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LETTER TO THE EDITOR

Interfacial wetting in a liquid binary alloy

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Abstract. We report the first study of interfacial wetting at the liquid–vapour surface of metallic gallium–bismuth alloys approaching the miscibility gap. Ellipsometry has been used to probe the interface continuously with increasing temperature along the coexistence curve. Below the monotectic (eutectic) temperature T_{mono} a liquid Ga-rich phase is in equilibrium with solid bismuth and the real part ϵ_1 of the complex dielectric function measured at the liquid surface clearly reflects Ga-like behaviour. Above T_{mono} the second liquid Bi-rich phase becomes stable and ϵ_1 changes from Ga-like to Bi-like behaviour. We conclude that the Bi-rich phase, which has the higher mass density, now covers the low-density phase. This can be consistently interpreted as complete wetting of the interface between the vapour and the Ga-rich phase by a coexisting Bi-rich layer.

Wetting phenomena and interfacial phase transitions are of growing interest in condensed matter physics. Since the time of Cahn's paper on *critical point wetting* [1] a variety of theoretical as well as experimental work has been published in this field [2–4]. However, in most cases only fluid systems whose intermolecular interactions are *not* governed by ionic or screened Coulomb forces have been considered. Although solid metal surfaces play some role as substrate materials the wetting behaviour of coulombic liquids such as molten salts or liquid metals is neither experimentally well established nor theoretically understood. This is rather surprising as alloys and their interfacial properties and wetting behaviour are of some technical importance. First experiments within the homogeneous series of the alkali metal–alkali halide systems have been reported: they show a growing trend of the fluid metals to be wetted by a salt-rich layer on going from the heavier (Cs–CsCl) to the lighter (Na–NaCl) systems [5, 6]. This trend is accompanied by a strong increase of the width of the miscibility gap in these systems [7] which reflects the sensitivity of thermodynamic behaviour to the gradual change of the intermolecular interactions in this series.

In order to study wetting phenomena of coulombic liquids and the interplay with bulk phase properties in more detail we have measured the complex dielectric function ϵ at the liquid–vapour interface of alloys using spectroscopic ellipsometry. The fluid gallium–bismuth system has been chosen for the following reasons: (i) it exhibits a miscibility gap with an upper critical point at 262 °C and a bismuth mole fraction $x_{Bi} = 0.3$ [8], (ii) the temperature range of melting points and critical point is experimentally easily accessible, (iii) the vapour pressure above the melt is low enough to probe the liquid–vapour interface and (iv), last but not least, the optical constants of the pure components are very different. This last point is particularly true for the real part ϵ_1 of the complex dielectric function below 2 eV in the infrared regime.

The ellipsometer that is used in this study is similar to that described by Stobie *et al* [9]. A polarized light beam hits the surface of interest at an angle of incidence ϕ_0 . The intensity

of the reflected light beam is modulated by a rotating polarizer, accumulated to obtain a suitable signal to noise ratio and finally Fourier transformed to determine the ellipsometric angles Ψ and Δ [10]. The complex dielectric function is then calculated within a simple two-phase model. As light sources, an Xe arc lamp and tunable lasers (Ti:sapphire and dye) have been employed which can be aligned to the ellipsometer using fibre optics. The principal arrangement of vacuum chamber, furnace and sample holder is demonstrated in figure 1. The alloy is heated in a molybdenum crucible with a resistance furnace in a UHV chamber. During the experiments a pressure of 10^{-6} Pa was achieved which was found to be sufficient to ensure no change of the optical constants within experimental errors over several days.

