Surface-Induced Giant Anisotropy in the Order Parameter Relaxation at $Cu_3Au(001)$

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We present a novel surface phenomenon found in the investigation of the ordering kinetics near the surface of $Cu_3Au(001)$. Monitoring different classes of Fourier components of the ordered $L1_2$ structure by time-resolved x-ray scattering, we found a giant anisotropy in the relaxation behavior. The layered structure normal to the surface relaxes ultrafast while lateral ordering occurs much more slowly ($\tau_\perp^{-1} > 20\tau_\parallel^{-1}$). We argue that the recently discovered oscillating segregation profile acts as a two-dimensional nucleating sheet for ordering wave vectors normal to the surface. [S0031-9007(97)03089-5]

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The investigation of the ordering behavior of first-order phase transitions has a long tradition. In particular, Cu_3Au is prototypical for a fcc ordering alloy in which the order parameter (OP) of the system is not conserved (NCOP) [1]. Equilibrium and nonequilibrium properties of the phase transition are well understood in the bulk [2–4]. Time-resolved x-ray experiments on bulk Cu_3Au systems have revealed ordered domains that appeared after a quench from a $T_i > T_0$ to $T_f < T_0$ (=663 K) nucleating from the metastable disordered phase. Information about the existence of antiphase boundaries (APB's) due to nucleation on the four simple cubic sublattices of the fcc structure and their spatial distribution can be extracted from the shape of the superstructure reflections [5], as from the anisotropic inverse widths which yield the average antiphase domain size for each type of APB. At long times after the quench the average domain size L grows with time t according to the Lifshitz-Cahn-Allen law, $L \sim t^{1/2}$, for curvature driven diffusion of domain walls [2,4,6]. In addition, critical divergence is found as the quench depth $\Delta T = T_0 - T_f$ goes to zero [6]. A deviation from the ideal Cu_3Au stoichiometry slows down the ordering kinetics and changes the growth law of the domain size [7].

In the last decade there have been many experimental and theoretical efforts to extend the understanding of first-order phase transitions from bulk to surface behavior [8,9]. Generally at the surface a broader variety of phenomena occurs than in the bulk, including surface segregation, surface relaxation, or a possible change in the order of the phase transition [10]. These phenomena depend on the surface orientation, the average composition, or the interaction strength at the surface. In this paper we address the so far open question how the ordering kinetics of a binary alloy and the resulting APB distribution after a quench to a metastable state is affected by the presence of a surface. As we will show by an x-ray scattering study on $Cu_3Au(001)$ there are indeed unexpected and rather dramatic surface phenomena in the relaxation of the OP. In the following we use the full four-component OP $\Psi = (\Psi_1, \Psi_2, \Psi_3, \Psi_4)$ associated with the $L1_2$ structure of the ordered Cu_3Au (for details see [11]), whereby Ψ_1 is related to ordering waves parallel to the (001) surface, while Ψ_3 describes ordering perpendicular to the (001) surface. The surface-related Ψ_1- and Ψ_3 components are experimentally accessible through the glancing-angle x-ray observation of the (100) and (110) surface superlattice reflections, respectively.

The x-ray experiments have been carried out at the X16A beam line of the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory [12] using the same sample as in the previous studies of the surface modified order-disorder transition and the surface segregation [10,13]. The bulk stoichiometry has been determined to be $x_{Cu}/x_{Au} = 3.237$. A routine UHV preparation provided an atomically clean and mirrorlike sample surface. Glancing angle fundamental Bragg profiles exhibited a resolution limited mosaic width of 0.01°. Thus, the surface region was close to a perfect single crystal.

The scattered intensity has been recorded with a linear position-sensitive detector providing scattering profiles in either an in-plane (2Θ) or the out-of-plane direction (α_f). In order to achieve surface sensitivity and depth resolution we used grazing angle diffraction [8] where the incident and the scattered beams are restricted to angles comparable to the critical angle of total reflection, α_c. A reduction of the scattering depth Λ down to 20 Å was achieved by choosing a wavelength of 1.73 Å, yielding $\alpha_c = 0.51°$. The phase transition temperature has been determined from the temperature dependence of the (100) superstructure intensities for different scattering depths, thereby confirming our earlier result that the surface- and bulk-related transition temperature $T_0 = 663$ K is the same, consistent with surface-induced in-plane disorder.

The crystal was mounted on a Ta plate and heated by a tungsten filament. Quenches were performed by shutting off the filament power to achieve cooling rates of

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0.55 K/sec measured by a thermocouple placed on the Ta plate near the edge of the crystal. The scattered intensity was then recorded while decreasing the temperature [14]. At the end of each cycle the shape anisotropy of the superstructure reflection was examined.

