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Solving the phase problem in surface crystallography: Indirect excitation via a bulk reflection

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We show that the phases of surface reflections can be determined by simultaneously exciting a surface and a bulk reflection at grazing incidence. The interference between the surface reflections excited by the incident and the bulk-diffracted waves has been observed for the Ge(113)-(3×1) reconstructed surface.

The phase problem is the fundamental problem of x-ray crystallography: a diffraction experiment commonly provides the amplitudes $|F_{\mathbf{h}}|$ of the structure factors $F_{\mathbf{h}} = |F_{\mathbf{h}}|\exp(i\alpha_{\mathbf{h}})$ while the phases $\alpha_{\mathbf{h}}$ remain unknown. Surface crystallography encounters the same problem. The vast majority of surface structures are solved by the classical methods of crystallography, involving the construction of structure models on the basis of Patterson maps and subsequent refinement using structure factor amplitudes.[1] Modern developments apply ''direct methods'' which derive phases from amplitudes using plausible assumptions (see Refs. 2,3 and references therein). Knowing the phases of some strong reflections enhances the applicability of direct methods.

The direct determination of the structure factor phases in a diffraction experiment can be achieved through the interference between different beams. An advantage of surface diffraction is the presence of the bulk crystal underneath which can be used to produce the reference beam. The method which we propose here involves the excitation of a strong bulk reflection while measuring a surface reflection far from it, which avoids the direct contribution of an incomparably large bulk diffraction signal. We choose diffraction conditions simultaneously exciting a surface reflection $\mathbf{h}$ and a bulk reflection $\mathbf{G}$. The bulk-diffracted wave, whose amplitude is compatible with the one of the incident wave, excites another surface reflection $\mathbf{h}' = \mathbf{h} - \mathbf{G}$, see Fig. 1. The diffraction signal is due to the interference between the incident wave scattered on $\mathbf{h}$ and the bulk-diffracted wave scattered on $\mathbf{h}'$. The conditions for the interference are varied by the angular deviation of the incident wave from the Bragg position for the reflection $\mathbf{G}$.

Before proceeding to further details of the suggested method, we discuss related experimental methods in both bulk and surface structure studies. In bulk diffraction, interference between different beams is achieved when two reciprocal lattice vectors, $\mathbf{H}$ and $\mathbf{G}$, simultaneously participate in the diffraction. Then, the measured intensity depends on the product of the three structure factors $F_{\mathbf{H}}F_{\mathbf{G}}F_{-(\mathbf{H}+\mathbf{G})}$ and is sensitive to the combination of phases $\alpha_{\mathbf{H}} + \alpha_{\mathbf{G}} + \alpha_{-(\mathbf{G}+\mathbf{H})}$ invariant with respect to the choice of origin.[4] Determination of these phase invariants by means of multibeam x-ray diffraction is a vigorously developing method of bulk crystallography.[5]

If the reciprocal-lattice vectors $\mathbf{G}$ and $\mathbf{H}$ are non-coplanar, the multibeam Bragg condition $|\mathbf{k}| = |\mathbf{k}+\mathbf{H}| = |\mathbf{k}+\mathbf{G}|$ can be satisfied with an arbitrary wavelength λ, because the Ewald sphere of any radius $k = 2\pi/\lambda$ can touch three points (0, $\mathbf{G}$, and $\mathbf{H}$) in reciprocal space. If the reflections $\mathbf{G}$ and $\mathbf{H}$ are coplanar, the wavelength is fixed, since three points in a plane uniquely define the radius of the sphere. Now, the deviation from the Bragg position can be varied by changing the wavelength of the incident beam. Coplanar three-beam bulk diffraction has recently been realized in the grazing incidence geometry by scanning the energy of synchrotron radiation.[6]

Interference between the incident beam and the beam diffracted from the bulk crystal is widely used in standing wave techniques to study positions of impurity atoms in surface layers. These techniques were applied under grazing incidence diffraction conditions.[7] However, they are not suited to study reconstructed surfaces, since the surface consists of the same chemical elements as the bulk crystal and hence the secondary radiation (fluorescence or photoelectron) intensities cannot be distinguished.

