experimental tests. We hope to be able to report on some results of these in the near future.

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The Phases of Forbidden Reflections*

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Dedicated to the memory of Professor Paul P. Ewald

Abstract

The invariant phases of large numbers of germanium triplets, consisting of one forbidden and two permitted reflections, have been determined experimentally. The forbidden reflections include members of the forms {200}, {222}, {420} and {442}. Phase effects in triplets containing members of the ultra-weak (forbidden) {622} and {640} were detected but were too weak to provide reliable phase indications. The phases of all triplets which include a forbidden reflection and the $\bar{3}\bar{1}\bar{1}$ reflection are observed to be negative. The phases of individual forbidden reflections, whose indices are described as summing to $(4n-2)$, are equal to $(-1)^n$. The imaginary part of the dispersion correction to the atomic form factors is relatively large (0·89 for Cu $K\alpha_1$ radiation): it makes significant contributions to the structure factors and the phases of the vanishingly weak forbidden reflections.

I. Introduction

Reflections whose indices sum to $4n-2$ are 'forbidden' in diamond-type crystals. Their structure factors, calculated for atoms in positions 8(a) of space group $Fd3m$ (Henry & Lonsdale, 1952), equal zero. In 1921, however, W. H. Bragg detected intensities diffracted by the forbidden 222 reflection of a diamond crystal.

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He explained his findings as follows; '... the properties of the atom in diamond are based on a tetrahedral not a spherical form. The tetrahedra point away from any (111) plane in the case of half the atoms in the diamond and towards it in the case of the other half. Consecutive (111) sheets are not exactly of the same nature; and it might reasonably be expected that they would not entirely destroy each other's effects in the second-order reflection from the tetrahedral plane. It is this effect which is now found to be distinct, though small' (Bragg, 1921).

Dawson (1967*b*) and Willis & Pryor (1975) have shown that 'forbidden' reflections are due largely to distortions of the bonding electron density distributions resulting from the packing of atoms into crystals, and to anharmonic thermal motions of the atoms. Experimental confirmation of the above has been provided by a series of investigations of the forbidden 222, 442 and 622 reflections of silicon and germanium by Batterman & Trucano (1972), Batterman & Hastings (1975) and Batterman & Tischler (1984). Measured values of the 222 intensities were in good agreement with Dawson's calculations. The structure factors of 442 and 622 were reported to be smaller than that of the 222 by almost two orders of magnitude. The effects of anharmonic thermal motion were demonstrated by measurements of the intensities of forbidden reflections at elevated temperatures.

The phases of germanium reflections displayed in an *n*-beam pattern, generated by rotation of the crystal about the forbidden [222] diffraction vector, have been investigated by Post, Nicolosi & Ladell (1984). All the triplet phases were determined, except for those of two interactions which were distorted by overlap effects.

In a recent study of *n*-beam patterns of germanium crystals rotated about [311], phase indications were observed in a number of weak triplet interactions, each of which involved one forbidden and two odd-index reflections (Post, Gong, Kern & Ladell, 1986). The forbidden reflections included members of the {200}, {222}, {420} and {442} forms.

Aside from the intrinsic interest in the determination of the phases of vanishingly weak forbidden reflections, it was also felt that the determination of the phases of those interactions could provide a useful check on the sensitivity of our phase-determining procedures. We have remeasured all the 'forbidden' interactions, using improved incident-beam resolution and longer counting times to increase their statistical reliability. The results are given below.

II. Experimental

Definitions of some frequently used terms may be helpful. 'R.l.p.s' refer to reciprocal-lattice points. The r.l.p. which passes through the surface of the Ewald sphere to generate three-beam diffraction is the 'transit' r.l.p. The two-beam 'pivotal' diffraction vector defines the rotation axis. The 'coupling' vector connects the tip of the transit vector to the tip of the pivotal vector. The transit and pivotal vectors are position vectors drawn from the origin of the reciprocal space. The symbol '*E*' indicates that the transit r.l.p. is entering and '*L*' that it is leaving the Ewald sphere.

In our experimental procedures we utilize a highly collimated monochromatic beam, an accurate 'biaxial' diffractometer, and an automated sequence of operations to collect and store intensity data. An essential feature of our apparatus is its 'monochrocollimator' ('m.c.c.') which provides a monochromatic incident beam whose divergence does not exceed 20″ in any direction. A photograph of the single-crystal diffractometer is shown in Fig. 1.

