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INTERFACE SCIENCE

Phase transitions in wetting films at the surface of Ga–Pb alloys

**Cyril Calmes · Donatella Giuranno ·
Dominique Chatain**

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Abstract Surface phase transitions at Ga-rich liquid surfaces have been investigated in Ga–Pb alloys with low lead content. In the region of the liquid–liquid miscibility gap, the Pb-rich liquid phase completely wets the surface of the Ga-rich phase at coexistence. Observations have been made of demixing and solidification of the Pb-rich liquid film. Ga-rich alloys, which are single-phase below the monotectic temperature, can be undercooled below the liquidus, as far as the metastable binodal line where the Pb-rich wetting liquid film forms and solidifies into thin {111} Pb crystals. These films completely redissolve upon reheating to the liquidus temperature. Freezing occurs at surfaces because of complete wetting of the liquid rich in the high melting point component and the hysteretic character of the solidification transformation. Such "surface" experiments allow assessment of the stable and metastable liquidus lines of the Ga–Pb phase diagram in the vicinity of the monotectic temperature.

Introduction

This paper aims to describe the phase transitions which occur at the surface of Ga-rich Ga–Pb alloys, at compositions in the vicinity of the Ga-rich end of the monotectic line. Liquid phase separation and solidification-melting are reported, and discussed in the context of bulk and surface phase transitions.

The physical origin of wetting films in systems with a liquid miscibility gap has been given by Cahn [1] in his seminal paper on critical wetting. Complete wetting of one liquid phase by the other takes place above a so-called wetting temperature, T_w, and up to the critical temperature of the gap. In the Ga–Pb system, the Pb-rich liquid completely wets the Ga-rich liquid surface in the whole range of temperature where the two liquids coexist [2, 3]. In addition, complete wetting extends well below the melting point of Ga, in a temperature range where the miscibility gap is metastable [4].

The thickness of the Pb-rich wetting film in equilibrium with the Ga-rich liquid is an open question. It is obviously limited by gravity because Pb is denser than Ga. In organic monotectic systems, attempts were made to use gravity forces in order to assess the range of the interactions that control the thickness of the wetting film [5]. Difficulties in equilibrating the wetting film prevented to draw general conclusions. Ga–Pb is a metallic system in which the interactions are short range. While the theory predicts that the thickness of the Pb-rich wetting film logarithmically thins with the height of the Ga-rich liquid, there is no indication on the absolute thickness of such a film. In the case of Ga–Pb alloys, we have found by Auger analysis, that the Pb-rich liquid film at stable and/or metastable coexistence with the Ga-rich liquid is thicker than 10–14 monolayers for both millimeter and micron-sized Ga-rich

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C. Calmes · D. Giuranno · D. Chatain (✉)
CNRS, Aix-Marseille University, CINAM-UPR3118, campus de Luminy, 13288 Marseille, France
e-mail: chatain@cinam.univ-mrs.fr

Present Address:
C. Calmes
Centre Microélectronique de Provence Georges Charpak, Ecole Nationale Supérieure des Mines de Saint Etienne, 880 route de Mimet, 13541 Gardanne, France

Present Address:
D. Giuranno
Istituto per l'Energetica e le Interfasi - CNR, Via de Marini, 6, 16149 Genoa, Italy

drops [2]. However, the actual thickness of the wetting film at coexistence could not be measured because the detection limit of the Auger in Ga–Pb has been reached [2].

Before addressing the phase transitions in the Pb-rich liquid wetting film, it is necessary to present all the available data on the phase diagram of Ga–Pb and the location of the prewetting line related to the complete wetting transition. The assessed phase diagram of Ga–Pb is shown in Fig. 1a [6]. Figure 1b shows the details of the Ga-rich side of the phase diagram, with the Pb atom fraction shown on a logarithmic scale. The liquidus, as well as both the stable and metastable binodal lines displayed in this figure, have been calculated using the compiled thermodynamic data of ref. [6]. Freezing at the surface of Ga-rich Ga–Pb alloys with low Pb contents was observed in a series of experiments aimed at measuring the surface energy of Ga–Pb liquids as a function of Pb chemical potential [7]. The experimental results, reported in Fig. 1b, show that the freezing temperatures of the alloys are actually located either on the metastable binodal line of the phase diagram, i.e., below the liquidus line, or at the monotectic (585.5 K) for the alloys which composition lies inside the miscibility gap. At the time when these experiments were performed, the freezing of Pb at the surface was assumed to occur at the liquidus line. However, that conclusion was incorrect as it will be discussed below, and was due to the omission of measurements of the Pb remelting temperature. One aim of this article is to redo some of these experiments to check the location of the liquidus and the binodal lines of Ga–Pb.

The prewetting line (Fig. 1b) associated with the wetting transition, which emerges from the metastable liquid miscibility gap at T_w, has been determined by two methods: measurement of the surface compositional transition by Auger analysis [4] and measurements of the surface energy of in situ prepared alloys by the sessile drop method [7]. The Pb atom fraction of the investigated alloys ranges between 5×10^{-6} and 1.5×10^{-2}. These compositions are accurate within 30% for the most dilute alloys [4] and 20% for the others [7]. The Auger experiments performed on small droplets have allowed the investigation of undercooled alloys well below the eutectic temperature (302 K): complete wetting of the metastable Ga-rich liquid extends at least down to 240 K, i.e., well below the melting point of Ga [4].

Both stable and metastable Ga-rich alloys with compositions lying between the prewetting and the binodal lines have surfaces that are enriched in Pb [2]. The thickness of the Pb-rich film is of the order of one monolayer until the Ga-rich liquid composition approaches the binodal line. The Pb-rich film thickness diverges logarithmically, because the interactions between Ga and Pb are short range [1, 2].

Experimental

Two types of Ga-rich liquid samples were investigated: (1) axisymmetric Ga-rich sessile drops with Pb contents either above or below the Ga-rich end of the monotectic line (1.6 at.% Pb [6]), and (2) Ga-rich alloys equilibrated in contact with solid Pb, at different temperatures below the monotectic temperature, T_{mono}.

