<table>
<tr><td> </td><td>Experiment title:
Structure of solid-liquid interfaces</td><td>Experiment number:
SI-678</td></tr>
<tr><td>Beamline:
ID15A</td><td>Date of experiment:
18.03.-27.03.01, 24.06.-02.07.01, 13.11.-20.11.01</td><td rowspan="2">Date of report:
05.08.2002

Received at ESRF:</td></tr>
<tr><td>Shifts:
48</td><td>Local contact(s):
Dr. Veijo Honkimäki</td></tr>
<tr><td colspan="3">Names and affiliations of applicants (* indicates experimentalists):
Dr. H. Reichert* , M. Denk*, S. Engemann*, I. Ramsteiner*, A. Schöps*,
Prof. H. Dosch (MPI für Metallforschung, D-70569 Stuttgart, Germany)
Dr. V. Honkimäki*, Dr. A. Freund (ESRF)</td></tr>
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Exact dates of beam times:

18.03.01	27.03.01	18 shifts	+9 shifts for setup
24.06.01	02.07.01	15 shifts	+9 shifts for setup
13.11.01	20.11.01	15 shifts	+6 shifts for setup

Interim Report:

The local point symmetry of short range order in simple monatomic liquids is one of the fundamental open questions in the science of condensed matter. The importance of the local liquid symmetry has long been highlighted by the conjecture of Frank, Bernal and Scott that simple liquids may be composed of icosahedral building blocks. However, these randomly orientated, mobile structures remained intrinsically inaccessible to experiments due to the unavoidable averaging involved in any scattering experiment which allows only to determine the isotropic radial distribution function. We have demonstrated the first successful x-ray observation of a fivefold local symmetry in liquid lead at the solid-liquid interface Pb(liq.)-Si(100) /1/. This unique information has become possible by exploiting two experimental devices: We have captured and aligned the local liquid building blocks at a properly selected wall and observed the point symmetry of the associated liquid scattering using evanescent x-ray waves as produced by total reflection at the internal wall-liquid interface.
It was the goal of the first period of this long term project to investigate solid-liquid interfaces systematically with special emphasis on the influence of the point symmetry of the single crystal surface and the degree of incommensurability between the solid and the liquid. We also started to investigate kinetic processes such as the inner oxidation of a deeply buried Si interface by a lead-oxide layer intervening between (bulk) liquid lead and clean Si(111).

Experiments

For the experiments we used the setup we have developed in two previous experimental campaigns (MI-339, SI-504, SI-583). We apply two different interface sensitive scattering techniques, namely grazing angle diffraction using the effect of total internal reflection at high photon energies and reflectivity measurements. This allows us to penetrate bulk solid substrates in order to determine the structure of liquids parallel and normal to the solid substrate. For the long term project ID15A supplied a new granite block which improved the stability of the setup in comparison with the previously used concrete block (SI-583) where we could not reach the stability that is mandatory for our experiments. The samples were prepared in Stuttgart and transported *in-situ* (UHV) to the ESRF. At the start of each experiment we have to assemble and configure our specially designed diffractometer which accounts for the setup time. At this point we want to emphasize that we continually improved the resolution and stability of our setup whithin this long term project. Most recently we have tested compound refractive lenses providing a focused high energy beam at the sample position. The sketch in Fig.1 shows the actual state of the setup.

With this setup we have achieved the required stability of the beam with respect to the sample (drift $<0.5\mu m$/shift and <10 µrad/shift) after an initial relaxation of the entire setup to an equilibrium temperature. For the experiments we used high energy x-rays (71.5 keV, bandwidth of 160 eV) optimized for liquid scattering experiments

