Surface phase transitions in liquid Ga-Bi alloys studied by optical second harmonic generation

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Cong Wang†, Detlef Nattland and Werner Freyland

Institute of Physical Chemistry, Physical Chemistry of Condensed Matter, University of Karlsruhe, D-76128 Karlsruhe, Germany

E-mail: `congwang@ihw.com.cn`, `detlef.nattland@chemie.uni-karlsruhe.de` and `werner.freyland@chemie.uni-karlsruhe.de`

Abstract. Optical second harmonic generation (SHG) as a particularly surface sensitive technique was employed for the first time to investigate the surface phase behaviour of a liquid alloy, Bi_xGa_{1-x}, in different heating and cooling cycles up to 280 °C. The aim of these experiments is to establish a relatively simple experimental access to the surface phase diagrams of liquid alloys. Measurements of the characteristic changes of the SH signal have been performed on pure Bi and different Ga-rich alloys ($x_{Bi} \leqslant 0.367$). In pure bismuth the melting and freezing of the surface is indicated by a distinct polarization dependent variation of the SH intensities. Of particular interest is the characterization of the wetting transition found in Ga–Bi recently at the monotectic phase transition ($x_m = 0.085$, $T_m = 222$ °C). Surprisingly, on first heating of the Ga-rich alloys up to 280 °C the SHG signals give no indication of the dramatic compositional change at the surface induced by the wetting transition. From these observations we conclude that the main source for the nonlinear polarization is the outermost layer of the alloy which in the wet and the non-wet state consists of an adsorbed Bi-rich monolayer. It is shown that SHG is very sensitive to structural changes at the surface. Most interestingly, on cooling of the Ga-rich alloys a Bi-rich film crystallizes on top of the bulk liquid alloy.

1. Introduction

Phase transitions at the surface of liquids are of particular interest in current research of surface physics and chemistry. They can be subdivided, on the one hand, into structural phase transitions with a change of the local symmetry longitudinal, i.e. in plane, and/or normal to the surface. A prominent example is surface freezing of alkanes where the surface solidifies at somewhat higher temperatures then the bulk [1]. On the other hand, there are surface phase transitions involving compositional changes like the wetting transition in a binary liquid mixture. Under partial wetting conditions below the wetting temperature phase A is exposed to the vapour. Above the wetting transition phase B completely wets phase A which loses the contact to the vapour phase. A very well studied system is methanol–cyclohexane [2].

The predominant intermolecular interactions of the above examples are van der Waals dispersion forces. However, in the last few years wetting transitions have also been observed in systems dominated by Coulomb forces [3]. Evidence for complete wetting and prewetting in K–KCl solutions was found by optical SHG [4] and by spectroscopic ellipsometry [5]: a

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† Present address: Centre of Material Physics and Chemistry, Faculty of Science, Beijing University of Aeronautics and Astronautics, 100083 Beijing, People's Republic of China
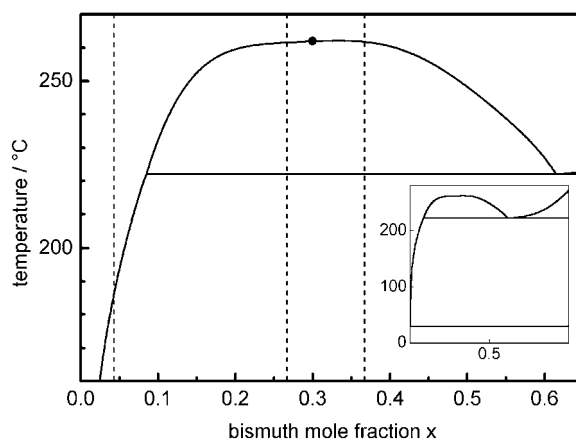
Figure 1. Section of the gallium–bismuth phase diagram [16]. The full circle is the upper critical point of the liquid–liquid demixing regime at $T = 262\,^\circ$C and $x_{Bi} = 0.3$. The horizontal line at the monotectic temperature $T_m = 222\,^\circ$C represents the location of four phase coexistence: solid bismuth, bismuth-rich liquid, gallium-rich liquid, vapour. The dashed lines show the compositions of the samples discussed in the text. The inset gives an overview over the entire phase diagram.

KCl-rich phase wets the interface between the bulk metal-rich solution and an inert window material. A complete wetting transition in the metallic alloy gallium–lead has been reported by Chatain, Wynblatt and coworkers using Auger electron spectroscopy and surface tension measurements [6]. Here, a lead-rich phase wets the interface between the gallium-rich bulk and the vapour phase.

Employing single wavelength ellipsometry a complete wetting film of about 50 Å was determined in gallium–bismuth [7]. It appears as if one crosses the monotectic temperature from below and enters the miscibility gap (see figure 1 for the phase diagram). Since the optical properties of gallium and bismuth are clearly different, spectroscopic ellipsometry can be used to determine the chemical nature of the film: despite its higher density a bismuth-rich film floats on top of a gallium-rich bulk phase [8]. Investigations by x-ray reflection gave valuable insight into the electron density profile normal to the surface. Tostmann *et al* have found a 30 Å thick bismuth-rich film with a considerably rough phase boundary towards the bulk gallium-rich phase. In addition, their experiments revealed that a bismuth monolayer is always present: at the surface of the wetting film and at the surface of the Ga-rich liquid alloy under non-wetting conditions with respect to temperature and bulk composition [9].

