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The Role of the Crystal Rotation Axis in Experimental Three- and Four-Beam Phase Determination

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Abstract

The geometry of four-beam diffraction and procedures for generating it systematically are described. These utilize relatively simple Renninger-type experimental arrangements. The four reciprocal-lattice points involved in each four-beam interaction are located at the corners of rectangles or symmetrical trapezoids in reciprocal space. One of the sides, or a diagonal, of each such quadrilateral serves as the axis of the azimuthal rotation of the crystal. Experiments designed to compare the relative merits of different types of rotation axes have been carried out. It is found that axes of twofold (or higher) symmetry provide advantages over alternate arrangements for experimental phase determination. Four-beam interactions are then generated systematically and in greater abundance than in all other n-beam interactions combined ($n > 2$). Such interactions usually provide stronger phase indications than comparable three-beam interactions. The experiments also showed that, although the phase of an 'invariant' quartet is clearly invariant to the choice of unit-cell origin, it is not necessarily invariant to a change of rotation axis from one two-fold axis to another.

I. Introduction

A. Four-beam diffraction

The use of four-beam diffraction data for the experimental determination of X-ray reflection

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phases is avoided by some investigators because of the presumed difficulties involved in the extraction of phase information from four-beam interactions (Chang, 1982; Han & Chang, 1983; Hummer & Billy, 1984). Many of the interactions detected in *n*-beam patterns involve four beams; in some experimental arrangements the *n*-beam data consist almost entirely of four-beam interactions. The latter usually display phase indications more clearly than do comparable three-beam data. It is evident that four-beam diffraction data could constitute valuable sources of experimental phase information, provided that the latter could be extracted from the diffracted intensities without undue difficulty.

Four-beam diffraction is generated systematically in Renninger diffraction experiments in which the crystal is rotated about an axis of twofold symmetry. Azimuthal rotation of the crystal then causes reciprocal-lattice points (r.l.p.s), which are arranged symmetrically 'above' and 'below' the equatorial plane of Fig. 1, to pass simultaneously through their diffracting positions to generate four-beam diffraction (*e.g.* *A* and *B* in Fig. 1). The four r.l.p.s, 0, *H*, *A* and *B*, are generally located at the corners of a rectangle or a symmetrical trapezoid. The rotation vector may serve as one of the sides of the rectangle or as one of the two parallel sides of the trapezoid. Three-beam diffraction can then be generated only when the 'transit' r.l.p., which traverses the surface of the Ewald sphere, lies in the equatorial plane and the indices of the diffraction vector which serves as the rotation axis are all even.

Four-beam diffraction may also be generated, though less systematically, in other experimental arrangements. A [311] Renninger scan of germanium with Cu $K\alpha_1$ radiation, which we discuss below, is a good example: 152 of 432 r.l.p.s which pass through the surface of the sphere in a 360° scan are involved in four-beam diffraction.

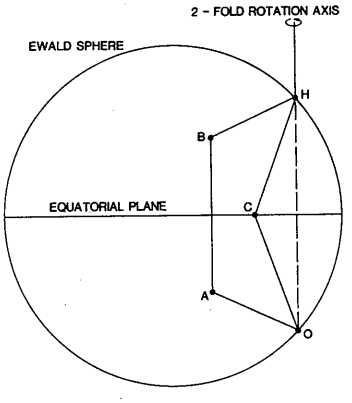

Fig. 1. Generation of symmetrical three- and four-beam interactions.

All the four-beam interactions discussed in these pages involve four coplanar r.l.p.s. Only such planar quartets can be brought systematically to their simultaneous diffracting positions to provide coupled four-beam diffraction for phase determination.

Seven invariant groups of structure factors (four triplets and three quartets) may be involved in establishing an invariant four-beam phase, compared to the single triplet which determines a three-beam phase (Fig. 2). As a result, the experimental determination of four-beam phases may be very difficult, but, as we demonstrate below, the extraction of useful phase information from four-beam data is relatively simple.