Here we report the results of two series of quenches to several final temperatures with varying scattering depths: (a) quenches to $T_f < T_0$ while monitoring the Ψ_1-related (100) surface reflection; (b) quenches to $T_f < T_0$ while monitoring the relaxation behavior perpendicular to the (001) surface via the Ψ_3-related (110) surface reflection.

First we turn to the relaxation of the in-plane OP components Ψ_1. Prior to the measurements the crystal was annealed at $T_0 + 26$ K for at least 15 min and subsequently at $T_i = T_0 + 6$ K for another 10 min. Figure 1(a) shows the evolution of the (100) surface Bragg peak. The time scale for the relaxation of the (100) Fourier component compares well with the values found in the bulk [2]. The same behavior is found for the (101) reflection associated with Ψ_2.

In order to check whether the growth of the lateral OP components occurred uniformly with depth we took the ratio $I(\Delta T, \Lambda_1, t)/I(\Delta T, \Lambda_2, t)$ for quenches with the same depth ΔT and different scattering depths Λ_i [15]. This ratio should be constant with time, if the OP growth is uniform. We found that the OP components Ψ_1 and Ψ_2, which are related to the ordering within the Cu-Au layers parallel to the surface, are not growing uniformly with depth; instead, the lateral order starts to grow in the bulk and is driven to the surface [9]. This behavior is consistent with the equilibrium phenomenon of surface-induced disorder where the surface exhibits a preference for the disordered state at temperatures below T_0.

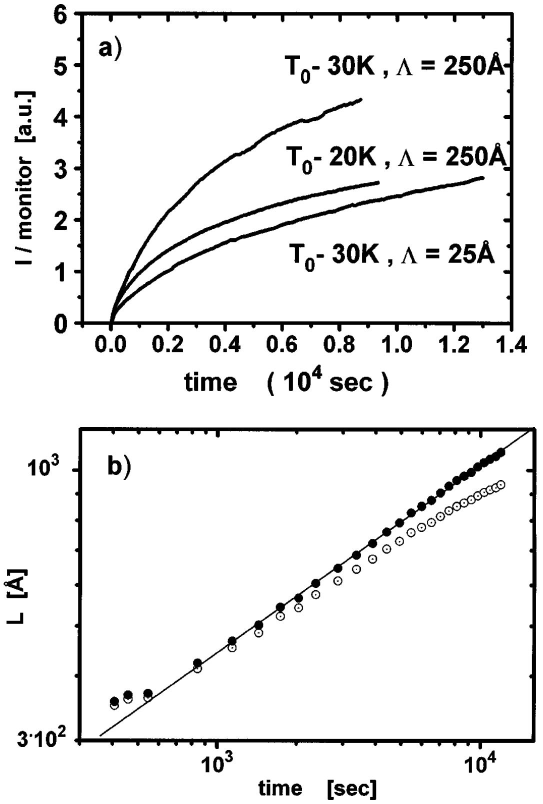

FIG. 1. (a) Time evolution of the α_f integrated (100) reflection after various quenches to $T_f < T_0$. (b) Time dependence of the domain size measured at the (100) reflection for a scattering depth of 370 Å after a quench to $T_f = T_0 - 20$ K (○ raw data, • resolution corrected). The growth of the domain size follows a power law (straight line).

The time evolution of the in-plane radial (100) profile has also been measured for a series of quenches with varying quench and scattering depths. Figure 1(b) shows some results of a detailed peak shape analysis. The domain size which is directly related to the (resolution-corrected) half width of the peak grows according to a power law $L(t) \sim t^a$ in the late time regime with $a = 0.36 \pm 0.02$. This is substantially smaller than the power law exponent of a Lifshitz-Cahn-Allen law for curvature driven growth of the domain size in NCOP systems. It can be understood by the fact that the sample has a small Cu excess compared to the correct Cu_3Au stoichiometry. Shannon *et al.* [7] found an analogous behavior with $a = 0.2$ or even a logarithmic growth in a Cu_3Au sample with a larger Cu excess of $x_{Cu}/x_{Au} = 3.76$ [16].

Now we turn to the relaxation of the Ψ_3 component. For a typical quench, while monitoring the associated (110) superstructure reflection at the $(11L)$ fundamental Bragg tail, the crystal was annealed at $T_i = T_0 + 26$ K for at least 15 min. Figure 2(a) shows the α_f integrated intensity of the profiles versus time, while Fig. 2(b) gives the time evolution of the intensity profile normal to the surface. The observed steep increase in the integrated intensities in Fig. 2(a) is due to a rapidly growing layered structure normal to the (001) surface and the lattice contraction during the quench. A quantitative comparison of Fig. 2(a) with Fig. 1(a) reveals that the relaxation times for the α_f integrated (100) intensities, $\tau_{\|}$, are at least 1 order of magnitude larger than for the (110) Fourier component, $\tau_{\perp}$, depending on quench and scattering depth [see the inset of Fig. 2(a)]. This reveals a giant surface-induced anisotropy in the relaxation of the different OP components. Note again that the bulk OP components show identical relaxation behavior.