Figure 2 displays a sketch of the experimental chamber that was originally designed to perform sessile drop surface energy measurements of Ga–Pb alloys [7]. All the Ga–Pb alloys were prepared in situ from 99.9999% pure Pb and 99.999% pure Ga from home-made syringes in this versatile ultrahigh-vacuum chamber (base pressure 4×10^{-7} Pa) to

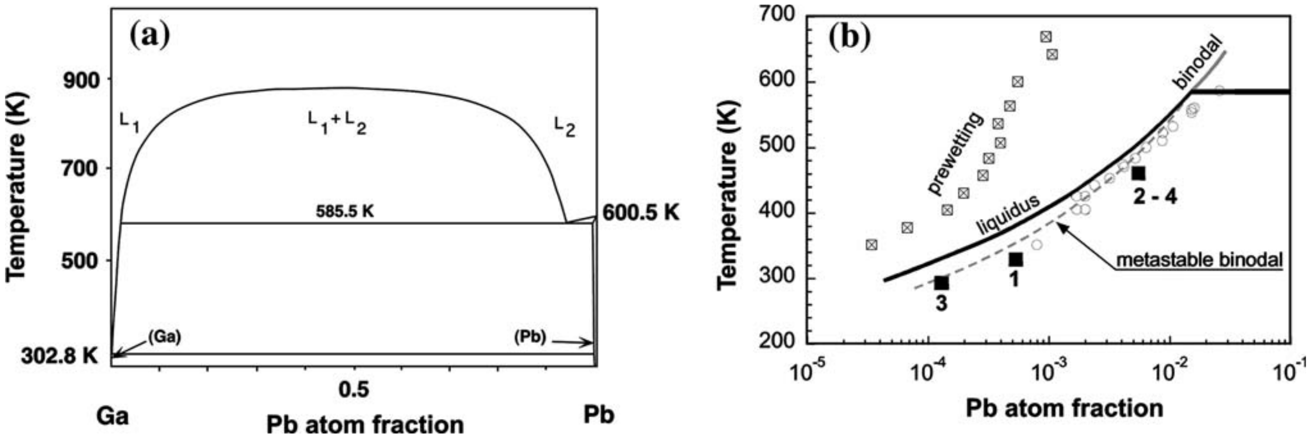

Fig. 1 **a** Ga–Pb phase diagram [6]. **b** Ga-rich side of the Ga–Pb phase diagram in the vicinity of the monotectic temperature showing the liquidus, the metastable binodal, and the prewetting lines (*crossed squares*). The Pb atom fraction is on a logarithmic scale. *Circles* are freezing temperature of the alloys investigated for surface energy measurements [7]. *Squares and numbers* refer to the previous surface freezing temperatures reported in literature, as described in the Discussion section

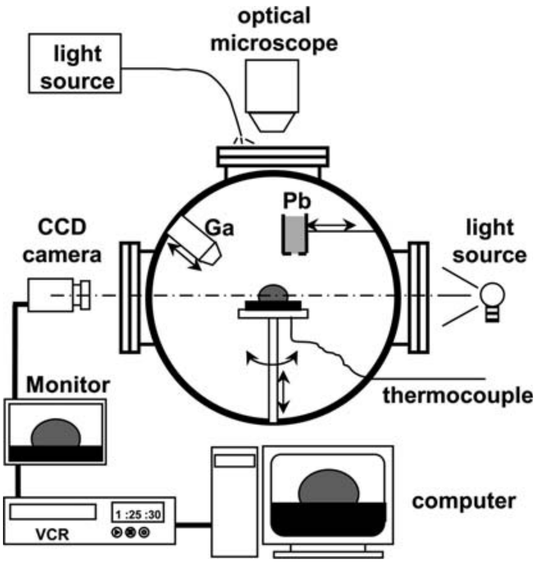

Fig. 2 Schematic diagram of the UHV chamber in which the experiments were performed

produce oxide-free surfaces [7]. The phase transitions that take place at the sample surfaces were observed in situ by optical means, through three windows.

The samples, which consist of millimeter drops on a horizontal substrate, can be positioned in the middle of the chamber between the side (vertical) windows and observed with a CCD camera connected to a video recorder and a computer. Alternatively, they can be raised close to the top window and observed with an optical microscope at a magnification of ×50.

Pure and alloyed drops were prepared in situ on a vitreous carbon platelet (20 × 20 × 2 mm^3) attached to a heating stage with tantalum clips. The heating stage is a 2.5-mm diameter graphite resistor (20 Ω) embedded in pyrolytic boron nitride, connected to a power supply with a 0.01-V resolution. Temperature monitoring and measurement are critical issues. In the temperature range used in this study (350–620 K), temperature can be varied by 1 K (±0.2 K) by varying the power supply voltage by 0.05 V. A chromel–alumel thermocouple in contact with the back side of the heating stage is used to measure the temperature. It is calibrated at the melting point of a pure Pb drop sitting at one end of the substrate. The actual temperature of the sample is determined from the departure of the measured temperature from the Pb melting point. This calibration is repeated after each change of the substrate position (tilt or rotation).

The volume and surface area of an axisymmetric drop can be calculated from its shadow profile, using NIH image analysis software [8]. The accuracy of these measurements is 5 and 2.5%, respectively. The compositions of the alloyed drops prepared by merging a pure Pb drop and a pure Ga drop can be determined from the volumes of the pure drops measured at the Pb melting point, where the density of Pb and Ga are 10.665 and 5.901 g/cm^3, respectively.

Results

For the sake of clarity, the experimental results are organized in two sections. In the first section, we report the morphological changes which take place during phase transformations in the Pb-rich wetting film located at the surface of the Ga-rich liquid phase, such as demixing and monotectic solidification. In the second section, the melting and freezing temperatures of the wetting Pb-rich film are presented and compared with the bulk transitions in the Ga–Pb phase diagram.

Morphology and phase transition in the Pb-rich wetting film

Demixing in two-phase drops

According to the phase diagram [6], equilibrated Ga-rich alloys containing more than 1.6 at.% of Pb (the composition of the Ga-rich end of the monotectic line) consist of a single liquid solution above the highest coexistence temperature on the liquid–liquid binodal, $T^{\max}_{\text{Liq–Liq}}$, and of coexisting Ga-rich and Pb-rich liquid solutions between $T^{\max}_{\text{Liq–Liq}}$ and the monotectic temperature T_{mono} (585.5 K). Between $T^{\max}_{\text{Liq–Liq}}$ and T_{mono}, in a two-phase sessile drop at equilibrium, the Pb-rich liquid partitions itself between the drop surface (because of complete wetting of the Ga-rich phase) and the drop bottom (because of gravity) [3], so as to encapsulate the drop. Here it is useful to stress that the thickness of the wetting film at the top of the drop depends on the height of the encapsulated Ga-rich liquid but not on the volume fraction of the Pb-rich liquid. When the temperature of a two-phase liquid drop equilibrated just below $T^{\max}_{\text{Liq–Liq}}$ is further lowered to a temperature that still lies above T_{mono}, a secondary liquid–liquid demixing occurs in each of the two coexisting phases, due to the changing mutual solubilities of Ga and Pb. Such secondary liquid demixing has been observed previously in the Co–Cu system [9].