B. Experimental phase determinations

Successful experimental determinations of large numbers of phases displayed by invariant three- and four-beam interactions in perfect centrosymmetric crystals of germanium and in mosaic crystals of zinc tungstate, lead molybdate and sulfamic acid were first reported by Gong & Post (1982), Nicolosi (1982) and Ladell (1982). Some of that material has appeared in print: Gong & Post (1983); Post (1983); Post, Nicolosi & Ladell (1984). The Gong & Post paper dealt with the experimental methods used to determine the phases of 53 *n*-beam interactions recorded in a [040] Renninger diffraction pattern of a crystal of zinc tungstate (space group $P2/c$). 17 of the interactions involved three beams; 36 involved four beams. Phases of structure factors were calculated using crystal data previously determined for the isomorphous nickel tungstate (Keeling, 1957). All three-beam phases were readily determined and all agreed with the calculated values.

Difficulties were encountered in initial efforts to carry out similar determinations using four-beam data. It was eventually recognized that all the experimental four-beam phase indications agreed with those calculated for either of the two triplets in which the rotation axis was involved (*e.g.* *RAB* and *RA'B'* in Fig. 2). The calculated phases of both triplets are

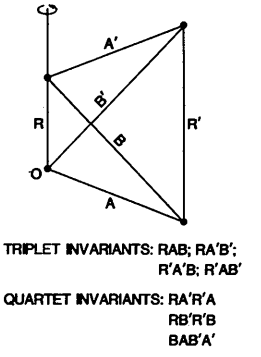

Fig. 2. Triplet and quartet invariants involved in a four-beam interaction.

Table 1. *Phase relations in P2/c*

Notation as in Fig. 2. $S(\ )$ refers to the 'sign of the structure factor whose Miller indices are in parentheses'.

1. $l=2n$: $S(hkl)=S(h\bar{k}\bar{l})$, $S(A)=S(A')$, $S(B)=S(B')$
   (*a*) If $S(A)=S(B)$, then $S(RAB)=S(RA'B')=S(R)$; $S(R'A'B)=S(R')$
   (*b*) If $S(A)=-S(B)$, then $S(RAB)=S(RA'B')=-S(R)$; $S(R'A'B)=-S(R')$
2. $l=2n+1$: $S(hkl)=-S(h\bar{k}\bar{l})$, $S(A)=-S(A')$, $S(B)=-S(B')$
   (*a*) If $S(A)=S(B)$, then $S(RAB)=S(RA'B')=S(R)$; $S(R'A'B)=-S(R')$
   (*b*) If $S(A)=-S(B)$, then $S(RAB)=S(RA'B')=-S(R)$; $S(R'A'B)=S(R')$

identical in $P2/c$ and in other centric space groups (Table 1).

The experimental data indicate that the phases displayed in four-beam interactions are not 'four-beam phases', *i.e.* they do not involve all four diffraction vectors that constitute the sides of the quadrilateral at whose corners the relevant r.l.p.s are located (Fig. 2). All the observed four-beam phase indications discussed above have been accounted for in terms of the identical phases of either one of the pair of triplets in which the rotation axis is involved. Diffraction vectors of the type R' (Fig. 2), however, appear to play no part in establishing the four-beam phase indications. A qualitative explanation has been given by Gong & Post (1983).

C. Rotation axes

The experiments with zinc tungstate, lead molybdate and sulfamic acid all involved rotation axes that served in each instance as one of the parallel sides of a symmetrical trapezoid or a rectangle in reciprocal space. It therefore seemed worthwhile to extend our investigation to include a study of the phase indications displayed by four-beam interactions in which the rotation axis is either a diagonal or one of the two non-parallel sides of its trapezoid. The [311] diffraction vector of germanium was selected for that purpose.