Several interference methods were proposed to study the

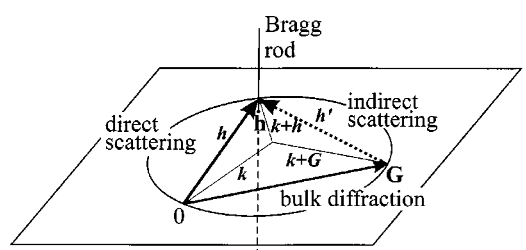

FIG. 1. Three-beam Bragg diffraction involving bulk and surface reflections. The Ewald sphere of radius $k = 2\pi/\lambda$ passes through the origin and the point $\mathbf{G}$ of reciprocal space and crosses the Bragg rod of the surface reflection $\mathbf{h}$. The diffracted wave at $\mathbf{h}$ is produced by direct scattering of the incident wave and, in addition, by scattering of the bulk-diffracted wave on the surface reflection $\mathbf{h}' = \mathbf{h} - \mathbf{G}$.

depth distribution of layers near the surface.[8,9] One possibility[8] is to use three-beam bulk diffraction with sufficiently large angular deviation of one of the beams. The weak beam serves as a phase-sensitive probe of the interference produced by the incident and strongly diffracted beams. Another approach[9] is to produce the second strong beam by reflection from a specially deposited gold film.

Our method has similarities with the techniques mentioned above in producing the second strong beam by diffraction from bulk crystal at grazing incidence[7,8] and detecting intensity of a weak beam diffracting from the surface structure.[8,9] In contrast to these methods, we use the interference illumination to study both in-plane and out-of-plane structure of the reconstructed surface. The bulk diffraction problem is treated in the standard two-beam approximation, using the well known solution of the dynamical diffraction problem under grazing incidence.[10]

The reciprocal space of the reconstructed surface consists of Bragg rods normal to the surface. The multibeam-diffraction requirement that all relevant reciprocal lattice points lie on the Ewald sphere is relaxed: the Ewald sphere should contain the points 0 and **G** and intersect the Bragg rod of the reflection **h**, Fig. 1. Therefore, a precise adjustment of the wavelength is not needed and there is no need to scan over the Bragg angle by tuning the wavelength. The Ewald sphere always intersects the superstructure rods and the crystal truncation rods, so that a large number of three-beam interferences can be measured for the full three-dimensional surface structure determination.

When the ideal crystal is illuminated by a plane wave $E_0\exp[i(\mathbf{k}_\parallel\cdot\mathbf{r}+k_z z)]$ at grazing incidence and the Bragg condition for the (bulk) reciprocal lattice vector **G** is met, the wave field at the crystal surface consists of three components: the incident wave, the specular wave $E_s\exp[i(\mathbf{k}_\parallel\cdot\mathbf{r}-k_z z)]$, and the diffracted wave $E_\mathbf{G}\exp[i(\mathbf{k}_\parallel\cdot\mathbf{r}-k_z' z+\mathbf{G}\cdot\mathbf{r})]$. The coherent superposition of these three waves illuminates the reconstructed surface of the crystal. If, additionally, the Bragg condition for the surface (fractional order) reflection **h** is met, the incident and the specular waves excite it. The bulk-diffracted wave $E_\mathbf{G}$ gives rise to an additional diffraction on the surface structure: the surface reflection $\mathbf{h}'=\mathbf{h}-\mathbf{G}$ diffracts simultaneously with the vector **h** and gives rise to a second diffracted wave coherent with the first one. The intensity measured at the position **h** is proportional to

$$I_\mathbf{h}=|F_\mathbf{h}(E_0+E_s)+F_{\mathbf{h}-\mathbf{G}}E_\mathbf{G}|^2. \tag{1}$$

It is worthwhile to note that the amplitude $E_\mathbf{G}$ is that at the crystal surface, which is different from the far field measured in a diffraction experiment.

The amplitude $E_\mathbf{G}$ is proportional to the bulk structure factor $F_\mathbf{G}$ and hence the intensity $I_\mathbf{h}$ depends on the phases of the structure factors in the combination $\alpha_\mathbf{G}+\alpha_{\mathbf{h}-\mathbf{G}}-\alpha_\mathbf{h}$, as is required by the invariance with respect to the choice of origin. The bulk structure is usually known. Once the origin is chosen, the phases of all bulk reflections are fixed and $I_\mathbf{h}$ depends on the phase difference of two surface reflections, $\alpha_{\mathbf{h}-\mathbf{G}}-\alpha_\mathbf{h}$. The intensity $I_\mathbf{h}$ can be varied by changing the angular deviation of the incident beam from the Bragg condition for the bulk reflection and thus varying the relative amplitude and phase of the waves E_0+E_s and $E_\mathbf{G}$.

