Structure-Factor Phase Information from Two-Beam Electron Diffraction

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The electron-induced characteristic x-ray emission from a noncentrosymmetric crystal shows a pronounced intensity difference when the Bragg condition is fulfilled for the G and $-G$ reflections, respectively, along a polar direction. This two-beam effect is demonstrated for GaAs and InP, and is a direct method of obtaining information about the phase of a structure factor and determining the sense of a polar direction.

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The absolute phase of a structure factor cannot be determined directly from a conventional diffraction experiment, whereas phase relationships can be determined when two or more Bragg beams are excited simultaneously, as has been demonstrated in electron diffraction[1] and x-ray diffraction.[2] Recent discussions of three-beam x-ray diffraction (incident beam and two Bragg beams) used to obtain phase information appear in Chang[3] and Juretschke,[4] and of the application of many-beam electron diffraction in Taftø and Spence.[5]

The phase of a structure factor depends on the choice of origin in the crystal unit cell. Localized excitations and inelastic scattering processes may act as a reference origin in the unit cell, and it is such localized processes that make it possible to obtain phase information and determine the sense of a polar direction of a noncentrosymmetric crystal, even in a two-beam case, by utilizing the anomalous dispersion where the energy of the incident x ray is close to the absorption edge of one of the elements present in the crystal.[6] Another class of experiments that relies on localized inelastic scattering processes comprises particle channeling,[7] and x ray[8] and electron diffraction[9,10] under standing-wave conditions. These are direct- rather than reciprocal-space techniques, and thus contain information about the phase with which the different elements contribute to a structure factor when localized element-specific signals are monitored. When one is dealing with crystal planes with inversion symmetry this phase information, although very powerful for locating small concentrations of atoms, may be considered rather trivial. In this paper we show that by detection of the variation of the electron-induced characteristic x-ray emission with the direction of an incident electron beam relative to a crystal plane without inversion symmetry, information about the phase of a structure factor may be obtained and the sense of a polar direction may be determined.

Ion-thinned crystals about 500 Å thick were studied with a 100-keV electron microscope equipped with a solid-state x-ray detector. Figures 1(a) and 1(b) show the normalized ratio between the $K\alpha$ counts of As and Ga for the (111) and (311) planar case of GaAs, and Fig. 1(c) shows the ratio between the $L\alpha$ counts of In and the $K\alpha$ counts of P for the (311) planar case of InP. A strong asymmetry is seen around parallel incidence. This is in contrast to the two-beam diffraction intensities which are symmetrical around parallel incidence according to Friedel's rule.[11]

For localized processes such as the ejection of

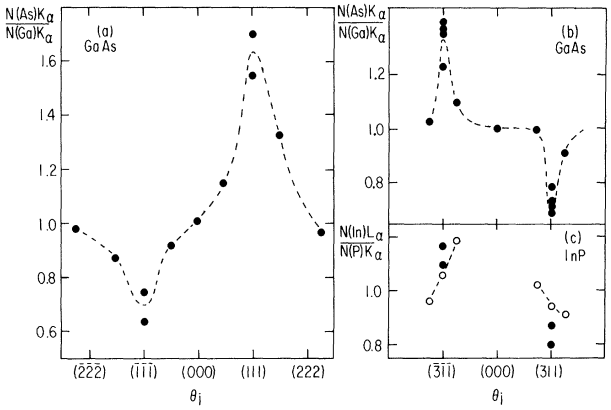

FIG. 1. Observed ratio between the x-ray counts from the two elements in (a), (b) GaAs and (c) InP for different angles between the incident electron beam and the Bragg reflecting planes (θ_i). (111), (222), etc., are the directions for which the Bragg condition is fulfilled for these reflections. The estimated crystal thickness was 500 Å (filled circles) and 700 Å (open circles). The angular spread of the incident beam was one quarter of the Bragg angle for the 311 reflection. The inaccuracies due to counting statistics are negligible. The spread in the experimental data for nominally the same experimental conditions is attributed to small variations in incident beam direction and crystal thickness.

