Experimental Evidence for an Interface Delocalization Transition in Cu_3Au

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The $Cu_3Au(100)$ surface has been studied close to the bulk order-disorder transition temperature T_0 by x-ray diffraction under total external reflection. The order-parameter profile which has been probed in various depths is analyzed in terms of a surface-induced disorder transition. It is demonstrated that the temperature dependence of the superlattice intensity is consistent with the assumption of a disordered surface layer which exists between the ordered bulk and the vacuum at temperatures below T_0 and grows logarithmically as T_0 is approached.

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The thermodynamic behavior of a semi-infinite system undergoing a first-order phase transition is particularly interesting close to its free surface, because the broken translational symmetry in the atomic arrangement and the atomic interactions may allow new phase transitions.[1] At the (100) surface of the binary alloy Cu_3Au, a continuous behavior of the surface order parameter in the neighborhood of its well-known order-disorder transition at $T_0=663$ K has been observed with LEED.[2] Lipowsky and co-workers[3] have analyzed semi-infinite systems within mean-field theory and found so-called surface-induced disorder (SID) transitions which are intimately related to wetting phenomena.[4] It turns out that at temperatures $T \leq T_0$ a disordered layer intervenes between the vacuum and the bulk [Fig. 1(a)] which grows to a macroscopic size as T_0 is approached [Fig. 1(b)]. By this process the interface between the disordered and the ordered phases becomes delocalized according to

$$L_t = L_0 \ln(1/t), \tag{1}$$

as long as short-range interactions govern the phenomena. (L_t is the mean position of the interface from the surface and $t=1-T/T_0$ the reduced temperature.) In the framework of this theory the continuous surface disordering originates from the exponential tail of the order-parameter profile which vanishes continuously at $z=0$ as the interface moves into the bulk. This situation corresponds in the context of wetting phenomena to a complete wetting at the wetting transition temperature (see, e.g., Ref. 4).

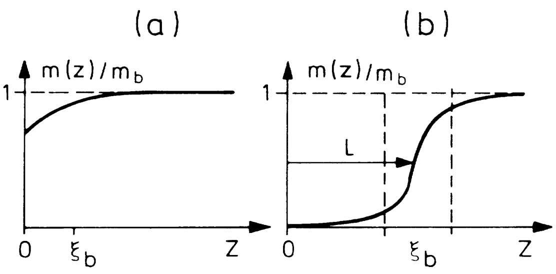

FIG. 1. Order-parameter profiles $m(z)/m_b$ associated with surface-induced disorder. The coordinate z measures the distance from the surface ($z=0$). ξ_b is the bulk correlation length and m_b the bulk order parameter. (m_b is set equal to unity in the main text.) (a) Onset of surface disordering; (b) advanced surface disordering with a delocalized interface at mean position $z=L$ from the surface.

In this Letter we consider the $Cu_3Au(100)$ surface. Although the continuous surface order parameter as found in the early work by Sundaram *et al.*[2] has meanwhile been confirmed,[5,6] the predicted growth of a disordered surface layer in the presence of the SID transition has not yet been observed. Since surface-induced disorder does not necessarily imply the existence of an interface delocalization transition,[7] it is highly desirable to subject this theoretical model to an experimental test. In this work we have studied the order parameter close to the $Cu_3Au(100)$ surface via the (001) superlattice reflection excited by evanescent x-ray fields. (In our notation the lattice constant is $a_0=3.705$ Å.) The scheme of the experiment is indicated in Fig. 2: When the incident x-ray beam (here with wavelength $\lambda=1.5$ Å) grazes the sample surface at an angle α_i below the critical angle α_c

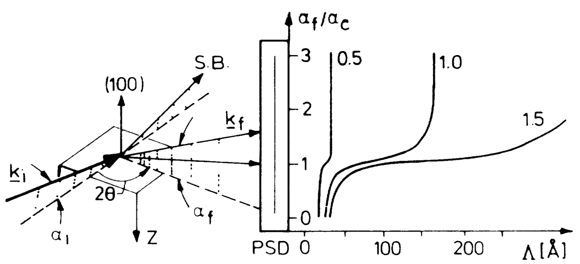

FIG. 2. Schematic experimental setup and the associated scattering depths Λ: $\mathbf{k}_{i,f}$ are the wave vectors of the incident and scattered x-ray waves; S.B. denotes the specularly reflected beam, PSD the position-sensitive detector. The scattering depths Λ are shown as functions of α_f/α_c for $\alpha_i/\alpha_c=0.5$, 1.0, and 1.5.

