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Tetra Point Wetting At The Free Surface Of The Binary Liquid Metal Gallium-Bismuth

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Beamline(s): X22B

Introduction: In recent years surface sensitive x-ray reflectivity studies established a phase diagram for the free surface of the binary liquid metal gallium-bismuth (GaBi) [1] that complements the bulk phase diagram, which had been known for a long time. The bulk phase diagram shows a consolute point at T_C=262°C, c(Ga)=70at% with a corresponding miscibility gap that starts at the lower monotectic temperature T_M=222°C. For $T<T_M$ (regime **I**), a Gibbs-adsorbed Bi monolayer resides at the free surface; however, a thick, Bi rich wetting film intrudes between the Bi monolayer and the Ga rich bulk for $T_M<T<T_C$ (regime **II**). In this period, we determined the surface transition temperature between of those two regimes in relation to the first order bulk transition temperature T_M. Furthermore, we have achieved new insights on the potential at free surface that drives this transition.

Methods and Materials: A sample with an overall Ga amount of 90 at% was contained in an UHV chamber. Surface sensitive x-ray reflectivity measurements were carried out over a temperature range from 200°C up to 270°C using the liquid surface reflectometer at Beamline X22B. To avoid temperature gradients a temperature-controlled radiation shield was installed above the sample.

Results: Fig. 1 shows the x-ray reflectivity at a fixed q_z = 0.8 $Å^{-1}$ while heating from 200°C to 255°C. From such a T-scan alone it is possible to get information on the thickness versus T behavior of the Bi-rich wetting film; however, from separate reflectivity measurements vs q_z we have obtained quantitative values for the temperature dependence of the film thickness. The higher the reflectivity at q_z=0.8$Å^{-1}$ the thinner is the Bi-rich wetting film [2]. The decrease of intensity from T=200°C towards T=222°C indicates the formation of the wetting film while approaching T_M and the liquid-liquid coexistence line, whereas the increase while heating above T=229.5°C indicates vanishing of the wetting film and hence a path leading off-coexistence. In Fig. 2 we compare the evolution of the Bi-rich film below T_M with the behavior as it vanishes for T>229.5°C. The abscissa is an "effective chemical potential" $\Delta\mu^-$ that is equivalent to the disjoining pressure in a one component systems and hence a measure of the surface potential that stabilizes the thermodynamically metastable thick Bi-rich film.

Conclusions: The observed formation and vanishing of the wetting film is governed by short-range forces as indicated by the logarithmic behavior on $\Delta\mu^-$ in Fig 2. The wetting transition at T_M is pinned at the bulk first order transition due to the topology of the phase diagram which enforces a path leading towards liquid-liquid coexistence at T_M in the same way as it leads off coexistence for this concentration of Ga at T=229.5°C. Since T_M is a temperature of four phase coexistence in the bulk (Bi-rich-, Ga-rich- , solid Bi- and vapor-phase coexist), the surface transition is properly described as tetra point wetting. A wetting phenomenon in binary systems which corresponds to the well-known triple point wetting phenomenon in one component systems [3].

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References:

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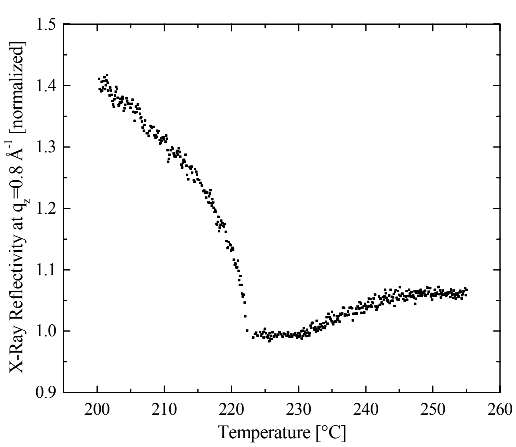

Fig.1: x-ray reflectivity at q_z=0.8 $Å^{-1}$ versus T normalized by its value at T=222°C.

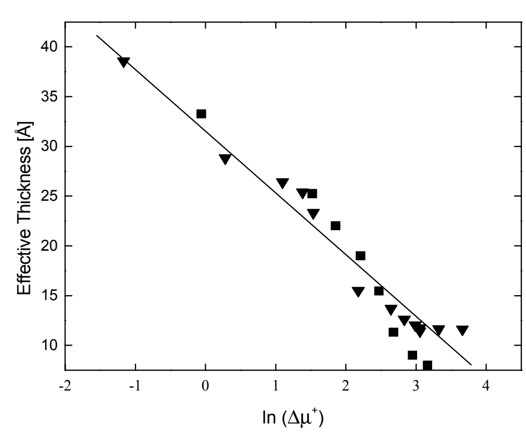

Fig. 2: slab thickness of the wetting film (squares) $T<T_M$, (triangles) T>229.5° versus log of the corresponding disjoining pressure.