Figure 3 shows pictures of an encapsulated Ga-rich drop after a small temperature decrease within the two-phase liquid domain, as seen from a side view using the CCD camera equipped with a zoom lens (Fig. 3a), and from a top view using the optical microscope (Fig. 3b, c). The original Pb-rich liquid volume fraction of this sample, about 10%, has partitioned itself between the thin wetting film and the very bottom of the two-phase drop. Upon secondary demixing, small droplets of the Pb-rich phase form within the bulk Ga-rich liquid, and similarly, small

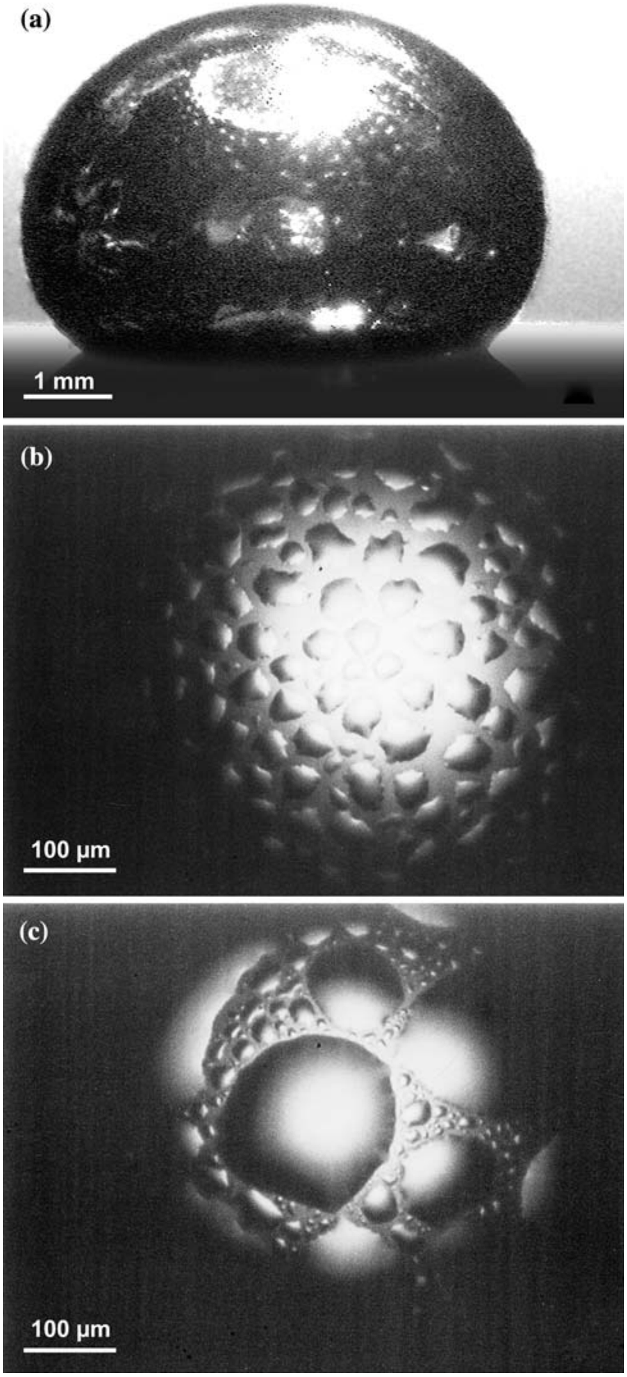

Fig. 3 Images of the rough surface of a Ga-rich drop with a large Pb content close to the monotectic temperature. **a** Lateral view of the appearance of the rough surface. **b** Optical microscope top view of the small drops of Ga-rich phase trapped inside the wetting Pb-rich film. **c** Same view of the Ga-rich drops which display some coalescence after 30 min

Ga-rich droplets nucleate and grow within the liquid Pb-rich film, as illustrated schematically in Fig. 4. The secondary demixing in the Pb-rich film produces a macroscopic roughening of the two-phase liquid drop surface (see Fig. 3). Just after the temperature decrease, many small blisters (corresponding to embedded Ga-rich droplets) appear and rapidly grow within the Pb-rich film (Fig. 3a, b). Long durations are required for the small blisters to merge into larger ones (Fig. 3c). Shaking of the sample accelerates coalescence of the blisters. However, the droplets trapped inside the Pb-rich film remain almost immobile and do not coalesce with the main Ga-rich drop underneath.

Two factors can contribute to the observed behavior of the Ga-rich drops trapped in the Pb-rich film: (1) buoyancy forces which drive the Ga-rich droplets toward the surface of the Pb-rich film, away from the main Ga-rich drop; and (2) coalescence of two trapped Ga-rich drops can only proceed by drainage of the Pb-rich layer which separates them, but drainage is impeded by an energy barrier associated with the compression of the composition gradients between the two liquid–liquid interfaces [10]. Some of the observed growth of the Ga-rich droplets with time could be the result of coarsening by Ostwald ripening.

Inside the main Ga-rich liquid, the Pb-rich droplets formed by demixing probably sink to the bottom of the drop, because of gravity and coalesce within the Pb-rich bulk phase there.

Solidification in two-phase drops

When the temperature of a Ga-rich drop encapsulated by a Pb-rich liquid film is lowered down to T_{mono}, the film undergoes monotectic solidification. As explained in the previous section, the surface of the two-phase drop first roughens. At T_{mono}, Pb solidifies in the liquid film that encapsulates the Ga-rich liquid and in the bulk Pb-rich liquid phase located at the bottom of the drop. These two successive phase transitions, demixing into two liquids, followed by solidification of Pb at T_{mono}, were observed for drops with Pb atom fractions $X_{\text{Pb}} = 1.8 \times 10^{-2} \pm 1.7 \times 10^{-3}$ and $1.5 \times 10^{-2} \pm 1.4 \times 10^{-3}$.