It is still an open question whether the monotectic phase transition (a bulk property) coincides with the wetting transition (a surface property). It is even not known of which order the wetting transition is in this system. If it is of first order it might be visible by its precursor in the homogenous phase, the prewetting transition. Thus, the location and identification of the surface phase transition lines in the phase diagram is of considerable importance. For further elucidation of these questions, it is useful to establish and employ a surface specific experimental method to probe the alloy surface continuously as function of temperature and composition.

Optical second harmonic generation (SHG), in principle, provides the demanded selectivity for structural and compositional changes at a surface. If one probes condensed matter with sufficiently intense laser light pulses the macroscopic polarization P is no longer proportional to the electric field strength E of the incident light. P can be now expressed as a power series of E. The second-order term describes second harmonic generation [10–12]. The
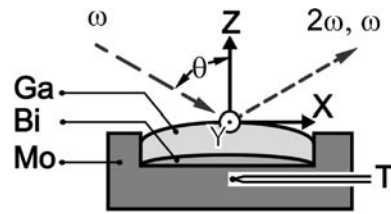
Figure 2. Schematic sketch of the sample with crucible (Mo) and the geometry of the experiment. Shown is a situation at the beginning of an experiment. Bismuth (still solid) is covered by liquid gallium. The plane of incidence is spanned by the coordinates X and Z; the plane of the reflecting surface is given by the coordinates X and Y. The angle of incidence Θ defines the geometry of the experiment for the fundamental ω and for the second harmonic light 2ω. It can be easily seen that the s-polarized light couples only to the Y coordinate, whereas the p-polarized light couples to both Z and X.

surface sensitivity arises from the following: within the dipole approximation SHG is forbidden in bulk media with an inversion centre. It is only generated at the surface where this symmetry condition is necessarily broken. Bulk contributions to the SH signal are expected through quadrupole source terms resulting from the multipole expansion of the nonlinear polarization. Usually they are much weaker then the surface terms, but this has to be verified critically in any case [13]. The SH intensity is proportional to the square of the effective surface second order polarization $P_s^{(2)}(2\omega)$, with the frequency ω of the incident fundamental electric field vector $E(\omega)$:

$$P_{s,I}^{(2)}(2\omega) = \chi_{s,IJK}^{(2)} E_J(\omega) E_K(\omega).$$

Here, $\chi_{s,IJK}^{(2)}$ is the second order susceptibility, a third rank tensor with 27 elements. I, J and K represent the Cartesian coordinates X, Y and Z, defined in figure 2. The numbers of non-zero and independent tensor elements are given by the symmetry at the surface. Different groups of tensor components can be probed and selected by varying the input and output polarization.

From the experimental point of view SHG can be easily adopted to study the liquid–vapour surface of a liquid alloy. This probably makes this technique for these systems a good candidate for a routine method to detect surface phase transitions. For metal molten salt systems it was demonstrated earlier [4]. This leads to two main objectives of this work: firstly, since in our opinion the SHG properties of liquid gallium, bismuth and its mixtures are not known, we have to learn which information can be extracted from the SH output; and secondly, we want to apply this knowledge to a systematic study of the surface phase behaviour as a function of temperature and bulk composition of liquid alloys with respect to structural and/or chemical alterations at the surface. First and interesting results are presented in this paper.

2. Experiment

The SHG experiment was described recently for the case of wetting studies in K–KCl solutions [4] and the principal experimental geometry is shown in figure 2. In brief, polarized fundamental laser light is reflected at the surface of the alloy under an angle of incidence of $\Theta = 70°$. Together with the fundamental a small portion of SH light generated at the surface is reflected from the surface. The fundamental intensity is greatly reduced with suitable filters. The SH photons are first analysed for the polarization state and then transformed to a circular polarization state to avoid corruption of the intensity measurement by the polarizing properties of the grating monochromator. This is introduced as an effective filter for the fundamental

photons and for parasitic stray light. Despite a mechanical damping of the optical table the liquid surface exhibits some surface waves which lead to small beam deviations. These are compensated using a focusing lens in front of the monochromator. The SH light pulses are detected with a photomultiplier.

Since surface SHG is usually weak one has to apply short and intense laser pulses. As fundamental light source we use a Q-switched Nd:YAG laser (Lumonics, Rugby) with a pulse duration of 4 ns, a pulse energy of 12 mJ and a repetition rate of 5 Hz. Next to the laser exit window a small portion of the fundamental is reflected into a KDP crystal in order to generate a reference SH signal, I_{ref}, detected with a second photomultiplier. Mostly, this signal is constant or drifts only weakly with time. As one varies the laser intensity the proportionality between I_{ref} and the sample signal, $I(2\omega)$, provides a test for the second harmonic nature of $I(2\omega)$.

The sample is contained in a molybdenum crucible which is heated by a resistance furnace. The temperature is measured with an Ni–NiCr thermocouple inside the bottom of the crucible. The absolute accuracy of the temperature measurement is 2 K; the temperature difference between the thermocouple and the temperature at the liquid surface is less then 3 K [14]. Sample, crucible and furnace are mounted inside a UHV chamber, which has been described previously [7]. Using a turbo pump and a liquid nitrogen cooling trap a vacuum of 10^{-7} Pa was obtained after baking out the chamber for about 12 h.