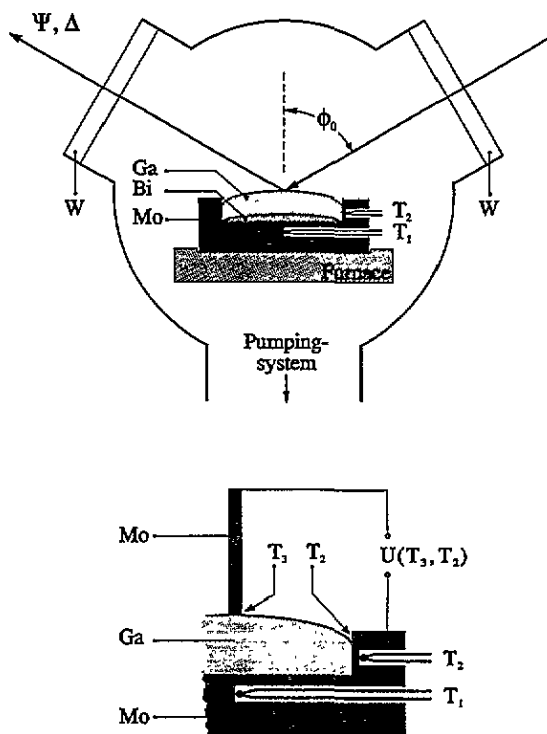


Figure 1. Top, a schematic drawing of the vacuum chamber, furnace, sample and reflection geometry of the ellipsometric experiment. ϕ_0 is the angle of incidence, Ψ and Δ ellipsometric parameters, W entrance and exit windows (quartz), T_1 and T_2 thermocouples measuring the temperatures T_1 and T_2 . Bottom, for temperature calibration at point T_3 the thermoelectric force $U(T_3, T_2)$ is measured. Under the experimental conditions we have a temperature gradient of $\Delta T = T_3 - T_2 \leq 3$ K.

Special attention was focused on the determination of the temperature in the bulk phase and at the liquid surface. Unfortunately, pyrometric methods for the absolute temperature determination are not suitable due to the poor black body characteristics of the liquid metal surface. As shown in figure 1, two thermocouples measure the temperature in the centre (T_1) and at the top edge (T_2) of the Mo crucible. Under the experimental conditions no significant difference between T_1 and T_2 was found but a gradient to the centre of the liquid surface (T_3) had to be considered. In order to quantify this a molybdenum rod was placed

in the centre of the liquid surface and the EMF of the following circuit was measured (see the lower part of figure 1): Mo (at 20 °C)–Mo|Ga (at T_2)–Ga|Mo (at T_3)–Mo (at 20 °C). The thermoelectric force $U(T_3, T_2)$ is given by the thermopowers of liquid gallium $S_{Ga}(T)$ [11] and of solid molybdenum $S_{Mo}(T)$ [12], respectively:

$$U(T_3, T_2) = \int_{T_2}^{T_3} S_{Mo}(T) dT + \int_{T_3}^{T_2} S_{Ga}(T) dT.$$

In the temperature range measured ($72\text{ °C} \leq T \leq 307\text{ °C}$) it was found that the temperature at the surface (T_3) was only a few kelvin below the temperature of the crucible (T_2). Additionally, the absolute values of T_1 and T_2 were calibrated when the ellipsometric experiment was finished and the sample was cooled down to room temperature: the monotectic point at 222 °C in the Ga–Bi phase diagram [8] was clearly visible as a plateau in the cooling curves.

All sample handling, the filling procedure and the mounting of the crucible in the UHV chamber were performed in an Ar glovebox ($\text{H}_2\text{O} < 1\text{ ppm}$, $\text{O}_2 < 2\text{ ppm}$). First bismuth (purity 99.9999%) was placed in the Mo cup and heated above the melting point to form a single flat drop at the bottom of the crucible. After solidifying it was covered with liquid gallium (purity 99.99999%) to make sure that ellipsometry measures the liquid Ga-rich phase at the top of the sample and not the solid precipitate. After connecting the chamber to the vacuum system and aligning it to the ellipsometer the spectra were recorded after equilibrating the sample at constant temperature. At each temperature step the composition of the liquid phase is given according to the phase diagram. The temperatures measured in two separate runs with overall compositions of $x_{Bi} = 0.085$ and $x_{Bi} = 0.28$ are indicated in figure 2.

