Direct Measurement of Crystallographic Phase by Electron Diffraction

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Three-beam diffraction is analyzed in a geometry appropriate for high-energy electron diffraction. An expression for the lowest-order correction to the kinematic intensity is derived, from which a prescription for measuring a crystallographic-phase invariant is obtained. This analysis is a good approximation for the diffraction observed in large-convergence-angle electron-diffraction patterns. Phase invariants are measured in the noncentrosymmetric crystal InP to an accuracy of $\pm 15°$. The technique provides a general and practical method for measuring phases.

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The phase problem has existed since the beginning of x-ray crystallography. In order to retrieve a crystal structure from a diffraction experiment it is necessary to know both the amplitude $|U_{\mathbf{g}}|$ and phase $\phi_{\mathbf{g}}$ of the Fourier components (structure factors) of the scattering potential, but in kinematic x-ray diffraction only the amplitudes are available. The absolute phase of a structure factor has no meaning because it is origin dependent, but combinations can be constructed which are origin independent and therefore, in principle, measurable. The best known of these phase invariants is the triplet $\theta=\phi_{\mathbf{h}}-\phi_{\mathbf{g}}+\phi_{\mathbf{g}-\mathbf{h}}$ where the reciprocal-lattice vectors involved, $\mathbf{g}$, $\mathbf{h}$ and $\mathbf{g}-\mathbf{h}$, form a closed triangle. Analysis of θ has formed the basis of the direct methods of crystallography.

It has been known for some time that in order to measure θ one must consider dynamical diffraction situations, the most obvious candidate being diffraction at a three-beam point.[1,2] Intensity anomalies are known to occur here and several attempts have been made to recover phase information, such as the value of θ in centrosymmetric crystals[3,4] (when it is always either 0 or π), or the polarity of ZnS-type crystals.[5] Further interest has recently been shown in analyzing x-ray three-beam diffraction,[6-8] but at present no simple, general, and practical method exists for measuring θ. In electron diffraction the problem is easy to set up in terms of a 3×3 matrix,[9] but in general, the solutions are intractable because of the strong diffraction. Indeed, until recently it has not been possible even to measure structure-factor amplitudes with high-energy electrons. However, a new large-angle convergent-beam diffraction technique has been developed which, with a simple geometry, gives many diffracted lines with measurable kinematic intensities.[10] The important extension of this work that we present in this Letter is that the same patterns contain many visible three-beam diffraction points, and that by analyzing the intensity distribution at these points we can recover phase information. An example of this "Vincent" pattern is given in Fig. 1; three-beam points are seen where the bright diffracted lines cross Kikuchi lines. The prescription for phase measurement which we describe below is general, and can be used in both centrosymmetric and noncentrosymmetric crystals. Importantly, only distances, and not intensities, need be measured on micrographs. It relies on the diffraction being relatively weak, but as the reciprocal-lattice vectors involved are large, this is not a stringent condition. As an example, we apply the method to measuring θ in the noncentrosymmetric crystal InP.

Our starting equations are a form of the Howie-Whelan equations[11] which are appropriate for diffraction near a three-beam point:

$$\frac{da_{\mathbf{g}}}{dz}=\frac{1}{2ik_z}\sum_{\mathbf{g}'}a_{\mathbf{g}'}(z)U_{\mathbf{g}-\mathbf{g}'}e^{i\Delta\mathbf{g}\mathbf{g}'z/2k_z}. \tag{1}$$