Special attention was given to the preparation of the samples and all handling was done in an Ar glove box ($O_2 < 2$ ppm, $H_2O < 1$ ppm) or under high vacuum conditions. We start with high purity gallium (99.9999% with respect to metallic impurities) and bismuth (99.999% with respect to metallic impurities, both supplied by Alfa/Johnson–Matthey or by ABCR GmbH). Bismuth ingots were filled in a syringe which was placed in an evacuated quartz tube above the molybdenum crucible. An induction furnace was used to heat up the bismuth ingots. The molten metal flowed through the syringe into the crucible leaving nonmetallic impurities stuck to the wall inside the syringe. The same procedure was applied for gallium which was poured on top of bismuth. Care was taken that the gallium is not heated above 40 °C in order to start the measurements with a low amount of bismuth in the liquid phase. The crucible was covered with a cap, evacuated and then transferred from the glove box to the UHV chamber. The cap was removed in the chamber under UHV conditions. Even this procedure is not sufficient to ensure an absolutely clean sample surface. We used an argon ion gun to get rid of visible impurities floating on the surface as well as of oxide layers [7].

In a typical experimental run we performed several heating and cooling cycles with a rate of 7.2 K h^{-1}. This fixed rate as set by the temperature controller was found to keep the sample close enough to equilibrium. The SHG output was measured for all polarization combinations with respect to the exciting fundamental and the reflected SH light: for p (s) polarization the E-field vector is parallel (normal) to the plane of incidence.

3. Results and discussion

We have studied the SH intensities reflected from the surface of various Ga–Bi alloys. The compositions are indicated as dashed lines in figure 1. The experimental results are displayed in the following figures as SHG intensities as a function of temperature. It seems to be reasonable to discuss and interpret our results along with their presentation. We have organized this section in the following form: in section 3.1 we show and discuss the results on pure bismuth; this is followed in section 3.2 by gallium-rich alloys with a bismuth mole fraction of $x_{Bi} < 0.085$, i.e. small enough to avoid the liquid–liquid demixing regime. In section 3.3 we present and discuss the results on alloys in the compositional range of the demixing gap ($0.085 < x_{Bi} < 0.615$).
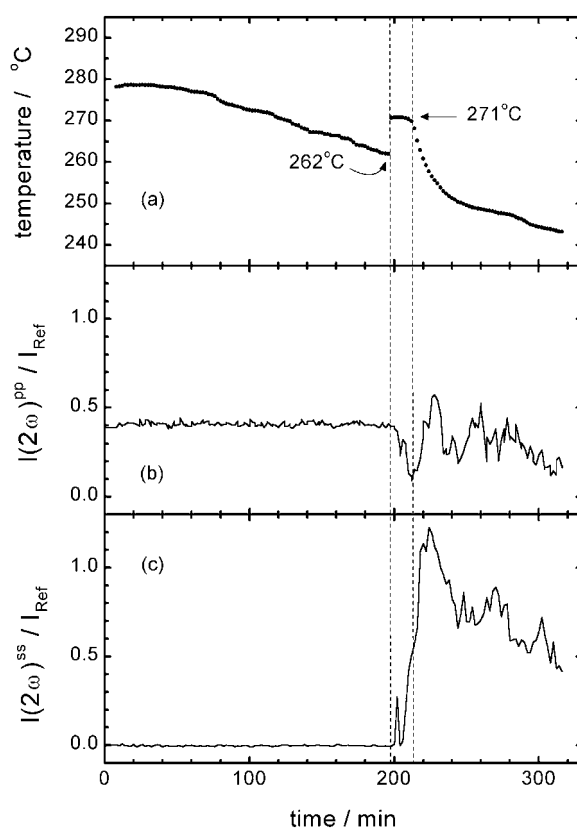
Figure 3. Pure bismuth. (a) Cooling curve: this sample undercools by 9 K and then jumps back to the melting point of bismuth at solid–liquid coexistence. (b) p-in p-out signal, (c) s-in s-out signal. For discussion of the figure see the text.

3.1. Pure bismuth

Figure 3 summarizes typical results of pure bismuth. The top part (a) of the figure displays the temperature of the sample, as measured on cooling by the thermocouple in the bottom of the molybdenum pan, versus time. The cooling curve exhibits the typical supercooling signature which is expected for bismuth. This particular bismuth sample (0.19 mol) remains liquid down to an undercooling of 9 K. For 15 min two phases coexist, a time period determined by the amount of bismuth, the heat capacities and the thermal coupling of the crucible to the environment. These undercooling phenomena lead to a discontinuity along the temperature axis. Therefore, if necessary we plot the SH intensities versus time instead of temperature and include the cooling curve.

The liquid–vapour surface of a simple liquid is expected to have $C_{\infty v}$ symmetry. In this case the second-order surface susceptibility $\chi_{s,IJK}^{(2)}$ has only seven non-vanishing tensor elements and only three are independent [15]: $\chi_{s,ZZZ}^{(2)}$, $\chi_{s,ZXX}^{(2)} = \chi_{s,ZYY}^{(2)}$, $\chi_{s,XXZ}^{(2)} = \chi_{s,XZX}^{(2)} = \chi_{s,YYZ}^{(2)} = \chi_{s,YZY}^{(2)}$. As shown in figure 2 the Cartesian coordinates X and Y define the liquid surface; X and Z are located in the plane of incidence. Under these conditions there is no s SHG on exciting either with p or s light. Four tensor components contribute to the pp SHG and only one ($\chi_{s,ZYY}^{(2)}$) leads to an sp signal.

