have phases restricted to special values – *i.e.* they might both be real or both imaginary – in which case they can only differ by 0 or  $\pi$ . In such a case the relationship can only be either  $\phi_1 = \phi_2$  or  $\phi_1 = \phi_2 + \pi$  and we can more profitably think of the *probabilities* of these relationships.

We have used as a measure of the probability that  $\phi_p = \zeta_q$  the expression

$$p_0 = \int_{-\pi/2}^{\pi/2} P_{\kappa_1, \kappa_2}(\theta) d\theta \quad (21)$$

and the indication that  $\phi_p = \zeta_q + \pi$  will thus have a probability  $p_\pi = 1 - p_0$ . With a relationship for which the distribution  $P_{\kappa_1, \kappa_2}(\theta)$  peaks at  $\theta = \pi$  the integral in equation (21) gives  $p_0 < 0.5$ .

The overall resultant probability that  $\phi_p = \zeta_q$ ,  $p_+$ , is given by

$$\frac{p_+}{1 - p_+} = \frac{\prod_{g=1}^t p_{0,g}}{\prod_{g=1}^t (1 - p_{0,g})} \quad (22)$$

where  $p_{0,g}$  is the value of  $p_0$  for the  $g$ th indication.

### Some results

The phase coincidence process was tested on two known structures: the photolysis product, space group

$P2_12_1$ , described by Karle, Karle & Estlin (1967) and, with the same space group, raffinose (Berman, 1970). The coincidences were sought from  $\Sigma_2$  listings derived from subsets of the largest  $|E|$ 's.

The results are given in Tables 1 and 2 and the final

column gives the actual magnitude of the error in the relationship. Only these relationships are listed for which  $q^2 \leq 2.00$  for the photolysis product and  $q^2 \leq 1.25$  for raffinose. The lower limit of  $p_+$  for both structures is 0.75.

Table 1. Test of phase coincidences for the photolysis product

The first two columns give the form of coincidence relationship and  $(hkl)$  is to be interpreted as  $\varphi_{hkl}$ . The final four entries are coincidence relationships between projection reflexions and the bracketed quantities in the third column are probabilities. The final three columns give angles in degrees.

$\varphi_p$	$\zeta_q = c\varphi_q + m\pi$	$q^2(p_+)$	$\varphi_p$	$\varphi_q$	$\Delta$
(2 1 1)	(2 1 15)	0.45	303	288	15
(2 4 1)	-(2 4 13)+ $\pi$	0.50	157	341	42
(2 6 8)	(6 4 8)+ $\pi$	0.50	168	312	36
(2 4 8)	-(2 6 8)+ $\pi$	0.51	19	168	7
(4 2 0)	(4 2 14)	0.58	180	168	12
(2 4 1)	-(6 4 1)	0.66	157	156	47
(4 4 8)	-(0 2 8)+ $\pi$	0.67	16	180	16
(6 4 1)	(4 4 1)	0.71	156	144	12
(6 4 6)	-(6 4 8)	0.72	86	312	38
(2 1 1)	-(2 1 15)+ $\pi$	0.74	303	288	51
(4 5 5)	(8 3 5)+ $\pi$	0.86	91	224	47
(4 5 7)	-(0 3 7)	0.87	266	90	4
(4 4 8)	(4 6 8)+ $\pi$	0.88	16	152	44
(4 2 12)	-(4 2 2)	0.93	338	332	50
(4 5 7)	(4 3 9)+ $\pi$	0.98	266	12	74
(6 4 1)	-(6 6 3)+ $\pi$	0.99	156	94	70
(0 5 7)	(4 3 7)+ $\pi$	1.05	270	134	44
(7 4 7)	(5 4 7)	1.07	182	215	33
(6 2 7)	(8 2 7)	1.09	265	289	24
(2 2 1)	-(2 4 1)+ $\pi$	1.10	348	157	35
(4 5 7)	(4 3 7)+ $\pi$	1.11	266	134	48
(4 4 8)	(4 6 6)+ $\pi$	1.12	16	318	122
(4 0 7)	(4 4 7)	1.17	90	146	56
(4 6 9)	(4 4 11)+ $\pi$	1.20	39	199	20
(4 5 5)	(0 3 5)+ $\pi$	1.22	91	270	1
(2 2 1)	-(6 2 1)	1.47	348	329	43
(4 4 8)	(6 4 8)+ $\pi$	1.52	16	312	116
(4 5 5)	(4 3 7)+ $\pi$	1.62	91	134	137
(2 6 8)	(4 4 8)+ $\pi$	1.63	168	16	28
(2 4 8)	(2 6 8)+ $\pi$	1.64	19	168	31
(6 4 6)	(8 4 6)	1.66	86	92	6
(2 4 5)	-(2 4 17)+ $\pi$	1.66	351	195	6
(2 4 1)	(2 4 17)	1.67	157	195	38
(2 4 10)	-(6 4 6)	1.71	220	86	54
(2 2 1)	(2 6 15)	1.73	348	326	22
(8 5 2)	-(4 5 0)	1.73	187	0	173
(8 5 0)	(4 5 2)	1.73	0	154	154
(6 4 6)	(6 6 4)+ $\pi$	1.75	86	333	67
(4 4 8)	-(6 4 8)	1.80	16	312	32
(0 5 7)	(4 5 5)+ $\pi$	1.81	270	91	1
(4 4 8)	-(4 6 8)+ $\pi$	1.82	16	152	2
(2 4 10)	(6 4 4)	1.84	220	199	21
(4 6 9)	-(4 6 5)+ $\pi$	1.84	39	212	71
(2 4 10)	(6 4 12)+ $\pi$	1.87	220	144	104
(4 5 7)	(2 5 7)	1.87	266	259	7
(6 4 1)	(6 2 1)+ $\pi$	1.89	156	329	7
(4 5 7)	-(4 3 9)	1.90	266	12	82
(2 6 8)	(2 2 4)	1.97	168	8	160
(2 2 1)	(2 4 1)+ $\pi$	1.97	348	157	11
(3 4 7)	-(5 4 7)	1.97	119	215	26
(2 4 8)	(4 6 8)+ $\pi$	1.99	19	152	47
(2 4 1)	-(2 6 15)	1.99	157	326	123
(0 5 7)	(0 3 7)+ $\pi$	(0.91)	270	90	0
(0 1 15)	(0 3 13)+ $\pi$	(0.78)	270	270	180
(4 2 0)	(6 2 0)	(0.78)	180	180	0
(4 2 0)	(4 0 0)+ $\pi$	(0.75)	180	0	0

