Thermodynamics of Surface Segregation Profiles at $Cu_3Au(001)$ Resolved by X-Ray Scattering

H. Reichert,[1] P. J. Eng,[2] H. Dosch,[3] and I. K. Robinson[2]

[1]*Sektion Physik der Universität München, D-80539 München, Germany*

[2]*University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

[3]*Institut für Materialwissenschaften der Bergischen Universität Wuppertal, D-42285 Wuppertal, Germany*

(Received 28 April 1994)

We demonstrate that crystal truncation rod scattering can ideally be applied to extract detailed information on surface segregation profiles in multicomponent systems. We present an x-ray study of the surface segregation at $Cu_3Au(001)$ at various temperatures above the order-disorder transition temperature. It exhibits a pronounced exponentially decaying, oscillatory behavior versus depth. The associated decay length Λ is found to obey $\Lambda \sim t^{-\nu}$, with $\nu = 0.49 \pm 0.04$ and $t = (T - T_{SP})/T$, and, thus, is related to the bulk order parameter fluctuations and the bulk spinodal temperature T_{SP}.

PACS numbers: 61.10.–i, 61.66.Dk, 82.65.Dp

Solid and liquid binary systems generally exhibit a more or less pronounced enrichment of one component at the surface. This phenomenon is called surface segregation. It plays a fundamental role in surface science, since it is universally present in binary systems and alters their surface thermodynamics. Moreover, surface segregation is also of enormous practical interest in materials science, as, for example, in the field of catalysis or in the design of tailored surface properties and layered structures. Surface segregation profiles in binary alloys have been studied theoretically [1] as well as experimentally via various surface tools [2], ranging from low-energy ion scattering (LEIS) [3] and Auger electron spectroscopy to low-energy electron diffraction [4,5]. In spite of all these efforts to obtain surface segregation profiles on an atomic length scale, the experimental evidence is still scarce. In this Letter we present an x-ray scattering study of surface segregation which provides detailed information about the temperature-dependent depth profile down to several layers with atomic resolution allowing for the first time to subject the phenomenon of surface segregation to a critical thermodynamic test.

We consider here the binary system Cu_3Au that has been studied in the bulk as well as at various surfaces [6]. Its most pronounced sublattice ordering behavior (first order phase transition at $T_c = 663$ K) has a thrilling implication for the surface segregation profile, even for temperatures well above T_c. Although the surface field responsible for the enrichment of one component (in this case Au) does not couple to the relevant order parameter of the order-disorder transition ("nonordering surface field"), the internal (antiferromagnetic nearest-neighbor) interactions still favor Cu-Au nearest neighbors, as evidenced by the existence of short range order (SRO) scattering at $T > T_c$. This conflicting situation should lead to a pronounced oscillatory segregation profile starting with an Au-enriched top layer followed by an Au-depleted second layer and so on. Quite generally, statistical mechanics predicts that any segregation profile should decay exponentially on the scale of the bulk correlation length ξ_b, provided that the surface does not evoke a new length scale. Until now, such an exponentially decaying, oscillatory segregation profile (which is predicted theoretically [7]), and especially its temperature dependence, has never been observed. Careful LEIS studies of the top layer composition of the $Cu_3Au(001)$ surface clearly showed though [3] that the outermost layer preserves an Au enrichment followed by an Au-depleted second layer up to temperatures $T \geq T_c + 400$ K. Several interesting questions arise from this observation: Is the observed Au concentration in the first and second layers indeed the tip of an oscillating depth profile? How does the phase transition influence the surface segregation? Which thermodynamic behavior and length scale is controlling the segregation profile?

In order to answer these questions we have investigated here the $Cu_3Au(001)$ surface at temperatures above T_c by means of x-ray crystal truncation rod (CTR) diffraction [8]. The truncation of the periodic crystal structure at the surface gives rise to an aditional Bragg scattering which is "rodlike" perpendicular to the truncation. Its intensity distribution along the rod carries detailed information on the microscopic morphology of the surface and the subsurface structure; thus, at the surface of binary alloys, any segregation induced deviation from the bulk stoichiometry alters the intensity distribution along the rod in a distinct way. As is well known, the bulk scattering from the ordered alloy ($T < T_c$) consists of fundamental and superstructure reflections originating from the average fcc lattice and the sublattice long range order (LRO), respectively [9]. At the (001) surface two types of crystal truncation rods occur [Fig. 1(a)]: "superstructure rods," such as the (10L) rod, linking superstructure reflections perpendicular to the (001) surface, and "fundamental rods," such as the (20L) rod, linking fundamental reflections with superstructure reflections. In the disordered state ($T > T_c$) the superstructure reflections disappear, as well as the associated superstructure rod. Thus, only the fundamental rods survive [Fig. 1(b)]. CTR diffraction has been exploited to extract information about structural properties of surfaces [8]. Here we use it to reveal the surface

