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Determination of Phase Using Multiple-Beam Effects*

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Abstract

It is shown that the absolute phase of a weak reflection can be obtained from an experimental integrated intensity measurement by taking into account multiple-beam effects. The absolute structure factor of the basis-forbidden 622 reflection in Ge has been measured. The contribution from weakly excited reflections whose phases are known acts as a reference wave for the reflection in question. It is further shown that, even in the limit of weak excitation of multiple beams, the intensity distribution in reciprocal space is determined by dynamical, not kinematical, theory. The remarkable result is demonstrated that several hundred beams are required to fully calculate X-ray multiple-beam effects, and an efficient approximation is presented for multiple-beam dynamical calculations with weak reflections. The intensity of weak multiple-beam effects, at least in the diamond structure, is roughly proportional to Z^4, where Z is the atomic number.

I. Introduction

X-ray scattering measurements can provide important information about the structure of crystalline materials. However, an unambiguous determination of structure requires knowledge of both the intensity and the phase of the scattered Bragg beams.

Generally, indirect phase information can be obtained through the use of a reference beam which is coherently related to the Bragg reflection being considered. One type of reference beam is created by the simultaneous excitation of a series of Bragg beams whose phases are known. The interaction of these multiple beams with the principal Bragg beam allows one to extract the phase of the principal beam.

In the present experiment we are interested in using the intensities and phases of weak quasi-forbidden reflections in the diamond structure to obtain detailed information about the charge distribution of valence electrons. The intensities, although quite weak, are measurable to fair accuracy using a synchrotron light source. We describe a method of measuring the absolute phase using many beam contributions from reflections far from the Ewald sphere. These extra beams are not negligible even under nominally optimized conditions, and affect the scattering in a way that allows one to extract the unknown phase.

The phases of the F's, the structure factors, for the allowed diamond-structure reflections are easily calculated from the known atomic positions. However, for basis-forbidden reflections ($h+k+l=4n+2$) it is the shape of the electron distribution around the nucleus that determines the value of F. For a spherical distribution, F is exactly zero. Thus for a

* The experimental work was part of a doctoral dissertation at Cornell Univ. See Tischler & Batterman (1984).

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basis-forbidden reflection, knowledge of the average crystal structure is not sufficient to determine the phase of these reflections. In fact, to extract the deviation from sphericity of the charge distribution from diffraction data, one needs an independent means of determining the phase.

For a normal Bragg reflection, multiple-beam effects can usually be ignored. However, for basis-forbidden reflections, multiple-beam contributions can, in some cases, be comparable in intensity to the principal reflection and can thus be used to derive phase information.

II. Theory

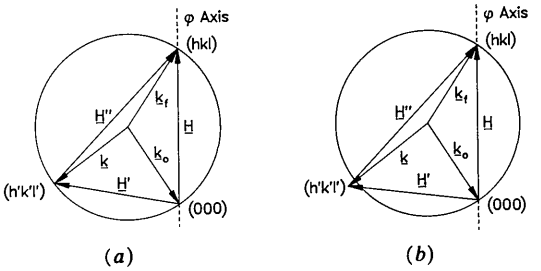
Consider the Ewald sphere construction when exciting a reciprocal-lattice vector **H** (Fig. 1). As we rotate the crystal through an angle φ around the vector **H** (*i.e.* normal to the diffracting planes), another reciprocal-lattice vector **H′** will also intercept the Ewald sphere. Due to the translational invariance of the reciprocal lattice, there exists a third vector **H″** such that $\mathbf{H}=\mathbf{H}'+\mathbf{H}''$. The pair of reflections **H′** and **H″** provide an alternative channel to scatter radiation coherently into the same direction as does **H**. This is the origin of the Renninger effect (Renninger, 1937, 1960) (also called *Umweganregung*).

If the reflection **H** is allowed, the effect of multiple reflections is relatively small. However, for basis-forbidden reflections, multiple-beam effects are very important. Fig. 2 shows a portion of a φ scan for the Ge 622 reflection using 1·511 Å radiation. The multiple reflections are the tall clipped-off peaks while the 622 is at the general background level. Some of the **H′**, **H″** pairs are indicated. A reflection pair such as $\mathbf{H}'=7\bar{1}1$ and $\mathbf{H}''=1\bar{3}1$ consists of two allowed strong reflections so that the individual channel **H′**, **H″** can be several orders of magnitude stronger than the basis-forbidden reflection. Note in Fig. 2 that the 222, although nominally forbidden, produces a small but detectable peak.

