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Oscillatory interfacial instabilities in binary metallic fluids

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Received 7 September 2005

Published 28 October 2005

Online at stacks.iop.org/JPhysCM/17/S3289

Abstract

Oscillatory wetting–dewetting instabilities at the liquid/vapour interface of Ga–Pb and, for the first time, of Ga–Bi alloys have been studied employing second harmonic generation and kinetic ellipsometry. Alloy samples prepared at x – T conditions inside the respective miscibility gap (Ga_{0.8}Bi_{0.2}: $T = 520$ K; Ga_{0.95}Pb_{0.05}: $T = 595$ K) show oscillations on the timescale of typically hours. The surface transforms back and forth from a Ga-rich non-wetting state to a complete wetting state where the Ga-rich bulk is covered with a Bi-rich (or Pb-rich) film. In the case of Ga–Bi the change of the wetting film thickness was characterized quantitatively with the aid of the ellipsometric measurements. It is consistent with a wetting–dewetting mechanism whereby the wetting film varies periodically between macroscopic and microscopic values. The phenomenon can be understood taking different emissivities of the wet and the nonwet state into account. They cause at otherwise constant conditions different temperatures of the sample, which has to adopt its phase compositions according to the respective phase diagram. This results in mass transport to and away from the surface. A model calculation on Ga–Bi taking these effects into account recovers in good quantitative agreement the oscillation period and the oscillations of the temperature as well as of the film thickness. Similarities and differences between Ga–Bi and Ga–Pb are finally considered.

1. Introduction

Recently we reported on the first observation of an interfacial oscillatory instability in a metallic fluid, the binary alloy Ga–Pb [1, 2]. This system is characterized by a liquid–liquid demixing

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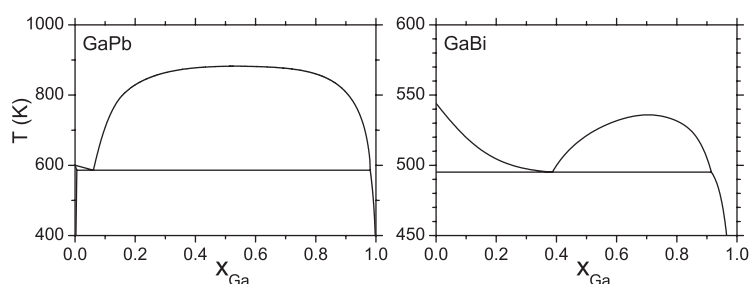


Figure 1. Phase diagram of Ga–Pb and Ga–Bi [3] in the temperature range of the miscibility gap.

gap with an upper critical temperature of 879 K, see figure 1 [3], and similar to the Ga–Bi system exhibits complete wetting transitions at liquid–liquid coexistence [4–7]. Probing the liquid/vapour interface by second harmonic generation (SHG) it has been found that the optical characteristics of the interface oscillate between those of the Ga-rich and Pb-rich phases when measurements were performed at a constant cooling rate or at constant temperature at conditions inside the miscibility gap [1]. These oscillations in the interface simultaneously induce temperature oscillations in the bulk fluid with the same period. The last phenomenon is a speciality of metals due to the high variation of their optical emissivities. A simple model considering a Rayleigh–Taylor instability has been developed to describe the film thickness evolution during wetting and dewetting. It is based on the Reynolds lubrication approximation for thin films [8, 9]. This model explains the main experimental features [14]. It is found that the interfacial oscillations are due to capillary–gravitation instability. Since the mass density of the Pb-rich liquid is larger than that of the Ga-rich one the film becomes unstable during its growth and part of it drops down. For understanding of the temperature oscillations the variation of the film emissivity with its thickness is essential [10]. Taking this into account, the model quantitatively describes the time evolution of the interfacial and temperature oscillations with the correct period.

In this contribution we present first experimental results of interfacial oscillatory instabilities in the Ga–Bi alloy. The liquid/vapour interface has been investigated by ellipsometry, which for the first time gives information on the time evolution of the Bi film thickness during wetting–dewetting. The results will be discussed in comparison with the observations for the Ga–Pb alloy. Of particular interest is the comparison with the model predictions.