 0031-9007/95/74(11)/2006(4)$06.00

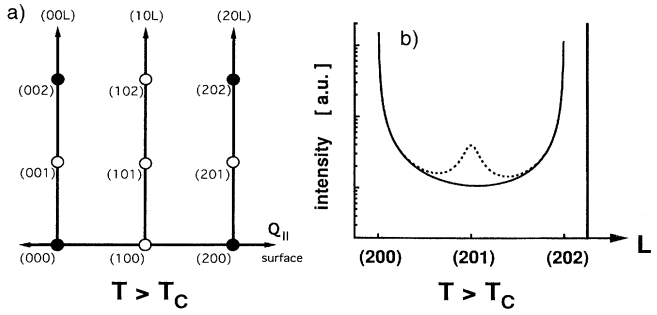

FIG. 1. (a) The reciprocal space in the h,l plane perpendicular to the surface. Full circles and lines correspond to the fundamental, open circles and the full line to the superstructure reflections and rods, respectively. (b) Calculated ($20L$) fundamental rod profiles above T_c for a surface without segregation (solid line) and a smooth, segregated surface (dashed line).

segregation profile. The structure amplitude of the fundamental rod can easily be derived:

$$F_{\mathrm{FR}}(Q_{\|}, q_z, T) = \delta(Q_{\|} - G_{\mathrm{HK}}) \times \sum_{n=0}^{\infty} [c_a(T,n) f_a + c_b(T,n) f_b] \times e^{iq_z n a_0/2} w_\rho(T,n), \quad (1)$$

where $c_i(n,T)$ and f_i are, respectively, the temperature-dependent concentrations and the associated atomic form factors including the Debye-Waller factors. The function $w_\rho(T,n)$ takes into account the microscopic surface roughness of a binary system (see below). The δ function holds for a perfect crystal with an ideal surface with microscopic roughness only and is broadened in the case of a nonvanishing mosaic width or a miscut of the surface due to steps and terraces (height-height correlation). The diffraction from a disordered alloy consists of a superposition of broad bulk SRO diffuse scattering and CTRs emanating from the fundamental reflections as already observed [10]. Without the tendency for surface segregation the CTRs are smooth and featureless [solid line in Fig. 1(b)]. The presence of the oscillatory surface segregation profile described above will introduce structure on the CTR in the form of a broad feature at the antiphase position $L = 1$ [dashed line in Fig. 1(b)] that preserves its delta-function cross section in $Q_{\|}$.

The x-ray experiments were carried out at the X16A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory [11] using the same sample as in a previous study of the surface modified order-disorder transition [12]. A measurement of the bulk composition using an electron microprobe (Cameca SX 50) disclosed an enhanced, laterally homogeneous bulk concentration of $c_{\mathrm{Cu},B} = 0.764 \pm 0.002$, presumably due to a long time interdiffusion effect brought about by the brazing of the crystal onto a Cu plate. The sample surface was prepared in a UHV routine procedure providing an atomically clean and mirrorlike surface. In addition, glancing angle fundamental Bragg profiles exhibited a resolution limited mosaic width of 0.01°, showing that the surface regime is close to a perfect single crystal.

