Temperature-Dependent Interfacial Stiffness of the Disorder Layer in a Thin Cu_3Au Alloy Film

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The order-disorder transition in a 170 Å thick $Cu_3Au(111)$ epitaxial alloy film is examined using x-ray diffraction techniques. Below the transition temperature T_0, a disordered surface layer of thickness l is detected. This layer exhibits wetting behavior, i.e., l increases, obeying a logarithmic growth law on approach to T_0. We show by a detailed analysis of the order parameter profiles that the stiffness of the order-disorder interface is temperature dependent, resulting in a nonuniversality of the wetting transition.

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First-order phase transitions in the presence of a surface or interface have been investigated in the past two decades in great detail [1]. It has been shown by theory [2,3] and experiment [4–7] that the surface-related phase transition is continuous and, consequently, surface critical exponents can be defined which have no counterpart in the bulk. It turned out that this surface scenario is mediated by a wetting transition which takes place close to the bulk phase transition at T_0 and which leads to a disordered surface sheet with temperature-dependent thickness l obeying the growth law,

$$l = \xi_b \ln[|t^*/t|], \tag{1}$$

where ξ_b is the bulk correlation length, t is the reduced temperature $(T - T_0)/T_0$, and t^* is the relative difference to an offset temperature of the wetting transition. A mean-field analysis assuming short-ranged forces [8] predicts that the emerging interface between the ordered bulk and the disordered wetting layer is smeared out by interfacial fluctuations to a width

$$\sigma_{\mathrm{od}} = \xi_b[\omega \ln(|t_r/t|)]^{1/2}, \tag{2}$$

where $\omega = k_B T_0/4\pi\tilde{\Sigma}\,\xi_b^2$ is a dimensionless capillary wave parameter related to the interfacial stiffness $\tilde{\Sigma}$ between the ordered and the disordered regions and t_r is the relative difference to the roughening temperature T_r of this interface. Recently, this scenario has been considered for the case of a temperature-dependent interfacial stiffness [9]. Since capillary waves are divergent in three dimensions, it was argued that interfacial fluctuations may lead to a weakening of the stiffness and to an increase of ω upon approaching the transition temperature T_0. In turn the width of the order-disorder interface [Eq. (2)] would exhibit a temperature dependence which deviates characteristically from the $[\ln(1/t)]^{1/2}$ behavior. From the theoretical point of view, different regimes of fluctuations can be distinguished [9], depending on the actual value of ω. A temperature dependence of $\tilde{\Sigma}$ results in a nonuniversality of the wetting transition [10].

Only very little experimental data are at hand for a critical test of this generic theoretical scenario. This holds in particular for the interfacial smearing σ_{od} which turned out to be an elusive experimental quantity [11]. In this Letter we present an x-ray scattering study of the order-disorder transition in a thin epitaxial $Cu_3Au(111)$ film and determine the microscopic order-parameter profile and its temperature dependence layer by layer.

Cu_3Au undergoes a first-order disorder transition from the $L1_2$ ordered structure to the fcc disordered phase at $T_0 = 663$ K. For semi-infinite $Cu_3Au(001)$ systems the existence of a disorder wetting and the associated continuous behavior of the topmost order have been demonstrated experimentally [4–6]. However, the detailed order profile, in particular the roughness of the order-disorder interface, could not be accessed by these experiments. Monte Carlo simulations [12] of thick $Cu_3Au(111)$ films bound symmetrically by two equal interfaces, on the other hand, showed that the wetting law (1) and the interfacial smearing (2) are fulfilled, although the prefactor in Eq. (2) could not be reproduced in this study. In our experimental x-ray study on a thin $Cu_3Au(111)$ film bound between vacuum and a Nb buffer we used the thin film geometry to achieve a fully coherent x-ray determination of the order-parameter profiles across the entire film. This allows for a microscopic insight into all details of disorder wetting.