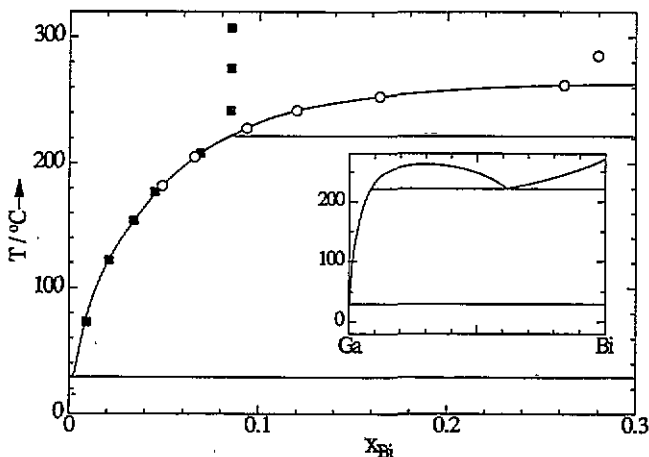


Figure 2. The Ga-rich part and a full (inset) representation of the Ga–Bi phase diagram [8]. Solid squares ($x_{Bi} = 0.085$) and open circles ($x_{Bi} = 0.28$) indicate the phase region where ellipsometric experiments were performed.

When adopting ellipsometry for the measurement of a liquid metal surface under vacuum conditions the following considerations have to be made. (i) Birefringence due to the mechanical stress of vacuum windows may influence the phase shift measurement Δ . Within one experimental run this was found to be constant but it has to be taken into account if

different experiments are compared (so far we are not able to calibrate this influence *in situ*). (ii) Mechanical shock sensitivity had to be minimized using pneumatic dampers to avoid surface waves. (iii) Even at a sample diameter of 30 mm the liquid surface is curved; this is shown nearly true to scale in figure 1. The reflected beam is slightly divergent and the intensity at the detector is reduced.

In the following we do not focus on the details of the measured spectroscopic properties of liquid Ga–Bi alloys [13]. Instead we consider here measurements of ε_1 at a certain energy (1.3 eV) as function of temperature and composition as a probe of the wetting behaviour. The main results for two samples measured at points in the phase diagram given in figure 2 are shown in figure 3: squares refer to a total composition $x_{Bi} = 0.085$, circles to $x_{Bi} = 0.28$ and numbers in figure 3 give the actual Bi content at coexistence of the liquid Ga-rich phase $x_{Bi,1}$. The sample with $x_{Bi} = 0.085$ has been measured at a solid angle of incidence $\phi_0 = 70^\circ$ and $\varepsilon_1(1.3 \text{ eV})$ was determined in two different ways. First, the subspectra in the Ti:sapphire regime ($1.20 \text{ eV} \leq \hbar\omega \leq 1.48 \text{ eV}$) were linearly interpolated to 1.3 eV taking the scattering of the datapoints in this energy range into account (solid squares in figure 3). The open symbols refer to Drude fits (free-electron model) to the whole spectral range. Below a temperature of 154 °C the error bars are larger due to the surface curvature which is reduced only at higher temperatures. The small error and the small systematic deviation of both evaluation procedures at 307 °C are remarkable! The data points may be represented by the solid line drawn in figure 3 and the temperature dependence of ε_1 is in very good agreement with that of pure Ga [14]. The main conclusion from this experiment is that within experimental error we do not observe any abrupt change of the optical properties on going from 72 °C to 307 °C for a total composition of $x_{Bi} = 0.085$.