inner-shell electrons from medium- and high-Z atoms, the corresponding x-ray yield is close to proportional to the intensity, at the atomic core, of the modulated wave field of the incident electrons.[12] Thus, in order to interpret the experimental results of Fig. 1, the important thing is to discuss the intensity distribution of the fast electrons in the crystal, i.e., the standing-wave pattern. For that purpose we will use the Bloch-wave approach.[13] The discussion will be restricted to qualitative two-beam considerations. In a two-beam situation, where only one Bragg beam is excited, there is generally one origin in the repeat unit which gives a real and positive structure factor. This origin, which coincides with the atomic planes in the simplest situation with inversion symmetry, will be referred to hereafter as the reference plane. Relative to the reference plane there is no basic difference between a situation with and without inversion symmetry as far as the standing-wave pattern is concerned. Thus previous discussions of two-beam situations[14] apply also when inversion symmetry is absent. In a two-beam situation two Bloch waves are excited. The total intensity of the wave field has often been expressed as a sum of the intensity contributions from the individual Bloch waves, resulting in a thickness-independent intensity modulation. In the upper part of Fig. 2 this intensity modulation is shown for three directions of incidence close to the Bragg reflecting position for the reflection G, viz., the direction that gives maximal intensity at the reference plane, the exact Bragg position, and the direction that gives minimal intensity at the reference plane. For 100-keV electrons the angle between these directions is typically 0.1° to 0.3° for a strong reflection, i.e., a considerable fraction of the Bragg angle, which is typically only 0.5°. The situation is identical near the Bragg position for the reflection $-G$. Thus the asymmetry around parallel incidence cannot be explained by treating the Bloch waves independently. However, if the coherence or interference term between the Bloch waves,[14] that gives rise to the well-known thickness oscillations of the Bragg diffraction intensities, is taken into account, an asymmetry around the reference planes results, and the standing-wave pattern changes with thickness. In particular, instead of a uniform intensity over the unit cell exactly at the Bragg position, we now have

$$I(x,z) = 1 - \sin(2\pi Gx)\sin(2\pi\Delta kz),$$

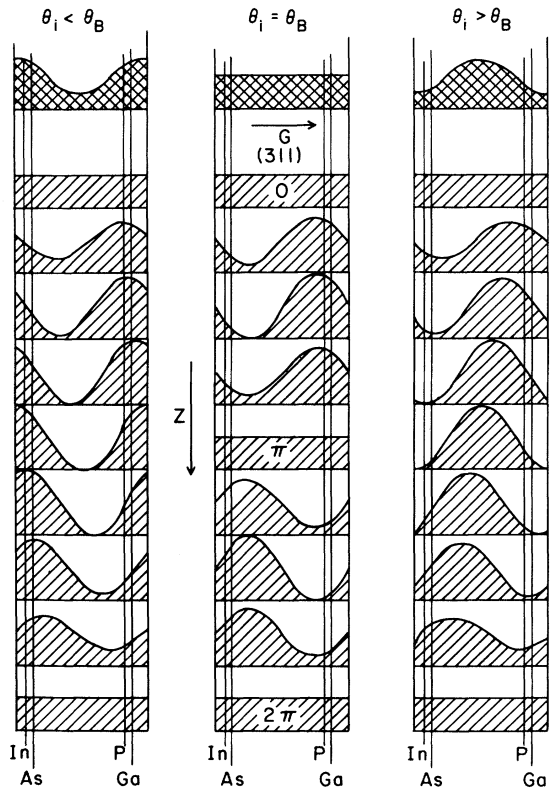

FIG. 2. Two-beam calculations of the electron wave field within the repeat unit for three directions of incidence close to the Bragg position for reflection G. The upper row (crosshatched) is the thickness-averaged wave field. The other rows show the wave field at increasing depth from the entrance surface. Zero is the entrance surface and 2π is one thickness period, which, for 100-keV electrons, corresponds to thicknesses of 750 and 820 Å for the (311) reflections of GaAs and InP, respectively. Also indicated are the positions of Ga and As in GaAs and In and P in InP along the 311 planes.