The difference between the lengths of the two parallel sides of a symmetrical trapezoid in reciprocal space must equal an even number of lattice repeat units parallel to the rotation axis. The difference between the magnitudes of the [311] and [622] of germanium does not satisfy that requirement. [622] is the only higher order of [311] accessible to Cu $K\alpha_1$ radiation. It is evident that the [311] axis of germanium cannot be one of the parallel sides of a symmetrical trapezoid in reciprocal space when Cu $K\alpha_1$ is used.

D. Research objectives

Two problems have been investigated. The first involved efforts to determine the range of validity of our procedure for determining the phases of four-beam interactions under the conditions outlined above, *i.e.* when the rotation axis is one of the parallel sides of the quadrilateral of r.l.p.s. The evidence cited above in support of that procedure is impressive but mainly empirical. Additional evidence is probably needed to justify its routine use for experimental phase determinations. Some of that evidence is presented below.

The second problem was concerned with the analysis of the phase indications shown in four-beam interactions when the crystal rotation axis is not parallel to any other side of its quadrilateral.

E. The use of germanium specimens

For experimental phase research, single-crystal specimens of germanium provide numerous advantages over most alternatives. Single crystals of high purity are readily obtainable. Accurate values of the lattice constant and the structure factors of all but some of the very weakest reflections are well known. The relations between features of experimental patterns and the invariant phases are most easily recognized in n-beam patterns of simple crystal structures, such as that of germanium. In Appendix I we show how the phases of the germanium reflections may be calculated for comparison with experimental results. One apparent disadvantage involved in the use of germanium specimens results from the fact that the phases of all but the very weakest triplets are positive (Appendix I). This has no significant effect on the phase analysis. The phase analysis is based entirely on the recognition of the distributions of the n-beam intensities about exact n-beam settings and on calculations which indicate whether the relevant transit r.l.p. is entering or leaving the Ewald sphere.

II. Experimental

The instrumentation and techniques used in this work as well as the procedures for extracting invariant phase information from n-beam intensities have been described by Gong & Post (1983) and Post, Nicolosi & Ladell (1984). The following summary is based on their work.

A. Instrumentation

One important change in instrumentation from that described previously should be noted here. Two channel-cut germanium crystals have replaced the flat silicon crystals previously used to monochromatize and collimate the incident beam. The germanium crystals are inclined to one another by 45° as shown in Fig. 3. The beam which emerges from the 'monochrocollimator', after a total of four reflections from (220) planes in the channel-cut crystals, is stable, monochromatic and well collimated. As seen in Fig. 3, the crystals are cemented to aluminium fixtures which were machined to orient the crystals at angles

0·5° less than the required Bragg angle. Each crystal is tuned to the Bragg angle by means of differential screws which flex the fixture and hold the crystal in place with a compression. This arrangement provides a convenient means of maintaining the requisite precise orientation of the monochromators. Stability is also enhanced by the two-channel arrangement which sends the emerging monochromatic collimated beam in the same direction as that incident upon the monochrocollimator; the divergence of the collimated incident beam does not exceed 15″ in any direction in the beam cross section, *i.e.* less than half the divergence provided by the original arrangement. Bartels (1983) has discussed the resolution of double-channel germanium (220) monochromators.

B. Phase determination procedures

The distribution of diffracted n-beam intensity is usually observed in the form of one of two possible three-stage sequences, which are conveniently designated as EA (enhancement followed by attenuation) or AE (attenuation followed by enhancement). If the EA sequence is generated while the transit r.l.p. is entering the Ewald sphere, a negative triplet phase is indicated. A positive triplet phase is indicated if the EA sequence is generated when the r.l.p. is leaving the sphere. Similarly, the AE sequence indicates a positive triplet phase if the transit r.l.p. is entering, and a negative phase if it is leaving.