2. Experimental details

Spectroscopic and single-wavelength ellipsometry have been employed to study the liquid/vapour interface of Ga–Bi alloys. The experimental set-up and the experimental procedure were described in detail recently [7]. In brief, polarized light is reflected under a well defined angle of incidence at the surface of the alloy. From the change of the amplitude ratio ($\tan \Psi$) and the phase shift (Δ) between the parallel and the normal component of the polarized field the complex reflection ratio is obtained: $\rho = \tan(\Psi) \exp(i\Delta)$ [11]. For the determination of ρ a phase modulation ellipsometer was employed in the experiments (UVISEL, Jobin–Yvon). The interpretation of ρ requires a model of the interface. Two limiting configurations are relevant here. In the simplest case of a two-phase model the interface can be described as the contact of two bulk phases (liquid alloy and ambient vapour phase) at which the composition profile is approximated as a step function. Here, ρ unambiguously yields the refractive index

n and the absorption constant k of the liquid metallic phase. If the liquid bulk phase is covered by a thin wetting film, which is relevant in the present context, ρ has to be interpreted in terms of a three-phase model consisting of the liquid alloy, the film of thickness h and the ambient medium. The film thickness can be evaluated from ρ once the complex indices of refraction of all three phases are known.

Surface second harmonic generation (SHG) has been used to study the surface of Ga–Pb alloys. The experimental set-up and the experimental procedure have been described in detail previously [12–14]. Since SHG is forbidden in isotropic bulk phases but allowed at surfaces, where the isotropic symmetry is broken, it is inherently surface specific. In the present problem it is used to determine qualitatively the chemical nature of the uppermost atomic layers of the Ga–Pb samples. The SHG intensities of a Ga-rich or a Pb-rich alloy differ noticeably [1]. The method is advantageous due to its experimental simplicity and its straightforwardness of the qualitative interpretation of the primary experimental intensity data.

Investigations of the surface of liquid metallic alloys require certain precautions to prevent the surface from being contaminated with impurities. All handling of the metals and preparation of the samples have been done in an Ar glove box. The crucibles with the solid metal mixtures have been transferred into an ultrahigh vacuum chamber in which additional cleaning steps with an Ar-ion sputter gun and a mechanical wire cleaner were accomplished (for further details see [7]). The crucible was heated with a resistance furnace from below. Hence, the alloy surface is open and is exposed to the vacuum environment of the UHV chamber. This geometry is the source of small thermal gradients across the sample. The radial gradient component could be estimated below 0.05 K mm^{-1} [1, 15]. For homogenization of the mixtures the samples have been heated above the demixing curve for several hours. Then, the alloys have been cooled down into the miscibility gap to prepare the complete wetting state. Here, the Ga-rich bulk phase is covered with a wetting film consisting of a Bi-rich phase or a Pb-rich phase, respectively. The optical experiments have been carried out at constant furnace temperature.

3. Results and discussion

3.1. Interfacial oscillations in gallium–bismuth

Representative of the alloys in the composition range of the miscibility gap of Ga–Bi we show in figure 2 the time evolution of the sample temperature and of the ellipsometric parameters Ψ and Δ of $\text{Ga}_{0.8}\text{Bi}_{0.2}$. The sample was cooled down from the homogeneous phase with a cooling rate of 25 K h^{-1} . As the furnace reached 552.5 K at 1.5 h on the timescale in figure 2 the temperature was set constant. This moment is marked in the upper panel of figure 2 with a straight line. Under the specific thermal conditions of the experiment the sample temperature approaches an average temperature of 520 K . It is remarkable to see strong and regular oscillations in the dense sequence of the Ψ – Δ data points (recorded every 5 s) obtained at a constant photon energy of 2.75 eV . We observed eight cycles until we stopped the experiment after about 40 h . The period is 4.26 h with a variation of only 0.1 h .

One oscillation, which will be analysed in more detail in the following, is highlighted in figure 2 with a dashed frame. The same dataset of Ψ and Δ can be seen in the inset of figure 3. Typically, Ψ and Δ start at angles of 39° and 119° , respectively, and decrease slowly in the first two hours. The progression of Ψ and Δ accelerates until a constant plateau is reached at 5.7 h ($\Psi = 36^\circ$, $\Delta = 117.5^\circ$). This plateau is stable for only 0.6 h . Then, Ψ and Δ jump back to the initial values with rates of 40° h^{-1} (Ψ) and 24° h^{-1} (Δ). It is an important observation that Δ reaches the plateau through a pronounced minimum and it leaves it through the same minimum documented by a few tens of data points. This undershooting is strictly reproducible and can be observed in each oscillation period.