Results

In a first set of measurements we investigated the system In(liq.)-Si(100). The signal to background ratio of this system is decreased by an order of magnitude compared to the previously studied system Pb(liq.)-Si(100). We focussed on two aspects: Resolving the *in-plane* structure of the system and the *out of plane* structure in comparison with the Pb(liq.)-Si(100) system. For the lead-silicon system we found a new (unexpected) length-scale (approx. 20 Å) for the density oscillations perpendicular to the interface. The indium-silicon system exhibits a similar (increased) length scale as can be seen in Fig.2. This additional length scale is not directly related to the atomic layering previously observed at Ga(liq.)-Diamond interfaces (Huisman et al., 1997). We attribute this new length scale to the changes in the in-plane structure in a thin liquid contact layer at the interface. So far we could resolve reflectivities up to $q_z=1Å^{-1}$. This allows us to resolve features in the electron density down to 5Å. The observation of atomic layering at the interface requires reflectivity measurements up to $q_z=3Å^{-1}$, which requires Si substrates with a roughness $<2Å^{-1}$. We have achieved this only recently (in collaboration with the optics group at the ESRF) by a gradual improvement of our preparation procedures. In order to exclude substrate effects (we penetrate 20mm of crystalline Si with the high energy beam) we have performed a set of reflectivity measurements at different azimuthal angles with respect to the substrate. The results prove the new length scale in the density profile to be independent of the azimuth. By a careful theoretical investigation of the excited Bragg reflections of the silicon substrate and a comparison with the transmitted intensity we could show that the features are not originating from the Si substrate. The complete modeling is currently underway. In Fig.3 the resulting electron density profile is shown. The main feature is the large density increase in a thick layer adjacent to the interface, which decays oscillatory to the bulk density of the liquid. The measurement of the *in-plane* structure factor turned out to be very time consuming. The critical angle of internal total reflection for this system is $\alpha_c=0.032°$ at an x-ray energy of 71.5 keV.
In order to avoid the footprint of the illuminating beam (vertical height 8µm) spreading into the bulk of the liquid the incident angle has to be adjusted between $\alpha_i=0.023°$ and α_c. So far we succeeded in determining the *in-plane* structure factor background free up to the second peak in the liquid structure factor (see Fig.4). The scattering depth is defined by the incidence angle to 70 Å. In order to determine the *in-plane* structure factor more precisely at reduced scattering depths we have recently increased the stability of the setup and the incident photon flux by an order of magnitude due to changes in the beamline optics /2/. This will allow us to determine the in-plane structure of the interface In(liq.)-Si(100) with comparable accuracy to the Pb(liq.)-Si(100) interface. To summarize this part we found evidence that the system In(liq.)-Si(100) shows similar behavior to the system Pb(liq.)-Si(100), where the interfacial liquid structure is determined by an abundance

of (noncrystalline) fivefold coordinated (dynamic) building blocks assembled at the top sites of the Si substrate.

In the following beam time we tried to tackle a frequently asked question about intervening oxide layers at the solid-liquid interface. For this purpose we prepared a thin lead-oxide layer of a thickness of approximately 250 Å between a (111) oriented Si surface and bulk liquid lead. During the experiments the sample was heated to 335°C > T_M^{Pb}. At this temperature lead is liquid while PbO-layer remains solid (the melting temperature for PbO is 888°C). Other Pb_xO_y components are less stable or energetically less favourably and therefore unlikely to be part of the layer. Hence, the oxide layer was solid at this temperature as could be verified during preparation at the free surface before contacting. In our previous experiments the oxide layer was completely removed by sputtering with argon ions prior to contacting the liquid with the clean solid surface. For the purpose of this experiment, however, the sputter process was stopped and the oxide covered liquid brought into contact with the clean silicon substrate. Immediately after contacting the sample was cooled to room temperature. Using x-rays we investigated then the structure of the interface. By scanning the incidence angle α_i and integrating the signal on the exit angle α_f at an *in-plane* momentum transfer q=2.18 Å, which is the position of the first peak in the structure factor of liquid lead, we could clearly identify the additional oxide layer at the interface. Due to the decreased electron density compared to bulk liquid lead the layer is producing a second interfacial peak in the incidence angle spectrum with a critical angle of α_c=0.26° (the broad peak at negative incidence angles is attributed to a bulk signal transmitted through the edges of the sample). The measurement of the *in-plane* structure factor with the interface aligned to both critical angles allows to determine the influence of an interfacial oxide layer onto the structure factor. At small scattering depths with respect to the Si (α_c=0.26°) the structure factor is entirely determined by the presence of the amorphous PbO-layer. We can clearly identify the first peak in the structure factor, whereas other maxima at larger momentum transfer values are absent. Tuning the incidence angle to the critical angle for pure lead in contact with Si (α_c=0.040°) the structure factor starts to resemble the structure factor of bulk liquid lead. A comparison with the bulk liquid structure factor taken from literature /3/ reveals the modifications of the structure factor due to the presence of the oxide layer.

