Accurate Structure-Factor Phase Determination by Electron Diffraction in Noncentrosymmetric Crystals

J. M. Zuo, J. C. H. Spence, and R. Hoier[(a)]

Department of Physics, Arizona State University, Tempe, Arizona 85287

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A solution to the phase problem is described which gives the phase invariant $\Psi = 2\phi_h - \phi_g$ for electron structure factors with phases ϕ_h and ϕ_g in noncentric crystals. The method exploits the high-voltage dependence of a minimum in convergent-beam transmission-electron-diffraction patterns in the systematics three-beam geometry. For CdS, with $h = (00\bar{2})$ and $g = (00\bar{4})$ we find $\Psi = 54.4° \pm 0.9°$. The error in the derived $(00\bar{2})$ x-ray structure-factor phase is 0.069°. The method is accurate enough to provide information on the bonding charge distribution in noncentric crystals.

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Despite considerable theoretical and experimental effort (see Ref. 1), the accurate measurement of the phases of structure factors in noncentric crystals remains an important unsolved problem in crystallography. Existing proposals[1,2] either lack accuracy, experimental verification, or are limited to centric materials of which large, perfect crystals can be grown. A solution to this problem, particularly for polycrystalline materials, would allow the ground-state crystal charge-density distribution to be synthesized for a wide range of real materials of known structure.[3] While "direct" statistical trial-structure methods have been successful in solving many crystal structures in x-ray crystallography, the problem of the direct measurement of the phases of low-order reflections remains. These phases are needed with high accuracy if the distribution of bonding electrons is to be determined in noncentric crystals.

In this paper we describe a sensitive method for measuring the phases of low-order electron structure factors U_g in noncentric crystals. These complex electron structure factors are related by the Mott formula[4,5] to the Fourier coefficients of electron charge density, the x-ray structure factors. For centric crystals of known structure only the amplitudes and signs of these need to be measured.[6,7] Our method gives a two-phase invariant from the systematics three-beam geometry by exploiting the accelerating voltage dependence of multiple electron scattering. The extended angular mapping of diffracted orders available in convergent-beam electron diffraction (CBED) has also allowed the development of a flexible method which does not require accurate selection of experimental parameters. By taking advantage of the submicron electron probe sizes available on modern electron microscopes, the method may be applied to polycrystalline materials, and is not restricted to the large single crystals needed for much x-ray and neutron-diffraction work. The sensitivity is, however, voltage dependent.

The theoretical work of Kambe[8] and of Gjonnes and Hoier[9] has shown that the diffracted intensity in the three-beam approximation depends on the sum of the phases of the three structure factors (the three-phase invariant Ψ), and that, for centric crystals, the elastic intensity is exactly zero at one of two readily identifiable points in a CBED pattern, depending on whether the phases sum to 180° or 0°. Recent work on nonsystematics three-beam theory[10-12] extended for noncentric crystals has shown that this zero then becomes a local intensity minimum, whose depth depends on the three-phase invariant. This work has suggested that a general method of accurate phase determination by electron diffraction may be possible,[2] based on measurements of these minima. Accuracy is limited, however, by the treatment of the inelastic background, which has a two-dimensional variation in the nonsystematics case, and which must be energy filtered for elastic Bragg scattering. The collection of one-dimensional elastic energy-filtered data in the systematics orientation proposed here are experimentally simple (and more accurate) since the CBED pattern may be scanned over the slit of an energy-loss spectrometer.[5]

The principle of our method is as follows. Consider a second-order reflection g at the Bragg angle in a noncentric crystal. The CBED experimental geometry[5] displays the entire rocking curve (over an angular range of less than twice the Bragg angle) in every diffracted order simultaneously as a disk. Choosing a point in the central disk defines the incident beam direction and conjugate points differing by reciprocal lattice vectors in all the other disks, and their excitation errors. For a certain range of accelerating voltage, the perturbation to the rocking curve for the second-order reflection g due to the unavoidable weak excitation of the first-order reflection h is shown below to be very sensitive to the sum of the phases of the two relevant structure factors. (Excitation of the third-order beam is much weaker.) By comparing the second-order beam's rocking curve with the results of many-beam calculations (including nonsystematic interactions for increased accuracy), the phase sum may be found. First, however, to aid understanding and to determine the region of the CBED pattern most sensitive to Ψ, we apply the "Bethe potential" correction[13] (for noncentric crystals) to two-beam theory. We define an electron wave vector $\mathbf{K}$ ($|K|=1/\lambda$) and electron structure factors $U_g=K/\xi_g=2\gamma m_0|e|V_g/h_p^2$, with V_g a Fourier coefficient of crystal potential. Consider the $(00\bar{2})=h$ and $(00\bar{4})=g$ systematics reflections shown in Fig. 1 in a noncentric structure. With structure-factor phases ϕ_g, the three-phase invariant is

$$\Psi=-\phi_g+\phi_h+\phi_{g-h}=-\phi(00\bar{4})+\phi(00\bar{2})+\phi(00\bar{2})$$
$$=2\phi(00\bar{2})-\phi(00\bar{4})\,. \tag{1}$$