After decreasing the temperature of a two-phase drop, equilibrated just above T_{mono}, the monotectic transformation takes place within a homogeneous Pb-rich liquid wetting film. According to the phase diagram, the liquid of monotectic composition transforms into a Pb-rich solid and a Ga-rich liquid. Through the side windows, we observe that solidification of the Pb-rich solid starts at the bottom of the drop in the Pb-rich phase and propagates at its surface. A few large platelets of Pb grow toward the top of the Ga-rich drop and eventually cover the whole sample surface. Using the optical microscope we could follow in situ the last moments of the phase transformation at the top of the drop, thanks to a large contrast between the solid Pb and the Ga-rich liquid. As the Pb crystal grows, the other product of the monotectic transformation, consisting of a

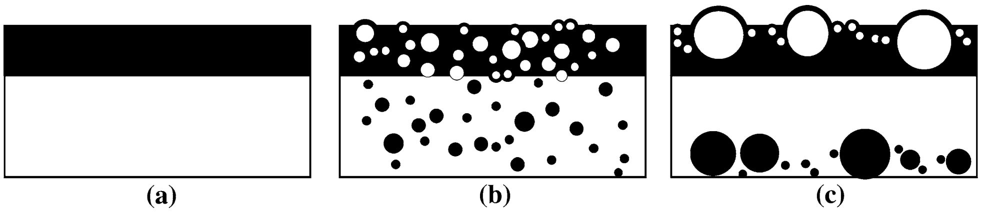

Fig. 4 Schematic diagram of the wetting Pb-rich layer on the coexisting Ga-rich phase after secondary demixing **a** the Pb-rich phase completely wets the Ga-rich one, **b** nucleation of Ga-rich (resp. Pb-rich) droplets in the film (resp. in the Ga-rich bulk), **c** coalescence of the Ga-rich droplets and sinking of the Pb-rich ones

few small Ga-rich droplets, is also seen to form. In situ optical microscope images of two Pb crystals approaching each other at the top of the drop are displayed in Fig. 5a, b. Figure 5b also shows the expected Ga-rich phase, which takes the form of strings of liquid inclusions. The Pb-rich crystals can be partially redissolved by raising the temperature slightly; a subsequent temperature decrease produces the regrowth of the left-over Pb crystal seeds into either almost hexagonal crystals or triangular dendrites, as shown in Fig. 5c. We conclude that the Pb crystals grown from the Pb-rich liquid film have their surface parallel to a {111} orientation. This is consistent with the recent STM investigation of Pb crystals grown at the surface of a Ga-rich liquid [11].

A partially frozen two-phase sessile drop was observed in a scanning electron microscope. The Ga-rich liquid which supports the solid Pb film did not solidify at room temperature. In Fig. 6, Pb appears in light gray and Ga is dark: the secondary electron contrast of Pb and Ga is the reverse of that of the optical images of Fig. 5. The low-magnification image shows the sessile drop wrapped by about ten thin Pb crystals. During the transfer of the sample to the electron microscope, parts of the Pb crystals at the top of the drop have sunk into the Ga-rich liquid underneath. This explains the dark Ga region at the top of the drop. The intermediate magnification image shows the boundaries between the individual Pb crystals, and the parallel strings of Ga-rich inclusions trapped within them. The highest magnification image shows that the shape of a Ga-rich inclusion in the Pb crystal has a threefold symmetry with three flat edges separated by three rounded ones. Because of the rapid diffusion of Pb in the Ga-rich liquid at a temperature close to the Pb melting point, the long string holes in the Pb crystal undergo Plateau-Rayleigh instability. The shape of the resulting inclusions seen in the largest magnification picture may be close to the equilibrium shape of a Ga-rich drop embedded in a thin Pb crystal. To the best of our knowledge, there is no literature data on those equilibrium shapes.

Ten micrometer sessile drops containing >70% of Pb were investigated in a previous experiment performed in a scanning Auger microscope. Upon cooling, the Pb-rich liquid wetting phase was observed to freeze into one single-crystal around the Ga-rich liquid core, and some of the Ga-rich liquid stemming from the monotectic transformation was randomly distributed on the Pb surface in the shape of droplets [12]. This suggests that the Pb-rich wetting film is thick at the scale of the drop.

Melting and freezing temperatures of one-phase and two-phase alloys

Alloyed-drop experiments

Phase transitions were first investigated in six alloyed drops, with Pb atom fractions ranging from 5.4×10^{-3} to 1.8×10^{-2} (±9.5%). Composition accuracy is limited by the precision of the measurement of the Pb drop volume, which is much smaller than that of the Ga drop for the alloys with a Pb content in the range used in these experiments. The alloyed drops were cycled in temperature, and optical observations were performed to check the reproducibility of the phase transitions taking place at the surface. The results are reported in Table 1 and plotted in Fig. 7.

The alloyed drops with Pb atom fractions of 1.5×10^{-2} and 1.8×10^{-2} were homogenized above T_{mono}, as explained in the previous section. Within experimental uncertainty, their Pb contents are a little higher than the Ga-rich end of the monotectic line (1.6 at.% Pb), consistent with the optimized Ga–Pb phase diagram [6]. Demixing occurs in the vicinity of the binodal temperature (i.e., the surface roughens as shown in Fig. 3a). This is followed by surface solidification of Pb at T_{mono} for both of the alloyed drops.

The four other alloyed drops contained Pb atom fractions are ranging from 5.4×10^{-3} to 1.05×10^{-2}. At these compositions, as the melt is cooled from the homogeneous liquid solution domain, the liquidus line is crossed first, with solid Pb expected to form upon cooling below the liquidus. Pb solidification is indeed observed; it occurs at the surface, with freezing taking place from the bottom of the drop to the top. Upon reheating, the solid Pb film at the surface is observed to be completely remelted at a reproducibly higher temperature than the first appearance of the solid on cooling.