(=7.8 mrad in our case), it creates an evanescent wave field inside the crystal which penetrates typically 50 Å below the reflecting surface. The (001) evanescent superlattice (SL) scattering is detected by a position-sensitive detector which measures the intensity distribution along the takeoff angle α_f between $\alpha_f/\alpha_c=0$ and $\alpha_f/\alpha_c=4$, and provides in this way a depth profile of the observed scattering.[8] The associated "scattering depths" Λ depend sensitively upon both angles[8-10] $\alpha_{i,f}$ and are shown in Fig. 2 as functions of α_f/α_c for $\alpha_i/\alpha_c=0.5$, 1.0, and 1.5 for the present case. This useful external control of the depth of the probe together with the straightforward interpretation of the scattering intensity (kinematic theory) makes this method an ideal tool to attack the task in hand. The necessary conditions are that the surface of the sample is flat so that the angle of incidence is well defined and also smooth to avoid unwanted diffuse scattering.[11]

The experiments were performed in the Hamburg synchrotron radiation laboratory (HASYLAB). The Cu_3Au single crystal had a flat and highly polished (100) surface which was cleaned by ion bombardment and annealing in ultrahigh vacuum until it showed the LEED pattern of the well-ordered surface. The sample was then transferred in a special UHV cell to the x-ray scattering station. While the temperature dependence of the (001) SL intensity was investigated in the temperature range between 523 and 677 K, the order-disorder transition was monitored by the α_f-integrated intensities collected by the position-sensitive detector [see Fig. 3(a) for $\alpha_i/\alpha_c=0.5$ and 1.5]. Inspection of Fig. 3(a) shows that for $\alpha_i/\alpha_c=0.5$, that is for small scattering depths Λ, already these α_f-integrated raw data exhibit the signature of a continuous phase transition and confirm in a straightforward way the results obtained by LEED[2,5] and spin-polarized LEED.[6] On the other hand, for increased values of Λ, as is the case for $\alpha_i/\alpha_c=1.5$, contributions of a first-order transition can be detected. We find within an accuracy of $\pm 0.5\,°C$ that the phase-transition temperature is independent of the distance of

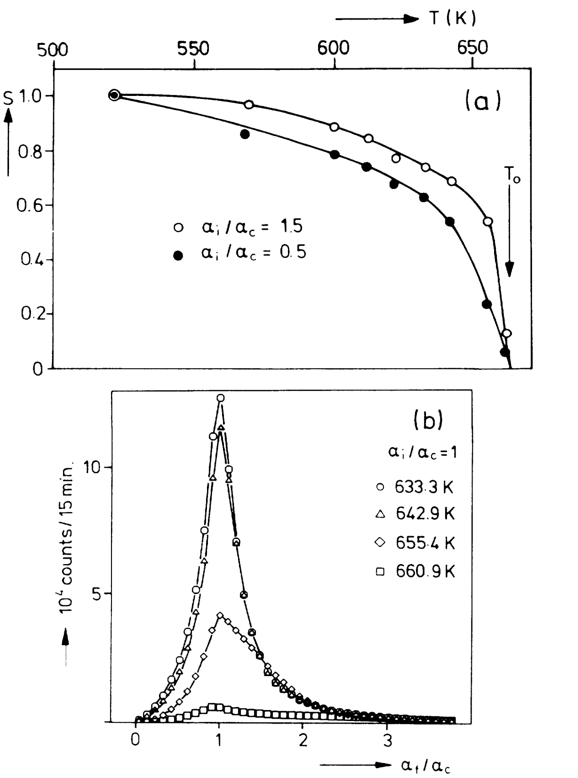

FIG. 3. (a) α_f-integrated raw data (S) as a function of the absolute temperature for $\alpha_i/\alpha_c=0.5$ and 1.5. The temperature T_0, where the (001) intensity vanishes, is indicated. The data are normalized to the intensities observed at $T=523$ K. (b) α_f distribution of the (001) intensities for $\alpha_i/\alpha_c=1.0$ at some representative temperatures close to T_0.

the surface. Much more detailed information on the order-parameter profile $m(z)$ associated with the SID is extracted from the α_f distribution of the SL scattering. A selection of our experimental findings is summarized in Fig. 3(b) showing the α_f distribution of the (001) intensity at $\alpha_i/\alpha_c=1$ for various temperatures. The scattering intensity recorded at $T=667$ K [not shown in Fig. 3(b)] is due to diffuse scattering from the sample and is subtracted from the signal in the subsequent data analysis. Note furthermore that the intensity maxima occur at $\alpha_f/\alpha_c\approx 1$, a refraction effect due to the transmission coefficient of the surface and the action of the scattering depth which can be understood in simple terms within a modified kinematic theory.[9,10] We mention here that the details in the α_f distribution of the recorded intensities are also affected by surface-roughness effects.[8]

