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A new x-ray diffraction method for structural investigations of solid-liquid interfaces

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A synchrotron x-ray diffraction method is presented for structural investigations of interfaces between low- Z substrates and heavier liquids. The method, similar to methods used in neutron scattering, is based on illuminating the interface through the solid substrate. The backgrounds arising from bulk scattering and the signal-to-background ratio are estimated and compared with experimental results. An ultrahigh vacuum (UHV) setup is described in which the atomic arrangement and roughness of clean interfaces can be studied *in situ*. Our first results illustrate the possibilities for both out-of-plane and in-plane diffraction studies. The specular reflectivity of the Ga/diamond(111)- 2×1 interface was measured for perpendicular momentum transfers up to $2.2\text{ \AA}^{-1}$. In an in-plane study of Ga/Si(111)- 7×7 the in-plane structure factor of Ga liquid within a depth of $\sim 50\text{ \AA}$ was compared to the structure factor of the bulk liquid. © 1997 American Institute of Physics. [S0034-6748(97)03211-5]

I. INTRODUCTION

Theoretical studies have predicted that a liquid in contact with a crystalline solid, orders at the interface over a depth of a few atomic layers.^{1,2} Near the interface, the liquid is expected to exhibit atomic layering in the direction along the interface normal as well as ordering parallel to the interfacial plane. Also the solid surface itself may undergo a structural change upon making contact with a liquid.³ Hardly any of the theoretical predictions concerning the structure of solid-liquid interfaces have been verified experimentally. The main reason for this is that the atomic structure and roughness of deeply buried solid-liquid interfaces and of solid-solid and liquid-liquid interfaces are difficult to probe. The only work reported so far concerns electrode/electrolyte interfaces,³⁻⁶ where voltage-dependent layering effects⁴ and restructuring at the solid interface³ have been observed.

Understanding the atomic-scale structure of solid-liquid interfaces is not only of interest for the verification of theoretical predictions. The properties of stratified ultrathin liquid boundary layers are thought to influence many everyday-life processes and to affect properties such as flow, lubrication, and wear.^{7,8} These boundary layers are also important in that they are likely to trigger heterogeneous nucleation, which is by far the most predominant and practically significant mechanism of solid initiation. Moreover, little is known about the interaction of liquid metals with solid surfaces in processes such as casting, moulding of steel and alloys, soldering, welding, and liquid-phase sintering. More insight may be acquired in layering effects in the liquid and in atomic-scale roughening of the solid surface upon chemical attack.

Like neutron scattering,⁹ the technique of x-ray diffraction may be applied to studies of buried interfaces because of

the large penetration depth of x rays in matter. In addition, the technique is nondestructive. Because of the small elastic scattering cross section of x rays, the kinematic scattering approximation is valid, i.e., complicating multiple scattering effects can be neglected. We use a transmission geometry in which the interface is approached from the side of a low- Z solid (see Fig. 1). When a heavier liquid is placed on top of the solid substrate, the interface acts as a totally reflecting mirror for grazing angles of incidence. In this way we use the liquid to change the Laue geometry into a Bragg geometry; thus we can perform Bragg scattering experiments analogous to studies performed on free surfaces.^{10,11} A prerequisite for obtaining sufficient count rates is to have a bright enough source. These experiments are best performed using undulator radiation from a third-generation synchrotron source.

Before the x-ray beam reaches the interface, macroscopic quantities of bulk material will be illuminated. This gives rise to a substantial background of undesirable bulk scattering. Since the relative contribution of Compton scattering to the total scattering cross section is larger for low- Z elements, there is a high Compton background from the solid bulk. The background scattering will also include thermal diffuse scattering from the solid substrate and, for momentum transfers where the liquid pair distribution function is nonzero, there will be a considerable contribution of diffuse scattering from the liquid. The background level, and the concomitant signal-to-background ratio, ultimately determines the feasibility of these studies.