We have then performed background subtracted reflectivity measurements up to a perpendicular momentum transfer q_z=0.6 Å^{-1}. The measurements were repeated several times within a single block of beam time. The results are summarized in Fig.7 which shows the measured reflectivity together with fits according to the electron density model shown in Fig.8. At temperatures below the melting point of lead we find a well defined oxide layer with sharp interfaces to the Si substrate and the (solidified) bulk lead. The thickness of the oxide layer is 250 Å. Upon melting the overall thickness of the layer between the silicon and the bulk liquid (lead) increases slightly. The roughness on both sides of the oxide layer increases, especially the roughness at the interface to the liquid lead. This leads to a damping of the Kiesig fringes for larger momentum transfer q_z. The more pronounced effect is the increase of the electron density in the oxide layer as a function of time. Since the oxide layer was stable at the free surface of the bulk liquid for several weeks before contacting the surface to the Si substrate, we attribute the tremendous increase in electron density at elevated temperatures to an internal (slow) oxidation process, whereby the oxygen is diffusing into the interface to the Si substrate forming an energetically favourable SiO_2 layer. As the electron density of the SiO_2 layer is almost identical to the electron density of the Si substrate the additional layer does not produce any prominent features in the reflectivity curves. The measurements demonstrate that our technique is well suited for the investigation of kinetic processes at deeply buried solid-solid interfaces /4/.

References

/1/ H. Reichert et al., Observation of five-fold local symmetry in liquid lead, Nature **408**, 839, (2000)
/2/ H. Reichert et al., Scattering methods for the investigation of deeply buried solid-liquid interfaces, in preparation.
/3/ Structure factors and pair correlation functions can be found at http://www.iamp.tohoku.ac.jp/database/scm/index.html
/4/ M. Denk et al., Kinetics of the oxidation process at a deeply buried solid-liquid interface, in preparation.