N-beam intensity profiles vary widely. If the magnitude of the two-beam structure factor is greater than those of either secondary reflection, the *enhancement* of the two-beam intensity may be barely or not at all detectable, but abrupt intensity *decreases* and recoveries to normal values are observed in almost all such interactions. These usually show significant asymmetry about the exact n-beam settings. The phase may then be deduced from the nature of the asymmetry, as shown in Fig. 4. The latter shows eight charts, each of which covers a 0·25° portion of a [311] Renninger scan. An n-beam interaction is shown near the center of each chart. The four upper charts show two four-beam interaction pairs (in and out); the lower charts show similar data for three-beam interaction pairs.

The legends above the diagrams list the relevant transit reflections and the azimuthal angles at which they occur. (See Table 2.) L indicates that the transit r.l.p.s are leaving the Ewald sphere and E indicates that they are entering. The intensity scales range from 9500 to 20 500 counts for the upper and from 12 500 to 17 750 for the lower diagrams.

Table 2. *Three-beam interactions in the asymmetric 90° angular range of a* [311] *scan of germanium*

All *hkl* indices listed sum to $4n$ or $2n+1$.

	hkl Transit	*hkl* Coupling	φ (°)*	2β (°)†	Intensity asymmetry	Dir.‡
1	$4\bar{2}2$	$\bar{1}3\bar{1}$	2·58	112·66	AE	*E*
2	$3\bar{1}5$	026	4·43	−66·73	EA	*L*
3	$60\bar{2}$	$\bar{3}13$	6·21	−52·88	EA	*L*
4	$4\bar{4}4$	$\bar{1}55$	10·23	−20·46	EA	*L*
5	$2\bar{4}2$	$15\bar{1}$	13·32	100·01	AE	*E*
6	$1\bar{5}1$	260	20·32	69·10	AE	*E*
7	$1\bar{3}3$	$24\bar{2}$	29·19	30·38	AE	*E*
8	$1\bar{1}3$	224	30·98	−112·66	EA	*L*
9	$5\bar{3}3$	$\bar{2}4\bar{2}$	37·45	51·73	AE	*E*
10	$3\bar{5}3$	$06\bar{2}$	37·89	55·55	AE	*E*
11	$\bar{1}3\bar{1}$	440	38·96	68·53	AE	*E*
12	$2\bar{2}4$	$13\bar{3}$	40·67	110·14	AE	*E*
13	$20\bar{2}$	113	42·64	−152·40	EA	*L*
14	$6\bar{2}0$	$\bar{3}31$	46·67	−52·88	EA	*L*
15	$4\bar{2}\bar{2}$	$\bar{1}33$	55·07	−110·14	EA	*L*
16	$3\bar{5}1$	062	62·30	−66·73	EA	*L*
17	$\bar{1}\bar{1}1$	$42\bar{2}$	64·76	112·66	AE	*E*
18	$1\bar{1}5$	$22\bar{4}$	66·68	100·01	AE	*E*
19	113	$20\bar{2}$	70·25	152·40	AE	*E*
20	404	$\bar{1}1\bar{3}$	72·51	68·53	AE	*E*
21	$3\bar{1}1$	022	76·20	−152·40	EA	*L*
22	$1\bar{3}1$	242	81·68	−112·66	EA	*L*
23	$0\bar{2}6$	$33\bar{5}$	86·56	55·55	AE	*E*
24	$5\bar{3}3$	$\bar{2}4\bar{2}$	89·19	−51·73	EA	*L*
25	$1\bar{5}1$	260	89·42	−69·10	EA	*L*

* φ refers to the azimuthal angle at which the interaction is observed.
† 2β is the angular interval between entering (E) and leaving (L) the Ewald sphere.
‡ Dir. indicates whether the transit vector is entering (E) or leaving (L) the Ewald sphere.