Precise values of the magnitudes and directions of all diffraction vectors involved in *n*-beam interactions are determined with the diffractometer. These are used in computer programs to establish the orientation of the reciprocal lattice relative to the incident beam and the instrumental axes. That information is used to calculate the crystal and detector settings required for the observation of all Renninger interactions and the profiles of the two-beam generalized inclination diffraction effects. This capability minimizes the possibility of incorrectly indexing *n*-beam interactions. Identification of relevant reciprocal-lattice vectors and the directions of their passage through the Ewald sphere can be confirmed by repeating the azimuthal scans of selected *n*-beam interactions *after moving the detector* from the setting at which it monitored the 'primary' (two-beam) reflection to those at which the diffraction profiles of transit reflections can be detected.

The thickness of the effective 'shell' of the sphere of reflection is non-uniform when crystal-monochromatized radiation is used. The thickness is a

Fig. 1. Biaxial diffractometer.

function of the divergence of the monochromatic incident beam, the spectral dispersion, and the deviation from strict parallelism of the X-ray wavelengths incident on the specimen. The resolution with which 'paired' interactions are recorded (*i.e.* those generated by a given r.l.p. as it passes into and out of the Ewald sphere) is generally significantly non-uniform (Ladell & Zola, 1985). To achieve equal half-widths for paired interactions, the m.c.c assembly was modified to permit rotation of the device about the incident-beam direction. The direction of maximum spectral dispersion was rotated into the plane containing the incident beam and the azimuthal rotation axis (*i.e.* the horizontal 'polar' plane). In that orientation, the thickness distributions of the hemispheric shells above and below the polar plane are equal.

Several paired interactions were measured using this modified arrangement. Comparison with interactions which had been recorded previously indicated significant improvements in resolution, but not enough, in our opinion, to warrant remeasuring an entire 180° Renninger pattern.

A second modification of the m.c.c. was implemented to improve counting statistics. It involved removal of the fourth reflecting face of the second grooved crystal of the m.c.c. and the rotation of the device to bring the collimated beam into the polar plane. This 'three-face' arrangement provided a 2·7-fold intensity increase without undue increase of beam divergence. Unfortunately, it also involved tilting the plane of maximum spectral dispersion by 65° relative to the polar plane. At that inclination, the widths of L interactions are greater, and the associated intensity dips smaller, than those of E interactions. It was felt that the substantial increase of incident-beam intensity outweighed the minor inconvenience resulting from the differences between the L and E profiles.

Three data sets have been measured. Each consisted of a 180° Renninger scan about the [311] rotation axis. In all, about 7×10^6 data points were collected. The two-beam 'background' intensity equalled about 6000 counts for the first two data sets and about 13 000 counts for the third set. Statistically significant dips in the two-beam intensity were observed at *all* calculated interaction settings. These varied from about 3% of the two-beam intensity for the weakest, to 38% for the strongest forbidden interactions. They ranged up to 50% for permitted interactions.

Additional details concerning the apparatus and techniques used in this investigation are given in Post, Nicolosi & Ladell (1984) and in Post, Gong, Kern & Ladell (1986).

The choice of [311] as the rotation axis made possible the recording of substantial numbers of n-beam interactions without detectable interferences owing to $\lambda/2$ contributions from the 622 reflection; 622 is a forbidden reflection.

III. Indices and phases

The indices of permitted reflections sum to $4n-1$, $4n$, or $4n+1$. Triplets of even-index reflections may include three terms each of which sums to $4n$, or one term which sums to $4n$ and two terms which sum to $4n-2$ ('forbidden'). Triplets of the latter type cannot be detected in Renninger patterns (James, 1963). Triplets of interest in this investigation, therefore, involve one forbidden and two odd-index reflections.

The sums of the phases of diffraction vectors which form closed polygons in reciprocal space are 'structure invariants'. We will be concerned mainly with 'triplet invariants'. The three diffraction vectors are related as follows:

$$\mathbf{H}+(\mathbf{K}-\mathbf{H})-\mathbf{K}=0. \qquad (1)$$

In the centrosymmetric germanium crystal structure $F(h, k, l)=F(-h, -k, -l)$. We will show below that, for forbidden reflections, $F(\mathbf{H})=F(h, k, l)=-F(-h, -k, -l)$. As a result, a change from a clockwise to counterclockwise summation of the terms in (1) leads to a change of the sign of the structure factor of the forbidden $\mathbf{H}$. The difference between the experimental triplet phase and the sum of the phases of the two permitted reflections is, of course, invariant, but that difference provides the sign of $\mathbf{H}$ in the clockwise sum and the sign of $-\mathbf{H}$ in the counterclockwise sum. In this manuscript all such summations will be carried out in a clockwise mode, *i.e.* in the sequence: transit, coupling, negative pivotal.