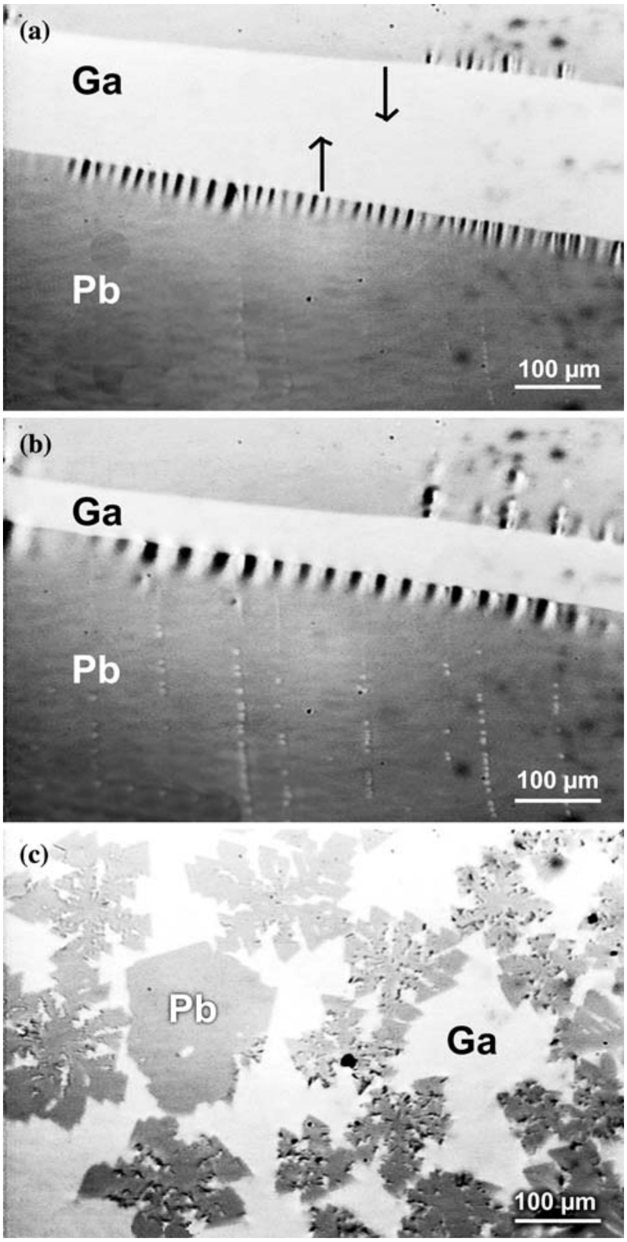

Fig. 5 Optical microscope images of the Ga-rich drop surface during in situ Pb solidification; solid Pb is darker than liquid Ga. **a**, **b** Two single crystals are slowly growing toward each other and contain strings of trapped Ga-rich liquid inclusions. About 10 s separate the two images (**a**) and (**b**). The wrinkles at the edges of the Pb crystals are due to the strain within the solid Pb platelet induced by the curvature of the drop. **c** Microstructure of rapidly regrown Pb seed crystals: most of them have dendrites made up of triangular crystals of Pb; one of them is an almost completely hexagonal crystal

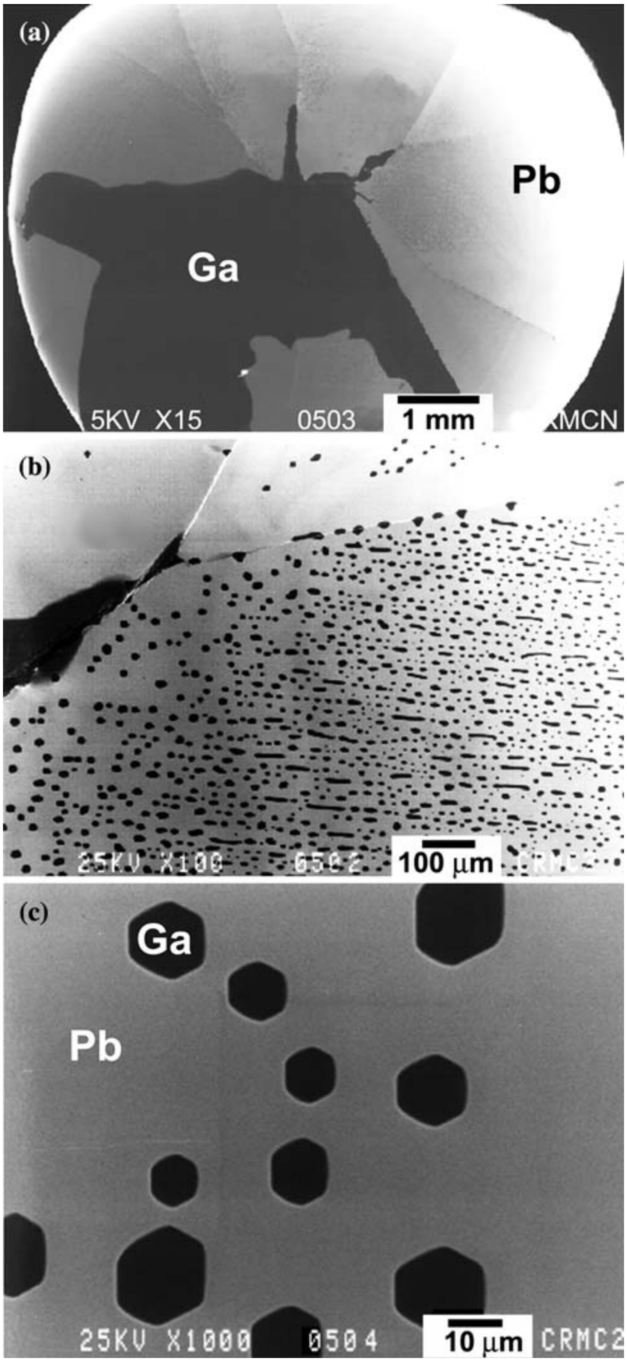

Fig. 6 Secondary electron images of a two-phase drop surface after Pb solidification. **a** The Ga-rich drop is wrapped by about ten Pb crystals. **b** Details of the junction of three Pb grains, with trapped Ga-rich inclusions. **c** Threefold symmetry of the Ga-rich inclusion

To explain these observations we propose the following sequence of events. As the liquid is cooled below the liquidus, nucleation of solid Pb from these alloys that are very dilute in Pb is suppressed. However, as the liquid composition reaches the metastable liquid–liquid binodal line, demixing occurs in conjunction with complete wetting, and the metastable liquid drop becomes encapsulated in a Pb-rich liquid surface film. Nucleation of solid Pb from this highly Pb-enriched layer occurs at much higher frequencies than from the homogeneous dilute solution. Nucleation of the solid Pb at the surface involves the creation of the solid/vapor Pb interface (560 mJ m^{-2} at the Pb melting point

Table 1 Results for the alloyed drops

X_{Pb} (at) (±9.5%)	m_{Ga} (g) (±5%)	m_{Pb} (g) (±5%)	$T_{Liq/Liq}$ (K) (±1 K)	$T_{Liq/Sol}$ (K) (±1 K)	Surface area (cm^2)	Pb thickness (μm)
5.4×10^{-3}	0.983	0.0157	493	504	0.98	3.0
5.7×10^{-3}	0.922	0.0157	495	502	0.96	3.1
1×10^{-2}	0.398	0.0120	526	536	0.53	2.1
1.05×10^{-2}	0.949	0.0300	547	554	0.78	2.3
1.5×10^{-2}	0.684	0.0311	598	587	0.65	–
1.8×10^{-2}	0.569	0.0311	610	586	0.55	–