A 170 Å thin $Cu_3Au(111)$ layer was grown using molecular beam epitaxy onto a 300 Å $Nb(110)/Al_2O_3(1120)$ substrate with growth parameters developed in [13]. After the surface order was checked by reflection high-energy electron diffraction, the sample was transferred into a portable UHV chamber equipped with Be windows. The actual x-ray study has been carried out at the C1 beam line of the Hamburg Synchrotron Radiation Laboratory (HASYLAB) equipped with a horizontal z-axis diffractometer. The experiments have been performed with a fixed x-ray energy of 11.0 keV. The sample temperature was monitored with a relative accuracy of 0.1 K using a thermocouple spring-loaded against the substrate.

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In order to follow the order-parameter profile across the film during the order-disorder transition we performed detailed scans through the (001) order reflection perpendicular to the film (q_z scans). As a reference and to monitor any structural changes accompanying the thin film phase transition, the fundamental ($11\bar{1}$) reflection profile has been measured at selected temperatures. In a finite slab of coherent thickness D the q_z diffraction pattern exhibits Laue oscillations with periodicity given by the number of fcc layers for the fundamental reflection and by the number of $L1_2$-ordered layers for the superlattice reflection. Disorder wetting in thin films can thus be directly observed by a distinct change of the periodicity of the order-related Laue oscillations (see Fig. 1b) which can be converted into a change of the number of ordered layers (see Fig. 1a). The aforementioned fluctuation-induced smearing of the order-disorder interface gives rise to a characteristic damping of the Laue oscillations (see Fig. 1b). It turns out that the smaller of the two interfacial roughnesses (σ_{bot}, σ_{od}) is responsible for the overall decay of the Bragg envelope while the damping of the oscillating pattern depends on the asymmetry ($\sigma_{\mathrm{bot}} - \sigma_{\mathrm{top}}$). This allows us in this case to distinguish between the top and the bottom profiles of the order parameter. Consequently, the wetting layer thickness $l(T)$ and the width of the order-disorder interface $\sigma_{\mathrm{od}}(T)$ associated with thin film wetting can be directly observed and precisely analyzed by comparing the thermal behavior of fundamental and order-related Laue-oscillation patterns.

For an arbitrary thin film order profile $\Psi(n)$ the coherent superlattice Laue pattern reads

$$I(q_z, \Psi) \propto \left| \sum_{n=1}^{N} F(q_z)\Psi(n)e^{i(q_z \cdot a_z \cdot n)} \right|^2, \qquad (3)$$

where F contains the atomic form factors of Cu and Au, a_z is the lattice spacing normal to the film, N is the number of lattice planes (here 90), $n = 1, 2, \ldots, N$ is the layer index (note that $n = 1$ corresponds to the surface and $n = N$ to the interface). A convenient analytical form for an order profile as shown in Fig. 1a is

$$\Psi(n) = \Psi_{\mathrm{hom}}\left[\tanh\left(\frac{n}{\sigma_{\mathrm{bot}}}\right) - \tanh\left(\frac{n - N}{\sigma_{\mathrm{od}}}\right)\right]; \qquad (4)$$

Ψ_{hom} is the homogeneous part of the order-parameter profile (see Fig. 1a). The tanh-functions accounted for the interfacial roughness σ_{bot} as well as for the thermal smearing σ_{od} [14].

The top curve of Fig. 2 shows the experimental results as obtained across the fundamental ($11\bar{1}$) reflection. The pronounced Laue oscillations are a direct evidence for the high structural quality of these binary films. The full lines are least-squares fits providing the fcc thickness