An atomically clean interface can only be prepared in an ultrahigh-vacuum (UHV) environment. The interface is made by first preparing a single-crystal surface free of contaminants. Subsequently, a clean drop of liquid metal is prepared by decanting a drop from the center of a melt.^{12,13} The

FIG. 1. Schematic of scattering geometry. The top panel shows a side view, the lower panel shows a top view. The incoming beam is represented by the wave vector $\mathbf{k}_i$, the outgoing beam by $\mathbf{k}_f$. The interface is illuminated from the substrate side with a monochromatic x-ray beam. After scattering, photons travel through the crystal again on their way to the detector. The momentum transfer $\mathbf{Q}$ is the difference between the wave vectors of the incident and scattered rays.

drop is then deposited *in situ* onto the crystal surface.

The outline of this article is as follows. In Sec. II, we will discuss our method. In Sec. III, we focus on the signal-to-background problem. We then present our setup in Sec. IV, and conclude by showing the first results obtained on the systems Ga/diamond(111)- 2×1 and Ga/Si(111)- 7×7 .

II. METHODS

A schematic of the scattering geometry is shown in Fig. 1. The interface, which lies in the horizontal plane, is illuminated from the substrate side by a monochromatic x-ray beam. After scattering from the interfacial region the photons travel through the crystal again on their way to the detector. We study low-Z substrates (diamond, silicon) in contact with heavier metals (gallium, indium). In diamond a photon beam of $0.5 \text{ \AA}$ wavelength is attenuated over a $1/e$ -depth of 8 mm. This enables scattering experiments to be performed on buried interfaces over illuminated areas comparable to those in conventional surface x-ray diffraction experiments.

The scattering geometry enables the measurement of in-plane intensity distributions and of diffraction intensities along the two-dimensional array of rods in reciprocal space arising from the truncation of the crystal lattice at the interface. For measurements along these nonspecular crystal truncation rods (CTRs),^{14,15} the angle of incidence can be chosen equal or smaller than the critical angle for total reflection. In that case, the penetration depth is limited to typically $50 \text{ \AA}$,¹⁰ which greatly enhances sensitivity to ordering effects at the

interface. One may also measure intensities diffracted from the interfacial region only, e.g., fractional-order peaks or diffuse scattering features associated with ordering of the liquid.¹⁶

To date, x-ray studies of solid-liquid interfaces have mostly been performed on electrolyte-electrode interfaces.^{3-5,17-19} In these experiments the contrast in electron density is the reverse of that in our method: the electrode is a high-Z metal, while the solution is watery. Therefore, in these scattering geometries, the interface is approached by the x-ray beam from the side of the solution. The electrochemical cells used in these studies can be divided into two classes: the "reflection geometry" cells and the "transmission geometry" cells. In the first a membrane is pulled taut over the working-electrode surface in order to minimize the volume of the solution layer through which the x rays must travel.⁵ Recently, this principle has also been applied in studies of the atomic arrangement at KH_2PO_4 surfaces in their growth solution²⁰ and to calcite cleavage surfaces in water.²¹ In the transmission geometry a thin slice of the interface is illuminated through the solution.¹⁷⁻¹⁹ The differences between the two types of cells have been discussed previously.²² Our method differs from these studies in one important aspect. For a geometry in which the beam illuminates the interface from the side of the crystal, most of the elastic scattering from the bulk is concentrated around the bulk Bragg points in reciprocal space. By avoiding these points one eliminates the elastic background scattering from the bulk solid. By contrast, illumination of a large volume of bulk liquid gives rise to a high elastic diffuse background at momentum transfers for which the liquid structure factor is nonzero.

III. THE SIGNAL-TO-BACKGROUND RATIO

In this section, we estimate levels of background scattering for the geometry of Fig. 1, and compare these with calculated yields from the truncated solid and with yields arising from ordering effects in the liquid near the interface. The estimated signal-to-background ratios will be compared with experimentally determined ratios.