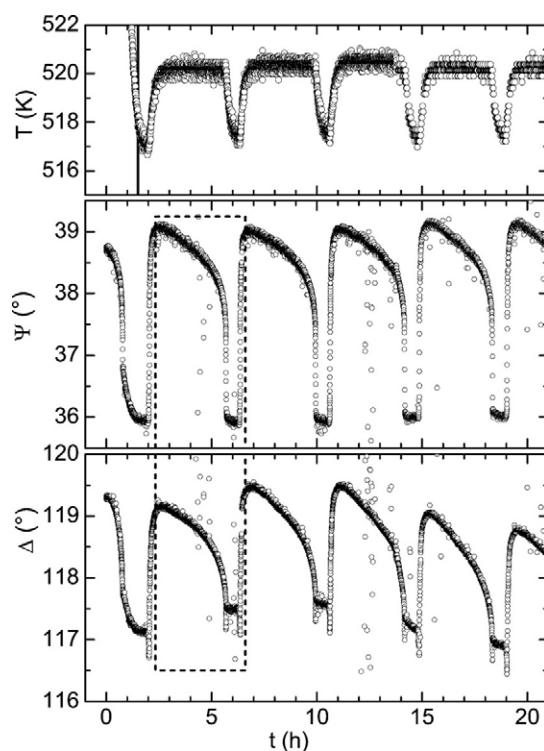


Figure 2. Oscillations in $\text{Ga}_{0.8}\text{Bi}_{0.2}$. Top panel: temperature behaviour during wetting–dewetting on account of the emissivity change of the surface. After the vertical bar the furnace temperature is set constant to 552.5 K. Middle and lower panel: ellipsometric parameters Ψ and Δ with time. Data in the dashed frame are discussed quantitatively in the text and figure 3. Note the regular appearance of the undershooting features in Δ before and after the plateau-like period. A few deviating and unphysical data points (see e.g. 12 to 13 h) are due to mechanical disturbances of the liquid surface. They are eliminated in figure 3.

The top panel of figure 2 shows the behaviour of the sample temperature while Ψ and Δ oscillate. At the beginning of the framed cycle the temperature ($T = 520$ K) is constant within the resolution of our measurement. As Ψ and Δ reach the plateau the sample temperature drops exponentially to $T = 517$ K with a time constant of $\tau = 0.25$ h. This, obviously, leads to an instability of the plateau phase and the initial state is recovered.

Qualitatively, the processes occurring at the sample surface can be understood quite easily (see also [2]). In the first hour of the experiment, when the furnace was continuously cooled down, the evolution of Ψ and Δ reflects the continuous increase of the wetting film thickness h as the system approaches the two-phase region. Typically for metallic systems h exhibits a logarithmic divergence as a function of the distance to the coexistence curve [7]. Thus, as the system enters the miscibility gap and the furnace temperature becomes constant, it is in the wetting state and a Bi-rich film phase completely covers the underlying bulk Ga-rich liquid. We have to assume that this wetting state is characterized by the plateau values of Ψ and Δ . Since the Bi-rich liquid has a higher emissivity than the Ga-rich phase the temperature of the sample is a bit lower with the wetting film than without. In turn, the compositions of the wetting film phase and the bulk phase have to be adjusted according to the phase diagram. This presumably destabilizes the film and leads to a dewetting of the sample. Consequently,

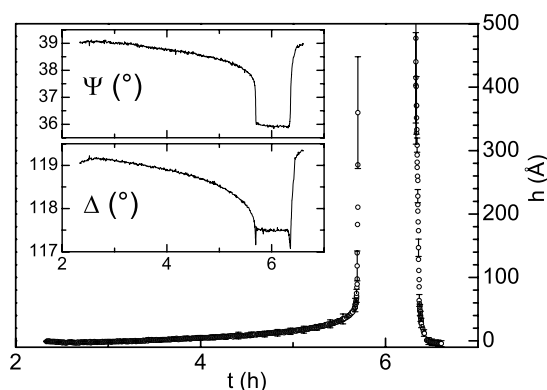


Figure 3. Evolution of the thickness h of the wetting film of $\text{Ga}_{0.8}\text{Bi}_{0.2}$ with time during one cycle of the oscillations, evaluated within the three-phase model from the Ψ - Δ couples shown in the inset. The increase of the error bar of h is due to the decreasing sensitivity of the three-phase model for h as an absorbing film grows. Within our model we can only give a lower limit for the wetting film thickness ($h > 500 \text{ \AA}$) in the plateau period (5.7–6.3 h).