The invariant phases of triplets of centrosymmetric reflections are displayed in n-beam patterns in the form of asymmetric distributions of diffracted intensities about exact n-beam settings (Post 1979, 1983). The nature of the asymmetry is determined by the triplet phases and the directions of passage of the transit r.l.p.s through the Ewald sphere. For an E transit r.l.p., a positive triplet phase is usually indicated by an initial gradual attenuation of the two-beam background, followed by an abrupt enhancement to values which may exceed the normal two-beam intensity and a final gradual return to background levels. The opposite sequence indicates a negative triplet phase. Both phase indications are reversed when the transit r.l.p. is leaving the sphere. Illustrative examples can be seen in Figs. 5(a) and 7(b) of Post, Gong, Kern & Ladell (1986).

Enhancement of the n-beam intensity to values greater than the average two-beam intensity is rarely observed when the structure factor of the transit or coupling term is much smaller than that of the pivotal reflection. The abrupt rise in the E case from the minimum, discussed in the previous paragraph, generally levels off and merges with the background when the two-beam value is reached. In such cases the intensity profiles resemble resonance curves from which the portions above average two-beam levels have been removed. Examples of such weak interaction profiles are shown in Figs. 2(*a*) and (*a*′).

As the investigation progressed and as increasing numbers of phases were determined, it became apparent that the experimental phases of all triplets which included one forbidden reflection were negative (see Appendix). We had earlier reported (Post, Gong, Kern & Ladell, 1986) that all triplet phases observed in [311] Renninger scans involving only permitted reflections were positive. In that report this was shown to be due to the nature of the diamond-type structure. In the next section we show that the phases of all the individual forbidden reflections which we investigated are given by $(-1)^n$ (where n is determined by 'sum $h+k+l=4n-2$').

IV. Experimental results and discussion

Renninger patterns are plotted as histograms in Figs. 2–6. The indices of the forbidden reflections, and the angles at which interactions occur, are listed above the histograms. Step intervals of 0·001 and 0·002° were used. Scan ranges equalled 0·1° for Figs. 2–5, and 0·25° for Fig. 6.

E and *L* pairs of interactions are used in the figures to illustrate experimental phase effects. Placing them side by side facilitates the detection of phase indications as well as the changes of *n*-beam intensity sequences with directions of passage of transit r.l.p.s through the surface of the Ewald sphere.

Experimental results are summarized in Table 1. The figure in which an interaction is displayed is listed in column *A*, the indices of transit and coupling r.l.p.s in *B* and *C*, and the angle at which interactions occur in *D*. *E* and *L*, in column *E*, refer to 'entering' and 'leaving' r.l.p.s. Because enhancement of intensities above two-beam values is rarely observed in interactions involving forbidden reflections, AE in column *F* refers to 'gradual attenuation of the two-beam intensity followed by abrupt return to two-beam values'; 'EA' refers to the opposite sequence, *i.e.* 'abrupt attenuation followed by gradual return to two-beam values'. The phases of the negative pivotal, transit and coupling terms are listed in that order under *G*. The relative decrease of intensity in each interaction is listed as a fraction of the average two-beam intensity in column *H*.

Triplet phases were determined using the procedures outlined in § III, and described in greater

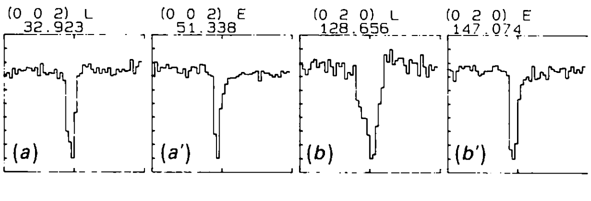

Fig. 2. Three-beam interactions involving {200} reflections.