Here the $a_{\mathbf{g}}(z)$ are the amplitudes diffracted into reflection $\mathbf{g}$ as a function of depth z in the crystal; in three-beam diffraction $\mathbf{g}$ and $\mathbf{g}'$ only take the values $\mathbf{0}$, $\mathbf{g}$, and $\mathbf{h}$. The geometry under consideration is summarized in Fig. 2. The $U_{\mathbf{g}}$ are electron structure factors, $\Delta_{\mathbf{g}\mathbf{g}'}=\{(\mathbf{K}+\mathbf{g})^2-(\mathbf{K}+\mathbf{g}')^2\}$, and $\mathbf{K}$ and k_z are the transverse and longitudinal components of the incident wave vector $\mathbf{k}$. A symmetric Laue geometry is assumed, and the initial conditions at the entrance surface ($z=0$) are $a_{\mathbf{g}}(z=0)=\delta_{\mathbf{g}0}$. We shall concentrate on diffraction into $\mathbf{g}$, although an identical analysis can be used for $\mathbf{h}$. Two-beam diffraction into $\mathbf{g}$ occurs all along the line PQ, but at special orientations (A in Fig. 2) three-beam routes become important. These will occur whenever the diffracted lines cross $\mathbf{g}-\mathbf{h}$ Kikuchi lines. The three-beam feature on the $\mathbf{g}$ line at B in Fig. 2 is obviously linked with that at C. At the exact three-beam orientation $OA=OB=OC=|\mathbf{K}_0|$, and if we write $\mathbf{K}=\mathbf{K}_0+\delta\mathbf{K}$, $\Delta_{\mathbf{g}\mathbf{g}'}$ becomes $\Delta_{\mathbf{g}\mathbf{g}'}=2(\mathbf{g}-\mathbf{g}')\cdot\delta\mathbf{K}$.

We use an iterative procedure to solve (1). The initial conditions serve as the zeroth-order amplitude terms $a_{\mathbf{g}}^{(0)}$, the first-order terms $a_{\mathbf{g}}^{(1)}$ give the kinematic approximation to two-beam theory, and inclusion of the two-path route $\mathbf{h},\mathbf{g}-\mathbf{h}$ in $a_{\mathbf{g}}^{(2)}$ is sufficient to introduce the phase triplet θ. It is convenient to use the dimension-

less coordinates

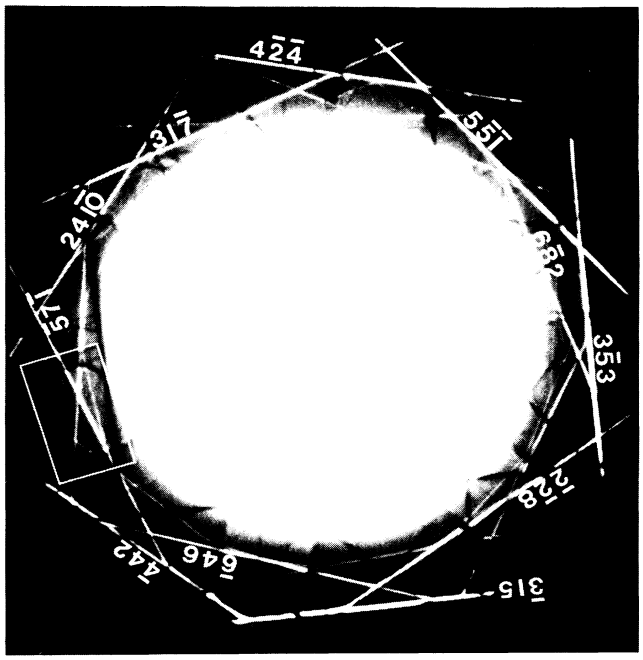
$$x=\mathbf{h}\cdot\delta\mathbf{K}\frac{t}{2k},\quad y=\mathbf{g}\cdot\delta\mathbf{K}\frac{t}{2k},\quad \beta_{\mathbf{g}}=|U_{\mathbf{g}}|\frac{t}{2k},\tag{2}$$