In parts (b) and (c) of figure 3 the normalized SH intensities $I(2\omega)^{pp}$ and $I(2\omega)^{ss}$ are shown. As long as the sample is liquid both signals are constant. In fairly good agreement with the above mentioned expectations we measure a strong $I(2\omega)^{pp}$ (0.41 ± 0.02), whereas $I(2\omega)^{ss}$ and $I(2\omega)^{ps}$ are below the noise level $(-0.002 \pm 0.004$ and $0.01 \pm 0.005)$. Finally, there is a small contribution in the $I(2\omega)^{sp}$ signal (0.033 ± 0.005). These findings are consistent with an in-plane disorder at the surface described by the point group $C_{\infty v}$. They give in turn some confidence that quadrupolar SHG contributions from the bulk do not play an important role. More evidence for this is given later in section 3.3.

If one looks at the signals in figure 3 in more detail it is found that they remain constant four to five minutes after the bulk phase begins to solidify. This implies that the nucleation process does not start in the footprint of the laser beam at the surface; it begins presumably at the crucible–sample interface. After this time period both signals dramatically change: $I(2\omega)^{ss}$ increases which means in turn that the symmetry of the surface decreases and the tensor component $\chi^{(2)}_{s,YYY}$ is no longer negligible. The highest surface symmetry with a non-zero $\chi^{(2)}_{s,YYY}$ element is C_{3v}, the symmetry class of the [111] plane of a close packed layer of bismuth atoms. This is a clear indication that in the footprint of the laser beam the sample surface becomes solid. The significance of the $I(2\omega)^{ss}$ intensity for the reduction of the symmetry at the surface is the reason why we include this signal in the figures and compare only the pp and the ss polarizations. The behaviours of the sp and the ps polarizations are in agreement with our conclusions. $I(2\omega)^{pp}$ first decreases and then becomes unstable. What values both signals $(I(2\omega)^{pp}$ and $I(2\omega)^{ss})$ approach depends on the actual symmetry of the crystal facet emerging at the surface and on its orientation with respect to the electric field vector of the laser beam.

Once the entire sample is solidified one would expect that the signals would become constant again. We observe a prolonged instability of the signals down to 240 °C in all polarization combinations, whose origin is presently not fully understood. One explanation could be that the surface does not come to a rest and that with further cooling the orientation of the crystal faces are unstable. Thermal gradients, thermal contraction of the sample, the anomalous volume jump on freezing (for both pure Ga and Bi the density of the liquid is higher than the solid) and correspondingly mechanical stress may lead to these continuous instabilities. On the other hand the laser also may alter the texture of the solid surface: in the laser spot on the sample surface we observed a regularly striped pattern which is different from the appearance outside the laser spot. These observations need further elucidation.

Not shown in figure 3 is the melting process: as long as the bismuth sample is solid both signals are unstable. When the bulk melts and a liquid phase appears at the surface the signals become constant again and the intensities approach the old values within the error bars.

In concluding this section we have demonstrated that the excitation of the second harmonic wave is clearly sensitive to structural changes at a metal surface. The melting transition at the surface from a disordered liquid to an ordered solid structure is clearly detected.

3.2. $Ga_{(1-x)}Bi_x$: $x_{Bi} < 0.085$

Exemplarily for this compositional range we discuss measurements on a sample with a nominal bismuth mole fraction of $x_{Bi} = 0.043$. According to the phase diagram [16] between the melting point of gallium and a temperature of 187 ± 1 °C the system consists of a gallium-rich liquid and of pure solid bismuth. As a consequence of the preparation method at the beginning of the experiment nearly pure liquid gallium covers solid bismuth. This situation is shown in figure 2. During the first temperature scan approaching the homogeneous liquid phase the laser beam probes the liquid gallium-rich phase, which becomes more and more enriched with bismuth. Since the surface tension of Bi is lower than that of Ga one expects the bismuth to
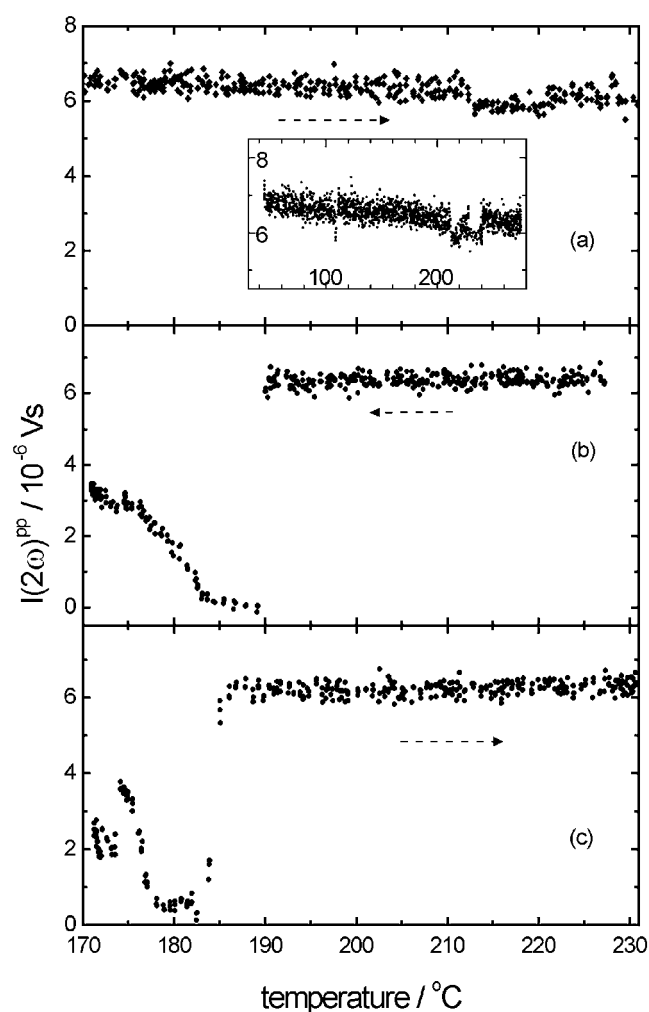
Figure 4. Ga–Bi alloy with $x_{Bi} = 0.043$ outside the miscibility gap. Sketched are the p-in p-out SH signals. Dashed arrows indicate increasing or decreasing temperature. (a) SHG with increasing temperature, first run. (b) SHG with decreasing temperature. (c) SHG with increasing temperature, second run. For discussion of the figure see the text.