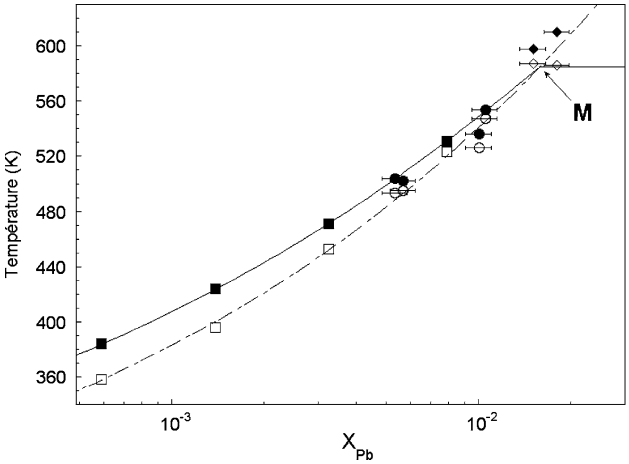

Fig. 7 Phase transitions of the Ga-rich drops. The *full and dashed lines* represent the liquidus and the metastable binodal lines, respectively, calculated from the study of Ansara and Ajersch [6]. The *filled circles* correspond to complete melting temperatures of the alloyed drops and the *open circles* indicate the "surface" freezing temperatures. For alloys with X_{Pb} higher than 1.5 at.% Pb, the *filled diamonds* correspond to demixing, whereas the *open diamonds* indicate the solidification temperature. The *squares* correspond to the side-drop experiments, the *filled squares* correspond to the equilibration temperatures of the alloys, and the *open squares* indicate their "surface" freezing temperature

[13]) to the detriment of the liquid/vapor interface (450 mJ m^{-2} at the Pb melting point [7]). This costs 110 mJ m^{-2} which is a lower energy than that of the solid Pb/liquid Ga interface which is of the order of 200 mJ m^{-2}. As suggested in the study of Chatain [14], this value is of the order of the sum of the Pb solid/liquid interfacial energy (150 mJ m^{-2} at the Pb melting point [15]) and of the Pb-rich liquid/Ga-rich liquid interfacial energy (40 mJ m^{-2} at the monotectic temperature [16, 17]). Since the Pb-rich liquid film is located at the drop surface, it is understandable that Pb solidification proceeds along the surface. Under this scenario, the locus of Pb solidification is expected to lie close to the metastable liquid–liquid binodal line. Once solid Pb has formed during cooling, it will gradually redissolve during reheating and vanish at the liquidus temperature.

The observed "melting" and "freezing" temperatures were reproducible within 1 K. They are reported in Table 1. They are also plotted in Fig. 7 together with the calculated metastable binodal and liquidus lines of Fig. 1b. The figure shows that within the uncertainty in concentration, the four alloys with Pb atom fraction below 1.5% froze in the vicinity of the metastable binodal line on cooling, and upon reheating, completed their melting process at the liquidus line. The freezing temperatures are in full agrement with the ones found in an earlier series of experiments aimed at measuring the surface energy of Ga–Pb liquids [7].

The freezing and complete remelting temperatures of the Pb-rich surface film on the alloy drops could not be detected for alloys with Pb atom fractions below 5×10^{-3}. The platelet formation was not seen at the expected binodal temperature, but at a much lower temperature (400 K). Instead, at $T_{Liq/Liq}$ (the metastable binodal line), the surface gets covered with a stiff skin well before the platelets become visible. This could be detected easily by shaking the drop. The stiff skin was also observed in the previous series of experiments for the most diluted alloys, and correlated with anomalies in surface energy measurement [7].

We have made a rough estimate of the maximum thickness of the Pb solid film which precipitates on the alloyed drops. The quantity of Pb, which has solidified, corresponds to a compositional jump of the liquid from the metastable binodal to the liquidus lines. If equally spread on the drop surface, the film thickness would be the ratio of the volume of the Pb rejected to the surface area of the drop. In Table 1, we have reported for each alloyed drop of composition, X_{Pb}, the average thickness of the Pb layer, e, calculated from the surface area of the drop, S, and the difference in Pb content between the liquidus and the binodal lines, ΔX_{Pb}, at the solidification temperature. We found an average thickness of about 2 μm.

After cooling to room temperature we have measured the thickness of the solid film formed at the surface of two drops with 6.7×10^{-3} and 9.2×10^{-3} Pb atom fractions in a scanning electron microscope. As the Ga-rich phase does not solidify, its composition in Pb remains close to the eutectic one (6×10^{-4} Pb atom fraction). The Ga-rich liquid beneath of solid Pb-rich film is not detected by EDS analysis with a 30-kV beam. This means that the solid

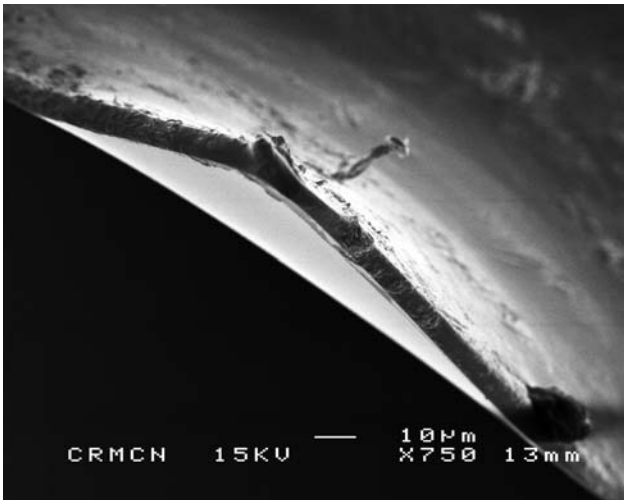

Fig. 8 Secondary electron image of a peeled back solidified wetting layer of Pb on top of Ga-rich liquid drop

Pb-rich layer must be thicker than 3 µm. Thus, we have peeled back the Pb film at the top of the samples and directly measured its thickness (see Fig. 8). For both samples the thickness of the solid Pb layer was found to be 6–7 µm. This is about the total amount of Pb solidified at the eutectic temperature, where the Ga-rich drop contains Pb. When compared to the 2 µm previously calculated, this means that after freezing at the surface and at the bottom of the drop, most of the Pb rejected from the Ga-rich liquid grows underneath the initial solid film formed at the surface.