the situation at the beginning and at the end of the selected time interval (dashed frame in figure 2) corresponds to the bare Ga-rich substrate. Bi is only Gibbs adsorbed at the surface in the first atomic layers on account of its lower surface tension.

Ellipsometry is particularly valuable to elucidate the interfacial structure of the present alloys. A rather full picture would be accessible if spectroscopic ellipsometry could be applied at various angles of incidence. But the need for UHV conditions requires the selection of a constant angle of incidence ($\Theta = 71.15^\circ$). In addition, we have to restrict ourselves to a single photon energy for the sake of time resolved measurements ($h\nu = 2.75 \text{ eV}$). Nevertheless, it seems to be worthwhile to evaluate the dense sequence of Ψ - Δ couples within the three-phase model to get insight into the evolution of the wetting film thickness with time. The film thickness is the only parameter in this model and wetting and dewetting is described solely by thickening and thinning of the wetting film. Even though one could think of various other wetting and dewetting modes, our data present a strong argument for the validity of the simple three-phase mechanism. It is well known that the ellipsometric angle Δ varies in a cyclic way if a transparent film (n is finite and $k = 0$) grows on an absorbing substrate [11]. These Δ oscillations will be damped if the film medium is absorbing. The undershooting features in the Δ sequence can be regarded as the signature of a damped oscillation.

As was pointed out above the application of the three-phase model requires the knowledge or the consistent choice of the complex dielectric function, $\varepsilon = \varepsilon_R - i\varepsilon_I$, of the bulk and the film phases. In our case the following choice seems obvious. First, we extract $\varepsilon_{\text{bulk}}$ from Ψ - Δ couples at the beginning of the cycle under consideration (2.5 h). Here, the bare bulk phase dominates. The evaluation within the two-phase model reveals $\varepsilon_{\text{bulk}} = -18.41 - 9.88i$. The complex dielectric function of the film was extracted from the Ψ - Δ data points in the plateau region. It is supposed that in this time interval (5.7–6.3 h in figure 3) the absorbing film is thick enough to mask the influence of the bulk phase. The light intensity that passes this macroscopically thick film and is reflected at the film-bulk interface is neglected. Under these conditions the three-phase model reduces to the two-phase model, regarding the film as a bulk phase. From the Ψ - Δ couples one obtains $\varepsilon_{\text{film}} = -14.2 - 12.0i$. The values of $\varepsilon_{\text{bulk}}$ and $\varepsilon_{\text{film}}$ lie between those of pure liquid gallium and pure liquid bismuth [7] at comparable temperatures.

Once these choices have been made all Ψ - Δ data pairs have been analysed individually within the framework of the three-phase model. Since the equations of Ψ and Δ as a function of the film thickness h cannot be inverted analytically to calculate h directly, we have to apply a nonlinear least square fitting routine to each dataset consisting of one pair of Ψ and Δ . The quality of the fit is measured with the quantity $\chi^2 = (\Psi_M - \Psi_F)^2 + (\Delta_M - \Delta_F)^2$ (index M, measured values; index F, fitted values). For 99% of the Ψ - Δ couples in the full time interval from 2.3 to 6.6 h χ^2 was below 0.1, which in turn means that $|\Psi_M - \Psi_F|$ and $|\Delta_M - \Delta_F|$ lie below 0.2° . Thus, the fitting quality in the whole range is satisfying. The error of the fitting parameter h , however, varies with the absolute value of h . Above a certain value of the wetting film thickness the three-phase fits are completely insensitive to a variation of h . This explains the strong increase of the error bars for h as function of the absolute value of h . In the time interval between 5.7 and 6.3 h we can only give a lower limit of 500 Å for the film thickness. We are aware that this procedure can only give an effective film thickness. A possible inhomogeneity of the wetting film is not discernable employing single-wavelength ellipsometry.