be adsorbed at the alloy surface. This was recently confirmed on an atomic scale using x-ray reflectivity and grazing incidence diffraction as microscopic probes [9, 17]. It was found that the monomolecular bismuth layer has the structure of a two-dimensional supercooled liquid.

In figure 4(a) we have plotted the $I(2\omega)^{pp}$ signals of the first temperature scan in the temperature range between 170 and 230 °C, where we expect the transition from two coexisting phases to one homogenous phase at 187 °C. However, the signal is nearly constant: it decreases only sightly in the temperature interval from 40 to 280 °C by 10% as shown in the inset of figure 4(a). This suggests that the monolayer segregation of bismuth is present up to this temperature, which is not surprising (see above).

Figure 4(b) shows the variation of the $I(2\omega)^{pp}$ signal as one cools the same sample down into the two-phase regime. It is striking to see a strong drop of the signal at 189 °C, which is

the liquidus temperature of the sample within the temperature error. In coincidence with the bismuth precipitation in the bulk the symmetry at the surface changes, i.e. bismuth crystallizes at the surface and wets the gallium-rich liquid. So far we cannot distinguish whether the wetting is partial or complete. The adsorbed bismuth monolayer forming the alloy surface on first heating can be probably regarded as the nucleation centre for the crystallization process. As such a sample is cooled further down one ends up with a thin but macroscopic crystal floating on the liquid.

In our opinion the drop of the pp signal to approximately zero is accidental. It depends on the type of crystal facet and its orientation with respect to the laser beam as the crystallization process sets in. Again, the recovery of the signal at lower temperature is not clear yet: movements of the bismuth crystals on cooling and/or altering of the surface morphology by means of the laser beam may explain this. All these effects will be objectives in future studies.

In figure 4(c) we depict the change of the $I(2\omega)^{pp}$ signal on a second heating of the sample. At first glance it is surprising to see that the pp signal jumps back to the liquid value about 5 K below the respective drop on cooling (figure 4(b)). Temperature gradients across the sample cannot be responsible for this kind of 'reversed hysteresis': at constant crucible temperature the sample surface is less than 3 K colder [14]. The most probable explanation for the reappearance of the liquid surface at a temperature 5 K below the phase line are local compositional inhomogeneities as a consequence of the finite solvation kinetics. The thin bismuth crystals on top of the gallium-rich liquid dissolve faster then the remainder, which is deposited in a more bulky form somewhere else in the sample. The dependence on cooling and heating rates is a subject of ongoing experiments. In addition, how far surface melting accelerates this process is an open problem.

3.3. $Ga_{(1-x)}Bi_x$: $0.085 < x_{Bi} < 0.615$

In this concentration range at temperatures above the monotectic point and below the critical point this alloy system exhibits a wide miscibility gap. Our main interest in employing the SHG technique is to detect the wetting transition which occurs as two liquid phases coexist. We discuss in detail the SHG results obtained for two alloy samples representative for the demixing regime. On passing the monotectic point [18]† at $T_m = 222\,^\circ\text{C}$ on heating the gallium-rich liquid is completely wetted by a bismuth-rich liquid film of mesoscopic thickness of a few tens of Ångstroms [7, 9]. We have measured the SH intensities at the surface of the liquid alloy with increasing temperature. Below 222 $^\circ$C the system consists of solid Bi at the bottom of the crucible covered by a Ga-rich liquid exposed to the laser beam. At 222 $^\circ$C the Bi-rich liquid phase becomes stable and completely wets the Ga-rich liquid leading to a drastic change of the chemical nature of the liquid surface. It is highly surprising to see in figure 5(a) that neither $I(2\omega)^{pp}$ nor $I(2\omega)^{ss}$ exhibits any change on first heating while the wetting film forms according to ellipsometric experiments [7]. The relative intensities in the temperature range plotted in figure 5(a) are: $I(2\omega)^{pp} = 0.59 \pm 0.03$ and $I(2\omega)^{sp} = 0.052 \pm 0.007$ which is considerably lower. $I(2\omega)^{ps} = 0.020 \pm 0.007$ and $I(2\omega)^{ss} = 0.011 \pm 0.005$ are close to the detection limit. This intensity pattern of the various polarization combinations is very similar to that found at the surface of pure liquid bismuth.

The important question arises why the wetting transition is not manifest in the SHG signals. At present we do not think that the heating rate of 7.2 K h^{-1} plays an important role in this case. In an ellipsometric experiment the film formed under comparable conditions [7]. Nevertheless, the dependence of the heating rate will be a subject of future studies. The fact that $I(2\omega)^{ss}$ is negligibly small excludes a substantial superposition of the SHG by fundamental stray light.

