Atomic-Scale Surface Demixing in a Eutectic Liquid BiSn Alloy

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Atomic-Scale Surface Demixing in a Eutectic Liquid BiSn Alloy

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Resonant x-ray reflectivity of the surface of the liquid phase of the Bi43Sn57 eutectic alloy reveals atomic-scale demixing extending over three near-surface atomic layers. Because of the absence of an underlying atomic lattice which typically defines adsorption in crystalline alloys, studies of adsorption in liquid alloys provide unique insight on interatomic interactions at the surface. The observed composition modulation could be accounted for quantitatively by the Defay-Prigogine and Strohl-King multilayer extensions of the single-layer Gibbs model, revealing a near-surface domination of the attractive Bi-Sn interaction over the entropy.

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imaginary parts of the dispersion correction, and \( \mu(E) \) is the photoelectric absorption coefficient.

The effect of \( f'' \) on the analysis can be neglected and the changes in \( f' \) are significant only near an absorption edge. Figure 1(a) shows \( f''(E) \) near the Bi L3 edge as obtained from an absorption measurement in a Bi foil. Figure 1(b) is the corresponding \( f'(E) \), calculated from \( f''(E) \) using the Kramers-Kronig relation [17]. Both agree well with theory [18,19]. The composition dependence of \( \langle \rho(z) \rangle \) was obtained by fitting the measured XR by the distorted crystal (DC) model for a layered liquid surface [7,8]:

\[
\frac{\langle \rho(z) \rangle}{\rho_\infty} = \sum_{n=1}^{\infty} \frac{e^{-(z-n\delta_n)/\sigma_n^2}}{\sqrt{2\pi}\sigma_n^2/d} \left( 1 + \delta_n Z'_{Bi} - Z'_{Sn} \right) \frac{c_n}{c} \tag{3}
\]

The progressive increase in the Gaussian width parameter \( \sigma_n^2 = \sigma_0^2 + (n-1)\bar{\delta}^2 \) with increasing layer number \( n \) describes the layering amplitude’s decay below the surface [8]. The layer spacing \( d \) is kept constant in this model due to similarity in size between Bi and Sn atoms. The bulk’s average effective electron number per atom is \( Z'_{\infty} = x Z'_{Bi} + (1-x)Z'_{Sn} \) and \( \delta_n = x_n - x \) is the difference in the Bi fraction between the \( n \)th layer, \( x_n \), and the bulk, \( x \). The corresponding atomic densities, \( c_n \) and \( c \), are determined from the atomic volumes \( v_{Bi} \) and \( v_{Sn} \): \( c_n = \frac{v_{Bi}}{v_{Sn}^n} c + c_n (1-x_n)^n v_{Bi} + c_n (1-x_n)^n v_{Sn} = 1 \). The contrast, \( (Z'_{Bi} - Z'_{Sn})/Z'_{\infty} \), varies strongly near the edge due to the variation of \( Z'_{Bi} \) from 0.43 at \( E = 12.00 \) keV to 0.27 at \( E = 13.418 \) keV (right axis in Fig. 1). This is the basis for the resonant XR method which allows us to separate out the density profiles of the two species [4,15].

Figure 2 shows Fresnel-normalized XRds \( R(q_x)/R_F(q_z) \) measured near the Bi L3 edge at the four energies marked by triangles in Fig. 1(b). The dashed line is calculated from the DC model for a layered interface assuming a uniform composition \( \delta_n = 0 \). The strong enhancement of the measured \( R(q_x)/R_F(q_z) \) over this line, evidenced by the peak at \( q_z \approx 1.0 \) \( \text{Å}^{-1} \), and the strong energy dependence of the low-\( q_z \) reflectivity, clearly indicate a significant surface segregation of Bi, and its variation with \( z \).

Three fits of the data by the DC model, Eq. (3), were carried out, assuming that only one \( (\delta_1 \neq 0, \delta_{n=2} = 0) \), two \( (\delta_{1,2} \neq 0, \delta_{n=3} = 0) \), or three \( (\delta_{1,2,3} \neq 0, \delta_{n=4} = 0) \) surface layers deviate from the bulk composition. All fits employed \( d = 2.90 \) Å, \( \sigma_0 = 0.30 \) Å, and \( \bar{\sigma} = 0.57 \) Å, derived from the energy-independent position, shape and intensity of the layering peak at \( q_z = 2.0 \) \( \text{Å}^{-1} \). The measured \( R(q_x)/R_F(q_z) \) of all four energies were fitted simultaneously, using the experimentally determined \( f'(E) \).