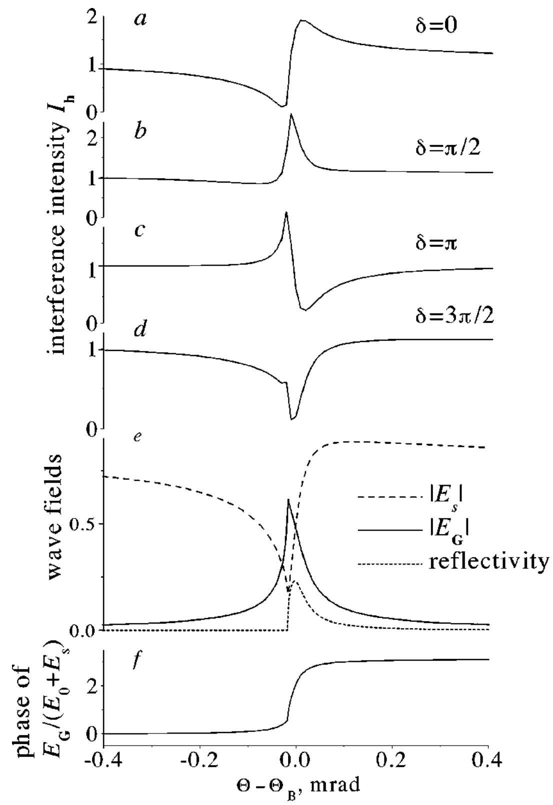

FIG. 2. (a)–(d) Calculated intensity $I_\mathbf{h}$ as a function of the angular deviation of the bulk-diffracted wave from the Bragg angle $\Theta-\Theta_B$ for a Ge crystal. The reciprocal lattice vector $\mathbf{G}=[220]$ is parallel to the surface, $\lambda=1.35$ Å, the incidence angle is equal to the critical angle. The ratio of the amplitudes of the surface reflections is $|F_\mathbf{h}|/|F_{\mathbf{h}-\mathbf{G}}|=1/3$, the values of the phase difference $\delta=\alpha_{\mathbf{h}-\mathbf{G}}-\alpha_\mathbf{h}$ are indicated. (e) Amplitudes of the specular $|E_s|$ and the bulk-diffracted $|E_\mathbf{G}|$ waves at the crystal surface and the reflectivity $R=|E_\mathbf{G}|^2\Phi_\mathbf{G}/\Phi_0$ (here Φ_0 and $\Phi_\mathbf{G}$ are angles between crystal surface and the incident and the diffracted waves, respectively). Note that the reflectivity is equal to zero for $\Theta<\Theta_B$ because of the trapping of the diffracted wave at the surface. (f) The phase difference between the waves $E_\mathbf{G}$ and E_0+E_s.

A demonstration of the magnitude and the angular scale of the interference is given in Fig. 2, where the intensity given by Eq. (1) is calculated for the Ge(220) bulk reflection and a hypothetical pair of surface reflections with amplitude ratio $|F_\mathbf{h}|/|F_{\mathbf{h}-\mathbf{G}}|=1/3$ and various values of the phase difference $\delta=\alpha_{\mathbf{h}-\mathbf{G}}-\alpha_\mathbf{h}$. The width of the peaks is given by the Darwin width of the bulk reflection. The width of the surface reflections is determined by the size of the coherently scattered domains of the reconstructed surface. It is usually large compared to the Darwin width and taken infinite in these model calculations. The calculations in Fig. 2 assume ideal collimation of the incident wave. Its divergence in the experiment will broaden the peaks. However, the decay of $I_\mathbf{h}$ for large angular deviations from the Bragg angle $\Theta-\Theta_B$ is proportional to $|\Theta-\Theta_B|^{-1}$, representing the kinematical limit of an interference phenomenon of dynamical diffraction, and still can be seen even with significant instrumental broadening.