Table 1. *Phases of 'forbidden' triplets (column headings are explained in the text)*

A	*B*	*C*	*D*	*E**	*F*†	*G*			*H*‡
						$(\bar{3}\bar{1}\bar{1})$	TR	CP	
	{200}								
2(*a*)	3 1 −1	0 0 2	32·923	*L*	AE	−	−	−	38
2(*a*′)	0 0 2	3 1 −1	51·338	*E*	EA	−	−	−	31
2(*b*)	3 −1 1	0 2 0	128·656	*L*	AE	−	−	−	19
2(*b*′)	0 2 0	3 −1 1	147·074	*E*	EA	−	−	−	31
	{222}								
3(*a*)	1 −1 −1	2 2 2	79·692	*L*	AE	−	+	+	33
3(*a*′)	2 2 2	1 −1 −1	100·299	*E*	EA	−	+	+	30
3(*b*)	5 −1 −1	−2 2 2	51·221	*L*	AE	−	−	−	13
3(*b*′)	−2 2 2	5 −1 −1	128·773	*E*	EA	−	−	−	12
3(c)	1 −1 3	2 2 −2	34·831	*E*	EA	−	−	−	19
3(c′)	1 −1 3	2 2 −2	178·723	*L*	AE	−	−	−	10
3(*d*)	1 3 3	2 −2 2	116·568	*E*	EA	−	+	+	13
3(*d*′)	1 3 3	2 −2 −2	243·423	*L*	AE	−	+	+	14
	{420}								
4(*a*)	1 1 −3	2 0 4	3·576	*L*	AE	−	+	+	11
4(*a*′)	2 0 4	1 1 −3	58·606	*E*	EA	−	+	+	11
4(*b*)	5 1 −3	−2 0 4	1·091	*L*	AE	−	−	−	6
4(*b*′)	−2 0 4	5 1 −3	99·583	*E*	EA	−	−	−	7
4(*c*)	4 −2 0	−1 3 1	87·834	*L*	AE	−	−	−	14
(4*c*′)	−1 3 1	4 −2 0	142·865	*E*	EA	−	−	−	12
	{442}								
5(*a*)	−1 −1 5	4 2 −4	85·013	*E*	EA	−	−	−	5
5(*a*′)	4 −4 2	−1 5 −1	94·981	*L*	AE	−	−	−	3
5(*b*)	4 −2 4	−1 3 −3	46·191	*E*	EA	−	+	+	5
5(*b*′)	−1 −3 3	4 4 −2	133·810	*L*	AE	−	+	+	7
5(c)	2 4 4	1 −3 3	141·927	*E*	EA	−	−	−	4
5(*d*)	−2 4 4	5 −3 −3	150·351	*E*	EA	−	+	+	5

* '*L*' indicates that the transit r.l.p. is leaving and '*E*' indicates that it is entering the Ewald sphere.

† 'AE' indicates 'attenuation followed by enhancement' and 'EA' indicates 'enhancement followed by attenuation' in an up-angle azimuthal scan.

‡ Percent deviation of the interaction minimum from the two-beam intensity.

detail by Post, Gong, Kern & Ladell (1986). Only the combinations '*L* AE', and '*E* EA' appear in columns *E* and *F*; both combinations indicate negative triplet phases. The phases of both permitted reflections in each triplet are known; the phase of the forbidden reflection is obtained by subtracting the two known phases from the experimental triplet phase.

{200} *interactions*

L and *E* pairs of interactions in which {200} reflections are involved are shown in Figs. 2(*a*), (*a*′) and (*b*), (*b*′). The phases of both permitted reflections ($\bar{3}\bar{1}\bar{1}$ and $31\bar{1}$) in Figs 2(*a*) and (*a*′) are negative. Subtraction of their phase sum from the observed negative triplet phase indicates that the phase of the third term, 002, is also negative. The same result is obtained for the phase of the 020 in Fig. 2(*b*).

{222} *interactions*

Four pairs of interactions are shown in Fig. 3. In Figs. 3(*a*) and (*a*′) the indices of the transit and coupling terms are 1, −1, −1 and 2, 2, 2. The phase of $\bar{3}\bar{1}\bar{1}$ is negative; that of $1\bar{1}\bar{1}$ is positive; the phase of 222 is therefore positive. The phases of both odd-index reflections in the triplet of Fig. 3(*b*) are negative, indicating that the phase of $\bar{2}22$ is negative. Similarly, the phases of $2\bar{2}2$ and $2\bar{2}\bar{2}$ in Figs. 3(*c*) and (*d*) are negative and positive respectively. Triplets involving the $\bar{2}\bar{2}\bar{2}$ reflection are not encountered in [311] scans of germanium with Cu $K\alpha_1$ radiation.