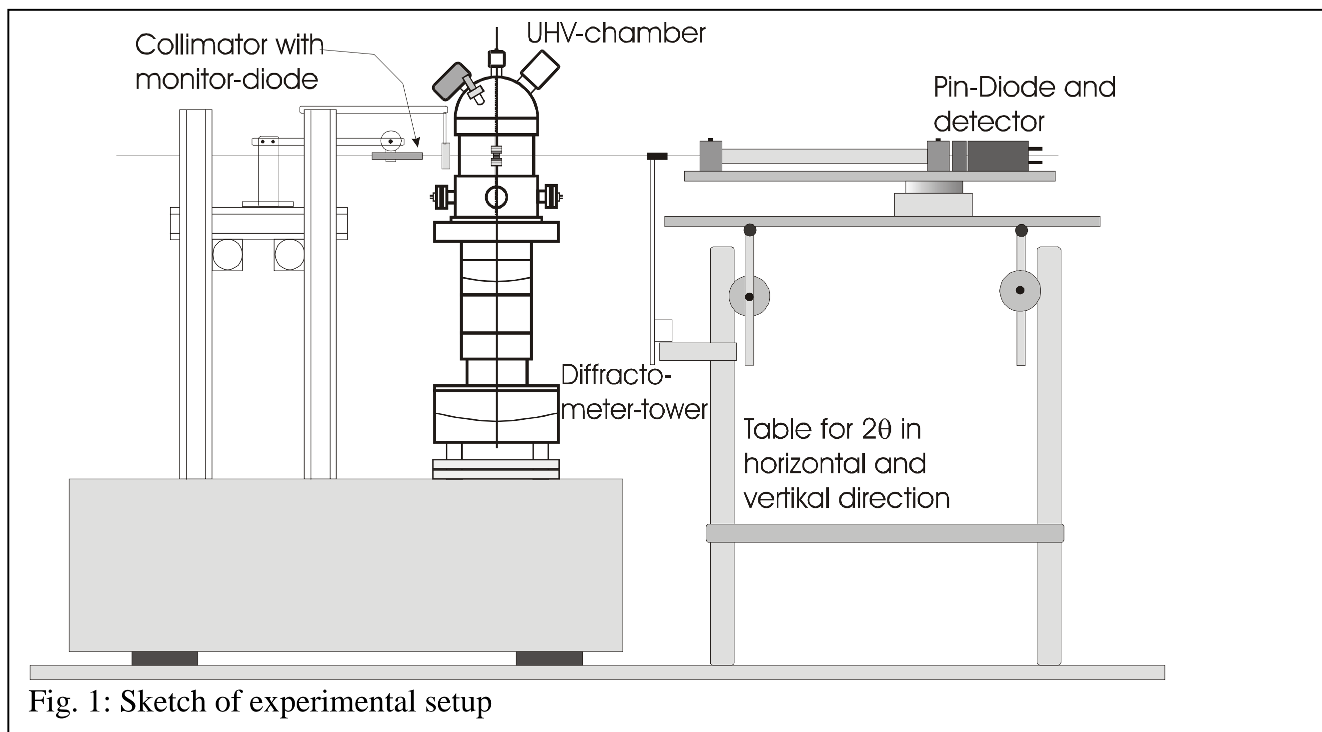

Fig. 1: Sketch of experimental setup

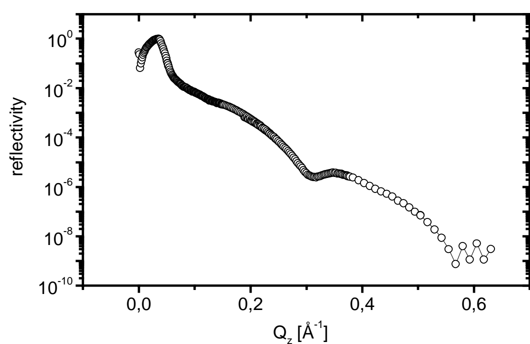

Fig.2 Reflectivity at the In(liq.)-Si(100) interface.

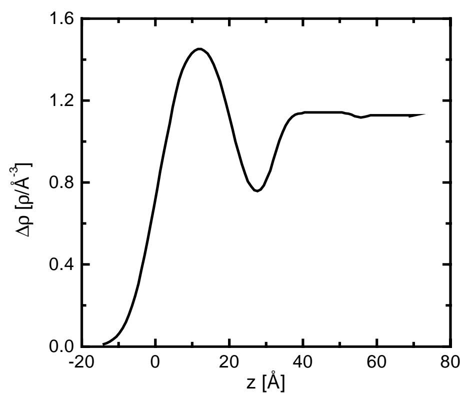

Fig.3 Electron density difference to the Si substrate.

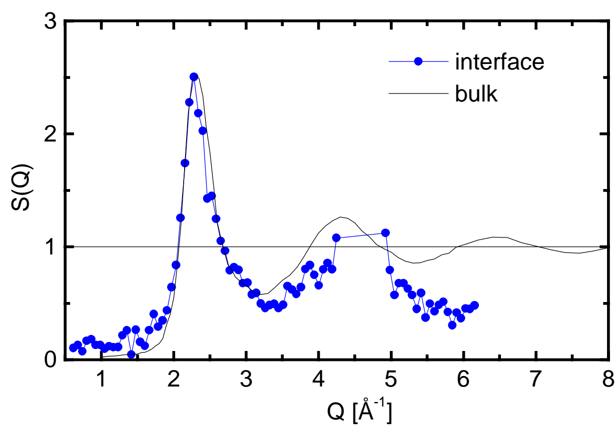

Fig.4 In-plane structure factor at the solid-liquid interface In(liq.)-Si(100).

