Depth-Controlled Grazing-Incidence Diffraction of Synchrotron X Radiation

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We show with both experiment and theory that a Bragg reflection from a crystal surface excited under grazing-incidence conditions is displaced from its reciprocal-lattice point. This new phenomenon allows for the first time a confirmation of the penetration depth of the scattered intensity on the scale of a lattice constant. The experiments presented show the possibility of a controlled depth probing of near-surface atomic correlations.

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Static and dynamic correlations of atoms near interfaces can be studied by use of x rays scattered at grazing incidence. When the angle α_i between the incident wave vector $\mathbf{k}_i$ and the interface is less than the critical angle $\alpha_c = \lambda(r_e\bar{\rho}_e/\pi)^{1/2}$ (λ is the wavelength, $\bar{\rho}_e$ the mean electron density, and r_e the electron radius), a specularly reflected beam appears and the evanescent wave within the less-dense medium decays exponentially with typical depths of 50 Å. To probe structural features near the interface it is necessary to measure a diffracted intensity at nonzero Bragg angles 2θ in order to provide a large momentum transfer $\mathbf{Q}_{\parallel}$ parallel to the interface (see Fig. 1). If $\mathbf{Q}_{\parallel}$ fulfills the Bragg condition, $\mathbf{Q}_{\parallel} = \boldsymbol{\tau}_{hkl}$ ($\boldsymbol{\tau}_{hkl}$ being a reciprocal lattice point in the interface), a Bragg beam is observed. A similar scheme has already been used to study the epitaxially grown Al-GaAs interface.[1] In a recent paper Dietrich and Wagner pointed out the use of grazing-incidence diffraction (GID) for probing the effect of a surface on critical behavior.[2]

Because GID intensities are observed in reflection, the momentum transfer Q_z perpendicular to the interface has to be carefully considered. In this Letter we show in fact with both experiment and theory that a GID Bragg intensity is displaced from its reciprocal lattice point along Q_z as a consequence of a length scale which is comparable to the penetration depth of the evanescent wave, but dependent on the momentum transfer Q_z in the scattering process. We indicate the potential for obtaining depth-resolved information about the structural properties parallel to the interface with the sensitivity of a single atomic layer through a simple control of this length.

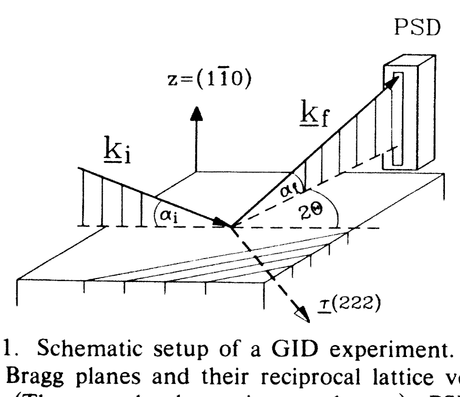

FIG. 1. Schematic setup of a GID experiment. The reflecting Bragg planes and their reciprocal lattice vector are shown. (The specular beam is not shown.) PSD is the position-sensitive detector.

By way of example we have investigated the Q_z structure of the (222) reflection from a (1$\bar{1}$0) surface of an Fe_3Al single crystal[3] using synchrotron radiation incident in the vicinity of the range of total reflection. The binary alloy Fe_3Al is characterized by $\bar{\rho}_e = 1.9$ Å^{-3} which gives a critical angle of $\alpha_c = 6.2$ mrad (for $\lambda = 1.5$ Å). The sample was mounted in a helium chamber on a two-circle diffractometer which sat on an optical bench whose tilt could be controlled with an accuracy of 0.1 mrad. The focused wiggler beam at the A1 station at the Cornell High Energy Synchrotron Source (CHESS) provided 10^{11} 8-keV photons/sec at the sample. The intensity profile of the GID Bragg reflection was probed perpendicular to the surface by measurement of the diffracted intensity at fixed $\mathbf{Q}_{\parallel} = \boldsymbol{\tau}_{222}$ as a function of the angle α_f between the diffracted beam and the surface (see Fig. 1). The angle α_f has been scanned between 2 and 25 mrad by a position-sensitive detector (PSD) for three different incident angles, $\alpha_i = 4.0$, 5.5 (below α_c), and 7.0 mrad (above α_c), with typical counting rates of order 10^2 counts/sec. After each scan the sample was rotated 5° around the surface normal. In this position, where the Bragg reflection is eliminated, we determined the background scattering from the sample. Since Compton and temperature diffuse scattering are proportional to the number of illuminated atoms, the α_f depen-