where t is the crystal thickness. Since the diffracted intensity is given by

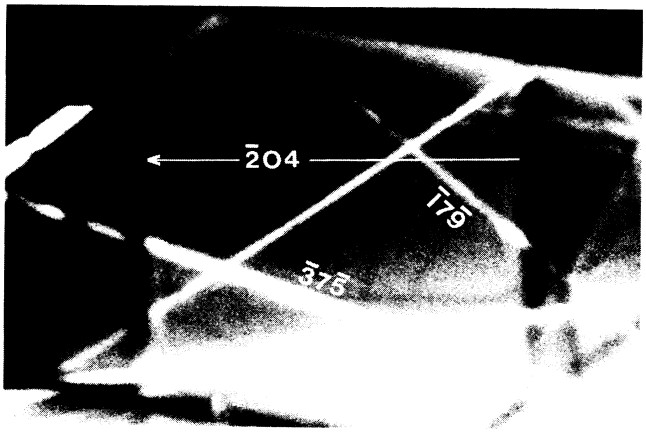
$$I_{\mathbf{g}}(x,y,t)=|a_{\mathbf{g}}^{(0)}(t)+a_{\mathbf{g}}^{(1)}(t)+a_{\mathbf{g}}^{(2)}(t)+\ldots|^2,$$

then, to third order in the potential U,

$$I_{\mathbf{g}}(x,y,t)=\beta_{\mathbf{g}}^2f^2(y)-\left[\beta_{\mathbf{g}}\beta_{\mathbf{h}}\beta_{\mathbf{g}-\mathbf{h}}\frac{f^2(y)}{x}\left\{1-\frac{f(y-x)}{f(y)}\cos x\right\}\right]\cos\theta+[\beta_{\mathbf{g}}\beta_{\mathbf{h}}\beta_{\mathbf{g}-\mathbf{h}}f(x)f(y)f(y-x)]\sin\theta,\tag{3}$$



(a)



(b)

FIG. 1. (a) Large-convergence-angle electron-diffraction pattern at the [$\bar{6}\bar{5}\bar{3}$] axis of InP. Accelerating voltage is 250 kV. (b) Enlargement of area shown in (a) showing intensity anomalies where diffracted lines ($\bar{3}7\bar{5}$) and ($\bar{1}7\bar{9}$) cross ($\bar{2}04$) Kikuchi lines.

where $f(X)=\sin(X)/X$ and $\theta=\phi_{\mathbf{h}}-\phi_{\mathbf{g}}+\phi_{\mathbf{g}-\mathbf{h}}$. The same expression can be used for diffraction into $\mathbf{h}$, but x and y must be interchanged and θ becomes $-\theta$. Thus, we have developed two correction terms to the kinematic result, each of which depends on the desired phase triplet θ. These are general expressions for all three-beam diffraction, though since they are essentially kinematic we should expect them to represent the true diffracted intensity most accurately when $\beta_{\mathbf{g}}\ll 1$ for all three $\mathbf{g}$'s. This will be satisfied for large voltages (large k), large $\mathbf{g}$ vectors (such as in Vincent patterns, giving small U's), and thin crystals (small t). In our analysis we shall need to know the position of the exact three-beam point which we do by observing the center of the diffusely scattered Kikuchi line. Thus, β cannot be made too small or this line will be too weak to be seen. A more detailed analysis[12] indicates that (3) and the prescription for measuring θ derived from it (see below) work well for β up to order unity.

Expressions of the approximate form of (3) have been derived before,[8] but, as mentioned above, they have not been used to develop a practical prescription for the measurement of θ. The strongest maxima and minima of $I_{\mathbf{g}}(x,y,t)$, i.e., the most obvious intensity anomalies, all lie along the ridge of the diffraction line of interest, at $y=0$. Setting $y=0$ in (3), the phase-dependent terms

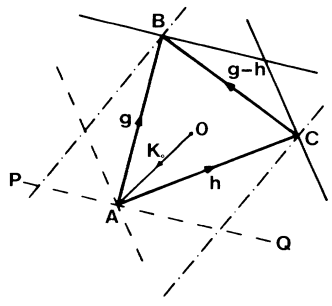


FIG. 2. Three-beam diffraction geometry. Dashed lines indicate incident orientations, full lines represent bright diffracted lines, and dot-dashed lines represent Kikuchi lines. See text for details.