The measurements were performed at the W1 wiggler

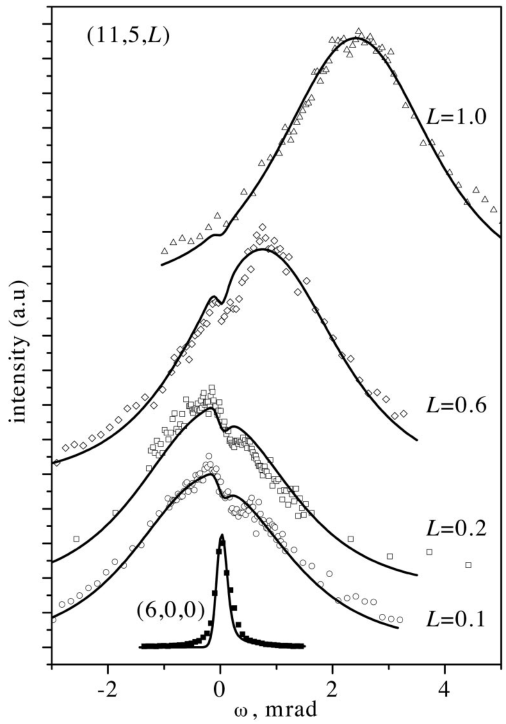

FIG. 3. Intensities of the $\mathbf{G}=[6,0,0]_{\mathrm{surf}}=[2\bar{2}\bar{0}]_{\mathrm{bulk}}$ bulk reflection and $[11,5,L]$ surface reflections of the Ge(113)-(3×1) reconstructed surface measured at the interference conditions with $\lambda=1.353$ Å as a function of the deviation $\omega=\Theta-\Theta_B$ from the Bragg angle of the bulk reflection Θ_B.

beamline of HASYLAB (DESY, Hamburg), on a Ge(113)-(3×1) reconstructed surface, the structure of which has been solved recently.[11] The deviation of the surface normal from the [113] direction was less than 0.1°. The crystal surface was cleaned under ultrahigh-vacuum (UHV) conditions by Ar^+ sputtering at 600 eV and annealing at 1050 K, followed by a slow cooling to room temperature. At room temperature, the LEED pattern exhibited sharp (3×1) spots. The measurements were carried out in UHV with a six-circle diffractometer (in the z-axis mode) using an in-vacuum x-ray detector.[12]

The measurements were performed as follows. The incidence angle was fixed to be less than the critical angle, to obtain a reasonable signal-to-noise ratio. The sample was rotated about its normal to find the bulk reflection. The intensity of the bulk reflection was measured as a function of the sample rotation angle ω. After the bulk reflection was measured, the detector was moved to the position corresponding the surface reflection and the intensity was measured in the same interval of ω.

We index the reflections with respect to the rectangular setting of the unit cell of the reconstructed Ge(113) surface of dimensions $12.0\times13.27\times18.76$ Å^3. The unit vectors of the surface reciprocal lattice are related to the standard notation for the cubic bulk unit cell by $[1,0,0]_{\mathrm{surf}}=\frac{1}{3}[1\bar{1}0]_{\mathrm{bulk}}$, $[0,1,0]_{\mathrm{surf}}=\frac{1}{11}[33\bar{2}]_{\mathrm{bulk}}$, and $[0,0,1]_{\mathrm{surf}}=\frac{1}{11}[113]_{\mathrm{bulk}}$.

Measurements with the bulk reciprocal lattice vector $\mathbf{G}=[6,0,0]_{\mathrm{surf}}=[2\bar{2}\bar{0}]_{\mathrm{bulk}}$, Fig. 3, were performed using the directly excited surface reflection $\mathbf{h}=[11,5,L]$. Hence, the reflection $\mathbf{h}'=[5,5,L]$ is excited indirectly. The wavelength $\lambda=1.353$ Å was chosen to provide nearly coplanar three-beam diffraction. The incidence angle was fixed at 3.8 mrad (0.8 of the critical angle) and the sample was rotated about its normal to find the bulk reflection $\mathbf{G}=[6,0,0]$. The intensity of the bulk and the superstructure reflections were measured as a function of the sample rotation angle ω, Fig. 3. The FWHM of the Bragg reflection (0.2 mrad) is large compared to the dynamical width and is given by the divergence of the incident beam. After the bulk reflection was measured, the detector was moved to the position corresponding the surface reflection $\mathbf{h}=[11,5,L]$ and the intensity was measured in the same ω interval for several values of L, see Fig. 3. The peaks of the surface reflections have a Lorentzian shape with the FWHM of 2.6 mrad given by the size of the coherently scattering domains of the reconstructed surface.