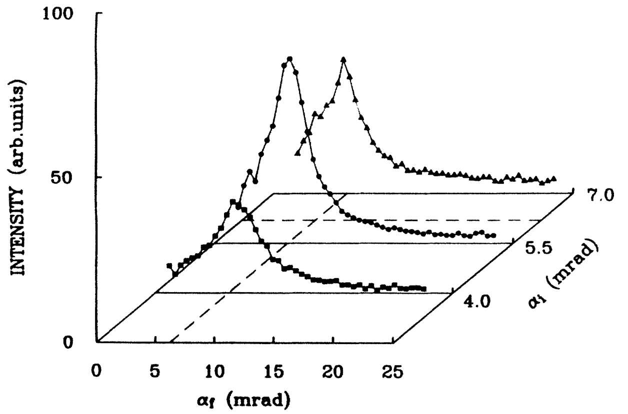

FIG. 2. Intensity profiles of the (222) GID Bragg reflection from a $(1\bar{1}0)$ surface of Fe_3Al measured with the geometry of Fig. 1. The dashed lines indicate the critical angle $\alpha_c = 6.2$ mrad.

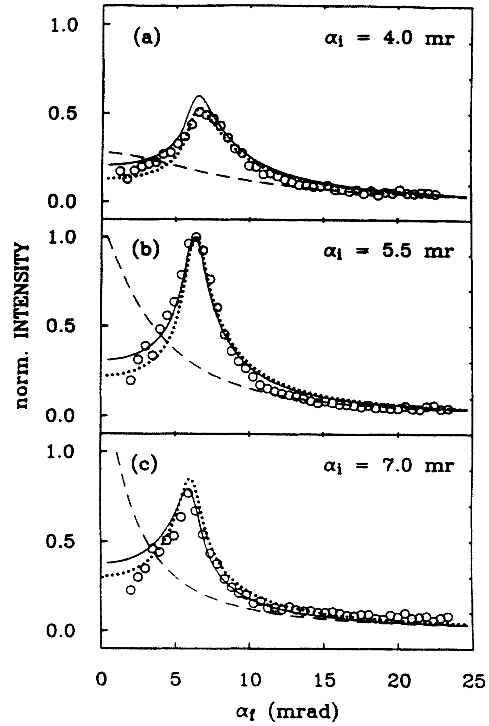

FIG. 3. Comparison of the experimental results with several theoretical treatments. The size of the data circles corresponds to the estimated experimental errors. The dashed curve is from Vineyard's DWA treatment. The solid curve is the present theory calculated from Eq. (5). The dotted curve is calculated from Eq. (6) with $p = 2$, i.e, the assumption that the first two layers on the surface are not ordered as the bulk and do not contribute to the Bragg peak. All theory curves are normalized to the peak intensity in (b).

dence of the diffuse intensity can be calculated from Eq. (2) (see below). The comparison between the observed and calculated diffuse intensity profiles exhibits absorption effects when α_i or α_f is less than 2.5 mrad. We attribute this to surface roughness. (The onset of surface-roughness effects at angles below 2.5 mrad has also been confirmed by the deviation of the observed specular intensity from Fresnel theory[4] for $\alpha_i < 2.5$ mrad.) Figure 2 shows our results for the measured intensity distributions after experimental elimination of the background scattering (Compton, temperature diffuse, and air scattering) and correction for the effective surface area and surface roughness. In each of the curves the intensity maximum is displaced from its bulk position ($\alpha_i = \alpha_f = 0$) by an amount comparable to α_c.

Since the crystal is mosaic a kinematic description of the experimental results should be applicable. Vineyard was the first to extend the kinematic theory to the regime of GID by introducing the distorted-wave approximation (DWA).[5] In this approach the evanescent wave created by the incoming beam ("distorted wave") determines the relevant penetration depth $l \approx (\lambda/2\pi)(\alpha_c^2 - \alpha_i^2)^{-1/2}$. The predicted (GID) Bragg peaks are centered at reciprocal lattice points and have Lorentzian-type shapes perpendicular to the surface. The comparison of the DWA predictions (dashed lines in Fig. 3) with our data points show that good agreement is achieved only for $\alpha_f \gg \alpha_c$ at the tails of the scattered intensities. In order to explain the observed peak shift we discuss in more detail the momentum transfer Q_z perpendicular to the surface. In the vacuum, Q_z is simply given by