A. Elastic scattering and Compton scattering

Consider the elastic scattering along a CTR for a buried interface.^{14,15} The integrated intensity in a transverse momentum scan, I_{int}^{el} , is given by²³

$$I_{int}^{el} = r_e^2 \frac{I_0 \lambda^2 A_s}{\omega A_u^2} F_{Lor} |F_{hkl}|^2 P \Delta \gamma C(\lambda, L), \quad (1)$$

where r_e^2 is the classical electron radius, I_0 the incident flux, ω the angular velocity with which the transverse scan is made, λ the photon wavelength, A_s the illuminated interface area, A_u the unit-cell area, F_{Lor} the Lorentz factor, $|F_{hkl}|$ the structure-factor amplitude of the unit cell at a point in reciprocal space given by the Miller indices (hkl) , P the polarization factor, and $\Delta \gamma$ is the angular range in the direction perpendicular to the interface over which the detector accepts scattered radiation. The correction factor $C(\lambda, L)$ accounts for the attenuation of the primary and scattered beams due to

absorption in the crystal. It depends on λ and on the total pathlength L traversed through the crystal. L in turn depends on the crystal shape and the orientation of the sample with respect to the incoming and scattered beams. We discuss the attenuation factor later.

Although crystallography is based on the measurement of integrated intensities, it is the peak counting rates that determine the feasibility of the experiment. If the angular divergence of the beam is smaller than the mosaic spread $\Delta\epsilon$ of the crystal, the peak counting rate Y_{sol}^{el} is given by

$$Y_{sol}^{el} \approx I_{int}^{el} \frac{\omega}{\Delta\epsilon} = r_e^2 \frac{I_0 \lambda^2 A_s}{\Delta\epsilon A_u^2} F_{Lor} |F_{hkl}|^2 P \Delta\gamma C(\lambda, L). \quad (2)$$

We account for the reduction in peak counting rate due to thermal vibrations of the atoms and atomic-scale interface roughness by writing the structure-factor intensity $|F_{hkl}|^2$ as^{23,24}

$$|F_{hkl}|^2 = \left| \sum_j f_j(Q) e^{-iQ \cdot r_j} e^{-B_j(Q/4\pi)^2} \cdot \sum_n \vartheta_n e^{in\psi_{hkl}} \right|^2. \quad (3)$$

Here, the first summation is over the atoms j in the unit cell at positions r_j . The parameter $f_j(Q)$ is the atomic form factor and B_j is the Debye–Waller parameter.²³ The second summation index n denotes the level at which the crystal lattice terminates. Each level has an occupancy ϑ_n and causes a phase shift $n\psi_{hkl}$ in the scattered beam.

The elastic scattering intensity from the liquid is estimated using the expression²⁵

$$Y_{liq}^{el} = r_e^2 I_0 \frac{N_{av} \rho_{liq}}{A_{liq}} A_s \Lambda f(Q)^2 S(Q) P \Delta\psi \Delta\gamma C(\lambda, L), \quad (4)$$

where N_{av} is Avogadro's number, A_{liq} the atomic weight, ρ_{liq} the mass density, Λ the penetration depth in the liquid, and $f(Q)$ the atomic form factor of the liquid in the independent atom approximation. $S(Q)$ is the liquid static structure factor which is well known for a monoatomic liquid.²⁶ $\Delta\psi$ is the opening angle of the detector in the plane parallel to the interface.

When estimating the diffuse background from a solid, one should consider both thermal diffuse scattering (TDS) and Compton scattering. For low- Z materials and energetic x rays, Compton scattering will be the main contributor,²⁷ hence we only consider the Compton contribution. Assume that the crystal is illuminated over a constant depth d over the whole active sample area A_s . The value of d is determined by the opening of the slits in front of the sample (incident slits) in the direction perpendicular to the interface. The modified background yield Y_{sol}^{Com} is given by²⁷

$$Y_{sol}^{Com} = r_e^2 I_0 \frac{N_{av} \rho_{sol}}{A_{sol}} A_s d \cdot R_B \cdot i(Q) P \Delta\psi \Delta\gamma C(\lambda, L), \quad (5)$$

where R_B is the Breit–Dirac relativistic recoil factor and $i(Q)$ is the modified scattering function which depends on the momentum transfer Q . The factor $(N_{av} \rho_{sol} A_s d / A_{sol})$ denotes the number of scatterers with atomic weight A_{sol} and mass density ρ_{sol} in an illuminated volume given by $A_s d$.