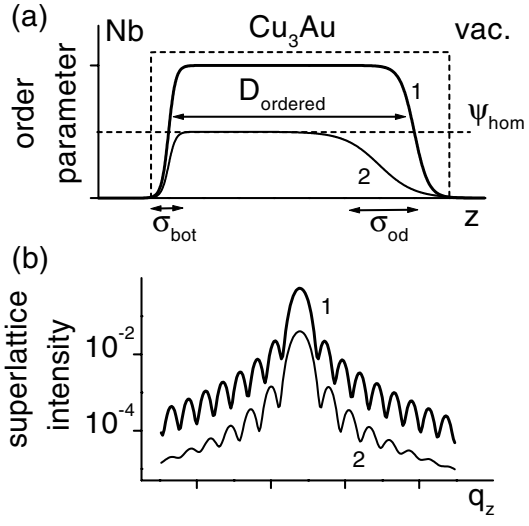

FIG. 1. (a) Sketch of a binary alloy film with fcc structure extending to a thickness D_{fcc} (dashed border). The film exhibits L_{12} order with thickness D_{ordered} which changes with temperature. (b) Resulting pattern in reciprocal space. The period of the superlattice reflection is temperature dependent. Notice that the oscillations are more pronounced for the symmetric profile (1) and strongly damped for the asymmetric profile (2).

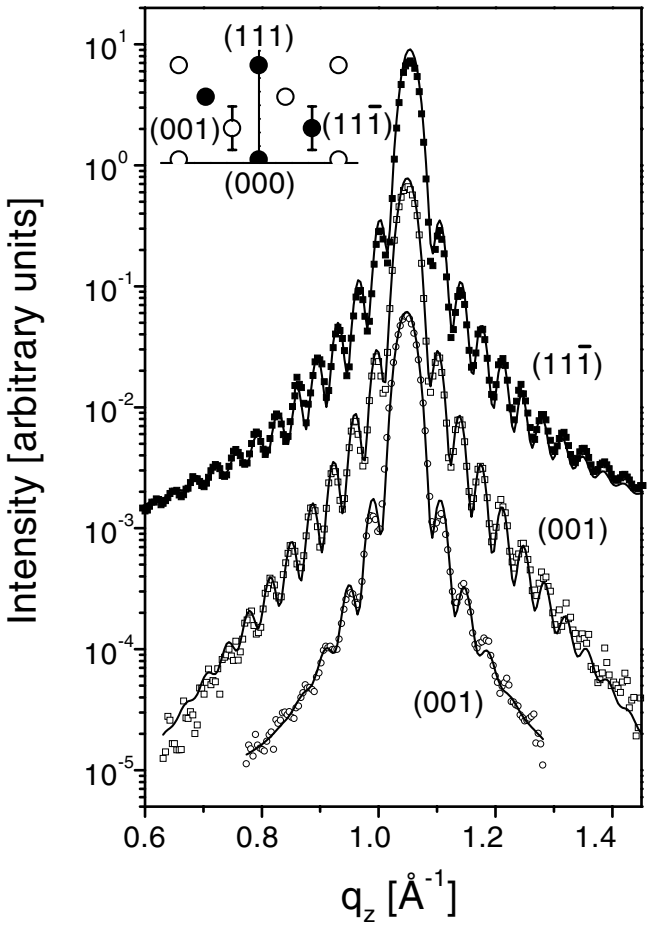

FIG. 2. Scans through the ($11\bar{1}$) fundamental (filled symbols) and (001) superlattice reflection (open symbols) at $T_0 - 94$ K (squares) and $T_0 - 8$ K (circles). The curves are plotted on the same scale. Straight lines are fits to the data according to Eqs. (3) and (4).

$D_{fcc} = (170 \pm 1.1)$ Å. The roughnesses have independently been measured by x-ray reflectivity to be $\sigma_{top} = (10 \pm 1.5)$ Å and $\sigma_{bot} = (6 \pm 0.3)$ Å. No noticeable changes of these structural parameters have been detected upon heating.

In contrast, the (001) superlattice Laue pattern exhibits pronounced changes both in the oscillation period and in the q_z-dependent damping of the oscillations (Fig. 2). A detailed quantitative analysis of these Laue patterns using Eqs. (3) and (4) provides the order-parameter profiles across the Cu_3Au film (Fig. 3): In the low temperature regime the order parameter profile adapts the form of the structural profile; i.e., the film is fully ordered and the larger smearing is located at the free film surface. Notice that upon heating the oscillation damping grows steadily while the overall decay of the Bragg tails does not change significantly. This observation together with the asymmetry arguments discussed above imply that the thermal smearing takes place at the top film interface of the Cu_3Au film.