Side-drop experiments

In a second series of experiments, which we will refer to as side-drop experiments, we have prepared Ga-rich liquid alloys with a Pb atom fraction below that of the Ga-rich end of the monotectic line, by equilibration of a Ga drop with a solidified Pb drop at temperatures below T_{mono}. A large solid Pb drop was first prepared on the vitreous carbon substrate, and a liquid Ga drop was put in side-contact with it at room temperature. Heating such a sample at a given temperature $T_{\mathrm{Liq/Sol}}$ allows dissolution of Pb in the Ga drop at a concentration, $X_{\mathrm{Pb}}^{\mathrm{LS}}$, given by the liquidus line of the Ga–Pb phase diagram (Fig. 1). Such samples allowed the investigation of phase transformations taking place at the surface of Ga-rich liquid alloys containing a Pb atom fraction of less than 10^{-3}.

Figure 9 illustrates the optical method used to investigate phase transitions at the sample surfaces. A light spot was reflected off the surface of the Ga-rich drop. As long as the drop is liquid, the spot is elliptical. After 1 h annealing at a given $T_{\mathrm{Liq/Sol}}$, the temperature of the drop was decreased at 0.5 K/min. At a certain temperature below the liquidus line, the shape of the reflected light spot changed from elliptic to jagged (see Fig. 8b, c). This is the signature of the crystallization of small Pb platelets at the surface of the Ga-rich liquid. As in the case of alloyed drop experiments, this solidification starts at the bottom of the drop and progresses toward its top at a constant temperature. A subsequent increase in temperature led to remelting of the thin Pb crystals, starting from the top of the liquid drop, and progressing down to the bottom. The surface was fully remelted at a temperature which was higher than the $T_{\mathrm{Liq/Sol}}$ at which the drop had first been equilibrated. This

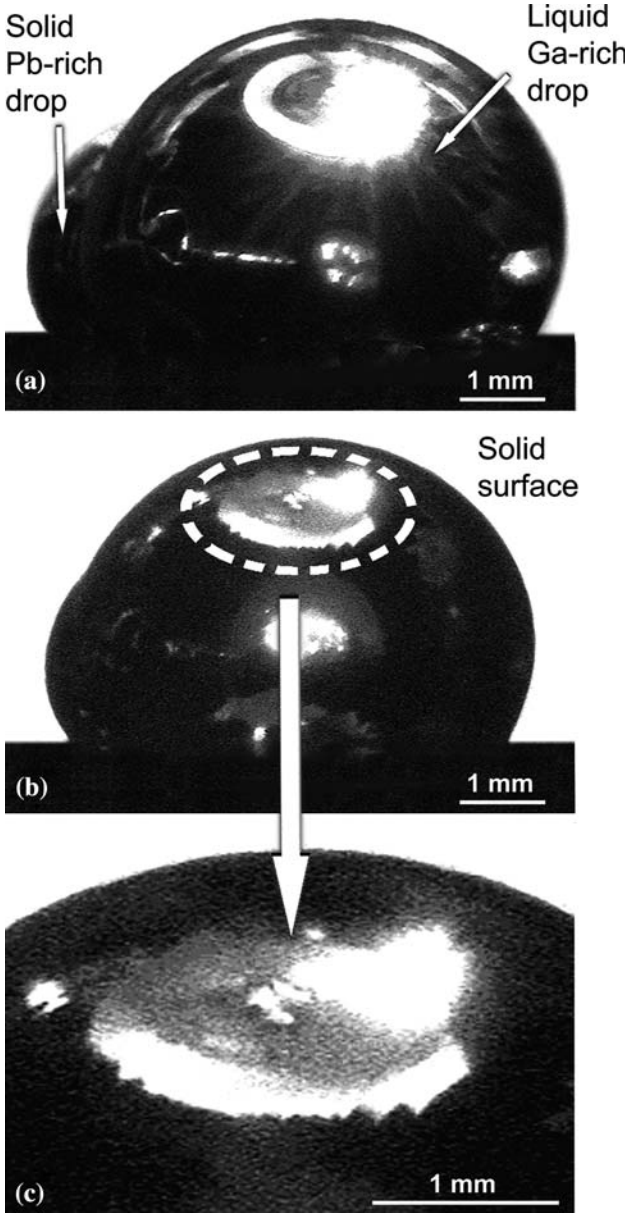

Fig. 9 Side drop sample. **a** Solid Pb on the left and a Ga-rich drop on the right. **b** Solid Pb on the left and Ga-rich drop with a "solid surface," on the right. **c** Faceted shape of the reflected light spot due to the presence of the Pb platelets

Table 2 Results for the side-drops

X_{Pb} (at.)	$T_{\mathrm{Liq/Liq}}$ (K) (±1 K)	$T_{\mathrm{Liq/Sol}}$ (K) (±1 K)
5.9×10^{-4}	358	384
1.39×10^{-3}	396	424
3.25×10^{-3}	453	471
7.90×10^{-3}	523	531

means that the Pb which redissolved in the Ga drop was partly provided by the large solid drop of Pb in contact with the Ga-rich drop.

Table 2 summarizes the compositions, $X_{\mathrm{Pb}}^{\mathrm{LS}}$, of the four liquid alloys determined from the calculated phase diagram [6] in conjunction with their equilibration temperatures $T_{\mathrm{Liq/Sol}}$, and their surface solidification temperatures. These data are also plotted in Fig. 7. In all four cases, the observed freezing temperatures fall almost perfectly on the metastable binodal line, at $T_{\mathrm{Liq/Liq}}$. We conclude that at a cooling rate of 0.5 K/min, in spite of the presence of a large Pb solid seed in contact with the Ga-rich drop, the Ga-rich alloy can be undercooled down to the metastable binodal line where a Pb-rich liquid surface film forms, before Pb solidifies. This provides further evidence that it is kinetically easier to form solid Pb from the Pb-enriched liquid phase which forms at the drop surface at the metastable binodal than directly from the dilute Pb in the Ga solution above the binodal, even in the presence of solid Pb. This surprising result demonstrates the important role played by complete wetting in the solidification and subsequent microstructure formation of monotectic alloys.