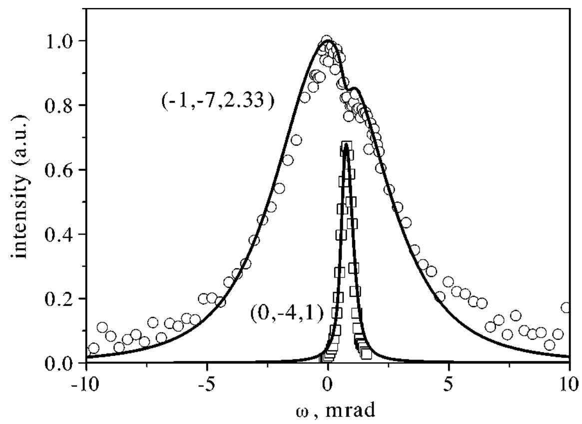

FIG. 4. Intensities of the $\mathbf{G}=[0,\bar{4},1]_{\mathrm{surf}}=[\bar{1}\bar{1}1]_{\mathrm{bulk}}$ bulk reflection and $[\bar{1},\bar{7},2.33]$ surface reflection of the Ge(113)-(3×1) reconstructed surface at three-beam interference with $\lambda=1.2$ Å.

The peaks clearly reveal, for $L=0.1$, 0.2, and 0.6, the dips whose position and width do not depend on L. When the value of L is increased to $L=1.0$, the surface diffraction peak is shifted to larger angles ω, the three-beam interference condition is destroyed and the dip vanishes. The curves in Fig. 3 are calculated by Eq. (1) with the structure factors determined from the known surface structure.[11] The phase difference between $[11,5,L]$ and $[5,5,L]$ reflections are $-63°$, $-56°$, and $-22°$ for $L=0.1$, 0.2, and 0.7, respectively. The calculated curves reveal dips (see Fig. 3) which agree well with the measured reflection profile. In the calculated reflection profile, the divergence of the incident beam parallel (0.2 mrad) and normal to the surface (1 mrad) has been taken into account. A small (0.1 mrad) systematic shift in the positions of the measured dips with respect to the calculated ones can be noticed in Fig. 3. We do not presently have an explanation for this shift.

Measurements with the out-of-plane bulk reciprocal lattice vector $\mathbf{G}=[0,\bar{4},1]_{\mathrm{surf}}=[\bar{1}\bar{1}1]_{\mathrm{bulk}}$, Fig. 4, were made at the wavelength $\lambda=1.2$ Å, to provide a maximum intensity of the incident beam. The directly excited surface reflection is $\mathbf{h}=[\bar{1},\bar{7},2.33]$, where the value of L is defined by the three-beam interference condition. As expected, the surface reflection shows a dip when the bulk diffraction takes place and provides the indirect excitation of the surface reflection $\mathbf{h}'=[\bar{1},\bar{3},1.33]$. The structure factors entering Eq. (1) in the case of the non-coplanar diffraction depend on the atom positions normal to the surface and can be used to solve the three-dimensional structure of the surface.

In conclusion, we propose to measure the phases of surface reflections by simultaneously exciting a bulk and a surface reflection. The proposed method differs from a usual three-beam diffraction experiment in several essential points. We excite a strong bulk reflection but measure an interference signal far from it. The bulk-diffracted wave is used to excite a second surface reflection. We do not need to solve the multibeam diffraction problem. We determine the amplitude of the bulk diffracted wave in the two-wave approximation and consider the surface scattering as a perturbation. A fine adjustment of the multibeam diffraction conditions is not necessary. The only requirement is that the Ewald sphere crosses the Bragg rod, which can always be achieved for a large number of surface reflections and crystal truncation rods far from the Bragg points. In the crystal truncation rods the bulk and surface contributions are coherently superimposed. While the bulk contribution is known, the amplitude and phase of the surface contribution is not known. The experimental determination of the phase therefore allows us to unambiguously determine the amplitude as well.

We performed first measurements on the Ge(113)-(3 $\times 1$) reconstructed surface, the structure of which has been recently determined. We measured the bulk and surface reflections and observed the expected interference modulations of the surface reflection when the bulk diffraction provides the indirect excitation of a second surface reflection. Systematic measurements of the surface reflection phases for unknown structures will help to decide between different structural models. Since it is possible to measure the phases for a large number of reflections in this way, direct methods of structure determination which have been proven to be effective in solving the structures of large organic molecules can be developed for surface structure determination.

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