The fit results are summarized in figure 3. In the first hours the film thickness increases only slowly to about 50 Å. Then the film thickness growth accelerates drastically to values above 500 Å. As the plateau phase becomes instable the system dewets through a continuous thinning of the wetting film within a period of 0.1 h. After 6.3 h the effective film thickness comes into a measurable range below 500 Å. The thinning of the film seems to occur with slightly different time behaviour than the thickening. The film thins with a more or less constant velocity down to microscopic values. An incubation period, visible as the film thickens in the range up to about 50 Å, is not observed. It is interesting to note that the undershooting feature in Δ can be consistently described within the three-phase model. The minima of Δ correspond to $h = 138$ Å and $h = 147$ Å, respectively. This is a thickness range where the three-phase model applies very well.

3.2. Model calculations for gallium–bismuth

Recently [16] we have extended our original model [1] for the oscillatory wetting instability in Ga–Pb by taking into account the influence of a vertical temperature variation in the liquid. According to this model the temperature evolution for the Ga–Bi alloy is determined by the heating from the heater below with constant temperature $T_F = 552.5$ K and radiation in vacuum above the liquid. Since the thermal diffusivity of the sample is large and the thickness $H = 2$ mm of the sample liquid is small, the temperature T in the Ga-rich liquid can be approximated as a uniform one satisfying the following energy balance:

$$H\rho_G c_G \partial_t T = \alpha(T_F - T) - \varepsilon\sigma_0 T^4. \quad (1)$$

Index G (or B) stands for a property of the Ga-rich (or the Bi-rich) alloy. The heat capacity $c_G = (1 - x_G^e)c_{Ga} + x_G^e c_{Bi}$ and the molar density $\rho_G = 1/[(1 - x_G^e)/\rho_{Ga} + x_G^e/\rho_{Bi}]$ of the Ga-rich liquid are approximated via linear combinations of the properties of the pure elements: $c_{Ga} = 25.9 \text{ J mol}^{-1} \text{ K}^{-1}$, $c_{Bi} = 25.5 \text{ J mol}^{-1} \text{ K}^{-1}$, $\rho_{Ga} = 89\,800 - 8.6T \text{ mol m}^{-3}$, $\rho_{Bi} = 51\,600 - 6.5T \text{ mol m}^{-3}$ [17]. Since the relaxation of the composition in the liquid is much faster than the oscillations, the average mole fraction of Bi in the Ga-rich liquid is always equal to the equilibrium one $x_G^e = (T - 490)/200$ approximated from the Ga–Bi phase-diagram at 520 K. The first term on the right-hand side of equation (1) describes the heat flow from the heater to the sample. It is equal to the difference between the temperatures of the heater and the sample multiplied by the effective heat transfer coefficient, which is estimated from the average temperature of the sample as $\alpha = 16.2 \text{ W m}^{-2} \text{ K}^{-1}$. The last term describes

the loss of heat due to radiation in vacuum, where ε is the integral emissivity of the sample and $\sigma_0 = 56.7 \text{ nW m}^{-2} \text{ K}^{-4}$ is the universal Stefan–Boltzmann constant.

The employment of equation (1) requires an adequate expression for the emissivity. Since the surface tension at the liquid/vapour interface of bismuth is lower than that of gallium, a Bi-rich wetting film forms on top of the bulk Ga-rich liquid. When the temperature approaches the bulk liquid–liquid coexistence curve a complete wetting transition occurs and a macroscopically thick Bi-rich liquid film develops at the liquid alloy/vapour interface. The effect of this Bi-rich liquid film with thickness h on the emissivity of the sample can be taken into account via the following expression [1]:

$$\varepsilon(h, T) = \varepsilon_B - \int_0^\infty \left[\varepsilon_B \exp\left(-\frac{16k_B T h}{3\hbar c \varepsilon_B} \sqrt{2\omega}\right) - \varepsilon_G \exp\left(-\frac{16k_B T h}{3\hbar c \varepsilon_G} \sqrt{2\omega}\right) \right] \times \frac{45\omega^3 \sqrt{2\omega} d\omega}{8\pi^4 [\exp(\omega) - 1]}, \quad (2)$$

where the emissivity of the Ga-rich and Bi-rich liquids is estimated by the linear combination $\varepsilon_X = (1 - x_X^e)(T + 140)/6250 + x_X^e(T + 100)/3000$ of the emissivity of the pure elements [18]. According to the Ga–Bi phase diagram the equilibrium mole fraction of bismuth in the Bi-rich liquid film is equal to $x_B^e = (588 - T)/143$ in the neighbourhood of 520 K. The characteristic thickness where $\varepsilon = (\varepsilon_G + \varepsilon_B)/2$ is about $0.07 \mu\text{m}$.