FIG. 2. Directions and angles defined for computing the absorption correction for a sample having the shape of a rectangular parallelepiped. The top panel shows a top view, the lower panel shows a side view in projection onto a plane containing the surface normal and the x axis. The sample area is shaded light; the footprint of the beam is represented by the shaded parallelogram. The different symbols are discussed.

B. Absorption

For calculation of the absorption correction factor $C(\lambda, L)$ we refer to Fig. 2. The crystal has the shape of a rectangular parallelepiped of width t . With respect to the incident beam, the normal of the long side of the crystal makes an angle σ in the horizontal plane and an angle α_i in the vertical plane. The intensity scattered over a slice of length dx at position x along the incoming beam path is given by

$$dI = KI_0 \exp[-\mu(\lambda)L(x)]dx. \quad (6)$$

Here, I_0 is the primary beam intensity and K is a proportionality constant. The linear absorption coefficient $\mu(\lambda)$ is approximately proportional to λ^3 far from the absorption edges. $L(x)$ is the total pathlength traversed by the rays, given by

$$L(x) = L_1 \cdot x + L_2, \quad (7)$$

where $L_1 \equiv \frac{1}{\cos\alpha_i} - \frac{\cos\sigma}{\cos(\sigma - \phi)\cos\alpha_f}$

and $L_2 \equiv \frac{W\cos\sigma}{\cos(\sigma - \phi)\cos\alpha_f}$.

We integrate along a line in the interface plane in the direction of the incoming beam, which reflects the experimental

condition described in this work. The incident slits in front of the detector are centered around the vertical rotation axis of the sample and determine the integration boundaries which range from w to $W-w$. After integrating over x , and normalizing the result to the length of the integrated range, we find

$$C(\lambda, L) \equiv \frac{I}{KI_0} = -\frac{e^{-\mu(\lambda)L_2}}{\mu(\lambda)(W-2w)L_1} \times \{e^{-\mu(\lambda)(W-w)L_1} - e^{-\mu(\lambda)wL_1}\}. \quad (8)$$

A special case arises for specular reflectivity, when $\alpha_i = \alpha_f = \theta$ and $\phi = 0$. Using $t = W \cos \sigma$ and redoing the integration we obtain

$$C^{refl}(\lambda, L) = \exp\left(\frac{-\mu(\lambda)t}{\cos \theta \cos \sigma}\right). \quad (9)$$

For our experimental geometry the active sample volume is relatively small and the regions contributing to the signal and background essentially coincide. Signal and background are therefore attenuated by the same factor.

C. Estimated and measured signal-to-background ratios

In order to obtain the signal-to-background ratio for a measurement along a CTR, we divide the peak counting rate given by Eq. (2) by the Compton background expressed by Eq. (5):

$$\frac{Y_{sol}^{el}}{Y_{sol}^{Com}} = \frac{A_{sol}}{N_{av} \rho_{sol}} \frac{\lambda^2 F_{Lor}}{d \Delta \psi \Delta \epsilon A_u^2} \frac{|F_{hkl}|^2}{R_B \cdot i(Q)}. \quad (10)$$