Figure 2 exhibits an excellent agreement of the three-layer model (solid lines) with the measurements, but a very poor agreement for the one- and two-layer models (inset). Table I lists the best-fit values of \( x_n' \) and \( \delta_{n}^\text{fit} = x_n' - x \) and the corresponding 95\% nonlinear confidence intervals \( Y(x_n') \) and \( Y(\delta_{n}^\text{fit}) \) determined from a six-parameter support plane analysis [20]. The most striking result is the nonmonotonic deviation \( x_n' \) of Bi from the 43\% bulk value, showing an enhanced composition of 96\% and 53\% in the first and third layers, and depletion down to 25\% in the second layer (see Fig. 3). Beyond the third layer entropy effects dominate the Gibbs adsorption and the layer and bulk concentrations cannot be distinguished. While demixing has not been previously reported in liquid alloys, similar decaying oscillatory composition profiles were dis-

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**FIG. 1 (color online).** Dispersion corrections (a) \( f'(E) \) and (b) \( f''(E) \) of Bi near the L3 absorption edge at \( E_{L3} = 13.418 \) keV. The right scale of (b) is the electron density contrast \( \Delta Z' / Z'_{\infty} = (Z'_{Bi} - Z'_{Sn}) / Z'_{\infty} \).

**FIG. 2 (color online).** XR of a uniform-composition surface. Inset: The \( E = 12.00 \) keV measured \( R/R_F \) with fits by the three models discussed in the text (lines). Error bars are smaller than the symbols’ size.
However, assuming a regular solution behavior with corresponding surface concentrations, we now compare our experimental observations with theory. Guggenheim’s [22] application of Gibbs theory [1] to regular solutions assumes the surface segregation to be restricted to a single surface monolayer. Assuming p nearest neighbors for each bulk atom in a layered lattice model, l p are within, and m p are in the adjacent layers. For a close-packed lattice, for example, p = 12, l = 0.5, and m = 0.25. The surface tension of the regular solution, γ_{AB}, follows from those of the pure components, γ_A and γ_B, as [22]

\[
\gamma_{AB} = \gamma_B - \frac{kT}{a_B} \ln \left( \frac{1-x}{1-x'} \right) + \frac{\omega}{a_B} \left[ l x'^2 - (l + m) x^2 \right]
\]

\[
= \gamma_A + \frac{kT}{a_A} \ln \left( \frac{x'}{x} \right) + \frac{\omega}{a_A} \left[ l (1-x')^2 - (l + m) (1-x)^2 \right].
\]

(4)

Here, x and (1 – x) are the bulk concentrations of atoms A (Bi) and B (Sn), while x' ≠ x and (1 – x') are the corresponding surface concentrations, a_A and a_B are the two atomic areas, and ω = 2ω_{AB} - ω_{AA} - ω_{BB} is the interaction parameter, defined by the A-B, A-A, and B-B atomic interaction energies. Extrapolated down to T = 142°C, γ_{Bi} = 398 mN/m, and γ_{Sn} = 567 mN/m, while a_{Bi} and a_{Sn} are calculated from the atomic radii. r_{Bi} = 1.70 Å and r_{Sn} = 1.62 Å assuming hexagonal close packing [23]. Treating Bi_{43}Sn_{57} as a perfect solution (ω/kT = 0), the Gibbs theorem, Eq. (4), yields γ_{AB} = 444 mN/m and x' = 0.904, below the experimental value x'(Bi) in Table I. However, assuming a regular solution behavior with ω/kT = 1 yields γ_{AB} = 432 mN/m, and x' = 0.941, which agrees very well with the experimentally derived x'(Bi) in Table I. Both γ_{AB} agree well with experiment and theory [24]. Note that γ_{AB} and x' are only weakly dependent on ω/kT due primarily to the logarithmic functional behavior and large surface tension difference of the two components, a_{Sn}γ_{Sn} - a_{Bi}γ_{Bi} = 2kT. This introduces a large uncertainty of ω/kT calculated from measurements of surface tension or surface monolayer composition. Resonant XR measurements of subsurface layer composition therefore present a unique opportunity to probe the nature of atomic interactions at the surface.

In spite of the good agreement above, confining the surface excess to a single monolayer is correct for perfect solutions only, but not for our case of a regular solution, as Defay and Prigogine [25] point out. They provide a correction for regular solutions, where the surface excess extends over two layers, the γ_{AB} values above do not change significantly, and the layers’ δ_n are related by

\[
\ln \frac{1 + \delta_2/x}{1 - \delta_2/(1-x)} = \frac{2\omega}{kT} \delta_2 - \frac{2\omega m}{kT} (\delta_1 - 2\delta_2) = 0.
\]

(5)

Expanding Eq. (5) to first order in δ_2:

\[
\delta_2 = \frac{2\omega mx(1-x)\delta_1}{kT - 2\omega lx(1-x)}.
\]