† The phases involved are: solid bismuth, bismuth-rich liquid, gallium-rich liquid, vapour.
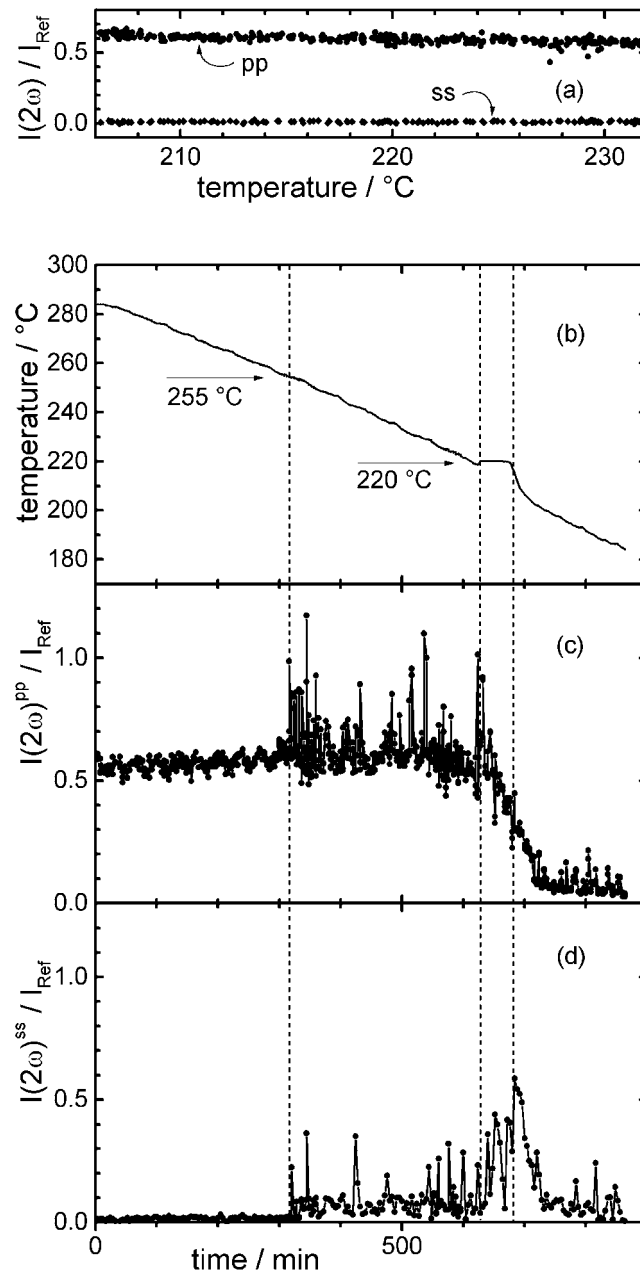
Figure 5. Ga–Bi alloy with $x_{Bi} = 0.367$. (a) pp and ss signals in the range of the wetting transition, first run. The appearance of the wetting film at $T_{mono} = 222\,°C$ is not visible in the signals. (b) Cooling curve, (c) pp signal and (d) ss signal. For discussion of the figure see the text.

Another explanation could be a strong quadrupolar bulk contribution to the second harmonic polarization which might hide the phase transition at the surface. The importance of making this estimation was recently pointed out by Shen [13]. The relevant length scale is half the penetration depth of the fundamental field in the liquid metal. The second-order polarization

as a function of the coordinate z along the surface normal is proportional to the square of the electric field which is given by: $E(z) = E(0) \exp(-z/\delta)$ with δ as skin depth. One can define a fraction y_{SHG} as follows:

$$y_{SHG}(30 \text{ Å}) = \left[\int_0^{30 \text{ Å}} \exp\left(-\frac{2z}{\delta}\right) dz \right] \left[\int_0^{\infty} \exp\left(-\frac{2z}{\delta}\right) dz \right]^{-1}.$$

The quantity $y_{SHG}(30 \text{ Å})$ gives the fraction of second harmonic radiation stemming from the first 30 Å under the assumption that the second harmonic susceptibility is entirely dominated by bulk contributions. Under these conditions and using the published absorption coefficients for gallium and bismuth [19, 20] one can estimate that a maximum fraction y_{SHG} of 30% to 50% of the SH signal could stem from the first 30 Å below the surface. The first 30 Å is the spatial region where the wetting phase transition takes place and where the composition changes drastically on wetting (from gallium rich to bismuth rich). That means that bulk contributions should definitely be influenced by the wetting transition. In addition the appearance of the wetting film generates new anisotropic regions normal to the surface which might also lead to additional dipolar contributions. However, the complete insensitivity of the SH signal to the wetting transition allows the conclusion that all these contributions are negligible. So, what is the source for the SH field in this system?

In our opinion a conclusive explanation is provided by new experimental results presented by Tostmann *et al* [9]: they have measured the angle of incidence dependent x-ray reflectivity, i.e. the Fourier transform of the electron density distribution normal to the surface, of gallium–bismuth alloys under wetting and non-wetting conditions. In both cases their reflectivity data can only be modelled under the assumption of a bismuth monolayer either on top of the bulk under non-wetting conditions or on top of the wetting layer under wetting conditions. Let us assume that the SHG is exclusively sensitive to the outermost layer in this system: it is possible that the wetting transition is not visible. In both cases it consists of a bismuth monolayer. This would imply that the strongest contribution to the second harmonic field stems from the anisotropy normal to the surface caused by the transition from the bismuth monolayer to the vacuum. The anisotropy due to the transition from the monolayer to the bulk volume seems to be at best of secondary importance. Weber and Liebsch treated the nonlinear second order susceptibility of metals within a local density functional approximation. They find that the main source for SHG is located in the exponential tail of the electron density extending into the vacuum hemisphere [21]. Thus, we arrive at the following conclusion: the SHG of this alloy system is highly sensitive to the first atomic layer! Since this layer consists in any case of bismuth, changes of the SHG signal is due to structural changes at the surface.