Discussion about surface freezing and freezing at surface

Two-dimensional surface freezing in Ga-rich monotectic Ga–Pb alloys has been addressed in several papers [18–21]. Surface freezing of liquids and surface melting of solids in single component systems are 2-D surface phase transitions that occur at temperatures which may be different from the bulk melting point. Surface freezing has been reported to occur in binary alloys, at temperatures above the liquidus temperatures. In-plane ordering in a single atomic layer at the surface of binary alloys has been identified in Au–Si [22] and Ga–Pb [18] "eutectic alloys." These transitions were found to be first order but without hysteresis during temperature cycling. However, whereas the eutectic temperatures are well-known, the eutectic compositions are not (0.186 ± 0.005 Si atom fraction for Au–Si [23] and between 5×10^{-5} [6] and 6×10^{-4} Pb atom fractions from extrapolation of the study of Predel [24]). Thus, if the alloy composition is not exactly eutectic, the surface ordering temperatures may be off-eutectic, and should be compared with a liquidus temperature. Surface phase transition in a binary alloy may be identified as such only under the condition that the bulk phase transitions in the same alloy have been properly located in the phase diagram. Here it must be recalled that the bulk freezing–melting transition is hysteretic. Melting takes place on the liquidus line but freezing typically occurs in undercooled liquid alloys. Since the location of the liquidus line in the Ga–Pb phase diagram has been assessed in this article, it is useful to discuss the location of the surface freezing transformation found for Ga–Pb alloys, on the basis of this phase diagram.

1. A 5.4×10^{-4} Pb Ga-rich alloy (see point labeled "1" in Fig. 1b) has been investigated by X-ray reflectivity and grazing incidence X-ray diffraction between 296 and 349 K [18]. According to the Ga–Pb phase diagram that we have re-assessed, this composition is hyper-eutectic (the eutectic composition occurs at a Pb atom fraction that is one order of magnitude lower, i.e., around 5×10^{-5} [6]). The liquidus and metastable binodal temperatures are 380 and 354 K, respectively. A first-order two-dimensional hexatic-to-hexagonal transition has been found to take place in the vicinity of 326 K in a single monolayer of Pb. Because this temperature is below that of the metastable binodal, the wetting Pb layer must be thick. However, it has been verified that the ordering takes place within a single Pb monolayer at the surface. Thus the alloy investigated must lie on the left of the binodal line: either the Pb content of the bulk alloy was overestimated or the temperature was underestimated.
2. The surface of a 5.2×10^{-3} Pb Ga-rich alloy (see point labeled "2" in Fig. 1b) has been investigated by Auger and XPS [19]. The surface of a 5.4×10^{-3} Pb Ga-rich alloy has been independently observed by second harmonic generation [20]. The liquidus and metastable binodal temperatures of the 5.2×10^{-3} (5.4×10^{-3}) Pb alloy are at 502 (505) and 486 (490) K, respectively [6]. Within 5 K around 461 K, as the temperature of the 5.2×10^{-3} Pb alloy was decreased, it has been observed that the Pb adsorbed layer thickness first slowly increased from 0.45 to 0.48 nm then jumped to 2.2 nm. Surface freezing of the 5.4×10^{-3} Pb alloy has also been observed in the vicinity of 461 K [20]. The first observation is typical of a logarithmic divergence of the thickness of the liquid Pb adsorbed layer as the binodal temperature is approached [2]. The second observation suggests that Pb freezing takes place once the thick wetting layer has formed at the binodal temperature. The surface transformations investigated for these alloys take place below both the liquidus and the metastable binodal

lines. Thus, such experiments do not prove the existence of surface freezing, but suggest that within the accuracy of temperature and composition measurements, freezing at the surface takes place when the thick Pb-rich wetting layer has formed, i.e., in the vicinity of the metastable binodal temperature.

3. For a 1.2×10^{-4} Pb Ga-rich alloy [20] (see point labeled "3" in Fig. 1b) no surface freezing was observed above 298 K. This is consistent with the location of both the liquidus and the metastable binodal temperatures of this alloy, i.e., 325 and 298 K, respectively.
4. A 5.6×10^{-3} Pb Ga-rich alloy (see point labeled "4" in Fig. 1b) has been investigated by spectroscopic ellipsometry by Bartel et al. [21]. This method does not allow the detection of a single monolayer adsorbed at the surface. The liquidus and metastable binodal temperatures of this alloy are 506 and 492 K [6]. A solid film has been found to form at the surface of the alloy at 461 K, i.e., below the metastable binodal temperature where the thick Pb-rich liquid film forms. In [21], the melting temperature of the surface film has also been investigated. It has been found to depend on the temperature at which reheating starts. Surface melting is 6 K above the surface freezing temperature when reheating starts from the surface freezing temperature, and 3 K below when reheating starts 7 K below the surface freezing temperature. These melting temperatures may be explained if the following experimental features are considered: (i) the film thickness is not homogeneous, and is thinner in the middle of the crucible, (ii) melting is observed at the center of the film (about 3% of the total surface), and (iii) the center of the Pb solid film dissolves first at a lower temperature than the actual melting temperature which is reached only once the whole film has been redissolved. Such an experiment suggests that the frozen film is a bulk solid which melts on a liquidus line.

All the experiments performed on surface freezing in Ga–Pb and reported above show that surface freezing takes place below the binodal line of Ga–Pb (see Fig. 1b). In addition, whereas surface ordering has been found not to be hysteretic [18, 22], the experiments reported in the study of Bartel et al. [21] show a hysteretic freezing–melting of the surface. Bartel et al. [21] point out that the thickness of the frozen film is still controversial: XPS and ellipsometry have measured 2 and 10 nm, respectively, whereas surface ordering has been reported to take place in one atomic layer [18].

Concluding remarks

The phase transitions at the surfaces of monotectic Ga–Pb alloys, which we have reported here, are directly related to the phase transitions indicated by the bulk phase diagram. Freezing of a Pb-rich phase at the surface of an originally homogeneous Ga-rich liquid solution occurs only after a completely wetting Pb-rich liquid forms at the surface as the binodal temperature is reached. The freezing–melting transition is found to be hysteretic while surface ordering like surface prewetting is not. We have also observed that surface freezing occurs on large drops when the Ga-rich liquid is in contact with solid Pb, for cooling rates of 0.5 K/min, under conditions where the solid Pb does not play its role of nucleant.

The existence in this system of complete wetting by the phase which contains the high melting point component is essential to the observation of freezing at surface. Our experimental setup cannot verify the first step of the freezing transition, namely the formation of a liquid Pb-rich film at the alloy surface; however, it is clear that the surface freezes only after the Pb-rich wetting film has formed. Complete redissolution of the solid Pb film takes place on the liquidus line. Surface freezing in Ga-rich Ga–Pb alloys observed by other authors occurs in the vicinity of the binodal line (see Fig. 1b). This suggests that freezing of the wetting Pb-rich film at the surface has been observed instead of surface freezing.

To draw valid conclusions on the location of the phase transitions that occur at surfaces of monotectic systems, sophisticated surface analysis techniques must be coupled with thermodynamic measurements, such as differential thermal analysis, to ascertain the location of the bulk phase transitions.

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