Let us evaluate the signal-to-background ratio for diamond(111). Our experimental conditions are: for $\Delta \epsilon = 1.75 \times 10^{-4}$ rad, $A_{sol} = 12$, $A_u = 5.51 \times 10^{-20}$ m², $\lambda = 0.7 \times 10^{-10}$ m, $\rho_{sol} = 3.51 \times 10^6$ g m⁻³, $\Delta \psi = 1.75 \times 10^{-3}$ rad, and $d = 1 \times 10^{-4}$ m. At $(hkl) = (1\ 0\ -3)$, for which $|Q| = 4.2$ Å⁻¹, $F_{Lor} = 3.1$ and, using Eq. (3), $|F_{1\ 0\ -3}|^2 = 1.7$. The values of the modified scattering function are tabulated and $R_B \cdot i(4.2) = 4.1$.²⁸ The structure factor $|F_{1\ 0\ -3}|$ includes the Debye–Waller factor²⁹ and the effect of roughness. For the diamond(111) sample used, the occupancies of the different levels at which the interface terminates follow a Poisson distribution with a second moment of 1.2 Å.²⁴ The roughness reduces the structure factor amplitude by a factor four. The Debye–Waller factor lowers the structure factor amplitude by only 4%. Substituting the above values in Eq. (10) yields a ratio $Y_{sol}^{el}/Y_{sol}^{Com} = 0.4$. From the experiment we find a ratio of 0.3, in good agreement with our estimate. We note that the experimentally observed signal-to-background ratio has been corrected for the dark countrate in the hutch, i.e., for all the detector counts not coming from the sample itself. The ratio $Y_{sol}^{el}/Y_{sol}^{Com}$ is plotted in Fig. 3 as a function of λ . For comparison, also a calculation assuming the same experimental conditions for a silicon(111) surface is shown.

Next we estimate the signal-to-background ratio for a measurement of the in-plane correlation function of the liq-

FIG. 3. Calculated ratio of elastic to Compton scattering yields for the $(hkl) = (1\ 0\ -3)$ reflection from a diamond(111) and a Si(111) surface as a function of wavelength λ . Parameters used in the calculation are given. The mosaicity and the roughness of both surfaces were assumed to be identical.

uid in the immediate vicinity of the interface.³⁰ Dividing Y_{liq}^{el} , given by Eq. (4), by the Compton background Y_{sol}^{Com} , given by Eq. (5), we find

$$\frac{Y_{liq}^{el}}{Y_{sol}^{Com}} = \frac{\rho_{liq}}{\rho_{sol}} \frac{A_{sol}}{A_{liq}} \frac{\Lambda}{d} \frac{f(Q)^2}{R_B \cdot i(Q)} S(Q). \quad (11)$$

Let us estimate the parameters for liquid Ga on a silicon(111) substrate. At the first maximum of the pair distribution function for bulk liquid Ga, $S(2.56) = 2.5$.³¹ Furthermore, $f(2.56) = 25.0$, $R_B \cdot i(2.56) = 4.5$,²⁸ $\rho_{liq} = 5.9 \times 10^6$ g m⁻³, $\rho_{sol} = 2.3 \times 10^6$ g m⁻³, $A_{sol} = 96.7$, $A_{liq} = 28.1$ and $d = 2 \times 10^{-5}$ m. The value of $\Lambda = 5 \times 10^{-9}$ m is the penetration depth of the transmitted wave in the liquid, which is exponentially damped (evanescent wave) for rays incident below the critical angle for total reflection.¹⁰ We calculate a ratio $Y_{liq}^{el}/Y_{sol}^{Com} = 0.8$. The experimentally determined ratio at the first maximum, after correction for the dark countrate equals $Y_{liq}^{el}/Y_{sol}^{Com} = 0.4$, which is in qualitative agreement with the prediction. The difference in estimated and measured ratios is most likely due to the crudeness in our estimate of the amount of bulk solid which is illuminated.

D. Reducing the Compton background

There are several ways of suppressing the Compton background. First, by choosing the smallest possible value of d , the illuminated volume of bulk solid is minimized, resulting in a maximum signal-to-background ratio. Second, one may utilize the high momentum resolution inherent to the use of synchrotron radiation. By reducing the momentum acceptance $\Delta \psi$ of the detector one suppresses the background accordingly, whereas the whole signal is still intercepted—provided the sample is well ordered. Crystal analyzers may be used for this purpose.