become

$$I_{\mathbf{g}}(x,0,t)=\beta_{\mathbf{g}}\beta_{\mathbf{h}}\beta_{\mathbf{g}-\mathbf{h}}\{(-1/x)[1-f(2x)]\cos\theta+f^2(x)\sin\theta\}\,. \tag{4}$$

Figure 3 shows a series of plots of this ridge intensity anomaly for various values of θ. If $I_{\mathbf{g}}(x,0,t)$ is differentiated with respect to x then the extremal values of x, which we write as x_e, satisfy

$$\tan\theta=\frac{(\sin2x_e)/x_e-\cos2x_e-1}{(\cos2x_e-1)/x_e+\sin2x_e}$$

$$=-\cot x_e=\tan(x_e-\tfrac{1}{2}\pi), \tag{5}$$

or, since the tangent function has a period of π,

$$\theta=x_e+(n-\tfrac{1}{2})\pi. \tag{6}$$

Thus, we see that a simple measurement of the position of intensity maxima and minima relative to the exact three-beam point $x=0$ gives us the desired phase triplet θ. If our attention is limited to the strongest extrema, which occur closest to the three-beam point, then n is 0 for the principal minimum and 1 for the principal maximum (Fig. 3). Therefore,

$$\theta=x_{\min}-\tfrac{1}{2}\pi=x_{\max}+\tfrac{1}{2}\pi. \tag{7}$$

Furthermore, the important result $|x_{\min}-x_{\max}|=\pi$ serves to define a distance scale in the electron micrograph. Thus, we have a prescription for measuring the phase triplet which is independent of structure-factor amplitude, voltage, and thickness, and in which only distances from the center of a Kikuchi line to the strong intensity anomalies need be measured. If only one of the principal extrema is detectable, we must use the definition of x (2) to define the distance scale, which will require a measurement of the crystal thickness t.

To demonstrate the method a study has been made of InP, which has the simple zinc-blende structure. The diffraction pattern used [Fig. 1(a)] is from the [$\bar{6}\bar{5}\bar{3}$] axis of a room-temperature sample with use of an accelerat-