The time evolution of the normalized profiles [Fig. 2(b)] is similar for all quenches and scattering depths. It starts with a diffuse-like line shape and ends very quickly with a line shape for a system which is long-range ordered in the direction perpendicular to the surface.

The material width parallel to the surface along the radial direction is independent of quench and scattering depth and keeps its value constant during the quench at 0.0062 ± 0.0002 reciprocal lattice units. Analyzing in detail the lateral shape of the fundamental Bragg tails [11], a step and terrace structure of the surface was derived revealing a step height of $a_0/2$ and terrace ledges

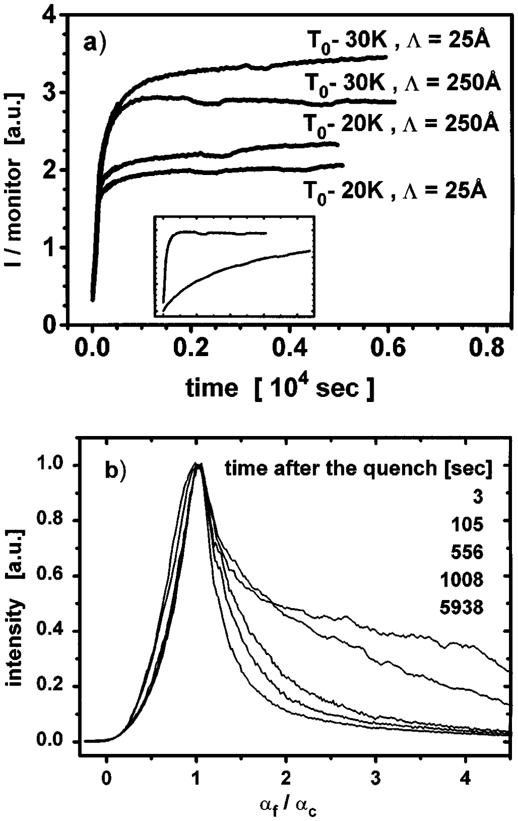

FIG. 2. (a) Time evolution of the α_f integrated (110) reflection after various quenches to $T_f < T_0$. The intensity recovers almost immediately according to the dropping temperature. The inset shows a direct comparison of the α_f integrated (100) (dashed line) and (110) (solid line) intensities for $T_f = T_0 - 30$ K and $\Lambda = 250$ Å on the same scale. (b) Normalized intensity profile perpendicular to the surface for the quench to $T_f = T_0 - 30$ K and $\Lambda = 25$ Å.

along the (110) direction corresponding to the radial direction at the (110) reflection. This prompts a static phase shift in the Au concentration profile perpendicular to the surface along the terrace ledges due to the preferred Au rich termination at the surface [13]. Thus, the $a_0/2$ steps force a static phase shift in the concentration profile along the terrace ledges in the disordered phase. Since the angular width at the (110) reflection stays constant during the ordering process, no additional APB's with a perpendicular component in the phase shift are created in the near surface region. This temporal behavior of the OP component Ψ_3 is completely different from the familiar bulk behavior [2,6,7].

In order to explain our observations we refer to a recent experimental investigation of the equilibrium surface segregation profile of $Cu_3Au(001)$ above T_0 [11,13]. The thermodynamic properties of the oscillatory, exponentially damped segregation profile have been related to the order-disorder phase transition of the system and the associated four-component OP Ψ. It was found that the decay length of the segregation profile is identical to the correlation length of the system which is diverging according to $\xi \sim t^{-\nu}$ with $\nu = 0.5$ and $t = (T - T_{SP})/T$ upon approaching the ordering spinodal temperature T_{SP} [11,17]. Thus, the surface-bound oscillatory concentration profile which is directly given by a local surface-induced OP component $\Psi_3 > 0$ can be viewed as a two-dimensional precursor of the low temperature ordered phase.

The layering in the direction perpendicular to the surface conforms to the $L1_2$ structure and exhibits therefore selected Fourier components of this ordered structure. Notice that all the quenches to $T_f < T_0$ discussed above start in the disordered phase where a segregated layer at the surface is always present. Since we argue that $\Psi_3 > 0$ at the surface acts as a nucleating sheet for layerwise ordering perpendicular to the surface, it is most instructive to investigate the relaxation behavior of the segregated layer during a quench within the disordered phase (i.e., $T_f > T_0$) which does not lead to bulk order.