The quality of the histograms of Figs. 3(*a*), (*a*′), (*c*), (*c*′), (*d*) and (*d*′) is much better than those of Figs. 3(*b*) and (*b*′). The former were scanned in 0·001° steps with a 15 s dwell time. The average two-beam count per step was 28 000 counts. These patterns are indicative of the improvement in direct phase determination possible with good counting statistics.

{420} *interactions*

Six interactions are shown in Fig. 4. As indicated by the histograms, these are much weaker than those observed for the {222} and {200} scans. In Fig. 4(*a*), the $11\bar{3}$ phase is positive. Since the phase of $\bar{3}\bar{1}\bar{1}$ is negative, the phase of 204 must be positive in order that the calculated triplet phase conform to the experimental negative value. Similar results are obtained from Figs. 4(*b*) and (*c*), *i.e.* the phases of $\bar{2}04$ and $4\bar{2}0$ are negative.

{442} *interactions*

Six very weak interactions are shown in Fig. 5. Although the stochastic noise (*ca* 75 counts) is relatively large, the interactions and the phase indications are clearly displayed. The minima of all the interactions occur at their calculated positions. The phases of the forbidden reflections were obtained as described above: the phases of $42\bar{4}$ and 244 are negative; those of $4\bar{2}4$ and $\bar{2}44$ are positive.

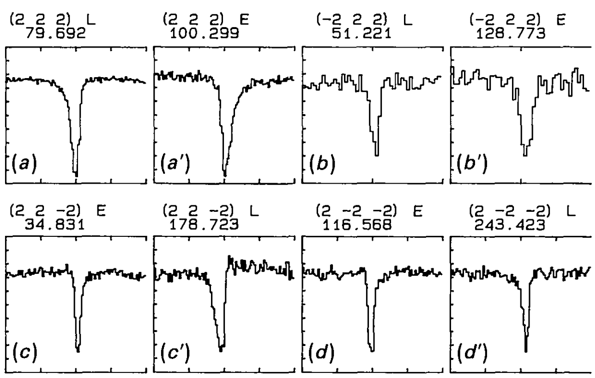

Fig. 3. Three-beam interactions involving {222} reflections.

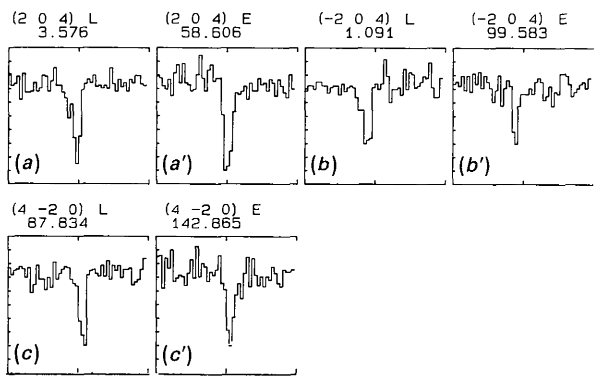

Fig. 4. Three-beam interactions involving {420} reflections

In Fig. 5 the large variations of the two-beam backgrounds because of relatively poor counting statistics tend to obscure the phase indications. However, our computer program sets the calculated three-beam interaction angle at the center of the corresponding chart, *i.e.* directly above the marker at the center of the lower margin. Note that in each case the minimum value of the intensity dip occurs at settings within one or two steps (7 to 14″) of the calculated setting. The asymmetries of the interaction profiles, in the form of abrupt dips followed by gradual recoveries, or the reverse, are also clearly visible.

In a thesis dealing with the *Temperature Dependence of Higher-Order Forbidden Reflections in Silicon and Germanium Using Synchrotron Radiation*, Tischler (1983) reported that the experimental structure factor of the 442 reflection of germanium at room temperature is positive (=0·098±0·0171 electrons). Our data indicate both positive and negative phases for different members of the {442} form, depending on the sum of the indices.

Unlike the phases of the triplets dealt with in this paper, the phases of *individual reflections*, particularly the very weak forbidden ones, are not invariant. Tischler, Shen & Colella (1985) have demonstrated that at elevated temperatures the contributions due to anharmonic thermal motions are sufficiently large to lead to changes of the phases of the 442 reflections in germanium and silicon. The phases which we discussed in the preceding paragraphs were determined from measurements made at room temperature.