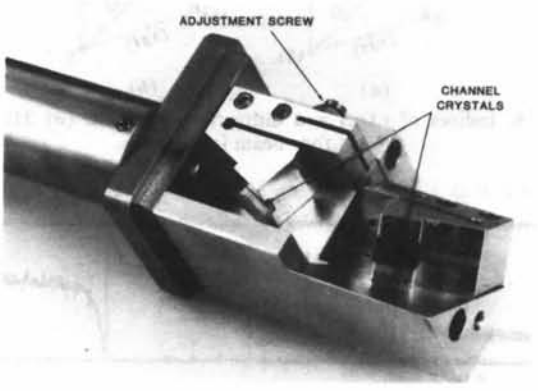

Fig. 3. Two channel-cut germanium (220) crystal monochrocollimator.

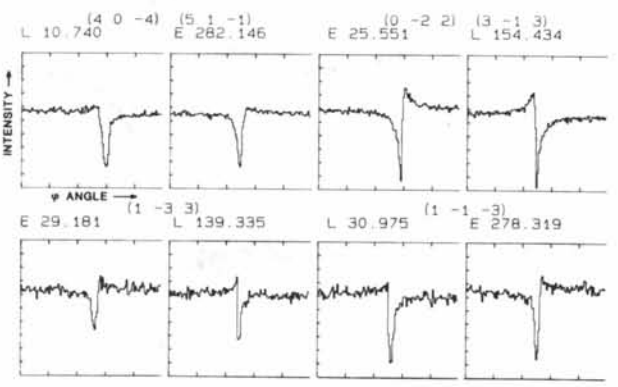

Fig. 4. Pairs of four-beam and three-beam interactions in a [311] scan.

C. *Invariance and rotation axes*

It is well known that the sum of the phases of a group of structure factors whose r.l.p.s lie at the corners of a closed polygon is invariant to the choice of unit-cell origin. The corresponding *phase indications* in experimental four-beam diffraction are not necessarily invariant to the choice of rotation axis. This is a consequence of the fact that those indications reflect mainly the identical phases of the two triplets in which the rotation axis is involved. As a result, the phase displayed by a given invariant quartet may change when the rotation axis is changed. This is shown in Table 1 for the special case of the space group $P2/c$. Similar results are obtained for all cases in which the space group determines the relative phases of pairs of structure factors, such as those of A and A' and B and B' (Fig. 2).

The four sides and the two diagonals of symmetrical trapezoids provide each such quadrilateral with six possible rotation axes. When the r.l.p.s at the endpoints of any one of those axes are in their diffracting positions, rotation about that axis brings the remaining two r.l.p.s to their simultaneous four-beam settings.

Chart recordings of four-beam intensities diffracted from a crystal of zinc tungstate rotated about [040] are shown in Fig. 5(a); the corresponding [060] data for the same trapezoid are shown in Fig. 5(b). Using the nomenclature of Fig. 2, the indices of the diffraction vectors of the trapezoid for the reflections involved in the four-beam interaction in Fig. 5(a) are: $R=[040]$, $A=[1\bar{1}0]$, $B=[\bar{1}50]$, $A'=[\bar{1}\bar{1}0]$, $B'=[150]$ and $R'=[060]$. All the charts were recorded over 1° ranges in steps of 0·002°. The dwell time at each step was 5 s. The intensity in Fig. 5(a) varied from 2900 to 6500 counts, and from 5600 to 7500 counts in Fig. 5(b). The charts to the left were recorded when the two transit r.l.p.s were emerging from the sphere, and those to the right were recorded when the transit r.l.p.s. were entering the sphere. The phases shown in the [040] and [060] charts are positive and negative respectively. (See above.)

This difference between the phases recorded for a given trapezoid may be surprising, but only if the dependence of the experimental phase indication on the rotation axis is ignored. The apparent anomaly vanishes when that dependence is taken into account.