In this Letter we apply a novel analysis of the evanescent scattering which is exclusively based on the scattering depth Λ and, in particular, does not require corrections for the surface transmission coefficient and for surface roughness (which is assumed to be constant in the discussed temperature regime[12]). For that the α_f scan

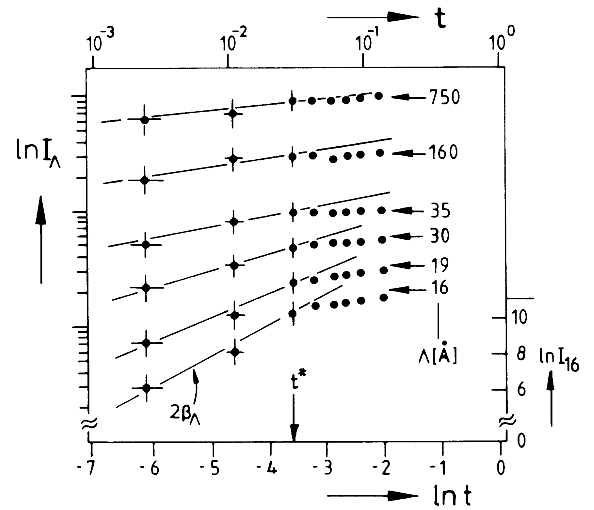

FIG. 4. Double-logarithmic plot of some observed values of $I_t(\Lambda)$ vs reduced temperature. Note that the intensities belonging to different Λ are shifted in order to accommodate them into one figure. The vertical scale is the same for all intensities and is shown explicitly for $I(16\ \text{Å})$ (right scale). The intensity error bars include the systematic errors due to the uncertainties in the grazing angles. For t^*, $2\beta_\Lambda$, and further explanation see text.

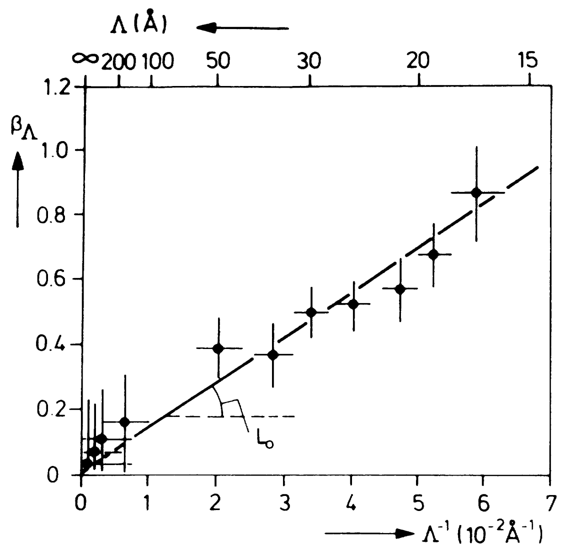

FIG. 5. Observed exponent β_Λ as a function of the reciprocal scattering depth Λ^{-1}. For explanation see text.

obtained by the detector is converted into a depth profile[8,10] as indicated in Fig. 2. The scattering intensities $I_t(\Lambda)$ associated with different scattering depths Λ are plotted versus the reduced temperature t on a double-logarithmic scale (Fig. 4). This representation of the data reveals a change in the temperature dependence of $I_t(\Lambda)$ at approximately $t^* \approx 4\times 10^{-2}$. In order to understand this observation we apply the following model.

At temperatures $t > t^*$ the onset of the SID takes place, i.e., the surface layer starts to disorder in the presence of a still ordered bulk [Fig. 1(a)]. This situation can be characterized by an order-parameter profile

$$m_t(z) = 1 - [1 - m_t(0)]\exp(-z/\xi_b), \quad t > t^*, \tag{2}$$

where $m_t(0)$ is the (continuous) order parameter of the top layer of $Cu_3Au(100)$ and ξ_b the bulk correlation length. The delocalization of the interface which separates the disordered surface layers from the still ordered bulk is observed in the asymptotic temperature regime $t \le t^*$ [Fig. 1(b)]. The full lines in Fig. 4 indicate the asymptotic slopes $\beta_\Lambda = d\ln I_t(\Lambda)/d\ln t$ which exhibit a distinct Λ dependence and provide the experimental evidence for a logarithmic interface delocalization. The order-parameter profile in this asymptotic regime may be written as[3]

$$m_t(z) = \begin{cases} \frac{1}{2}\exp(z - L_t)/\xi_b, & 0 \le z \le L_t, \\ 1 - \frac{1}{2}\exp(L_t - z)/\xi_b, & z \ge L_t \end{cases} \tag{3}$$