Table 2. Test of phase coincidences for raffinose

The format is as in Table 1.

$\varphi_p$	$\zeta_q = c\varphi_q + m\pi$	$q^2(p_+)$	$\varphi_p$	$\varphi_q$	$\Delta$
(3 10 7)	-(3 10 5)+ $\pi$	0.61	291	263	14
(7 4 3)	-(7 4 13)	0.82	284	78	2
(6 7 11)	-(6 7 13)+ $\pi$	0.84	126	349	65
(7 4 5)	-(7 4 3)	0.85	81	284	5
(2 10 3)	-(6 8 3)	0.91	59	253	48
(5 1 14)	-(5 1 10)+ $\pi$	0.92	124	233	177
(7 2 9)	(7 2 1)	0.97	241	225	16
(7 4 13)	(7 4 5)	0.98	78	81	3
(7 3 11)	-(7 9 11)	0.99	136	219	5
(7 7 5)	-(3 7 1)+ $\pi$	1.00	269	22	111
(1 8 21)	-(1 6 17)+ $\pi$	1.07	7	156	17
(3 11 11)	-(7 9 11)+ $\pi$	1.07	353	219	32
(2 10 8)	-(6 8 8)+ $\pi$	1.09	68	91	21
(2 10 7)	-(2 10 9)+ $\pi$	1.10	273	296	29
(5 7 2)	(5 7 14)+ $\pi$	1.13	348	109	59
(4 4 21)	-(2 4 17)+ $\pi$	1.16	151	299	32
†(2 0 3)	-(2 14 3)+ $\pi$	1.17	270	261	9
(2 7 5)	(2 7 17)+ $\pi$	1.20	215	67	32
†(2 0 3)	(2 14 3)	1.23	270	261	9
(3 7 11)	-(3 7 1)+ $\pi$	1.25	147	22	11
(0 7 20)	(0 7 8)+ $\pi$	(0.92)	90	270	0
(0 1 18)	(0 1 6)+ $\pi$	(0.87)	270	90	0
(0 6 12)	(0 6 4)	(0.86)	180	180	0
(0 7 12)	(0 7 20)	(0.85)	90	90	0
(2 0 3)	(4 0 17)	(0.83)	270	270	0
(0 7 20)	(0 1 6)	(0.82)	90	90	0
(0 5 16)	(0 9 16)	(0.82)	270	90	180
(0 7 8)	(0 7 21)+ $\pi$	(0.81)	270	90	0
(0 6 12)	(0 6 14)+ $\pi$	(0.78)	180	0	0

† For explanation see text.