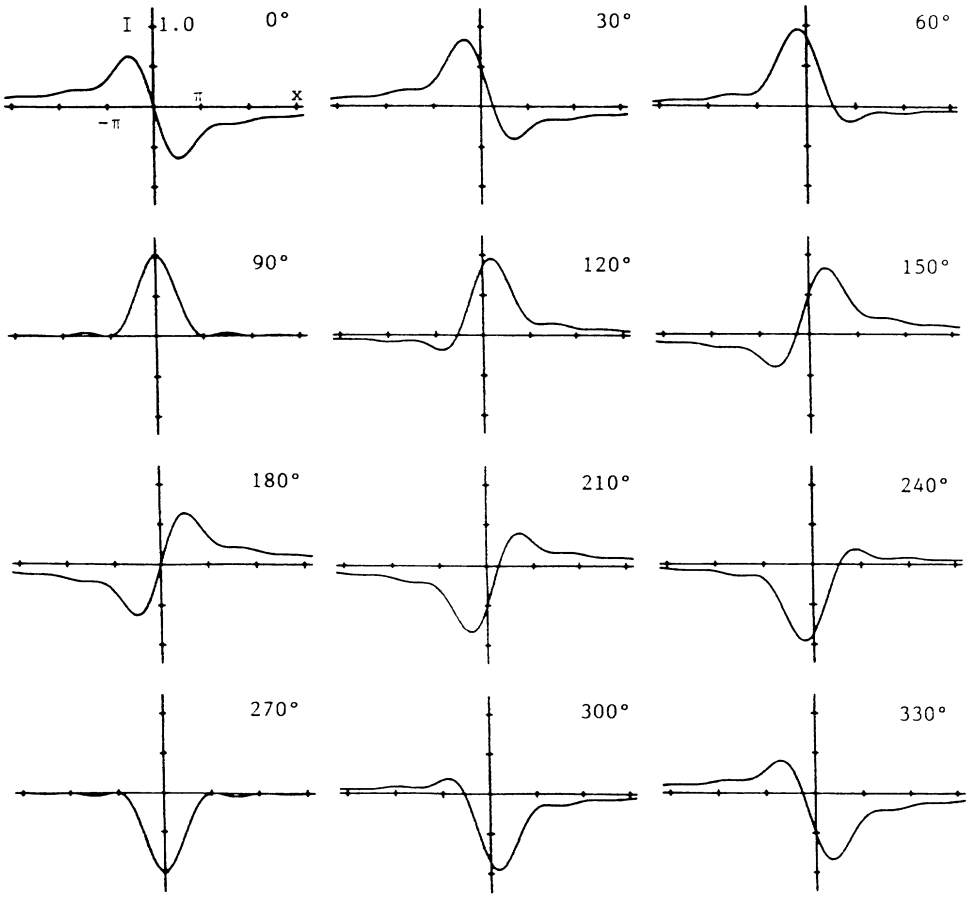


FIG. 3. Diffracted-line intensity anomalies about exact three-beam point ($x=0$) as a function of phase triplet θ. x positive goes into the Kikuchi band.

ing voltage of 250 kV. This high-index axis was chosen to provide a clear pattern with not too large a number of lines. The diffracted lines were indexed by matching to computer simulations of the pattern. A few examples of each of the possible reflection types $h+k+l=4n+m$, $m=0,1,2,3$, are labeled in the figure. The presence of $(4n+2)$-type reflections, which are systematically absent in the similar but centrosymmetric diamond structure, gives rise to phase triplets θ which are neither 0 nor π; it is these phases which were measured. In particular, we have concentrated on the triangle of vectors $(\bar{3}7\bar{5})$, $(\bar{1}7\bar{9})$, and $(\bar{2}04)$ [Fig. 1(b)] in which the Kikuchi band $\mathbf{g}-\mathbf{h}=(\bar{2}04)$ is of the $4n+2$ type, and $\mathbf{g}$ is either $(\bar{3}7\bar{5})$ or $(\bar{1}7\bar{9})$. With use of the atomic form factors given by Doyle and Turner,[13] with In at (0,0,0) and P at $(+\frac{1}{4},+\frac{1}{4},+\frac{1}{4})$, the phase triplets are predicted to be $\theta_{\bar{3}7\bar{5}}=(180+39.2)°$ and $\theta_{\bar{1}7\bar{9}}=(180-39.2)°$. These are centered about a value of 180° because the interaction between electrons and atoms is basically attractive. The crystal thickness has been estimated from subsidiary fringes on the $(\bar{3}15)$ diffracted line to be 1100 Å.[10] Reference 13 then gives values of $\beta_{\bar{3}7\bar{5}}=0.90$, $\beta_{\bar{1}7\bar{9}}=0.62$, and $\beta_{\bar{2}04}=1.36$. These do not include Debye-Waller factors, but are nevertheless a little larger than the optimum. They are not large enough to invalidate the method,[12] but will give rise to a greater uncertainty in the final results.

The positions of the intensity extrema along the diffracted lines were found by microdensitometer traces along the lines. The diffuse background, which includes the Kikuchi line profile, was determined by parallel scans away from the diffracted line and subtracted from the line intensity. The resulting elastic intensity has a profile similar to those of Fig. 3. The distance scale to be used in the analysis was obtained both from the maximum-minimum separation (7) and from the thickness measurement using (2). These agreed to within 20%. The prescription (7) also requires our knowing the exact position of the three-beam point. This was taken to be where the Kikuchi line profile has its maximum gradient. The related anomalies along the $(\bar{3}7\bar{5})$ and $(\bar{1}7\bar{9})$ lines were both analyzed, giving the phase triplets as $\theta_{\bar{3}7\bar{5}}=(180+36)°\pm15°$ and $\theta_{\bar{1}7\bar{9}}=(180-43)°\pm15°$. These agree well with the Doyle-Turner values and also establish the polarity to be as given above. The main sources of error are in the measurement of the positions of the intensity extrema and the exact three-beam point, and in the neglect of higher-order terms in the intensity expression. With a more elaborate analysis, it is expected that the errors quoted above can be reduced. Other factors, such as absorption could also affect the analysis—this will be addressed in future work.