An unusual example of the resolution attainable in investigations of forbidden reflections is shown in Fig. 6. Three interactions, all involving forbidden

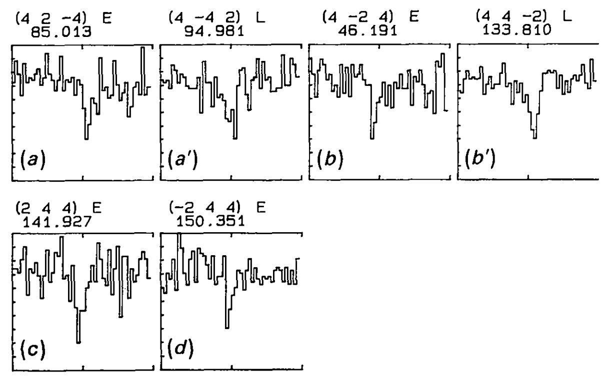

Fig. 5. Three-beam interactions involving {442} reflections.

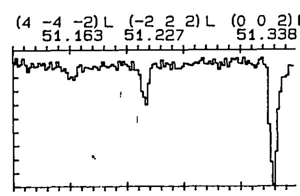

Fig. 6. Resolution of adjacent *n*-beam interactions.

reflections, are observed within a total azimuthal range of 0·17°. There is no visible evidence of the effects of overlap, even in the case of the two interactions separated by only 0·05°. Examination of the figure reveals that all three triplets have negative phases. The indicated phases of the three forbidden reflections are: $4\bar{4}\bar{2}$ positive; $\bar{2}22$ negative; and 002 negative.

V. Phases and anomalous scattering

The experimental phases reported in this paper are based on diffracted intensities. They therefore include substantial contributions from the large imaginary part of the anomalous scattering of Cu $K\alpha_1$ radiation by germanium ($f''=0{\cdot}89$).

Dawson (1967*a*) described procedures for the inclusion of effects due to f'' in his structure-factor formalism. He chose to omit them from his calculations of the structure factors of diamond and silicon, pointing out that, in those cases, such contributions could be reduced to negligible proportions by suitable choices of X-ray wavelengths.

The phases of all the forbidden reflections which we investigated are given by $(-1)^n$, where $n=(h+k+l+2)/4$. Our investigation was, however, limited to room-temperature studies of reflections which did not extend very far out into reciprocal space. At higher temperatures anharmonic effects make large contributions to the structure factors, comparable to, or even larger than, those due to f'' (Willis & Pryor, 1975). Under such conditions, measurements of the phases of high-index forbidden reflections would undoubtedly have indicated deviations from the simple $(-1)^n$ rule.

For the purpose of this discussion, the Dawson (1967*a*) expressions for the structure factors of the forbidden reflections may be summarized in the form:

$$F(hkl)=(-1)^n(hkl/|hkl|)A. \qquad (2)$$

A is a factor which does not change sign in the range of $\sin\theta/\lambda$ of interest, and hkl refers to the product of the indices. The expression implies that the structure factors of forbidden reflections go to zero, and need not be considered, when one or more indices equal zero. Nevertheless, strong phase indications are detected in n-beam interactions which involve reflection of the forms {200} or {420}. Ewald & Heno (1968) have pointed out that three-beam interactions would not be detectable if the magnitude of any one of the structure factors equalled zero. The possibility that the magnitudes of reflections of the forms {200} and {420} are not equal to zero must therefore be taken seriously. The problem warrants further study.

It is clear that the Dawson analysis is valid for cases in which anomalous scattering is negligible or absent. Our measurements, however, do not fall into that category. As a result, differences between the Dawson predictions and our experimental results are to be expected. Such differences occur when a change in the sign of the hkl product is not offset by a corresponding change in n in (2).

If we use our expression $(-1)^n$, we find that the structure factors of 'Friedel pairs', $F(h,k,l)$ and $F(-h,-k,-l)$, have opposite signs. [Let $n=(h+k+l+2)/4$ and $m=(-h-k-l+2)/4$. Then $m+n=1$; thus m and n have different parities.] Thus the phase angle is zero for one member of the Friedel pair and 180° for the other. Dawson has shown that Friedel's law is not obeyed when atomic form factors include significantly large values of f'', and that it *is* obeyed, even in the non-spherical-atom treatment, when f'' is negligibly small or absent. When, as in our experimental measurements, f'' represents a dominant portion of the effective atom form factor, it leads to the observed 180° shift of the phase angle in going from h, k, l to $-h$, $-k$, $-l$.