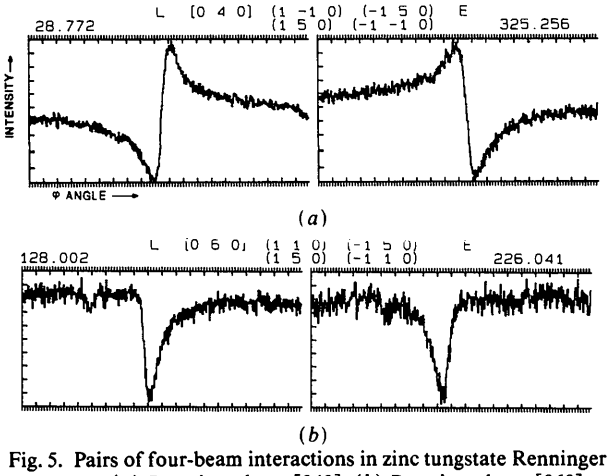

Fig. 5. Pairs of four-beam interactions in zinc tungstate Renninger patterns. (a) Rotation about [040]. (b) Rotation about [060].

D. *The 222/444 experiment*

We made use of the phenomenon discussed in the preceding paragraphs to investigate the range of validity of the four-beam procedure. A [222] chart of germanium is included in Post, Nicolosi & Ladell (1984). Only one of the maxima in the chart (their Fig. 4) is due to a four-beam interaction. Some properties of that maximum are listed in their Table 2 (item no. 7). The diffraction vectors and the associated r.l.p.s are shown in Fig. 6.

The structure factors of 222 and 444 equal 1·09 and −109·0 respectively. A triplet phase is determined by the sum of the phases of its component structure factors. The amplitudes of the latter play no direct part in determining the phase, though they may affect its visibility in experimental patterns. The 222/444 experiment provided an opportunity to note the effect of a change of rotation axis, from a very strong [444] to the very weak [222], on the resultant phase indications.

The four-beam interaction in the [222], scan is shown in Fig. 7(a) for transit r.l.p.s entering the Ewald sphere. The indicated phase is 'negative'. The corresponding [444] chart is shown in Fig. 7(b). It indicates a 'positive' phase. The phase difference is due to the difference between the phases of the diffraction vectors that serve as the rotation axes. In Fig. 7(a), the

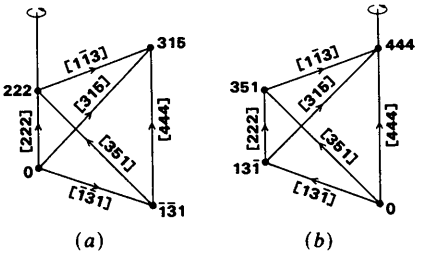

Fig. 6. Indices of r.l.p.s and diffraction vectors in (a) 222 and (b) 444 four-beam interactions.

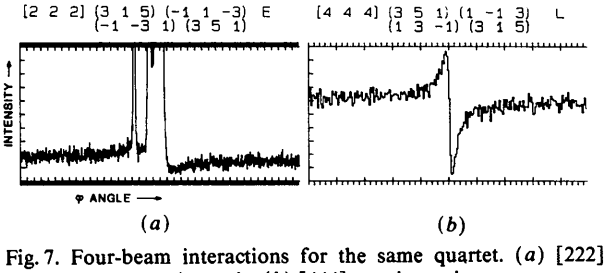

Fig. 7. Four-beam interactions for the same quartet. (a) [222] rotation axis. (b) [444] rotation axis.

angular range shown is 5°, the step interval 0·005°, and full scale is 200 counts. In Fig. 7(*b*), the angular range is 0·5°, the step size 0·002°, the intensity scale of the plot varies from 3100 to 5100 counts.

E. The [311] *n-beam pattern of germanium*

The [311] *n*-beam pattern of germanium appears to conform to *C2l* symmetry (Buerger, 1942). The azimuthal angle φ is measured from a mirror plane. The transit vectors that give rise to interactions at angle φ are leaving the Ewald sphere when those at 180-φ are entering and *vice versa.* Also, all interactions are repeated every 180° with the roles of the coupling and transit vectors interchanged.