Two other methods reduce the Compton component by energy selection. The first one is known as the Warren–Mavel fluorescence excitation method,³² the second one is a method which involves a diffracted-beam crystal

FIG. 4. Schematic of x-ray scattering chamber with an enlarged view of the liquid pouring assembly and the sample mount. The chamber is mounted onto a horizontal liquid surface diffractometer.

monochromator.³³ Here, we will only discuss the first one. The photon energy is chosen to be just above a K-absorption edge of a metallic foil placed in the scattered beam path. The elastically scattered x rays excite fluorescence in the foil whereas the lower-energy Compton rays cannot. Recording the fluorescence is therefore a measure of the elastic scattering signal.

To reduce the Compton scattering background from the diamond bulk, we have successfully applied the Warren-Mavel method. As a fluorescent medium we used a thin yttrium foil in front of the detector. Using the tunability of the undulator the incident photon energy was set 20 eV above the yttrium K 1s binding energy (17.038 keV). Employing this detection mode, we achieved an improvement in the signal-to-background ratio of a factor of two. The signal is lower by a factor of 15 due to the loss in solid angle over which scattered rays are detected (only 20% is detected) and due to the relative inefficiency of the recording process itself. If the intensity is reduced too much, the dark count in the experimental hutch becomes the main source of the background scattering, and part of the gain of using the Warren-Mavel method is lost. The detection efficiency and gain in signal-to-background ratio are in good agreement with a previous application of this fluorescent detection method.³⁴

If the Compton background cannot be eliminated from the measured intensity, the optimum wavelength is a tradeoff

between a favorable signal-to-background ratio (long wavelength) and a hardly attenuated signal (short wavelength).

IV. EXPERIMENT

A. UHV chamber

A schematic of the UHV scattering chamber is shown in Fig. 4. It fits onto a horizontal diffractometer equipped with the standard Huber goniometer head 5203.2.³⁵ The chamber is fitted with a 35 l/s turbomolecular pump and a 20 l/s ion pump. One design consideration was that the chamber must be stand-alone. Therefore the turbomolecular pump is connected through an all-metal, right-angle valve so that it can be switched off, leaving the pumping to the ion-pump only. This makes the system safe against power failures, when it is left unattended. After a bakeout at 160 °C the base pressure is less than 4×10^{-10} mbar.

The x-ray beam enters and leaves the vacuum chamber through a cylindrical Be window (radius 50 mm) which permits 360° access. The height of the window is 50 mm, which allows the in- and outgoing beam to make an angle of maximally 23° with respect to the interface. The largest in- and outgoing angles determine the range of momentum transfers in the direction perpendicular to the surface (for specular reflectivity the maximum momentum transfer is $7 \text{ \AA}^{-1}$ at $0.7 \text{ \AA}$ wavelength). The Be window was brazed into stainless

TABLE I. Summary of experimental parameters.

	Ga/diamond(111)-2×1	Ga/Si(111)-7×7
Undulator type at ID10, magnet period	standard, 46 mm	small gap, 26 mm
Undulator gap (mm)	10.08	21.68
Monochromator reflection	asymmetric diamond (111)	symmetric diamond (220)
Resolution in $\Delta E/E$	5.9×10^{-5}	2.3×10^{-5}
Wavelength (Å)	0.727	0.478
Energy (keV)	17.058	25.947
Transmission of straight-through beam	25%	11%
Incident flux (ph s ⁻¹ mm ⁻² at 100 mA)	2.2×10^{12}	9.6×10^{12}
Beam size at sample (μm)	200×120 (H×V)	100×20 (H×V)
$\Delta Q_{\parallel} \times \Delta Q_{\perp}$ (Å ⁻¹)	0.017×0.066	0.014×0.002

steel extensions welded to 150 mm flanges. Three buttresses were welded on each flange for additional support. The Be-window assembly, made by Brush Wellman Inc.,³⁶ has a thickness of 0.020" (0.5 mm). The Be material is of the type S-200-F, containing as the main contaminant 0.08 wt. % Fe. Prior to installation, the Be assembly was baked in vacuum up to 300 °C and found to be leak tight.