In figures 5(b) to 5(d) we show a cooling cycle of the same sample ($Ga_{0.633}Bi_{0.367}$) starting in the homogenous liquid phase region at 283 °C. Part (b) is the cooling curve of this experiment showing a weak undercooling before bismuth precipitation sets in at the monotectic point. Down to this point both SHG signals, $I(2\omega)^{pp}$ and $I(2\omega)^{ss}$, show two distinct domains corresponding to the homogenous phase region and the demixing gap below 255 °C. This temperature, as measured at the bottom of the crucible, has to be calibrated with the help of the monotectic point. Taking this into account, the occurrence of the two phase region lies 3 K below the phase line published earlier [16], which is in acceptable agreement. Above 255 °C the signals display the well known signature of a second-order polarizability of a surface that is horizontally isotropic: $I(2\omega)^{pp}$ is the strongest signal (0.58 ± 0.04), $I(2\omega)^{sp}$ is one order of magnitude lower (0.050 ± 0.007) and the ps (0.012 ± 0.013) and ss intensities (0.016 ± 0.006) are again close to the detection limit. Why the pp signal displays a weak modulated structure is not yet clear. A probable explanation considers interference patterns arising from the modulation of the optical path length between the entrance and exit windows acting as an interferometer.

The optical path is varied by the volume contraction of the sample on cooling: two maxima have a separation of roughly 3 K. Using a typical coefficient of linear expansion of 10^{-5} K^{-1} for the liquid and a sample thickness of 7 mm, the surface of the sample is moved down by approximately 200 nm. At the given angle of incidence this reduces the optical path between the entrance and exit windows of our vacuum chamber by approximately one wavelength.

As soon as the sample approaches the demixing regime the character of the SH signals change strongly. In comparison to the homogenous phase region the average values of the intensities change. $I(2\omega)^{pp}$ increases only by 5%, $I(2\omega)^{sp}$ by a factor of three, $I(2\omega)^{ps}$ grows by a factor of eight and $I(2\omega)^{ss}$ by a factor of five. But the most obvious difference is that the signals no longer exhibit a Gaussian distribution if one averages the intensities in the temperature range from 255 °C down to 219 °C. As one can see in figures 5(c) and 5(d) there are frequent spikes leading to a strongly fluctuating second harmonic, which is observed in all four polarization combinations. This implies that the symmetry and/or the chemical nature of the outermost layer fluctuates strongly in the footprint of the laser beam as one passes through the demixing gap downwards.

As a first explanation we assume that in the demixing state the outermost layer consists of an adsorbed monolayer of bismuth. Underneath this monolayer there is the bismuth-rich wetting film, which encapsulates completely the gallium-rich bulk phase. As one cools the sample down both the wetting film phase and the bulk phase have to adjust their compositions as described by the phase diagram. Thus, the film phase has to accumulate bismuth which has to be supplied by the gallium-rich bulk phase. If the kinetics of this process is diffusion controlled this may lead temporarily to a depletion of bismuth. In this situation the film free energy may be reduced by dissolving the bismuth monolayer and, as a consequence, a strong change of the electron density at the surface should result. In other words, there are two competing mechanisms to diminish the total free energy: Gibbs adsorption requires formation of a Bi monolayer; the approach to phase equilibrium of the wetting film may destroy this monolayer. In addition, convective flow may also contribute to the mass transport necessary to achieve equilibrated phases. This might lead to the fluctuating intensity. We are aware that these scenarios are somewhat speculative and qualitative. They raise new questions like the following: why is this process observable on the experimental time scale and what SHG output is expected for liquid gallium in comparison to liquid bismuth? To our knowledge this has not yet been measured. The critical reader may add an alternative scenario that involves impurities floating at the surface. But this would not explain why the intensity fluctuations do not occur in the homogenous phase and in the demixing range on heating.

Before reaching the monotectic point this sample undercools by about 1.5 K. At the phase transition three condensed phases are in equilibrium: solid bismuth, bismuth-rich liquid and gallium-rich liquid. Which of them actually forms the reflecting surface is not *a priori* clear. As one can see in figures 5(c) and 5(d) for these conditions a reduction of the pp signal and an enhancement of the ss signal occurs. Once the phase transition is completed and the liquid Bi-rich phase has vanished this trend continues: the ss and the sp signals become stronger than $I(2\omega)^{pp}$. This clearly indicates that solid bismuth crystallizes at the surface. For further evolution of the signals with decreasing temperature the same considerations as in the preceding subsections hold. The end of this particular experiment at about 180 °C is given by a violation of the specular reflection condition. The reflecting crystal facets developing at the surface may be somewhat declined with respect to the liquid surface: the reflected beam is no longer properly aligned and all signals decrease. If one inspects the sample surface with the naked eye one finds thin crystalline slabs on top of the liquid.