From these results we can deduce several thermodynamic quantities in a rather straightforward way: the thickness $l(T)$ of the disordered layer (Fig. 4a), the order parameter $\Psi_1(T)$ at the top layer (Fig. 4b), and the width σ_{od} of the order-disorder interface (Fig. 4c). $\Psi_1(T)$ [open symbols in 4b] exhibits a distinct power law behavior as a function of the reduced temperature t with a power law exponent $\beta_1 = 0.85 \pm 0.03$. This deviation from mean-field behavior ($\beta_1 = 0.5$) is in reasonable agreement with LEED investigations [5] and indicative of strong interfacial fluctuations.

The detailed observation of the thermal behavior of the interface topology associated with the wetting transition in this thin film is the main result of this Letter (summarized in Fig. 4b, 4c, and 4d): Within the temperature range screened by the experiment the wetting layer thickness $l(T)$ grows to a thickness of 25 Å, following the growth law predicted in Eq. (1). (Note that every data point is extracted separately from a fit to the experimental scattering profiles and no functional relation was assumed *a priori*.) The amplitude of the growth law was determined to 7.54 ± 0.29 Å, which is in good agreement with published values of the bulk correlation length at coexistence [15]. In addition, we are able to determine the hitherto unknown onset temperature for disorder wetting from the parameter t^* to be $T^* = T_0 - 160$ K. The interfacial width σ_{od} is shown in Fig. 4c as a function of the logarithm of the reduced temperature. Notice first that σ_{od} merges

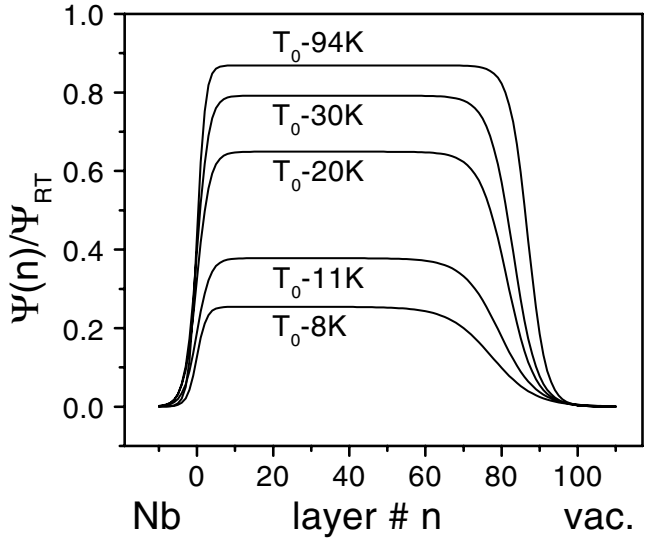

FIG. 3. Order-parameter profiles as a function of temperature. The uppermost and the lowest curves are the models for the straight lines in Fig. 2.