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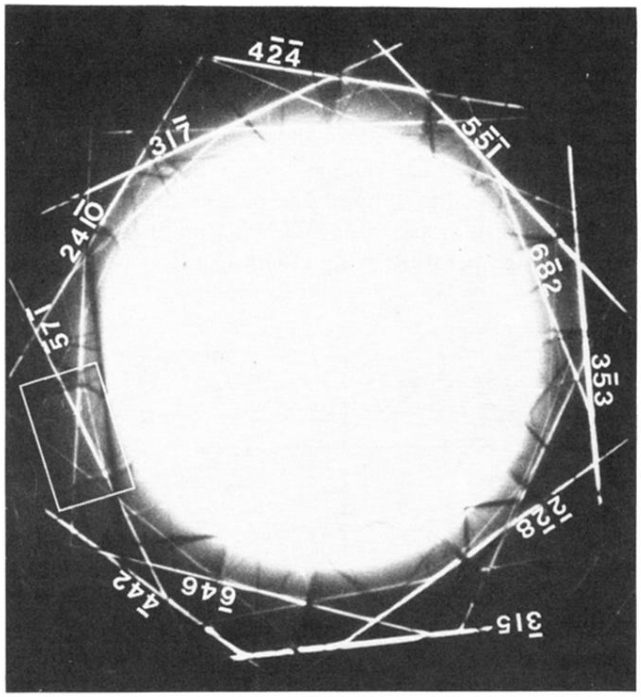
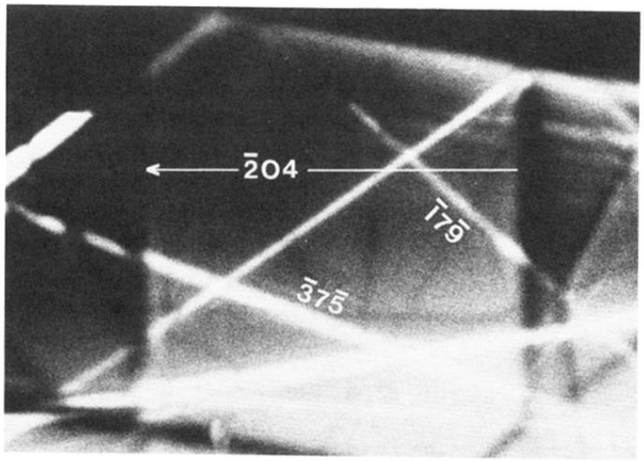
[1]W. N. Lipscomb, Acta Crystallogr. **2**, 193 (1949).
[2]K. Kambe, J. Phys. Soc. Jpn. **12**, 13 (1957).
[3]M. Hart and A. R. Lang, Phys. Rev. Lett. **7**, 120 (1961).
[4]B. Post and J. Ladell, Acta Crystallogr., Sect. A **43**, 173 (1987).
[5]K. Ishizuka and J. Tafto, Acta Crystallogr., Sect. B **40**, 332 (1984).
[6]H. J. Juretschke, Phys. Rev. Lett. **48**, 1487 (1982).
[7]Q. Shen, Acta Crystallogr., Sect. A **42**, 525 (1986).
[8]G. Thorkildsen, Acta Crystallogr., Sect. A **43**, 361 (1987).
[9]C. J. Humphreys, Rep. Prog. Phys. **42**, 1825 (1979).
[10]R. Vincent and D. M. Bird, Philos. Mag. A **53**, L35 (1986).
[11]A. Howie and M. J. Whelan, Proc. Roy. Soc. London, Ser. A **263**, 217 (1961).
[12]D. M. Bird and R. James, to be published.
[13]P. A. Doyle and P. S. Turner, Acta Crystallogr., Sect. A **24**, 390 (1968).



(a)



(b)

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