Figure 6 shows the second harmonic intensities of Ga$_{0.733}$Bi$_{0.267}$ on cooling. Comparable to the last example we observe unstable signals in the liquid–liquid demixing regime. However,
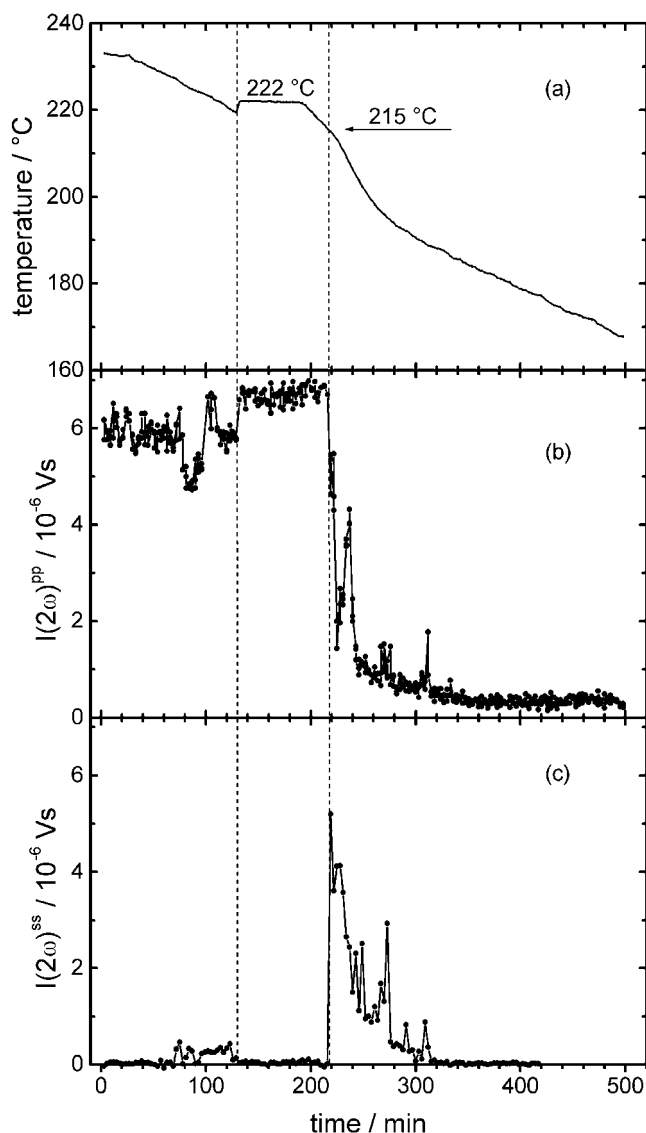
Figure 6. Ga–Bi alloy with $x_{Bi} = 0.267$. (a) Cooling curve, (b) pp signal and (c) ss signal. For discussion of the figure see the text.

at the monotectic phase transition the situation is different. All signals show the signature of a liquid with an adsorbed and disordered, i.e. isotropic, bismuth monolayer as can be seen by the following relative intensities: $I(2\omega)^{pp} = 0.58 \pm 0.02$, $I(2\omega)^{sp} = 0.048 \pm 0.006$, $I(2\omega)^{ps} = 0.010 \pm 0.004$, $I(2\omega)^{ss} = 0.003 \pm 0.003$. The range of these signal patterns extends down to 215 °C when this sample is back in the two-phase region consisting of a Ga-rich liquid and solid bismuth. This means that the crystallization history is different compared with the sample of figure 5. In this case solid bismuth does not show up in the footprint of the laser. But below 215 °C $I(2\omega)^{ss}$ is suddenly switched on: it grows by a factor of 100. The surface symmetry is reduced at least to C_{3v}. Now the crystalline slab has formed and

can be detected by SHG. Why the crystallization process at the surface is different in the two samples is not yet clear: small temperature gradients across the sample could play an important role; concentration gradients resulting in surface tension gradients and a Marangoni flow can influence the surface structure; metastable undercooling of the Bi layer at the surface has also to be considered. All these problems are open for further studies.

4. Conclusions

Second harmonic generation at the surface of the gallium–bismuth system is strongly sensitive to structural changes at the surface. This holds in particular for order–disorder surface phase transitions. A slight reduction of the symmetry at the surface (from $C_{\infty v}$ to C_{3v}) is visible by strong changes of the SH signals. In this way a freezing of Bi-rich films on top of the Ga-rich liquid alloy is clearly detected for the first time in the vicinity of the monotectic point. We have no success in applying SHG for the study of the wetting transition occurring in this system, which was one of the aims when we started these experiments. In this system SHG is insensitive to chemical changes in the first few tens of Ångstroms below the surface. We argue that this may be due to the location of the main source of nonlinear polarization at the outermost layer of the liquid surface. It consists in the wetted and the non-wetted state of a segregated monolayer of bismuth with an isotropic in-plane structure. One can turn the tables: these findings open new perspectives for the understanding of SHG at metal surfaces. A wetting transition can be regarded as a microscopic tool to change the composition near the surface drastically whereas the top layer remains constant. Thus, the change of the SHG signals tells us where the nonlinear source is located.

Applying the special SHG sensitivity to order–disorder transitions at the surface of bismuth–gallium samples we observe on *first* heating a persistent disordered, i.e. liquid, state at the surface. On cooling solid bismuth crystals appear at the sample–vapour interface despite the fact that the crystals are more dense than the liquid underneath. How far this depends on the wetting transition occurring in this system or on the presence of a segregated bismuth monolayer is an open and interesting question.

Acknowledgments

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