φ regions in Fig. 2 labelled *J*, *B* and *I* are seen to be free of strong multiple reflections. However, if the basis-forbidden reflection is extremely weak, as in the present case of the Ge 622, the multiple-beam contributions are significant even in these regions in φ. Significant effects are observable when the vector **H′** is as much as the Ewald sphere's radius distant from the sphere's surface. This can be put in another way. Although the intrinsic widths of the strong Bragg reflections are in the arc-second regime, a significant multiple-beam contribution is observable when a multiple-reflection node is tens of degrees in φ removed from the exact Bragg condition for the principal reflection.

It is our goal to extract the structure factor F_{622} for germanium from a measurement of the integrated intensity of a θ scan for three values of φ centered in the regions *J*, *B* and *I* in Fig. 2. The measured integrated intensities range over an order of magnitude among the three regions. Simple two-beam theory would require equality of these values. We will show that these large variations are due to different multiple-beam contributions in the three φ regions. A proper *N*-beam dynamical calculation of the integrated intensity shows that these three disparate measurements are consistent with a single signed value of F_{622}.

Initially we chose eight beams in each φ region whose reciprocal-lattice point lay within 5% of the Ewald sphere's radius of the Ewald sphere defined by the ⟨622⟩ vector and the incident-wave vector (Tischler & Batterman, 1984). These eight beams were put into the *NBEAM* program of Colella (1974) to



(*a*) (*b*)

Fig. 1. Ewald sphere showing excitation of a three-beam case. (*a*) shows (*h′k′l′*) exactly on the sphere; (*b*) shows (*h′k′l′*) slightly off the sphere, but note that for the total process we still have the condition that $\mathbf{H}=\mathbf{H}'+\mathbf{H}''$, and **H** still lies exactly on the Ewald sphere.

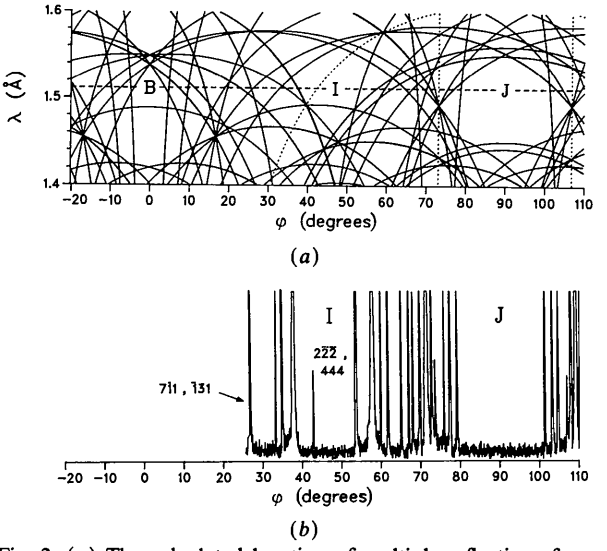


Fig. 2. (*a*) The calculated location of multiple reflections for a fixed 622 primary Bragg reflection for a range of wavelengths. The dashed line is at 1·511 Å, and the dotted curves are multiple reflections involving a 222-type reflection. (*b*) Experimental intensity *versus* φ for the Ge 622 reflection at 1·511 Å. The multiple reflections are the tall peaks and the general background is mostly due to F_{622}. The regions labelled *J*, *B* and *I* refer to areas mentioned in the text. Note the small multiple reflection due to a 222 reflection.

compute the integrated intensity by dynamical theory (Tischler & Batterman, 1984).

The results were encouraging and led to a consistent value of F_{622} for the three regions. However, as we included more beams in the calculation within a spherical shell with an outer diameter equal to twice the radius of the Ewald sphere, it became apparent that the full contribution of the multiple reflections was not covered by merely eight beams.

Fig. 3 shows the calculated integrated intensities using up to 30 beams for each of the three regions *J*, *B* and *I*. The symbols are from a full calculation using the *NBEAM* program. They indicate that the multiple-beam contributions in regions *J* and *B* have not reached their asymptotic values. Also clear is a practical limit to further complete calculations, since for a single 30-beam rocking curve, one point on the curve required 4·5 h of CPU time on a superminicomputer.

To complete an *N*-beam calculation at only one value of θ would require diagonalization of an $N \times N$ complex array which would take some nine days for $N = 400$. An approximation was employed to reduce this computation to the equivalent of the diagonalizing of N 3×3 arrays requiring only a few minutes of CPU time.

The approximation is based on the fact that all beams derived from reciprocal-lattice points far off the Ewald sphere are very weak, and thus they couple weakly to one another. Each $\mathbf{H}'$, $\mathbf{H}''$ pair scatters coherently with, but independently of, all the others. We show that this approximation agrees very well with the exact calculations that extend to 30 beams.