For reciprocal lattice vectors forming a closed loop, Ψ is independent of choice of origin. Unlike the nonsystematics three-beam case, only two phases are involved. The rocking-curve intensity observed in a CBED disk is given in two-beam theory as a function of excitation error S_g by

$$I_g(S_g)=\frac{U_g^2\sin^2[(\pi t/K)(K^2S_g^2+U_g^2)^{1/2}]}{K^2S_g^2+U_g^2}\,, \tag{2}$$

where t is the thickness of the crystal. We note that Eq. (2) is independent of Ψ. The perturbation to the two-beam form due to the excitation of the weaker systematics beam h is expressed by Bethe's second approximation, applied to the noncentric case.[11] This requires that U_g in Eq. (2) be replaced by an effective structure factor

$$|U_g^{\rm eff}|^2=|U_g|^2\left\{1-\frac{|U_h||U_{g-h}|}{KS_h|U_g|}\cos\Psi+\left[\frac{|U_h||U_{g-h}|}{2KS_h|U_g|}\right]^2\right\}, \tag{3}$$

which now depends on Ψ. Figure 2 shows $|U_g^{\rm eff}/U_g|$ for various values of the phase Ψ with $|U_i|$ fixed. We restrict attention to the region near $S_g=0$, where the Bethe approximation is most accurate (i.e., for $|S_g|\ll|S_h|$ and $|S_h|\gg|U_{\max}|/2K$, with $U_{\max}$ the largest U). Figure 2 shows that $|U_g^{\rm eff}|$ is most sensitive to changes in Ψ near its minimum,

$$\left\{\frac{|U_g^{\rm eff}|}{|U_g|}\right\}_{\min}=|\sin\Psi|\ \text{ for }\ 2KS_h=\frac{|U_h||U_{g-h}|}{|U_g|\cos\Psi}\,. \tag{4}$$

Thus to obtain sensitivity to phase in disk g near S_g=0, we require S_h to satisfy the (material's dependent) constant of Eq. (4). Now if $S_g=0$ then the Ewald sphere geometry requires $2KS_h=h^2$ in Eq. (4). Using the definition of U_g to solve for γ, and the expression $V_A=m_0c^2(\gamma-1)/|e|$ for high voltage, we find

$$V_A=\frac{m_0c^2}{|e|}\left[\frac{h^2h_P^2|V_g|\cos\Psi}{|V_h||V_{g-h}|2m_0|e|}-1\right], \tag{5}$$

where h_P is Planck's constant and h is a reciprocal lattice vector. Equation (5) reduces to an approximate form of the critical-voltage formula for $\Psi=0$ or π (centric crystals). The critical voltage corresponds to a choice of V_A which makes $|U_g^{\rm eff}|=0$. Here we have extended the theory to noncentric crystals and found the voltage V_A at which, for a given phase, $U_g^{\rm eff}$ is a minimum near $S_g=0$, and therefore most sensitive to phase. Since, however, the excitation error S_h in Eq. (3) is used as a variable in CBED experiments, the choice of accelerating voltage is no longer critical (each CBED disk displays intensity over a range of S_g values). An error in choosing V_A (and thus K) may be compensated for by changing S_h (i.e., looking at a different part of the CBED disk). Unlike the critical-voltage method (which is restricted to centric crystals), our method also allows independent refinement of several reflections, rather than giving a relationship between structure-factor amplitudes.

These considerations can be illustrated with an example. For CdS, with $g=(00\bar{4})$ and $h=(00\bar{2})$, $|U_h|=0.0577$, $|U_g|=0.0142$, and $\Psi=55.332°$ for neutral

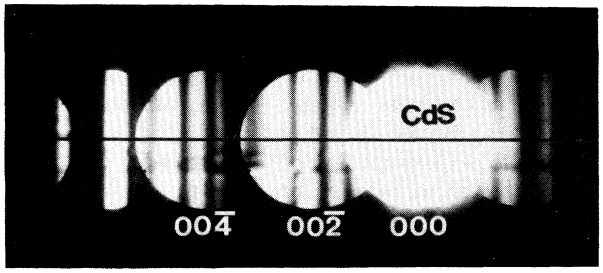

FIG. 1. Experimental $(00h)$ systematics CBED pattern recorded at 120 kV from CdS. The intensity scans in Fig. 3 were taken along the line shown.