These tables show a number of interesting features. Firstly there is a high frequency of cases where the related reflexions have two indices in common. A phase relationship can only be found in a number of different ways if the reflexions have at least one index

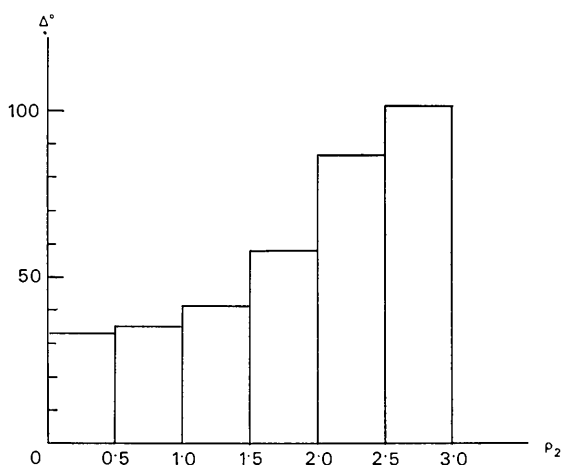


Fig. 2. The mean error of the coincidence phase relationships for the photolysis product for ranges of  $q^2$ , the computed variance.

in common; with two indices in common they can be related by more routes and hence the likelihood of finding a low variance or high probability is enhanced.

Another point concerns the two phase relationships marked with a dagger in Table 2. Because the structure factor is imaginary,

$$\phi_{203} = -\phi_{203} + \pi$$

and the two relationships are in fact identical. These two entries could be combined to give a single relationships of variance 0.60 which would then be the smallest variance found for this structure.

A summary of the photolysis product results, which were more extensive than those given in Table 1, is shown in Fig. 2 in the form of a histogram giving the mean error for various ranges of  $q^2$ . This confirms that the values of  $q^2$  are a reasonable relative, although not absolute, measure of the reliability of the relationships.

### The efficient use of phase relationships

The process of solving crystal structures by the phase permutation method as incorporated in the computer program *MULTAN* (Germain, Main & Woolfson, 1970) certainly goes more smoothly if one has a large starting set of phases, but normally the size of starting set is limited by the number of phase combinations it is practical to explore. In fact the *MULTAN* routine *CONVERGE* found the following starting point for raffinose.

<i>h</i>	<i>k</i>	<i>l</i>	$\phi$	
0	0	12	180°	From $\Sigma_1$
0	1	6	90°	
3	0	18	360°	
4	0	17	90°	
4	1	0	360°	
0	2	4	0°, 180°	To fix origin and enantiomorph
2	9	3	45°, 135°, 225°, 315°	
3	10	5	45°, 135°, 225°, 315°	
5	8	4	45°, 135°, 225°, 315°	

If any pair of these reflexions were related by the coincidence method then it would be possible to reduce the number of combinations explored. In fact Table 2 does not show any relationships between them. However we do have the relationships

$$\phi(0\ 1\ 18) = \phi(0\ 1\ 6) + \pi$$

$$\phi(3\ 10\ 7) = \phi(3\ 10\ 5) + \pi$$

and accepting these would enable the starting set to be increased without any penalty of having extra phase combinations to be explored.

A second approach is as follows. A number of the strongest coincidence relationships are accepted – as an example –

$$\phi(3\ 10\ 7) = -\phi(3\ 10\ 5) + \pi$$

and then in the  $\Sigma_2$  listing whenever  $\phi(3\ 10\ 7)$  appears there is substituted  $-\phi(3\ 10\ 5) + \pi$ . This is done for a number of relationships so that some reflexions disappear (temporarily) from the  $\Sigma_2$  listing while some others appear with increased frequency. The *CONVERGE* routine is then run with the modified  $\Sigma_2$  listing and the effect of the modification is that, for example, the reflexion with indices 3 10 5 will have a higher likelihood of appearing in the starting set. If it does, then both 3 10 5 and 3 10 7 can be included with permuted phases which always differ by  $\pi$  so that there are four possibilities for the two phases together.

Before the *FASTAN* routine of *MULTAN* is begun the  $\Sigma_2$  listing must be restored to its original state for it is wise to let the coincidence-related reflexions refine independently in the tangent-formula process.

Tests have indicated that this procedure is worthwhile and can greatly help in solving some structures. The coincidence routine is now being incorporated as an option in the *MULTAN* package.

We are grateful to the Science Research Council for financial support for this project. Our gratitude is also due to the staff of the Computing Laboratory of the University of York for their assistance and for the services of the University ICL 4130 computer.

### References

- BERMAN, H. M. (1970). *Acta Cryst.* **26**, 290.  
 COCHRAN, W. (1955). *Acta Cryst.* **8**, 473.  
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274.  
 GRANT, D. F., HOWELLS, R. G. & ROGERS, D. (1957). *Acta Cryst.* **10**, 489.  
 KARLE, I. L., KARLE, J. & ESTLIN, J. A. (1967). *Acta Cryst.* **23**, 494.  
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.  
 WATSON, G. N. (1966). *A Treatise on the Theory of Bessel Functions*. 2nd ed. Cambridge Univ. Press.