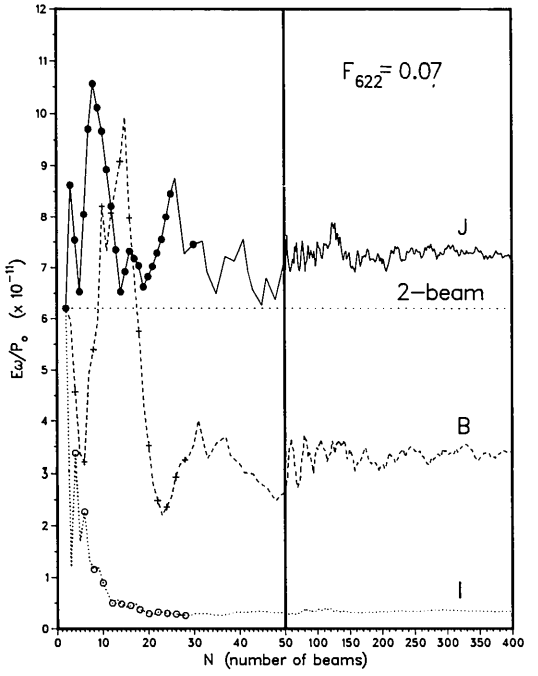


Fig. 3. Calculated integrated intensities *versus* number of included beams for the three regions *J*, *B* and *I*. The markers are from a complete dynamical calculation of the rocking curve using the *NBEAM* program for up to 30 beams. The lines are calculated results using the weak-beam approximation outlined in the text.

The approximation scheme was developed by keeping firmly in mind that these are very weak reflections and that primary extinction is totally negligible. A simple view of the problem is that the multiple reflections and principal reflection represent separate and coherent scattering channels. So it should be possible to determine separate amplitudes for these outgoing waves and then add them coherently to get the final outgoing amplitude. Neglecting polarization for the moment, we could write $F_{\text{total}} = F_{622} + \sum F_i$, where F_{622} is the 622 structure factor, F_{total} is the F one might naively calculate from the integrated intensity using kinematical theory (Warren, 1969), and F_i is proportional to the scattered amplitude (as is a structure factor) of the $\mathbf{H}_i'$, $\mathbf{H}_i''$ pair. Since the scattering is weak, each F_i may be obtained from a separate three-beam calculation. Using this method F_{total} is accurate to ~5%.

In fact, the above procedure can be made to work by using the actual scattered amplitude and properly including polarization. Since the vectors $\mathbf{H}_i'$ and $\mathbf{H}_i''$ do not have a simple orientation with respect to the plane of incidence, σ and π polarizations are mixed and so scattering amplitudes cannot simply be added as scalars.

For a given angle and set of $\{\mathbf{H}_i'\}$, the *NBEAM* program computes the amplitudes of both the σ and π outgoing waves for both σ and π incident waves. These complex four-vectors (denoted by $\mathbf{E}$) are what should be added, not the simple scalar amplitudes (the F's). Thus, $\mathbf{E}_{\text{total}} = \mathbf{E}_{622} + \sum \mathbf{E}_i$, where $\mathbf{E}_{\text{total}}$ is the total outgoing amplitude, $\mathbf{E}_i$ is the contribution from $\mathbf{H}_i'$, $\mathbf{H}_i''$, and E_{622} is the amplitude from F_{622}.

We further assume that the integrated intensity is proportional to the square of the modulus of the scattering amplitude when θ is at the exact nodal position of the forbidden reflection. This assumption removes the need to compute a rocking curve to calculate integrated intensity. The above assumptions can be expressed as:

$$E\omega/P_0(N) = \alpha |\mathbf{P} \sum_{i=0}^{N} E_i|^2 \qquad (1)$$

where $\mathbf{P}$ is a 4×4 diagonal matrix representing the polarization,* and $i = 0$ is the two-beam case. Note that the $\mathbf{E}_i$ from an $\mathbf{H}'$, $\mathbf{H}''$ pair are added coherently, and the scaling parameter α is derived from a complete rocking-curve calculation of a two-beam case.

* $\mathbf{P}$ is a diagonal matrix with P_{11} and P_{22} equal to the fraction of the incident beam polarized perpendicular to the plane of diffraction, and P_{33} and P_{44} are equal to the fraction of the incident beam polarized parallel to the plane of diffraction.