The crystal is mounted in a sample holder and kept in place by Ta clamps. The sample is heated either by radiative heating, electron bombardment, or by resistive heating. The electrons are accelerated towards the back of the sample directly (silicon) or onto a Ta backplate on which the sample is mounted (diamond). In this way temperatures well in excess of 1000 °C can be reached at pressures below 1×10^{-8} mbar. The temperature is measured with a W/Re thermocouple and monitored with an optical pyrometer.

B. Liquid pouring assembly

The liquid drop to be deposited onto the solid substrate has to be free of contaminants. Our preparation method, first proposed by Norris and Wotherspoon,^{12,13} is based on the fact that contaminants (mainly oxides) will float to the surface of the liquid, allowing clean material to be decanted from the center of the melt. We have slightly adapted this method for our experiments with liquid Ga (purity 6N). The liquid metal column is held in an alumina tube and prevented from spontaneously dripping through the exit aperture by choosing the diameter of this aperture which is small enough (0.8 mm). If an excess pressure is exerted by an alumina plunger onto the liquid in the tube, drops will be forced through the aperture. The tube and plunger were heat cleaned in a furnace for several hours at 900 °C, and afterwards degreased ultrasonically in acetone and ethanol. After assembly and baking, the first seven or eight drops were decanted into a Ta drip tray before the actual sample was poured onto the substrate. The cleanliness of the drops was checked in a separate experiment using Auger electron spectroscopy (AES). After three to four drops, the liquid surface was found to be free of oxygen to within the detection limit of 2% of the surface area. No evidence of other contaminants was found.

C. Scattering geometry

X-ray diffraction measurements were performed at the TROIKA undulator beamline (ID10) of the European Syn-

chrotron Radiation Facility in Grenoble, France.³⁷ Due to its high brilliance, this beamline is well suited for these studies. The UHV chamber is mounted onto the horizontal diffractometer, which is operated in the z -axis mode³⁸ or in the reflectivity mode.³⁹ In the z -axis mode different values of the perpendicular momentum transfer along the CTRs are selected by varying the exit angle α_f , while keeping the angle of incidence α_i fixed below the critical angle for total reflection (typically 0.07°–0.12°). In-plane momentum transfer values are set by moving the detector to different scattering angles in the horizontal plane. In the specular reflectivity mode, the chamber is tilted in the vertical plane by an angle θ , while the detector is simultaneously moved in the vertical plane by an angle 2θ . The diamond monochromator of the TROIKA beamline was set to select a given wavelength in Laue geometry. Experimental parameters of studies of the Ga/diamond(111)-2×1 and the Si(111)-7×7 interfaces are summarized in Table I.

V. RESULTS AND DISCUSSION

In this section, we illustrate the possibilities for scattering studies out of the plane of the interface as well as in the interface plane. More details can be found elsewhere.⁴⁰ Specular reflectivity experiments were performed on the Ga/diamond(111)-2×1 interface.⁴⁰ As a substrate we used a synthetic, high-quality type-Ib diamond(111) crystal ($7 \times 6 \times 1.3$ mm³) polished to within 0.3° of the true crystallographic (111) plane. The crystal surface was polished and rinsed and then flash heated to 1000 °C *in vacuo*. This procedure is known to yield an atomically clean surface exhibiting a clear three-domain (2×1) LEED pattern.⁴¹