The presence of a large f'' also results in an apparent ambiguity in the determination of the invariant phase of triplets which contain a forbidden reflection. In the usual case, involving three 'permitted' germanium or other diamond-type reflections, the sum of the three phases is independent of the sense (clockwise or counterclockwise) in which the sum is taken. In such cases, in which the real parts of the atomic form factors have significant magnitudes, the inclusion of a small f'' in the form factor will usually lead to a minute change in the phase sum when the sense of the summation is changed. However, when the f'' is the dominant term in the form factor, as is often the case in forbidden reflections, the change in the sense of the summation leads to a shift of 180° in the phase, giving rise to the phase ambiguity mentioned above.

VI. Summary

(1) All of the calculated n-beam interactions accessible to Cu $K\alpha_1$ radiation in [311] scans of germanium have been detected and measured using a biaxial diffractometer and procedures discussed in § II.

(2) The triplet phases of large numbers of interactions which involve forbidden reflections have been determined experimentally. Scan ranges of 0·1° were used in most experiments. We could not detect significant differences between the intensities at the edges of the scan ranges and the average two-beam intensities (Figs. 2–6).

(3) Small half-widths of interaction dips, such as those reported above, appear to be characteristic of Renninger patterns of very weak interactions recorded by rotation about a strong primary reflection. The effects of the very minor perturbations due to the weak interactions on the strong background reflection are not detectable at angular settings only a few

hundredths of a degree removed from the interaction center.

(4) The phases of three interactions, each involving one forbidden reflection, which occurred within a 0·17° range were determined (Fig. 6). No effects due to overlap were detected even though two of the interactions were separated by only 0·05°.

(5) The phases of triplets which include one forbidden reflection are negative if the indices of the negative pivotal vector sum to $4n-1$, and positive if the indices sum to $4n+1$. (See Appendix.)

(6) The magnitude of f'' may have significant effects on the indicated phases of very weak forbidden reflections.

APPENDIX

Triplet phases in diamond-type crystals (one 'forbidden' and two 'permitted' odd-index reflections)

If the sum of the diffraction vectors $\mathbf{H}+(\mathbf{K}-\mathbf{H})-\mathbf{K}=0$, the triplet phase is a structure invariant. The sum of the indices of the vectors ('forbidden', 'coupling' and 'negative pivotal') is given by either

$$[4n(1)-2]+[4n(2)-1]+[4n(3)-1]=0 \quad (A1)$$

or

$$[4n(1)-2]+[4n(2)+1]+[4n(3)+1]=0. \quad (A2)$$

The n's are integers.

The phases of 'permitted' reflections (whose indices sum to $4n-1$, $4n$, or $4n+1$) equal $(-1)^n$. The sum of the indices of the 'forbidden' terms may be written in two equivalent ways: $4n+2$ or $4n-2$. When the latter is used, the phase of the forbidden reflection, obtained by subtracting the sum of the phases of the two permitted reflections from the experimental triplet phase, is also equal to $(-1)^n$.

The sums of the indices of the coupling and negative pivotal reflections must be both of the same type, *i.e.* $4n-1$ or $4n+1$ for $(A1)$ and $(A2)$ to be realized. The two cases are considered separately.

A. Permitted reflections whose indices sum to $4n-1$

Equation $(A1)$ reduces to

$$n(1)=-[n(2)+n(3)]+1. \quad (A3)$$

If $n(2)$ and $n(3)$ are of the same parity, $n(1)$ must be odd. The individual reflection phases will then be $---$ or $-++$. If $n(2)$ and $n(3)$ differ in parity, then $n(1)$ must be even and the individual reflection phases will be $++-$ or $+-+$. In all cases the triplet phase is negative. These correspond to the cases discussed in this paper (the indices of the negative pivotal vector, $-\mathbf{K}$, are $-3, -1, -1$). The observation that the phases of all the forbidden triplets are negative for these cases is accounted for.

B. Permitted reflections whose indices sum to $4n+1$

Equation $(A2)$ reduces to

$$n(1)=-[n(2)+n(3)]. \quad (A4)$$

If $n(2)$ and $n(3)$ are of the same parity $n(1)$ is even. The individual reflections are then $+--$ or $+++$. If $n(2)$ and $n(3)$ differ in parity, $n(1)$ is odd; the individual reflections are then $-+-$ or $--+$. In all cases (B) the triplet phase is positive.

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