Evidence for Surface Relaxation and Surface Layering in Liquid Sn

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Introduction

Rice and coworkers [1] predicted that the atoms at the free surface of a liquid metal should be ordered, forming a nanoscale quasi-crystalline structure confined to the near-surface region between two disordered bulk phases of the vapor and the liquid. This surface layering phenomenon has been recently experimentally discovered for three high surface-tension metals: Hg [2], Ga [3], In [4] and the low-surface tension metal K [5]. The signature of layering in the x-ray reflectivity curve is the appearance of a quasi-Bragg peak arising from constructive interference of waves diffracted by the ordered surface layers.

In addition to surface layering we report evidence for surface relaxation in liquid Sn. Liquid Sn is the first monatomic liquid for which surface relaxation has been observed.

Results

The UHV chamber and the details of sample preparation procedure of the liquid metal sample have been described previously [4, 6-8]. Direct observation of surface structure of liquids is complicated by thermally excited capillary waves at the surface. However, recent development of theoretical and analytical treatment of capillary wave excitation spectrum made it possible to separate the structural properties of the surface from its dynamics [5, 7, 8]. Fig. 1 shows a resulting surface structure of liquid Sn obtained by applying this analysis to x-ray specular reflectivity measurements and x-ray off-specular diffuse scattering. The strong peak at 2.3 Å^{-1} is a signature of surface-induced layering found previously in Ga, In, K and Hg. The layering peak position and height are consistent with the standard "distorted crystal" layering model, however at 0.9 Å^{-1} data deviates from standard behavior in a form of low-angle shoulder, indicative of high-density surface structure.

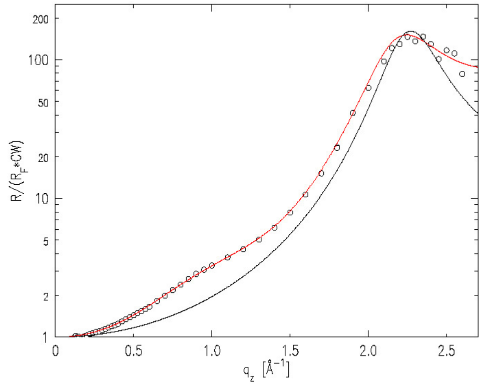

Fig. 1: The structure factor (squared) of the Sn surface as derived from the measured reflectivity (open circles). The black line describes the standard layering density model. Red line is a fit to the surface relaxation density model described in Fig. 2.

X-ray Grazing Incidence Fluorescence and Resonant X-ray Reflectivity measurements provide conclusive proof that this high-density feature is associated with packing of Sn atoms at the surface, rather than presence of impurities. Theoretical density model capable of explaining this anomalous surface structure calls for reduction of the spacing between the surface and the first sub-surface monolayers, reminiscent of a surface relaxation behavior regularly observed in crystalline surfaces. Electron density profile distribution normal to the liquid-vapor interface shown in Fig. 2 with solid line corresponds to surface structure fit shown with red line in Fig. 1. Theoretical density models which preserve regular spacing of standard layering model but introduce denser packing of atoms within the uppermost layers are not consistent with experimental results.

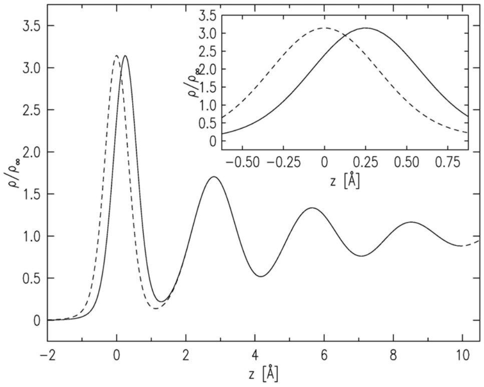

Fig. 2: Electron density profile of liquid Sn along surface normal z, showing the standard layering model (dashed line) and surface relaxation model (solid line) with 10% reduction in spacing between two uppermost surface layers. Inset shows the difference between models in greater detail.

Discussion

One of the possible reasons for the surface relaxation structure reported here is the strong Sn-Sn pairing observed previously in the bulk liquid phase [9, 10]. The reasons for relaxation are the same as in the case of solid crystalline surfaces: reduced number of near-neighbors for surface atoms requires anisotropic distribution of preferentially bulk-oriented bonds, resulting in a reduced spacing between surface and first sub-surface layers. Clearly, the origins of the observed increased surface density in liquid Sn warrants further investigation.

Acknowledgments

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