The measured specular reflectivity is shown in Fig. 5 as a function of $Q_{\perp}$ up to a value of 2.2 Å^{-1} . The data are compared with two model calculations. In the first calculation a density profile is assumed which increases monotonically from the average electron-density value of diamond (1.06 Å^{-3}) to that of liquid Ga (1.63 Å^{-3}). The profile is broadened due to the surface roughness of the diamond substrate. The corresponding specular reflectivity is a Fresnel curve with an additional Debye–Waller factor. Clearly, a smooth electron density profile is too simple to offer an explanation for our observations. In the second model calculation, the density profile includes a layering oscillation in the liquid density at the interface. The quasi-Bragg peak at 1.4 Å^{-1} is evidence of a stratified liquid with a layering period

FIG. 5. Reflectivity of the Ga/diamond(111) interface at 25 °C. The measured reflectivities (filled circles) are obtained from transverse momentum scans. The solid curve represents a model calculation assuming a diamond surface with a rms roughness of 1.2 Å in contact with liquid Ga exhibiting layering near the interface. The dashed curve is a model calculation assuming the same interface (with a rms roughness of 1.1 Å) but without layering. The inset shows selected transverse momentum scans across the reflected beam, with an offset to the zero of the background yields. The scans were made by rocking the sample around the angle θ within the scattering plane, at values corresponding to $Q_{\perp}$ of 0.6, 1.1, and 1.6 Å⁻¹.

of ~ 3.8 Å. Details of these models are published elsewhere.⁴⁰ Although very different for high momentum transfer, for smaller momentum transfer (<0.9 Å) the two model calculations give very similar results and the fits are almost indistinguishable. Hence, the best-fit rms values for the interface roughness for the two models are very similar, with 1.2 Å for the smooth and 1.1 Å for the layered-liquid model. These values correspond well with the value for the rms surface roughness of the clean diamond(111)- 2×1 surface.²⁴

For the Ga/Si(111)- 7×7 system we have measured the in-plane pair distribution functions in the interface region of the Ga liquid and in the bulk liquid.⁴² The substrate was a polished single crystal Si(111) sample ($10\times 4\times 1.4$ mm³) oriented to within 0.1° of the true (111) direction. Before insertion into the UHV chamber, the Si specimen was subjected to a modified Shiraki etch.⁴³ After baking, the sample was flash-heated for 5 s to 1100 °C. This resulted in a (7×7) reconstruction; the width of fractional-order reflections indicated a correlation length of 350 Å. A superposition of six different scans across the peak of the in-plane (transverse) structure factor of supercooled Ga (25 °C) in contact with Si(111)- 7×7 is shown in Fig. 6. The x-ray beam was incident at 0.05°, below the critical angle for total reflection. This reduces the penetration depth to ~ 50 Å in the Ga liquid. Shown for comparison is the structure factor for the bulk liquid which was obtained by having the beam incident at an angle above the critical angle for total reflection. The structure factor for bulk liquid as measured with x ray and neutron diffraction by Narten³¹ agrees well with our bulk measurements. For the range of $Q_{\parallel}$ values shown in Fig. 6, the transverse structure factor from the liquid layer shows no apparent deviation of the bulk structure factor,⁴² within the

FIG. 6. Transverse structure factor of bulk Ga (filled circles) and that of Ga near the interface within a $1/e$ -depth of ≈ 50 Å (open circles) at 25 °C. The solid line represent the bulk structure factor of liquid Ga at 20 °C, as given by Narten (Ref. 31).

error of measurement. Due to the large scatter in the data of the liquid near the solid surface, a meaningful comparison is difficult.

Our method of examining buried interfaces should be applicable in several areas of interface research. This approach not only allows determination of the structure of a liquid metal in contact with a solid but may also be utilized in other fields, such as crystal growth and heterogeneous nucleation. Even for interfaces of two similar materials, such as a crystal and its melt, an analysis of the distribution of intensities along nonspecular CTRs is possible, since the intensity distribution mostly depends on the structure and morphology of the ordered crystal.²⁰ The range of applications may also be extended to studies of solid-solid interfaces, solid-state reactions and metal-semiconductor contacts.

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