70 three-beam and 19 four-beam interactions are generated in the asymmetric 90° range of a [311] Renninger scan; 108 r.l.p.s pass into or out of the sphere in that angular range (two transit r.l.p.s are involved in each four-beam interaction). 45 of those triplets and 9 quartets include at least one forbidden reflection. We have observed interesting and unexpected phase effects in our analyses of those interactions. The results are being rechecked and will soon be submitted for publication. The present discussion is therefore limited to the 25 three-beam and the ten four-beam interactions that involve only 'permitted reflections'.

Relevant data for the 25 'permitted' triplets are listed in Table 2. As indicated in Appendix I, the phases of all these triplets are positive. Data for the ten permitted quartets are listed in Table 3. The phases of the three-beam interactions were discussed above in § II*D*.

The r.l.p.s are located at the corners of rectangles in seven of the ten four-beam cases that we are considering, and at the corners of symmetrical trapezoids in the remaining three. The phase analysis for the rectangular arrays is straightforward. The phase that is displayed is, as we have noted previously, the phase of either of the triplets in which the [311] is involved. The analysis is essentially identical with that used when the rotation axis is one of the parallel sides of a trapezoid. The phases of six quartets were readily determined in that way.

A complication was encountered when the interaction at $\varphi = 16{\cdot}78°$ was analyzed. In that interaction, the rotation axis [311] is the diagonal of the rectangle whose sides are [202] and [11$\bar{1}$]. As shown in Fig. 8, rotation about the diagonal causes one r.l.p., the [11$\bar{1}$], to enter the Ewald sphere when the [202] leaves. The phases of the two triplets are identical. They cancel one another and the interaction yields no phase information.

Phase cancellation, however, does not necessarily result in the vanishing of the four-beam intensity. The intensity would vanish if the components of the diffracted resonance interaction above and below the average two-beam intensity were identical. That is rarely the case. In the general case, we observe either a symmetrical increase or, as in the 16·78° interaction, a symmetrical dip in the diffracted intensity.

Table 3. *Four-beam interactions in the asymmetric* 90° *range of a* [311] *scan of germanium*

All *hkl* indices listed sum to $4n$ or $2n+1$.

	hkl Transit	*hkl* Coupling	T/R*	φ (°)	2β (°)†	Intensity asymmetry	Dir.‡
1	51$\bar{1}$	$\bar{2}$02	*T*	10·74	−88·60	EA	*L*
	40$\bar{4}$	$\bar{1}$15			−88·60		*L*
2	11$\bar{1}$	202	*R*§	16·78	−180·00	—	*L*
	202	11$\bar{1}$			180·00		*E*
3	51$\bar{3}$	$\bar{2}$24	*R*	24·84	−83·25	EA	*L*
	2$\bar{2}$4	135			−83·25		*L*
4	0$\bar{2}$2	33$\bar{1}$	*R*	25·57	128·86	AE	*E*
	31$\bar{3}$	02$\bar{2}$			128·86		*E*
5	5$\bar{5}$1	$\bar{2}$60	*R*	26·94	30·39	AE	*E*
	2$\bar{6}$0	171			30·39		*E*
6	33$\bar{3}$	044	*T*	44·30	−88·60	EA	*L*
	0$\bar{2}$2	333			−88·60		*L*
7	2$\bar{6}$0	171	*R*	57·32	−30·39	EA	*L*
	5$\bar{5}$1	$\bar{2}$60			−30·39		*L*
8	53$\bar{1}$	$\bar{2}$42	*R*	58·40	−83·25	EA	*L*
	24$\bar{2}$	153			−83·25		*L*
9	33$\bar{5}$	04$\bar{4}$	*R*	59·68	60·65	AE	*E*
	0$\bar{4}$4	35$\bar{3}$			60·65		*E*
10	4$\bar{4}$0	$\bar{1}$51	*T*	77·86	−88·60	EA	*L*
	5$\bar{1}$1	$\bar{2}$20			−88·60		*L*

* T/R refer to trapezoidal or rectangular arrangement of r.l.p. quartets.
† 2β represents the angular interval between r.l.p.s entering and leaving the Ewald sphere.
‡ Dir. indicates whether r.l.p. is entering (*E*) or leaving (*L*) the Ewald sphere.
§ [311] serves as the diagonal of this rectangle.