(6)

For nearly perfect solutions (ω/kT ≪ 1) Eq. (5) yields a negligible δ_2: 0 < δ_2 ≪ δ_1. For ω/kT ≥ 1, however, δ_2 and δ_1 are of opposite signs and |δ_2| may become comparable to |δ_1|. This prediction is qualitatively consistent with the demixing observed here. For example, when ω/kT ≫ 1, Eq. (6) can be simplified further: δ_2 = -(m/l)δ_1. For Bi_{43}Sn_{57}, m/l = 0.5 and the Gibbs-predicted x'(Bi) = 0.90 (or δ_1 = 0.47) yields δ_2 = -0.23, δ_3 = 0.12, and δ_4 = -0.06 [26]. These values, shown as δ^DP in Table I, agree well with δ^FI obtained from the three-layer model fits. The smallest value of the interaction parameter ω/kT for which satisfactory agreement with

TABLE I. Density model parameters x'_n and δ^FI_n = x'_n - x_n, and confidence intervals Y(x'_n) and Y(δ^FI_n) obtained from the three-layer model fits compared to theoretical δ^DP_n and δ^SK_n derived from the Defay-Prigogine and Strohl-King models.

<table>
<thead>
<tr>
<th>n</th>
<th>x'_n (Bi)</th>
<th>Y(x'_n)</th>
<th>δ^FI_n</th>
<th>δ^DP_n</th>
<th>δ^SK_n</th>
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<tr>
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<td>0.53</td>
<td>[0.51, 0.56]</td>
<td>0.47</td>
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<tr>
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<tr>
<td>3</td>
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<td>[0.50, 0.56]</td>
<td>0.10</td>
<td>[0.07, 0.13]</td>
<td>0.12</td>
</tr>
<tr>
<td>4</td>
<td>0.43</td>
<td>[0.00, 0.01]</td>
<td>0.00</td>
<td>[0.00, 0.00]</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

FIG. 3 (color online). Electron density profiles as derived from the fits to the reflectivities shown in Fig. 2. Inset: the bulk-normalized differences in electron density of Bi and Sn, (ρ_{Bi} - ρ_{Sn})/ρ_m.
the Defay-Prigogine model could be obtained (by treating $m$ as an adjustable parameter) is $\omega/kT = 2.3$. Stroh and King [27] suggest a multilayer, multicomponent model, where no expansion is used, and $x_n$ are obtained iteratively, until convergence to a self-consistent composition profile is reached. A good agreement of this theory with our Bi-Sn measurements is obtained when $\omega/kT = 1.0$-1.7. Typical $\delta_n^{sk}$ values are listed in Table I. As observed, the Stroh-King model provides composition profiles very similar to those of the Defay-Prigogine model, albeit with slightly different $\delta_n$ values, thus supporting our overall conclusions.

Theoretically, $\omega$ and the enthalpy of mixing, $\Delta H_m$, are related by $\omega = \Delta H_m/\left[x(1-x)\right]$. In practice, however, bulk thermodynamic quantities were often found to yield inaccurate values for surface quantities. For example, organic [28] and metallic [29] mixtures exhibit significant disagreements between $\omega$ values derived empirically from surface tension measurements and from bulk caloriometry. For Bi-Sn, reported values of $\Delta H_m$ range from endothermic values of 80 to 140 J/mol [12] to an exothermic value of $-180$ J/mol [13]. These values lead to $\omega/kT > 0.2$, i.e., an almost perfect solution, and an insignificant $|\delta_2| < 0.01$. On the other hand, the value of $\omega/kT = 10$ that we previously found necessary to account for the observed 35% Bi concentration enrichment at the surface monolayer at the BiIn eutectic is of the same order of magnitude as the value we find necessary to account for the present observation of surface segregation in Bi-Sn. $\omega/kT = 1.0$–2.3. Unfortunately we do not have an explanation for the origin of the discrepancy in the values of $\omega/kT$ and this suggests an urgent need for both further theoretical studies of surface demixing as well as experimental investigations of similar effects in other binary alloys. In particular, the Bi-Sn system appears to be the only liquid alloy for which clear evidence for multilayer surface demixing has been found. The case for new studies is strongly reinforced by the existence of a growing class of surface-induced ordering phenomena that have been observed in metallic liquids. In addition to the surface demixing reported here, these include layering [7–11], relaxation [11], segregation [2–4,30], wetting transitions [14,31], and surface freezing [32]. Finally, there is a basic unresolved question of whether the surfaces of liquid metals are fundamentally different from those of nonmetallic liquids [33].

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[26] Equation (6) yields $\delta_3$ from $\delta_2$ and $\delta_4$ from $\delta_3$.