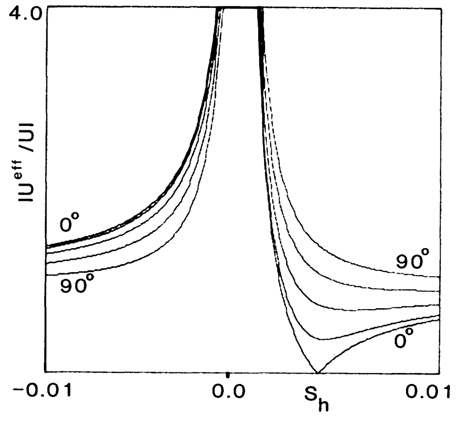

FIG. 2. Plots of $|U_g^{\rm eff}/U_g|$ against S_h (in Å^{-1}) for various values of the phase invariant Ψ, showing greatest sensitivity to Ψ at the minimum.

atoms (room temperature, $V_A = 120$ kV). We take $a_0 = 0.41348$ nm and $c_0 = 0.6756$ nm. Then at $S_g = 0$, $2KS_h = 0.088$, which is sufficiently close to the value $2KS_h = 0.363$ of Eq. (4) to allow accurate refinement (Fig. 2 shows that for $\Psi = 55°$ the curves change slowly, and hence the choice of S_g is not critical). Here $2KS_h$ varies from 0.2 to 0.022 across the disk, and a 1° change in Ψ leads to a 1% relative change in $U^{\text{eff}}(00\bar{4})$. This produces a readily detectable change in I_g, as shown below. Equation (3) also shows how insensitive the $(00\bar{4})$ intensity is to $|U(00\bar{4})|$, and how sensitive it is to $|U(00\bar{2})|$ (see below). For example, a 3% change in $|U(00\bar{4})|$ leads to only a 0.1% change in $|U^{\text{eff}}(004)|$. Thus (and in view of the relatively large size of g) the use of scattering factors for neutral atoms (rather than ions) is a good approximation for $|U(00\bar{4})|$.

Convergent beam patterns were recorded on film from crushed samples of single-crystal CdS at 300 K in a Philips model EM400 transmission electron microscope at 120 kV. Patterns such as that shown in Fig. 1 showing strong $(00h)$ systematics were read into a VAX750 computer using a flat-field, charge-coupled device camera and light table. The intensity around the outside of the CBED disks was used to estimate the inelastic background. This was assumed one-dimensional and subtracted. By comparing different scans taken parallel to the systematics line, we find the experimental accuracy in the intensity ratios to be 6%.

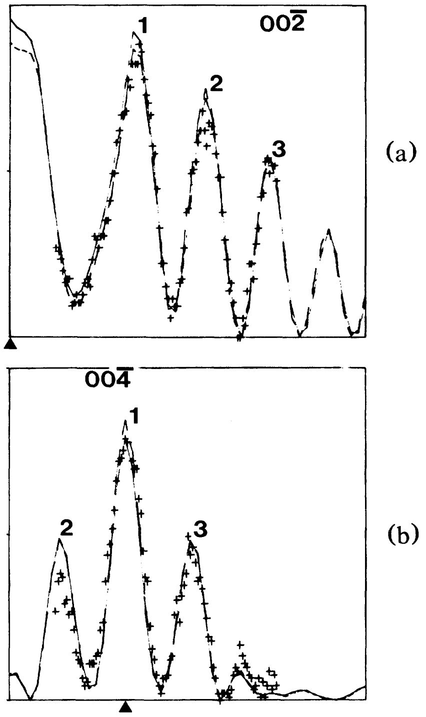

FIG. 3. (a) Comparison of experimental (crosses) and best-fit calculated (continuous line) results for the $(00\bar{2})$ CBED intensity in CdS. Maxima 1, 2, and 3 are most sensitive to $|U(00\bar{2})|$. The dashed curve is a calculation for a 1% increase in $|U(00\bar{2})|$ from best fit. (b) Similar to (a) for the $(00\bar{4})$ rocking curve. The marker indicates the Bragg condition in both figures. The dashed curve is a calculation for a 1° decrease in Ψ from best fit.