Figure 3 displays the temperature and the α_f integrated intensity of the (110) surface Bragg peak versus time as observed after a quench from $T_i = T_0 + 96$ K to $T_f = T_0 + 26$ K. Notice that in this temperature regime the scattered intensity originates exclusively from a segregated layer at the surface. The thickness of this layer is growing during the temperature quench to $T_f > T_0$. The observed increase in the intensity is induced both by the lattice contraction noted above and the growth of the segregated layer. As can be seen, there is no time lag between the decrease in temperature and the increase in Bragg intensity, thus, the kinetics of surface segregation above T_0 was beyond our time resolution. In fact, we could use this intensity curve as a monitor for the temperature at the surface during the quench. Upon this quench the thickness of the segregated layer increases only slightly from 4.0 to 5.2 Å [13], which should not

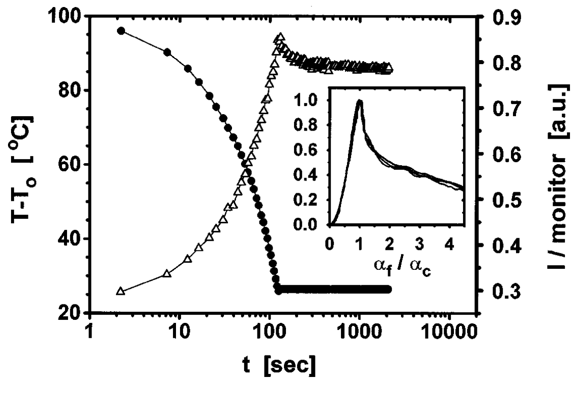

FIG. 3. Time evolution of the (110) Fourier component after a quench from $T_0 + 96$ K to $T_0 + 26$ K. Triangles mark the increase of the α_f integrated intensity, filled circles the decreasing temperature. The inset shows the intensity profile perpendicular to the surface for an incidence angle of $\alpha_i = 0.8\alpha_c$ at times $t = 2$, 44, 130, and 2088 s after the quench has been started.

lead to a noticeable change in the out-of-plane profile as observed (see inset of Fig. 3).

To summarize, we have shown that the symmetry break induced by the presence of a free surface has an unexpected large influence on the ordering kinetics of a system which undergoes a discontinuous order-disorder transition. At the $Cu_3Au(001)$ surface the (110) and (100) superstructure reflections associated with the OP components Ψ_1 and Ψ_3 revealed a giant anisotropy in their temporal behavior with $\tau_\perp^{-1} > 20\tau_\parallel^{-1}$ [18]. This unexpected anisotropy is caused by surface segregation which induces a layered structure perpendicular to the surface. We propose that the segregated layer acts as a two-dimensional nucleus for the Ψ_3 component of the ordered $L1_2$ structure. Most interestingly, the layered structure is induced at the surface and propagates immediately into the bulk, while lateral order (Ψ_1 component) is built up in a slow nucleation and growth process, initiating in the bulk and proceeding to the surface. The observed lateral ordering at the (001) surface is achieved in accordance with the well-known ordering behavior of the bulk.

Clearly, the broken translational invariance at the surface has given rise to an anisotropy in the relaxation times of the different types of OP components of at least 1 order of magnitude depending on the quench and scattering depth. This ultrafast relaxation of one OP component is currently not covered by any theoretical concept and raises questions on the underlying growth mechanism in the presence of a new surface-induced topological nucleus (2D nucleus).

Close to the surface the three relevant components Ψ_1, Ψ_2, and Ψ_3 of the OP can evolve locally only into two of the four possible ordered states of the $L1_2$ structure [12] since Ψ_3 is constrained to $\Psi_3 > 0$ due to the preferred enrichment of Au at the surface. The bulk, however, evolves equally into the four possible ordered states. This leads to the conclusion that not only the growth of the OP components, but also the distribution of antiphase domain boundaries, is highly anisotropic. Thus, we suggest that the constraints for the development of the antiphase domain boundary structure in the near surface region are set by the surface segregation and the morphology of the surface.

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[14] Prior to the quench the diffractometer was aligned to the Bragg position associated with T_f.

[15] We had not been able to determine the exact relaxation times τ (100) since the crystal never reached its equilibrium state. Therefore $I(\Delta T, \Lambda, t = \infty)$ remained undetermined.

[16] Careful fitting favors power-law growth to logaritmic growth $L(t) \sim [\log(t)]^m$ to any power m for our sample with a more stoichiometric composition.

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