$$k_z^{(f)} - k_z^{(i)} = (2\pi/\lambda)[\sin\alpha_f + \sin\alpha_i].$$

Since the index of refraction is complex,[6] $n = 1 - \delta - i\beta$ (where $2\delta = \sin^2\alpha_c$, $\beta = \mu\lambda/4\pi$, and μ is the linear absorption coefficient), this quantity becomes within the sample[7]

$$Q_z' = k_z^{(f)\prime} - k_z^{(i)\prime} = (2\pi/\lambda)[(\sin^2\alpha_f - 2\delta - 2i\beta)^{1/2} + (\sin^2\alpha_i - 2\delta - 2i\beta)^{1/2}]. \tag{1}$$

This can be verified by application of Snell's law to both $\mathbf{k}^{(i)}$ and $\mathbf{k}^{(f)}$ and neglect of nonlinear terms. (We use primes to denote quantities within the sample.) The appropriate length which describes GID correctly is the depth for which the scattered intensity is reduced by $1/e$. This depth Λ, which we call "scattering depth," is coupled to the momentum transfer perpendicular to the surface through $|\mathrm{Im}Q_z'|^{-1}$. Using Eq. (1) we get

$$\Lambda = \lambda/2\pi(l_i + l_f), \tag{2}$$

$$l_{i,f} = \tfrac{1}{2}\sqrt{2}\{(2\delta - \sin^2\alpha_{i,f}) + [(\sin^2\alpha_{i,f} - 2\delta)^2 + (2\beta)^2]^{1/2}\}^{1/2}. \tag{3}$$

These equations show explicitly the symmetric influence of α_i and α_f upon Λ which can be understood from the reciprocity theorem in optics where source and point of observation are interchanged.[8] Figure 4(b) illustrates for our system Fe_3Al the behavior of Λ with α_f for various incidence angles α_i. Consider first the scattering depths associated with α_i below α_c: There, the scanning of the α_f provides a variation of the depth Λ between the minimum value $\Lambda_{\min} \approx \lambda/4\pi\alpha_c$ and a maximum $\Lambda_{\max} \approx (\lambda/2\pi)(\alpha_c^2 - \alpha_i^2)^{-1/2}$, which is independent of α_f. Thus, for example, at an incidence angle $\alpha_i = 4.0$ mrad a depth between 20 and 50 Å is ranged. The situation is qualitatively different in the case where α_i is above α_c. The upper limit of Λ is then merely determined by photoelectric absorption and therefore increases continuously with α_f up to several hundred angstroms, whereas the minimum depth is $\lambda/2\pi\alpha_c$, which is 40 Å in our case. This angular dependence of the scattering depth has crucial consequences for the intensity distribution of a GID Bragg reflection, as will be shown below. An immediate consequence of the small number of atomic layers involved is that the GID Bragg node is extended in k space normal to the surface allowing Bragg intensity external to the crystal. We note here that for α_i and α_f below α_c the z component of the momentum transfer disappears within the sample, since $\mathrm{Re}(Q_z') = 0$ [Eq. (1)]. This can be seen in Fig. 4(a) which shows $\mathrm{Re}(Q_z')$ vs α_f for different incidence angles α_i calculated for the system Fe_3Al. The negligibly small value of $\mathrm{Re}(Q_z')$ remaining in the regime $\alpha_{i,f} < \alpha_c$ is due only to photoelectric absorption and thus of order $\mu/\alpha_i \approx 10^{-3}$ Å^{-1}. Therefore, even though the vacuum value Q_z is nonzero in this regime, the momentum transfer within the sample is parallel to the surface. Within the kinematic theory the scattering law of the GID Bragg reflection is, in the z direction,

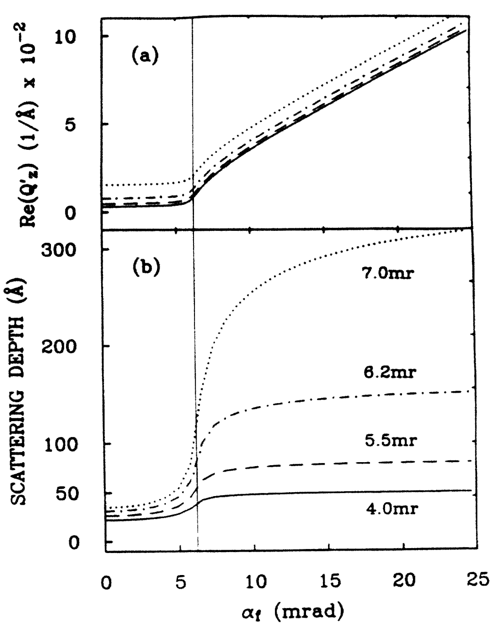

FIG. 4. (a) z components of the momentum transfer within the sample and (b) scattering depths in the binary alloy Fe_3Al vs scattering angle α_f for various incidence angles α_i. The different curves represent corresponding values of α_i in (a) and (b). The vertical line indicates the critical angle.