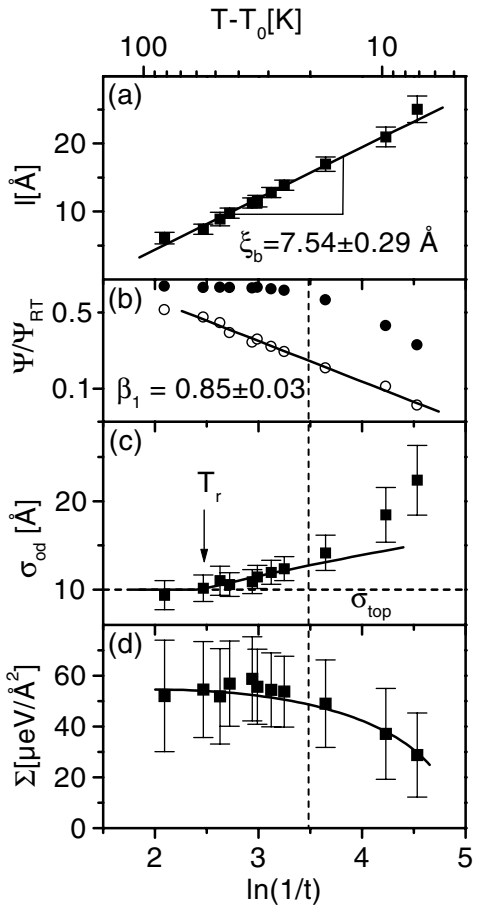

FIG. 4. (a) Thickness l of the disordered layer and (b) order parameter in the first (top) layer (open symbols) and in the center of the film (filled symbols) as a function of the reduced temperature on a (double)-logarithmic scale. The straight line is a fit with parameters stated in the plot. (c) Roughness of the order-disorder interface σ_{od} as a function of the logarithm of the reduced temperature. The full line is a fit assuming a $[\ln(1/t)]^{1/2}$ behavior [Eq. (2)]. (d) Interfacial stiffness $\tilde{\Sigma}$ as calculated from the experimental data in (c); the full line is a guide to the eye. For explanations of ξ_b, β_1, T_r, and σ_{top} see main text.

into $\sigma_{\text{top}} = (10 \pm 1.5)$ Å for low temperatures (horizontal dashed line). We conclude from this observation that the order-disorder interface takes over the static roughness of the surface (conformal roughness). With the emergence of a disordered layer additional thermal roughness is observed. In the following discussion we separate the thermal from the static roughness. In a region up to 20 K below T_0 the growth of σ_{od} can be described by Eq. (2) with a temperature-independent prefactor (solid line), but at higher temperatures significant deviations from (2) can be detected. Here we estimated the roughening temperature T_r of the order-disorder interface to be $T_r = T_0 - 60$ K. Although there is no detailed experimental investigation of the roughening in bulk Cu_3Au, Monte Carlo simulations on wetting of (100) antiphase boundaries [16] show the existence of a roughening temperature well below the order-disorder transition. Interestingly, the increase of σ_{od} and therefore the weakening of the order-disorder interface sets in where the "bulk" order parameter in the center of the film (filled circles in Fig. 4b) starts to decrease more rapidly (see vertical dashed line). Apparently the associated decreasing energy difference between the ordered and the disordered phase (associated with the interfacial stiffness) is the driving force for the strong increase of the interfacial fluctuations.

The increase of the interfacial smearing σ_{od} together with the surface exponent $\beta_1 = 0.85$ can be taken as evidence for the dominant role of fluctuations at higher temperatures. Note here that the order-disorder transition stays first order (as manifested in a pronounced hysteresis when cycling through the transition) while the disorder wetting transition is fluctuation dominated. In order to estimate the contribution of fluctuations on the stiffness of the order-disorder interface we calculated the interfacial stiffness $\tilde{\Sigma}$ from the width σ_{od} using the correlation length ξ_b as determined from Fig. 4a. The results are plotted in Fig. 4d: the interfacial stiffness drops by nearly 50% in the temperature range screened by the experiment. The related capillary wave parameter ω (the ratio of thermal to interface energy) stays constant at ≈ 1.45 in the region where the solid line in Fig. 4c describes the data and then rises up to 2.7. From the value of $\omega = 1.45$ we may calculate the surface exponent β_1 through a nonuniversal relation [12], ending up with $\beta_1 = 0.96$. This calculated value is in remarkable agreement with the independently determined experimental value 0.85 ± 0.03.

In conclusion, we have unambiguously shown that the width of the order-disorder interface during the disorder wetting transition grows in an amount incompatible with mean-field theory assuming short-ranged forces. We therefore conclude that interfacial fluctuations lead to a decrease of the interfacial stiffness, resulting in a nonuniversality of the wetting transition.

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