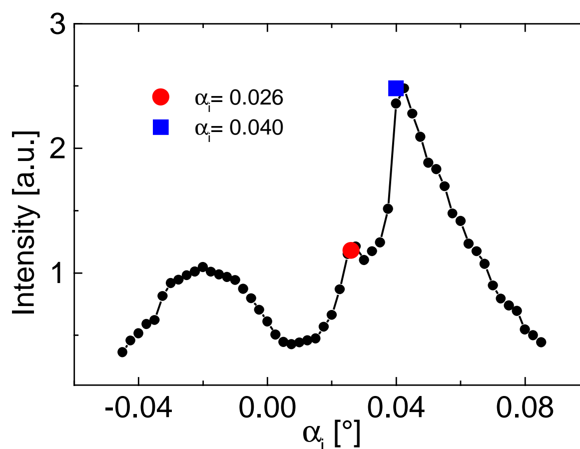

Fig.5 Incident angle scan at the first sharp diffraction peak of the structure factor of liquid lead.

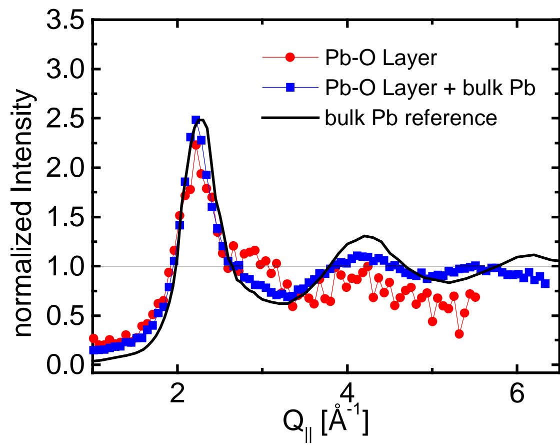

Fig.6 Measured in-plane structure factor at various incident angles.

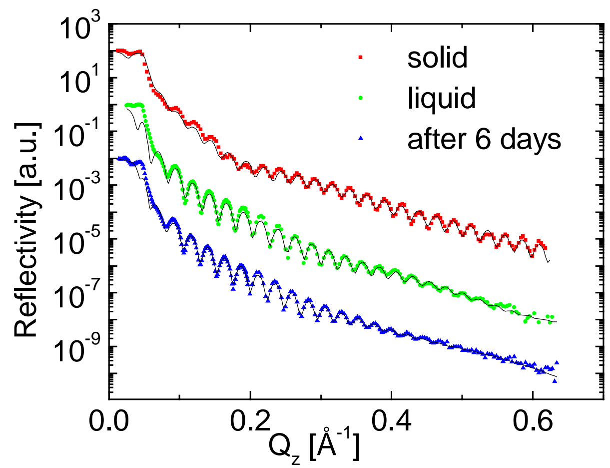

Fig.7 Reflectivity from an intermediate oxide layer

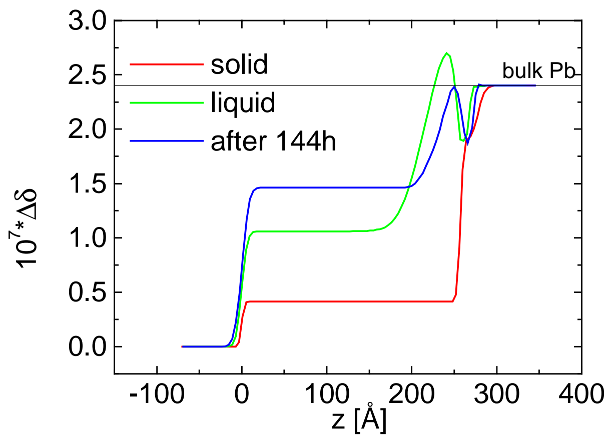

Fig.8 Electron density model for the reflectivity Shown in Fig.7