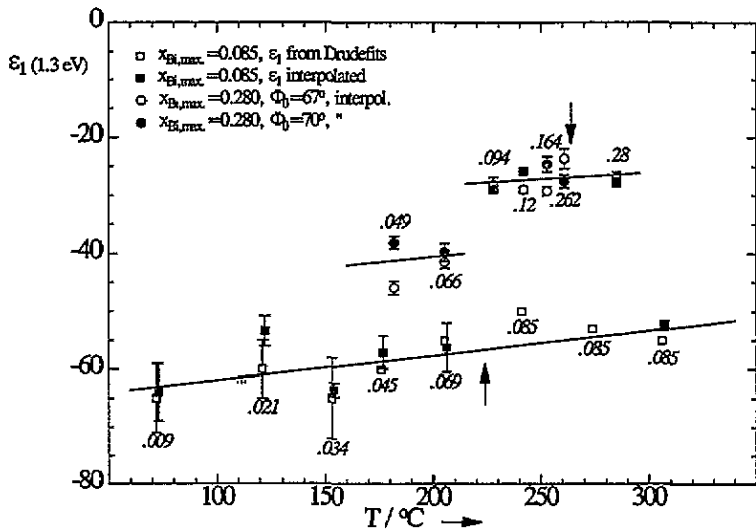


Figure 3. The real part of the dielectric function ε_1 at constant energy (1.3 eV) and as a function of temperature and composition. Squares refer to a total composition of $x_{Bi} = 0.085$, circles to $x_{Bi} = 0.28$. Solid and open symbols refer to different evaluation procedures or different angles of incidence (for details see text). The arrows indicate the temperature where the two samples reach the homogeneous phase.

The sample with $x_{Bi} = 0.28$ was measured at two different angles of incidence ($\phi_0 = 67^\circ$ (open circles) and $\phi_0 = 70^\circ$ (full circles)). Datapoints shown in figure 3 are calculated by

the interpolation method described above and the deviation between 70° and 67° gives a reasonable estimate for a realistic relative error of ε_1 . The absolute values at 182 °C and 205 °C show a significant offset compared to the values measured at $x_{Bi} = 0.085$. Careful data analysis revealed a birefringent contribution of the windows which was shown to be constant during one experimental run and evacuation period.

Taking this into account figure 3 clearly shows ε_1 increasing towards the value of pure bismuth ($\varepsilon_1 = -13.5$ at 1.3 eV and at 295 °C [15]) in the temperature range between 228 °C and 285 °C. The initial abrupt increase coincides with the monotectic temperature $T_{mono} = 222$ °C and the onset of the second liquid Bi-rich phase. The latter dominates the optical properties of the liquid surface for all higher temperatures. Since the Bi-rich phase has the higher mass density [16] this phenomenon only can occur if the contact angle between both phases is zero, which corresponds to complete interfacial wetting of the Ga-rich phase by the Bi-rich phase. Presumably the wetting transition between the completely wet state and the non-wet or partially wet state is not visible in this system due to the monotectic solidifying below 222 °C. To the best of our knowledge this is the first time that interfacial wetting has been observed in a metallic liquid binary alloy under thermodynamic equilibrium conditions along the coexistence curve. Grugel and Hellawell [17] as well as Perepetzko *et al* [18] have suggested that the Cahn mechanism should play an important role for the morphological structures of alloys solidified via a monotectic reaction. Perepetzko *et al* found solid Ga droplets wetted by a Bi-rich layer. These findings are consistent with our results on the optical properties of the surface of a demixed thermodynamically stable liquid.

A striking feature is the fact that the heavier phase intrudes between the lighter phase and the vapour since the density differs considerably: $\rho = 6.3$ g cm⁻³ at $x_{Bi} = 0.1$; $\rho = 8.8$ g cm⁻³ at $x_{Bi} = 0.6$ [16]. The thickness of gravitationally thinned layers was first experimentally studied and discussed in terms of existing theoretical predictions for van der Waals systems by Kwon *et al* [19]. For the thickness and its height dependence of wetting films in metallic systems no such theoretical predictions exists. If our experimental results are analysed within a Drude slab model (substrate–film–ambient medium) consisting of pure gallium as substrate and of pure bismuth as film we conclude that our data are consistent with 50 Å as a lower-limit estimate for the film thickness. In the gallium–bismuth system the phase with the higher mass density is the phase with the lower number density and contains the more volatile component to a much larger extent [20]. This obviously is a situation that favours wetting [2]. The results of Perepetzko *et al* indicate that this mechanism cannot be the only driving force towards wetting since their experiments were not performed in equilibrium with the corresponding vapour phase but in an inert carrier fluid. The specific character of the screened Coulomb (metallic) interactions obviously plays an important role.

In summary, we have measured the complex dielectric function by ellipsometry in the IR/VIS optical range of gallium–bismuth alloys at the liquid–vapour interface at two-phase coexistence. The data in the liquid–liquid demixing regime clearly indicate that an interfacial wetting transition must occur near the monotectic triple point. This is consistent with first observations at the fluid–wall interface in these alloys obtained in an experiment using second-harmonic generation (SHG) as an interface sensitive tool [21].

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