Table 1. *Parameters and calculation results for the* Ge 622 *reflection for three regions in germanium*

Region	*J*	*B*	*I*
φ	90·1	0·01	45·37
$\lvert E\omega/P_0\rvert$exp. ($\times 10^{-11}$)	9·730	4·3295	0·5433
F_{622}	+0·0818*	+0·0766	+0·0814
	$\langle F_{622}\rangle = 0{\cdot}080(3)$ (3·7%)		

* The other roots of equation (2) give an F_{622} for the *J*, *B* and *I* regions of −0·093, −0·039 and +0·050, respectively.

Since each $\mathbf{E}_i$ is treated independently and assumed not to be a function of the value of F_{622}, each $\mathbf{E}_i$ may be obtained from a simple three-beam calculation using 000, 622 and $\mathbf{H}_i'$ ($\mathbf{H}_i''$ is implicitly included). The three-beam calculation yields $\mathbf{E}_i+\mathbf{E}_0$ by the above assumptions.

The procedure for calculating $E\omega/P_0$ was first to pick an approximate value for F_{622}, called F_0, and calculate the two-beam amplitude $\mathbf{E}_0$ and the N three-beam amplitudes ($\mathbf{E}_i+\mathbf{E}_0$). $\mathbf{E}_0$ was vectorially subtracted to leave the individual $\mathbf{E}_i$'s. We then calculated a complete two-beam rocking curve to get α. With α, $\mathbf{E}_0$ and a list of the N $\mathbf{E}_i$'s, we get that

$$E\omega/P_0 = \alpha|(F_{622}/F_0)\mathbf{P}\mathbf{E}_0+\mathbf{P}\sum_{i=1}^{N}\mathbf{E}_i|^2. \qquad (2)$$

We have implicitly assumed that $\mathbf{E}_0$ is proportional to $\mathbf{F}_0$ (true for weak reflections), and that there is no polarization mixing in the two-beam case. Note that with this procedure the required computer time only increases linearly with the number of beams N. For a normal eigenvalue problem, the time would increase as N^3.

Fig. 3 shows both the justification for this approximation scheme and the reason for including 400 ($\mathbf{H}'$, $\mathbf{H}''$) pairs. The makers in Fig. 3 are the integrals of complete dynamical rocking-curve calculations where the full matrix was diagonalized (the $N=30$ dot required ~4·5 h of CPU time), and the lines are obtained from the approximations outlined above. In all three regions, the fit is excellent. The significant variations in $E\omega/P_0$ as a function of N show the extent and importance of multiple-beam contributions. Clearly, in our present situation, several hundred beams are needed to compute the asymptotic multiple-beam contribution.

For the diamond structure, which is centrosymmetric, the phase of any F can be only 0 or π, thus all F's are either positive or negative real. This simplifies the problem. The difficulty is that the sign of F for the forbidden reflections is not intuitively obvious. To get the signed value of F_{622}, one adjusts F_{622} until the calculated (2) and measured $E\omega/P_0$ agree for each φ position. This is quickly done since (2) only requires a summation over the previously calculated $\mathbf{E}_i$'s.

The $\mathbf{E}_i$'s are not sensitive to the value of F_{622}: *i.e.* the amplitude of the multiple-beam contributions at a given node in k space is independent of the value of F at the node and is a coherent uncoupled contribution. It is therefore added as an amplitude with appropriate phase to the two-beam value at the node. Because of the qudratic nature of (2), two values of F_{622} are possible for each φ point, but only one value is consistent for all three regions.

III. Results

These experiments were done at CHESS (Cornell High Energy Synchrotron Source). Details of the experiment are given in Tischler & Batterman (1984).

The measured integrated intensities are converted to absolute units by a measurement of the Si 533 allowed reflection whose F is known (see Tischler & Batterman, 1984). The experimental absolute integrated intensities for the three regions are shown in Table 1 and range from $9{\cdot}7\times10^{-11}$ to $0{\cdot}54\times10^{-11}$. For each φ region a value of F_{622} is calculated by comparing the experimental integrated intensity with the results of the 400-beam calculations, using the parameters listed below.* The average F_{622} fitting all regions is $F=0{\cdot}080(3)$. The relative error of only 3·7% is remarkable when one considers that the experimental intensities range over a factor of 20 in the three regions.

IV. Discussion of results

Experimental X-ray measurements of multiple-beam effects have heretofore required three to eight beam contributions to explain experimental intensities. In the present case, we show that regions nominally free of multiple reflections can still have multiple-beam contributions comparable to that of the primary forbidden reflection. Furthermore, one must include several hundred reflections; a situation more to be expected in electron diffraction than X-ray diffraction.

Furthermore, even though each contributing beam is extremely weak, it must be added as a coherent amplitude to the primary reflection to get the net field. This is more a dynamical problem than a kinematic one from this point of view.