To close the problem a model for the thickness evolution of a Bi-rich film as a function of time is required. This has been derived in [16] on the basis of the hydrodynamic equations in the film and in the underlying bulk liquid and the stability analysis of the Bi-rich wetting films. Obviously, the Bi-rich film on the top is colder and the film on the bottom is warmer than the Ga-rich liquid. The temperature difference ΔT between the films will generate a Bi composition gradient in the Ga-rich liquid, $-(\partial_T x_G^e) \Delta T / H$, since a Ga-rich liquid with uniform composition $x_G^e(T)$ is super- and under-saturated in respect to the films on the top and bottom of the crucible, respectively. Of course the presence of this constant gradient does not affect the average composition $x_G^e(T)$ but it will result at constant temperature in a permanent flow of Bi atoms from the warmer Bi-rich liquid to the cooler Bi-rich film. Hence, the thickness evolution of the wetting film at the sample/vapour interface will obey the following modified equation [16]:

$$\partial_t h = -\beta^2 \sigma_{GB} H h / 4 \eta_G R^2 - \rho_G (\partial_T x_G^e) [H \partial_t T / 2 - D \Delta T / H]^\# / \rho_B x_B^e, \quad (3)$$

where because of the strong inequality, $T \gg \Delta T$, all the specific constants are taken at temperature T . The first term on the right-hand side of equation (3) results from the relaxation of the Bi-rich film thickness as a result of collecting and falling down of the unstable Bi-rich droplets. Here β is the static Bond number, $\sigma_{GB} = 0.07 (1 - T/535)^{1.3} \text{ N m}^{-1}$ is the interfacial tension between the Ga-rich and Bi-rich liquids [19], $R = 21 \text{ mm}$ is the radius of the sample, and the viscosity of the Ga-rich liquid $\eta_G = (1 - x_G^e) 0.436 \exp(478/T) + x_G^e 0.446 \exp(771/T)$ (in cP) is calculated as the linear combination of the viscosities of the pure liquids [20]. The last term in equation (3) accounts for increase/decrease of the film thickness due to adsorption/desorption of bismuth from the bulk to the film. The molar density of the Bi-rich phase is calculated here via $\rho_B = 1 / [(1 - x_B^e) / \rho_{Ga} + x_B^e / \rho_{Bi}]$ and the diffusion coefficient of Bi in the Ga-rich liquid is approximated by the Stokes–Einstein relation $D = k_B T / 3\pi \eta_G d_{Bi}$, where $d_{Bi} = 1.17 \text{ \AA}$ is the diameter of the Bi^{3+} ion. During cooling across the liquid–liquid miscibility gap the solubility of Bi in the Ga-rich phase decreases. Since a wetting film of the

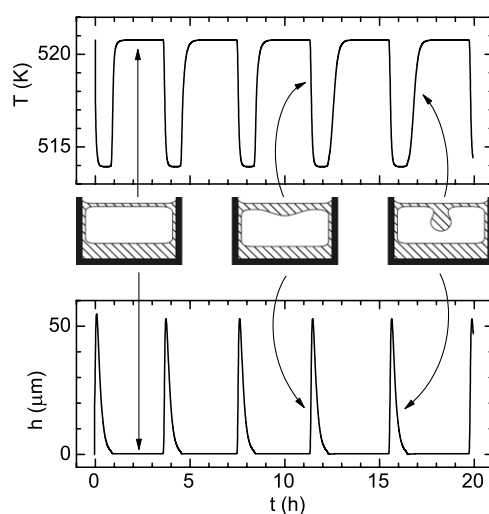


Figure 4. Evolution of the temperature of the sample and the thickness of the wetting film in $\text{Ga}_{0.8}\text{Bi}_{0.2}$ during the wetting–dewetting process as calculated with the hydrodynamic emissivity model (for the parameters see text). Different states of the demixed sample during the wetting–dewetting process are shown schematically: a wetting film of the Bi-rich phase (hatched area) thickens, then becomes unstable and finally drops back into the reservoir at the bottom of the crucible.

