Atomic Layering Structure at the Surface of Liquid Sn

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Abstract

- We report X-ray measurements of liquid Sn which confirm the existence of atomic layering at the surface
- Deviation of the surface structure factor for liquid Sn from the standard layering model behavior (Ga, In, K, etc) can be explained by presence of high-density layer at the surface
- The high-density layer is an intrinsic property of Sn, rather than a result of contamination or oxidation at the surface

Introduction

•**Background**

-Surface-induced atomic layering is the formation of well-ordered atomic layers parallel to the surface of a bulk liquid. This results in an oscillatory surface-normal density profile, with an atom-sized period and a decay length into the bulk of a few atomic diameters.

-Atomic surface layering has been theoretically predicted to occur in liquid metals by S. Rice in 1974, and has been confirmed experimentally 20 years later in a number of liquid metals such as Hg, Ga, In, K and several binary liquid metal alloys. On the other hand studies by Chacon (2001) conclude that under the right conditions non-metallic liquids could also exhibit layering.

•**Our results:**

–We have studied the atomic layering structure of the surface of liquid Sn by the methods of X-ray reflectivity and diffuse scattering.

–By deconvolving the capillary wave contributions from the reflectivity measurements we were able to obtain the intrinsic surface structure factor for liquid Sn.

–The surface structure factor exhibits a peak at q_z^{peak} =2.3 Å^{-1} , indicating the presence of surface-induced layering in liquid Sn, similar to that found for other metallic liquids.

–The surface structure factor deviates at low q_z from a standard layering model. The deviation indicates the presence of a high-density layer at the surface.

•**Proof:**

–The high-density layer at the surface an intrinsic property of the liquid Sn and is not due to some Gibbs monolayer (i.e. Bi, Pb, etc) at the surface!

Figure 1: X-Ray Reflectivity Data

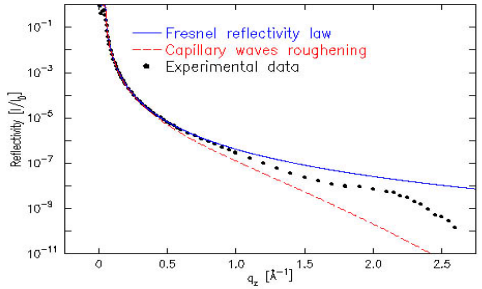

Fig. 1: A plot showing a raw reflectivity data (points), the Fresnel reflectivity curve that is expected for ideally flat surface (solid black line) and the Fresnel reflectivity convolved with thermally excited capillary wave contributions (dashed red line). The shallow, but distinct, quasi Bragg peak at ~2.2 Å^{-1} indicates the presence of surface-induced layering in Sn.

Figure 2: Structure Factor for Sn

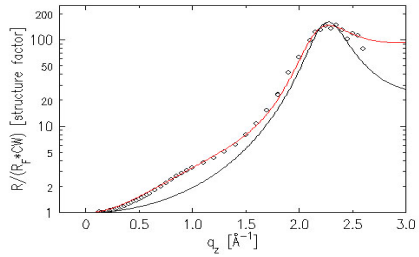

Fig. 2: Reflectivity normalized by Fresnel and capillary wave contributions (circles), also known as surface structure factor. The peak at q_z^{peak}=2.3 Å^{-1} corresponds to atomic layering feature with atomic spacing of Sn d = 2.8 Å ($q_z^{peak} \approx 2\pi/d$). The black line shows a fit to the standard layering model, with equally spaced atomic layers of the same density. Deviation from this model at q_z ~0.5-1.5 Å^{-1} indicates a more complicated surface structure. Red line shows a fit to the data assuming a high surface density model shown with red line in Fig. 3.

Figure 3: Density Profile

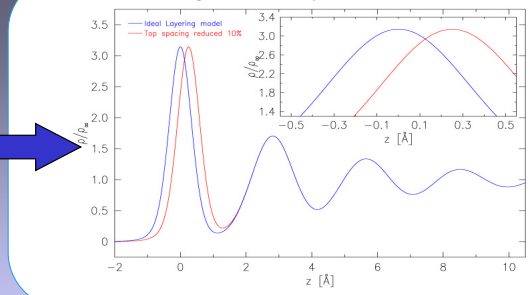

Fig 3: Surface-normal density profile ρ(z) describing the surface-induced layering, normalized to the bulk density value: Blue line corresponds to the standard layering model which assumes equidistant spacing and the same average density for each layer. Red line represents the model describing non-standard structure of liquid Sn – uppermost atomic layer is more densely packed, resulting in 10% reduction in the layering spacing (see red curve in Fig. 2). The rest of atomic layers are not affected.

Figure 4: Fluorescence Data

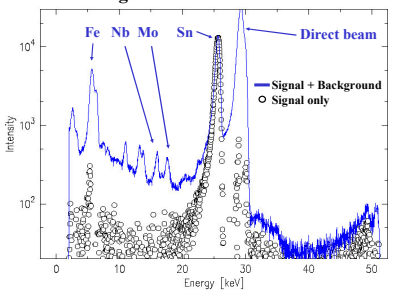

Fig. 4: Spectrum of x-ray induced fluorescence: before (solid line) and after (circles) background subtraction.

None of the non-Sn fluorescent peaks (Fe, Nb, Mo, etc.) in the raw data are present after background is subtracted.

The precision of this method would allows detection of a fraction of a monolayer at the surface.

Figure 5: Resonant Edge of Sn

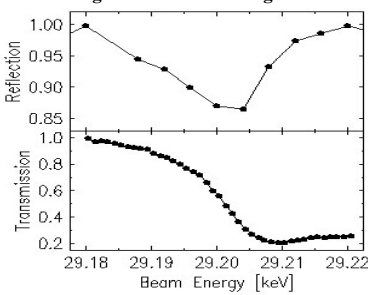

Fig. 5: Additional test for possible sample contaminants consists of scanning through the K-edge of liquid Sn.

Upper inset: effective reflectivity at 0.3 Å^{-1}, reduced by ~ 15% at the resonant energy (29.20 keV)

Lower inset: transmission through a Sn foil

Figure 6: Resonant Reflectivity

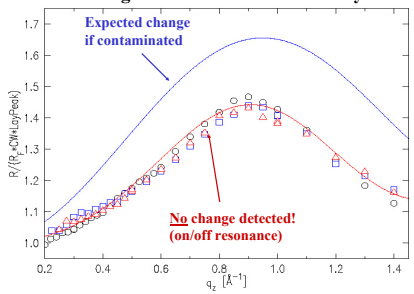

Fig. 6: Low-angle peak in the reflectivity at resonance energy edge (red triangles), compared to the reflectivity taken off-resonance (black circles, blue squares).

Red line: fit corresponding to density profile depicted in Fig. 3.

Blue line: simulation assuming the layer is anything other than Sn.

The reflectivity remains unchanged on- an off- resonance

Low-angle peak must be an intrinsic property of Sn!

Summary

- Surface induced atomic layering is confirmed for liquid Sn
- The reflectivity curve shows a fundamentally different layering from the standard layering structure found for other metals (Ga, In, K, etc)
- Energy-dispersive x-ray fluorescence and resonance x-ray reflectivity data confirm the absence of any foreign chemical species or contaminants at the surface, down to sub-monolayer quantities. This suggests that the higher-density layer is an intrinsic feature of liquid Sn
- The fitting indicates that the low-angle reflectivity feature is consistent with an uppermost atomic layer of Sn having a 10% shorter layer spacing than the bulk's first coordination sphere radius, resulting in a higher-than-average density at the surface

Acknowledgements

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