The theory shows that the multiple-beam contribution $E_{\text{mult}}=\sum_{i=1}^{N}E_i$ is independent of F_{622} [see (1)]. To probe this point further, we investigated the shape of the diffraction curve, *i.e.* $I(\theta)$ at fixed φ. The shape of the reflection curve in all cases depends upon the effective crystal thickness as determined by the absorption coefficient or effective extinction depth,

* Parameters used in the calculations: $a_0=5{\cdot}657764$, $\langle u^2\rangle=0{\cdot}02187$, $\lambda=1{\cdot}511$ Å, $f'=-1{\cdot}190$, $f''=0{\cdot}987$, $\theta=62{\cdot}345°$. For a two-beam case, with $f=0{\cdot}08$, $E\omega/P_0=8{\cdot}09741\times10^{-11}$.

whichever is shorter. Since the reflection strength for all N beams is very low, the self-extinction depth is quite large.

We calculated the $I(\theta)$ curve as F_{622} approached zero. As F_{622} becomes smaller, $E_{\rm mult}$ is virtually unchanged and there remains a narrow rocking curve at the 622 position whose strength is determined by the excitation of the N beams. There is no general background scattering in reciprocal space because of n-beam effects. What appears is a node of reflectivity at the reciprocal-lattice point even as the structure factor F_{622} goes to zero.

These results indicate that even extremely weak multiple-beam effects cannot be treated kinematically. There is a dynamical interaction of beams whenever a Bragg condition is satisfied, *i.e.* wherever $\mathbf{k}_f$ in Fig. 1 is at a node of the reciprocal lattice.

When a dynamical reflection is extremely weak, the integrated intensity for a given F is the same as that calculated from the kinematic expression, which is proportional to F^2. However, the interaction of the beams is clearly dynamic in origin. For any region of k space near a reciprocal-lattice point, the scattered intensity contributed by each of the N beams is essentially zero because we are so far removed from satisfying the Bragg condition for those reflections. However, if the $\mathbf{k}_f$ vector approaches a node of the reciprocal lattice, even if the node has a zero structure factor, a sharp, albeit weak, reflection will appear.

We investigated the general strength of the n-beam effect as a function of the atomic number Z. We calculated n-beam integrated intensities for the 622 reflection, at identical φ and λ/a_0. In the I region of Ge, $E^{\rm Ge}_{\rm mult}=0{\cdot}038$, and in the corresponding region of Si, $E^{\rm Si}_{\rm mult}=0{\cdot}0075$. The ratio of $E^{\rm Ge}_{\rm mult}/E^{\rm Si}_{\rm mult}=5{\cdot}07$, which is very close to the ratio $(Z_{\rm Ge}/Z_{\rm Si})^2$. Thus, the intensity of multiple-beam contributions for the two materials scales as Z^4. This explains why multiple-beam effects are much more important in Ge than Si and is consistent with our experimental results reported in Tischler & Batterman (1984). It appears that a simple condition governs the weak multiple-beam contributions; each pair of reflections satisfying $\mathbf{H}'+\mathbf{H}''=\mathbf{H}$ contributes as the product of the two intensities as if they were sequential reflections.

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Determination of the Velocity of Sound in Crystals by Time-of-Flight Neutron Diffraction

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Abstract

In a neutron Laue (time-of-flight) experiment, the nature of the thermal diffuse scattering by elastic waves depends on the ratio, β, of the sound velocity in the crystal to the neutron velocity. For slower-than-sound neutrons, there is a certain range of β for which a 'wavelength window' appears in the incident beam; TDS is forbidden for all wavelengths lying within this window. The window is best observed in back scattering, and for a scattering angle close to 180° the centre of the window coincides with the Bragg wavelength. At the edges of the window, the TDS intensity rises abruptly to two sharp peaks, one due to phonon emission and the other to phonon absorption. The sound velocity is derived by measuring the time of flight of either peak. The method is illustrated by applying it to pyrolytic graphite, which was examined using the neutron spallation source ISIS.

Glossary of symbols

$b_\kappa^{\rm coh}$	coherent scattering length of atom κ
$\mathbf{B}$	reciprocal-lattice vector
c_g	group velocity of sound
c_s	phase velocity of sound
$\mathbf{e}(\kappa \mid j\mathbf{q})$	polarization vector of atom κ excited by mode of vibration $(j\mathbf{q})$
E_0, E	initial and final energies of neutron
$G_j(\mathbf{Q})$	structure factor for one-phonon scattering
$\hbar$	Planck's constant/2π

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