$$S = \sum_{m,n=0}^{\infty} \exp(-iQ_z' z_m + iQ_z'^{*} z_n), \tag{4}$$

where z_m is the z component of the vector $\mathbf{R}_m$ of unit cell m. Carrying out the sums and neglecting terms higher than second order in Λ^{-1} (see Ref. 5) we find

$$S \approx \frac{(\Lambda/a_0)^2}{1 + \{(2\Lambda/a_0)\sin[\mathrm{Re}(Q_z')a_0/2]\}^2} \tag{5}$$

(a_0 = lattice constant). The behavior of S as a function of α_f is considerably different if $\alpha_f \leqslant \alpha_c$ or $\alpha_f > \alpha_c$. For $\alpha_f \leqslant \alpha_c$, the sine function in Eq. (5) is a constant close to zero [see Fig. 4(a)], and in this regime we have $S \approx \Lambda^2$, i.e., the intensity increases quadratically with increasing scattering depth. On the other hand, for $\alpha_f > \alpha_c$ the increasing $\mathrm{Re}(Q_z')$ tends to decrease the intensity and counters the action of Λ. Thus an intensity maximum is predicted at a nonzero value of α_f close to α_c. This qualitative discussion is confirmed by a detailed calculation giving the intensity profiles (full lines in Fig. 3) in good agreement with our experimental results.[9] The peak-shift phenomenon is to our knowledge the first direct experimental confirmation of the scattering depth associated with GID on the scale of a lattice constant.

A closer inspection of Fig. 3 reveals differences outside the experimental error between the calculated full lines and the measured profiles which are substantial at small values of α_f. A possible explanation of the discrepancies is that the crystal surface was not ideal, for example, because of the presence of an oxide layer. Assuming that p layers at the surface do not contribute to the Bragg intensity (but still contribute to the refraction index), we find the modified form of the scattering law

$$S_{-p} = \exp(-2pa_0/\Lambda)S, \tag{6}$$

where S is given by Eq. (5). The dotted lines in Fig. 3 show the intensity profiles[9] if two layers at the surface are removed from the scattering process ($p = 2$). We find, indeed, an improvement in the fit to the experimental data. It is important to point out that the major effect of the exponential function in Eq. (6) is an intensity change of the scattering profiles which is partly removed because of the normalization to the peak in Fig. 3(b). However, this could be readily detected by a reference measurement with a clean surface.

We conclude that the α_f-resolved GID experiments can provide a sensitive depth profiling of near-surface atomic correlations. Information on the behavior of a particular crystal structure property, say $p(z)$, with depth z can be extracted by such experiments. The proposed measurements actually provide the Laplace-transformed quantity

$$p(\Lambda)=\Lambda^{-1}\int_0^\infty e^{-z/\Lambda}p(z)\,dz, \tag{7}$$

and $p(z)$ can be obtained by the inverse transformation.[10] The method described here complements in an important way other surface scattering techniques such as direct two-dimensional scattering and standing waves[11]: The present procedure does not require perfect crystals, and the diffraction phenomena can be described by straightforward kinematic theory. The depth of the probe can be easily varied within tens of angstroms. This has a potential for a wide range of applications. Examples of some intriguing problems of current interest are the behavior of a crystal surface in the neighborhood of the melting point and the depth profile of radiation damage near crystal surfaces, as in ion-implanted semiconductors.

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[9]The theoretical curves include the vertical divergence of the incident beam ($\Delta\alpha_i=0.4$ mrad) and the spatial resolution $\Delta s=200\ \mu$m of the PSD (giving $\Delta\alpha_f=0.44$ mrad).

[10]Consider the case where the obtained data $p(\Lambda)$ are fitted by a power series in Λ, i.e., $p(\Lambda)=\sum_n b_n\Lambda^n$. Then $p(z)$ is simply given by

$$p(z)=\sum_n(b_n/n!)z^n.$$

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