where x is the distance from the reference plane. For convenience, the reference planes, which are parallel to the Bragg reflecting planes, are assumed to be normal to the entrance surface of the crystal. z is the distance from the entrance surface, and Δk, which is proportional to the structure factor, is the difference between the wave vectors for the two Bloch waves (see Ref. 13 for details). Figure 2 shows also the intensity modulation for different thicknesses when the interference term is included. In addition, the positions of the two different types of atoms in GaAs and InP relative to the reference planes along the (311) direction are shown. Note that for a thin crystal the wave field is enhanced at the Ga planes and reduced at the As planes, in agreement with the observed decrease in the ratio between the

$K\alpha$ intensity of As and that of Ga close to the Bragg reflecting position for the 311 reflection [Fig. 1(b)]. The increased ratio near the $\bar{3}\bar{1}\bar{1}$ Bragg position is explained similarly. Here we obtain the standing-wave pattern by a mirror operation around the reference plane in Fig. 2. For InP we observe an additional asymmetry around the Bragg position, with enhanced x-ray emission from In when the angle between the incident beam and the Bragg reflecting planes is smaller than the Bragg angle [Fig. 1(c)]. This asymmetry can be explained qualitatively by considering the thickness-averaged modulated wave field in the upper part of Fig. 2, and it is a consequence of the large difference in scattering amplitude between In and P resulting in the reference planes being much closer to the In atoms than to the P atoms. For GaAs such an asymmetry is, as expected, not observed, since Ga and As have very similar scattering amplitudes so that their distances from the reference plane are almost the same. For the (111) planar case of GaAs the asymmetry around parallel incidence can be explained similarly.

For the dense (111) reciprocal lattice row, quantitative comparison requires the inclusion of more beams, whereas close to the Bragg reflecting position for the (311) reflection the two-beam approximation is good. More important here is the diffuse scattering out of the direct and Bragg reflected beam. Figure 3 shows the normalized thickness-integrated wave field for different crystal thicknesses at the Ga and As atoms when the (311) reflection is at the Bragg position obtained by introducing an exponential attenuation of the direct and Bragg beams (absorption) and assuming the electrons being scattered out of these beams to produce x rays like a plane wave (see Ref. 14). Note that the asymmetry attenuates rapidly with thickness, and thin crystals, generally thinner than 1000 Å, are needed. This is no severe restriction of the technique when one uses a modern electron microscope capable of forming an intense electron probe with a diameter as small as 100 Å, in that thin areas of this size can be obtained by a variety of crystal thinning techniques. The main limitations are, rather, the experimental problems in detecting the x rays from light elements ($Z < 10$), and electron-induced radiation damage, which, at the present status of instrumentation, makes it difficult to apply the technique to a large number of interesting problems in organic crystallography.

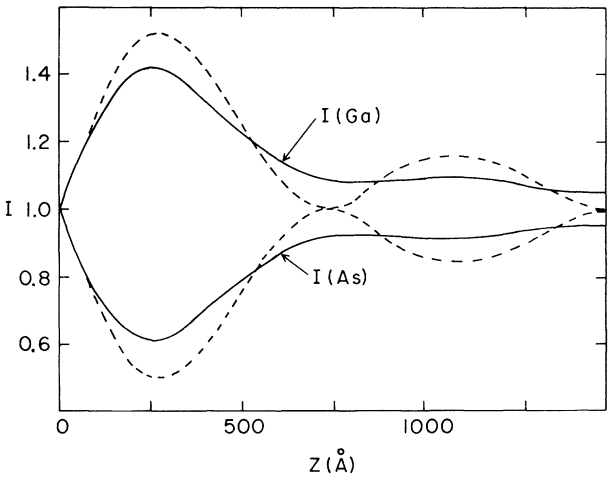

FIG. 3. The thickness-integrated wave-field intensity at the two planes of atoms in GaAs when the (311) reflection is at the Bragg position. The full and dotted lines are with and without diffuse scattering included, respectively.

In conclusion, we have shown that, by detection of electron-induced localized secondary emission, a two-beam diffraction experiment contains structure-factor phase information, and such information is obtainable from crystal grains smaller than 1000 Å. This provides a new technique for testing centrosymmetry of a crystal. In particular, the sense of a polar direction and thus the absolute orientation of a noncentrosymmetric crystal can be determined from simple two-beam arguments.

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