The effects of rotation about [311] are increased when the r.l.p.s are arranged at the corners of a symmetrical trapezoid. The usefulness of our four-beam procedure derives mainly from the fact that when the rotation axis is an axis of twofold symmetry the phases of both triangles in which the rotation axis is involved are identical. The phase that is displayed by a four-beam interaction may then be identified with the phase of a triplet.

The phases of the two corresponding triangles are not necessarily identical when the [311], or a similar low-symmetry axis, is used as the rotation axis. Less convenient procedures must then be used to determine the 'four-beam' phase. Additional criteria for

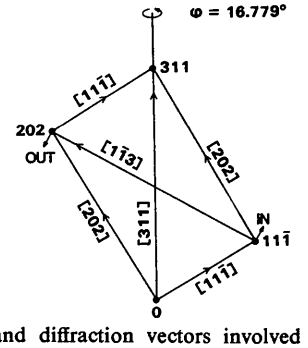

Fig. 8. Indices and diffraction vectors involved in rectangular quartet rotated about a diagonal.

choices of rotation axes in Renninger scans to be used for phase determination have been given by Post, Nicolosi & Ladell (1984).

APPENDIX I

[Invariant triplet phases of diamond-type crystals

[In this Appendix we assume the validity of the 'conditions limiting possible reflections' as given in *International Tables for X-ray Crystallography* (1969), Vol. I, for positions 8(*a*) in *Fd*3*m*.]

The structure factor may be written as $F(hkl) = 8f \cos 2\pi(h+k+l)/8$. Indices that sum to $4n+2$ for individual reflections have structure factors whose magnitudes equal zero. Those are not considered here.

The indices of individual reflections are either all even or all odd. For the former, the sum of the indices equals $4n$; for the latter the sum is $4n \pm 1$. In either case, the phase of an individual reflection is positive if n is even and negative if n is odd.

We are concerned with invariant triplet phases; these are equal to the sums of the phases of three diffraction vectors which form triangles in reciprocal space. Invariance requires that all three reflections have even indices or that two have odd indices and the third even. The indices of the three reflections must sum to zero.

In the case of even-index reflections, all reflection phases as well as the corresponding triplet phase will be positive if all n's are even. Since odd-index reflections must occur in pairs in invariant triplets, the third reflection will have even indices. We write the relations among the three as:

$$4(n1) = [4(n2) \pm 1] + [4(n3) \pm 1].$$

In order that $n1$ be an integer, it is necessary that the ± 1 terms cancel. This requires that one of the right-hand terms be of the type $4n+1$ and the other of the type $4n-1$. It follows that

$$4(n1) = 4(n2) + 4(n3),$$

a condition that is satisfied only if all the n's are even or if two of the n's are odd. For either of these cases the triplet phase will be positive.

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The Effect of Measured *vs* Conventional Polarization Factors in Structure Refinements*

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Abstract

The polarization ratio K is measured for LiF (200) and graphite (00.2) monochromators at different X-ray wavelengths. In each case the kinematical value $\cos^2 2\theta_M$ is a poor approximation, and the actual value of K may exceed the dynamical limit $\cos 2\theta_M$. An explanation is offered in terms of a model that includes secondary extinction. The effects of an incorrect value of K are studied by refining the model for a ruby standard crystal. The positional parameters are not affected, but the scale, extinction and thermal parameters change. The effects are, however, smaller than the ones observed in the structural parameters due to termination of the data set at lower $\sin\theta/\lambda$ values.

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