$(t \le t^*)$. We note without proving that the recorded evanescent SL intensities $I_t(\Lambda)$ are proportional to $|m_t(\Lambda)|^2$, $m_t(\Lambda)$ being the Laplace transform of $m_t(z)$ (see Ref. 8), and thus

$$I_t(\Lambda) \sim \left| \Lambda^{-1} \int_0^\infty m_t(z)\exp(-z/\Lambda)dz \right|^2. \tag{4}$$

From Eqs. (3) and (4) we conclude that the relation

$$I_t(\Lambda) \sim |\exp(-L_t/\Lambda) - \tfrac{1}{2}(\xi_b/\Lambda)\exp(-L_t/\xi_b)|^2 \tag{5}$$

should describe the observed SL intensities in the asymptotic regime. In the derivation of Eq. (5) we have assumed that $\xi_b/\Lambda \approx a_0/\Lambda \ll 1$. Note that the first term in Eq. (5) accounts for the motion of the interfacial position, while the second term can be treated as an intensity correction due to the finite width ξ_b of the interface. Since ξ_b/Λ as well as ξ_b/L_t are small in the temperature range $t \le t^*$, we may discard the second term by setting $\xi_b \approx 0$ and study a steplike interface. The corresponding SL scattering then obeys the simple law $I_t(\Lambda) \sim \exp(-2L_t/\Lambda)$. Let us assume now that the position L_t of the interface diverges logarithmically with t [Eq. (1)]; then we end up with a characteristic power law for $I_t(\Lambda)$, namely

$$I_t(\Lambda) \sim |t|^{-2\beta_\Lambda} \text{ with } \beta_\Lambda = L_0/\Lambda. \tag{6}$$

In other words, the observed asymptotic slopes at $t \le t^*$ in the double-logarithmic plot of Fig. 4 are predicted to scale with $1/\Lambda$, if Eq. (1) is fulfilled. This assertion is tested in Fig. 5 where the experimental values of β_Λ are plotted versus $1/\Lambda$. Indeed, we find that our data fulfill to a good approximation the linear relation $\beta_\Lambda \propto 1/\Lambda$.

The straight line is a least-squares fit to the data and describes an order-disorder kink moving with $\ln(t)$ into the bulk. The slope of the straight line provides the amplitude L_0 of the logarithmic growth to be

$$L_0 \approx 3a_0. \quad (7)$$

Since we are dealing with a first-order transition, L_0 should be of order of the lattice constant; thus, the observed value is quite reasonable. We conclude that this is a first experimental evidence for an interface delocalization transition. Since our data are consistent with a $\ln(t)$-like divergence of the interface position, the SID transition in Cu_3Au in the present temperature range is not significantly influenced by long-range interactions which may be present.

Indications of a logarithmic growth of an interfacial layer have already been reported by Frenken and van der Veen[13] who investigated the Pb(110) surface close to the bulk melting point. Since their technique (ion channeling and blocking) is not sensitive to long-range order, it is not clear whether they have observed a SID transition in this system. However, it is nonetheless interesting to compare the amplitudes L_0 of the logarithmic growth in the two systems. According to Ref. 13 the thickness of the surface premelting layer in Pb(110) grows with an amplitude $L_0 \approx 2.5a_0$, a value which is virtually identical with our result for Cu_3Au ($\approx 3a_0$). Surface-induced order-disorderer transitions in binary alloys (as discussed here) and premelting transitions may be regarded as very different physical phenomena; note, however, that both effects occur close to a three-phase coexistence region,[14] and so they are describable by the same thermodynamics. The almost equal values of the amplitude L_0 in these two transitions seem to reflect the fact that they are both wetting phenomena. It would be interesting to investigate how close to T_0 the relation (1) remains valid until the effective interface potential is dominated by long-ranged interactions. This would be observable as a crossover from a $\ln t$- to a $t^{1/3}$-like growth of the disordered layer.

Finally, we indicate the further analysis of the data in the regime $t > t^*$. Consider again the associated order-parameter profile $m_t(z)$ of Eq. (2). Since $\xi_b = O(a_0)$, the disorder is limited to the outermost layer; therefore, the temperature dependence of the SL intensity is much less pronounced. From Eqs. (3) and (4) we find for small ξ_b/Λ the relation

$$1 - I_t(\Lambda)/I_\infty(\Lambda) = \{2\xi_b[1 - m_t(0)]\}/\Lambda. \quad (8)$$

Thus, evanescent SL intensities provide the quantity $\xi_b[1 - m_t(0)]$. Its reliable quantitative determination requires a meticulous experimental study of the left-hand side of Eq. (8). Experiments of that kind are under way.

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