Bi-rich liquid is already formed and, in addition, the undercooling applied is far away from the spinodal curve, the homogeneous nucleation in the bulk is unfavourable. This leads to a surface-directed phase separation via the Bi-rich wetting film resulting in adsorption of the Bi excess on the sample surface. The superscript # indicates that the term in the brackets should be taken equal to zero when $H\partial_t T > 2D\Delta T/H$ and $h = 0$. This means that no desorption is possible when the Bi-rich film is not present on the surface.

The predictions of our model with $\beta = 0.04$ and $\Delta T = 0.000\,002$ K are presented in figure 4. As is seen, the temperature and film thickness oscillations correspond well to our experimental observations. Note that the maximal film thickness in the Ga–Bi case is two orders of magnitude larger than in the Ga–Pb case [1]. However, this is not surprising since the temperature of the Ga–Bi liquid is close to the critical one. Hence, the density difference between the Bi-rich and Ga-rich liquids is small and for this reason the Bi-rich film is more stable against gravity. For clarity we have included in figure 4 a sketch of different states of the demixed sample during the oscillatory instability.

3.3. Comparison with gallium–lead

In order to compare with the Ga–Bi system, we briefly summarize the main characteristics of the interfacial oscillatory instabilities observed recently for the Ga–Pb system. These were detected at the liquid/vapour interface by SHG-intensity measurements and as such did not give direct information on the time evolution of the wetting film thickness or the kinetics of wetting or dewetting. However, from the oscillating SHG signal a clear discrimination between a completely wet state (Pb-rich film at the interface) and nonwetting configuration (Ga-rich surface) could be made. Inside the miscibility gap oscillations occurred on cooling and heating, and also at constant temperatures. An example of the latter is given in figure 5, where the time dependence of the SHG intensity is compared with the corresponding time

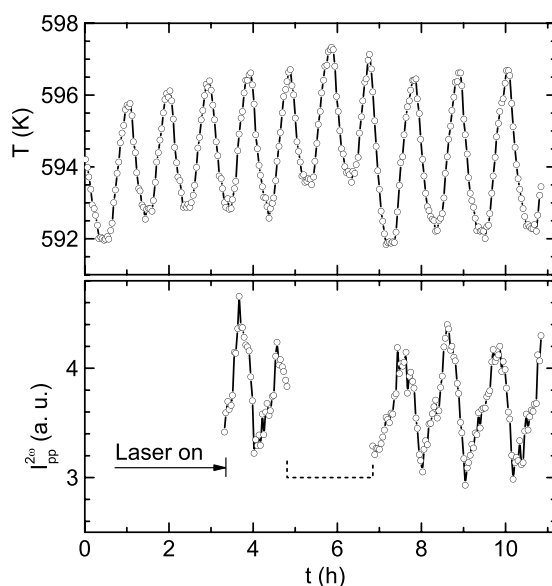


Figure 5. Oscillations in $\text{Ga}_{0.95}\text{Pb}_{0.05}$. Top panel: temperature behaviour during wetting–dewetting on account of the emissivity change of the surface at constant furnace temperature. Lower panel: SHG intensity $I_{pp}^{(2\omega)}$ with time. The Nd:YAG laser was switched on at about 3.3 h. In the time interval indicated by the horizontal dashed bracket the sample surface was observed visually.

variation of the sample temperatures. In all experiments a strong coupling of the interfacial oscillations and the bulk temperature oscillations was observed, as is confirmed by the results on Ga–Bi. This correlation has been explained by the thickness dependent emissivity changes at the interface—specific to metals—during wetting and dewetting and is quantitatively taken into account in the model calculations [1]. Various influences on the stability of oscillations and their characteristics have been studied, including the effect of laser and lamp irradiation (figure 5), or a transverse temperature gradient. The latter can overdamp the oscillations; see also [16]. In comparing Ga–Pb with Ga–Bi two significant differences must be stated. The period of oscillation in Ga–Bi is ~ 4 h, which is roughly a factor of four longer than in Ga–Pb. In addition, in Ga–Pb the formation of a lens was regularly observed at the interface on cooling and at constant temperature, which is not visible in Ga–Bi. The amplitude of the temperature oscillations in both systems is comparable in magnitude and slightly depends on the experiment conditions, i.e. measurements on cooling or at constant temperature.