In view of the insensitivity of the $(00\bar{4})$ intensity to $|U(00\bar{4})|$, we do not include it in our refinement parameters. The Debye-Waller factors and the position parameter $u = 0.37717(8)$ were obtained from recent x-ray work.[14] The final refinement therefore included (1) phase invariant Ψ, (2) a starting value of $|U(00\bar{2})|$ obtained from tables,[15] (3) absorption coefficients, and (4) specimen thickness. The high voltage and incident beam direction (the center of the Laue circle in the nearest zero-order Laue zone) were found from the positions of higher-order Laue zone lines in the central disk.[5] Figures 3(a) and 3(b) show a comparison of experimental data with the results of 32 beam Bloch-wave dynamical calculations. All beams of appreciable intensity are included, including nonsystematics. The algorithm treats noncentric crystals in the form of a parallel-sided plate, which may be inclined to the beam, with absorption. Higher-order Laue zone effects are included, using the renormalized eigenvector method.[5,16] A listing of the program has appeared.[17] The refinement parameters were adjusted for best fit, with use of a method described earlier.[5] As shown by two-beam theory, the outer fringes of the $(00\bar{4})$ were found to be most sensitive to thickness, and gave a value of $t = 86.50$ nm. Absorption coefficients $U'(g)$ were obtained by matching the asymmetry in the central disk, with each of the reflections satisfied in turn. For noncentric structures the $U'(g)$ and $U(g)$ are each the complex Fourier coefficients of real potentials. Our use of a real constant for the ratio of these complex coefficients assumes that the phase of the absorption potential is equal to that of the elastic-scattering potential; however, our results are very insensitive to changes in $U'(g)$. The results obtained were $U'(00\bar{2})/U(00\bar{2}) = 0.08$ and $U'(00\bar{6})/U(00\bar{6}) = 0.13$, with $U'(00\bar{4})$ negligible. The refinement of the remaining parameters Ψ and $|U(00\bar{2})|$ was based on the sensitivity of the $(00\bar{2})$ rocking curve (near its center) to $|U(00\bar{2})|$ and that of the $(00\bar{4})$ curve to Ψ. In Fig. 3(a), maxima 1 was found to be most sensitive to $|U(00\bar{2})|$, with the other maxima less sensitive. A 1% change in $|U(00\bar{2})|$ causes a 6.8% change in the ratio R' of maxima 1-3. None are very sensitive to Ψ. The best fit shown gives the value $|U(00\bar{2})| = 0.0565 \pm 0.0006$. The error was estimated from the following expression:

$$\left(\frac{\Delta U_g}{U_g}\right)^2 = C_1\left(\frac{\Delta I_g}{I_g}\right)^2 + \left(\frac{\Delta t}{t}\right)^2 + 0.25\left(\frac{\Delta E}{E}\right)^2 + C_2\left(\frac{\Delta U'_g}{U'_g}\right)^2 . \quad (6)$$

The 6% error in the experimental data gives $C_1 = 0.02$. Errors in thickness and E are both 0.5%. A 10% error in $U'(00\bar{2})$ causes a 3.3% change in R' giving $C_2 = 0.002$. Errors in other parameters are negligible. Thus the error in $|U(00\bar{2})|$ is found to be about 1%. The refinement of Ψ is completed last, using the $(00\bar{4})$ rocking curve shown in Fig. 3(b). For the ratio R of the heights of maxima 1-3, many-beam calculations show that a 1% change in $|U(00\bar{2})|$ leads to a 2.3% change in R, while a 1° change in Ψ causes a 7.6% change, revealing the high sensitivity of our method. For the best fit shown, we find

$$\Psi = 54.4^\circ \pm 0.9^\circ .$$

The error is obtained from a quadrature sum of the phase changes due to errors in intensity measurement, the measured $|U_g|$, absorption factors, and thickness. These were 0.8°, 0.3°, 0.3°, and 0.2°, respectively. If we assume $\phi(00\bar{4}) = 2.94^\circ$ (known), the Mott-Bethe formula[4,5] gives the corresponding error in the deduced x-ray structure-factor phase $\phi_{\text{xr}}(00\bar{2})$ as $\pm 0.069^\circ$. By comparison, recent x-ray work on acentric crystals[1] gives errors of 20°.

In conclusion, we have discovered a method for accurately measuring a sum of phases of two structure factors in noncentric crystals by transmission electron diffraction, and applied it to the case of CdS. The method uses one-dimensional data sets from the systematics orientation and is most sensitive for a certain range of high voltage. The resulting phase measurements are sufficiently accurate for the study of bonding in known structures, and may also be used to assist in solving few-parameter unknown crystal structures by x-ray diffraction.

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[a] Permanent address: Department of Physics, University of Trondheim-NTH, 7034 Trondheim, Norway.

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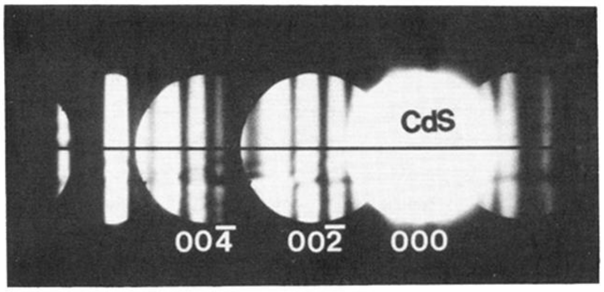

FIG. 1. Experimental (00*h*) systematics CBED pattern recorded at 120 kV from CdS. The intensity scans in Fig. 3 were taken along the line shown.