In figure 6 the temperature oscillations and the evolution of the Pb-rich wetting film thickness are presented resulting from the model calculations. In the present simulations the specific constants of the Ga–Pb alloy were taken from [1], while the other parameters were as follows: $\alpha = 7.6 \text{ W m}^{-2} \text{ K}^{-1}$, $\beta = 0.02$, $T_F = 715 \text{ K}$ and $\Delta T = 0.1 \text{ K}$. It can be seen that the model calculations of the temperature oscillations are in qualitative agreement with the experimental observations. The variation of the Pb-rich wetting film thickness corresponds well to the periodicity of the SHG intensity. Completing the Ga–Pb section it is worth noting that the oscillations at constant temperature were not effective here in every experimental run. According to the model description a transverse temperature variation in the alloy has to be considered to rationalize these observations [1]. At present its influence has not been studied in detail experimentally.

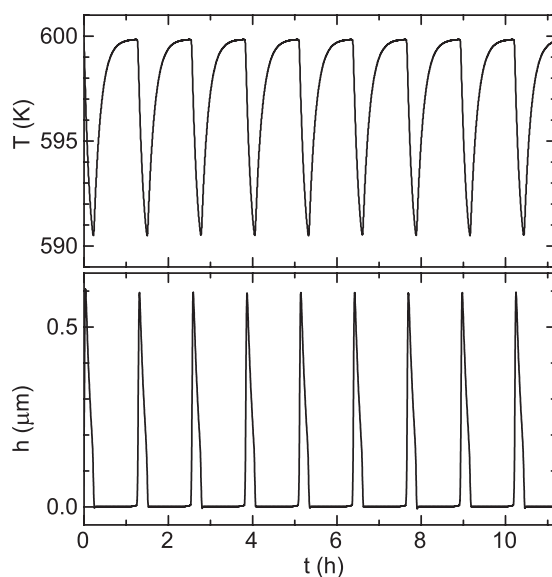


Figure 6. Evolution of the temperature of the sample and the thickness of the wetting film in $\text{Ga}_{0.95}\text{Pb}_{0.05}$ during the wetting–dewetting process as calculated with the hydrodynamic emissivity model (for the parameters see text).

4. Conclusions

The interfacial and bulk oscillatory behaviour of the liquid alloys gallium–bismuth and gallium–lead has been studied at conditions inside the miscibility gap. For this, the interfacial characteristics have been probed by surface sensitive methods, second harmonic generation intensity measurements and kinetic ellipsometry. These investigations show a close similarity of the main features of the oscillatory instabilities in both systems: (i) the optical characteristics of the interface oscillate between that of a gallium rich phase and that of a bismuth or lead rich phase, the latter representing the respective complete wetting films; (ii) the oscillation periods are long, of the order of hours; (iii) the interface and temperature oscillations are strongly correlated. This last phenomenon is due to the corresponding variation of the interfacial emissivities which is quantitatively described by appropriate model calculations. The ellipsometric results for the first time give a detailed and quantitative insight into the wetting–dewetting kinetics. Whereas the wetting film growth is slow, exhibiting logarithmic time dependence, the dewetting step is relatively fast. Ellipsometric determinations of the wetting film thickness are limited to a maximum value of about 500 Å, the extension to higher macroscopically thick values is estimated by hydrodynamic model calculations. In this model the oscillatory behaviour is explained by a Raleigh–Taylor or capillary–gravitation instability. It describes the temperature oscillation frequency and amplitude in accordance with the experimental observations. It also confirms that the temperature oscillations are a clear consequence of the wetting film oscillations.

Acknowledgments

This work was supported through the Centre for Functional Nanostructures of the Deutsche Forschungsgemeinschaft (DFG-CFN: www.cfn.uni-karlsruhe.de). RT is grateful to Deutsche Forschungsgemeinschaft for a Mercator visiting professorship.

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