We performed a detailed study of the temperature dependent intensity distribution along the ($10L$) superstructure rod and the ($20L$) fundamental rod for $L = 0-1.3$ by scanning the rod intensity parallel to the surface at each setting of L [see inset of Fig. 2(b)] with a resolution of $\Delta L = 0.02$ reciprocal lattice units. Since the superstructure reflections and the associated superstructure rods disappear at $T = T_c$, these intensities were used to determine the transition temperature and to monitor any eventually present LRO close to the surface [Fig. 2(a)]. We found within our surface sensitivity that the transition temperature is depth independent as reported previously [12]. The ($20L$) rod was examined in the temperature range between $T_c + 1$ K and $T_c + 216$ K. This allows us to subtract the SRO diffuse scattering which is broad in $Q_{\|}$ and—in our case—at least 1 order of magnitude weaker compared to the CTR intensity [see inset of Fig. 2(b)]. Figure 2(b) shows our measured CTR profiles for various tempera-

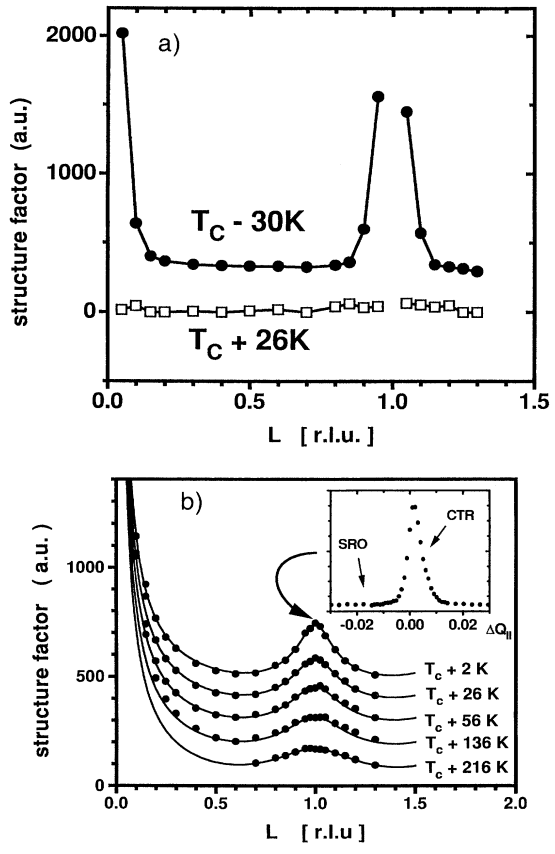

FIG. 2. The decay of the CTR structure factor with temperature versus perpendicular momentum transfer in reciprocal lattice units (for clarity the rods are shifted by a constant offset). (a) The ($10L$) superstructure rod; the solid lines are a guide for the eye. (b) The ($20L$) fundamental rod; solid lines are fits according to the model described in the text. The inset shows a rod profile at $L = 1$ parallel to the surface for $\Delta Q_{\|} = (0,k)$ which remains sharp.

tures above T_c. Each point was obtained by integration of the peak in $Q_{\parallel}$, subtraction of the diffuse scattering, and correction for the changes in active sample area.

Interestingly, we indeed observe a temperature dependent broad feature around $L = 1$ that persists up to the highest measured temperature. Without applying a detailed analysis, the clear Lorentzian line shapes of the feature around $L = 1$ immediately demand an exponentially decaying deviation from the average fcc structure factor. We therefore chose the following function to describe the layer dependence of the Au and Cu composition:

$$c_{\mathrm{Au}}(T,n) = 1 - c_{\mathrm{Cu}}(T,n) = c_{\mathrm{Au},B} + \Delta c(T)\,(-1)^n \times \exp[-n/\Lambda(T)], \quad (2)$$

where $\Lambda(T)$ is so far an unknown decay length. The bulk Debye-Waller factors were taken from Chipman [13]. The surface roughness in this binary system was described by starting with a dense top layer (which can exhibit surface segregation) and subsequently introducing a certain fraction $\beta < 1$ of vacancies which act on Cu and Au sites. In our model the nth layer then has β^{n+1} vacancies [8], i.e., $w_\rho(T,n) = 1 - \beta^{n+1}(T)$. In order to test the sensitivity of the results on the assumptions for the roughness we applied three different models, β being temperature independent, and β varying both linearly and exponentially with temperature. Several unknown parameters in the model have been extracted from the $(20L)$ rod in the ordered state, where the scattering at $L = 1$ is dominated by bulk LRO. At $T = T_c - 30$ K, we find $\beta = 0.15$, surface-enhanced Debye-Waller factors of $\langle u_S^2\rangle/\langle u_B^2\rangle = 1.15$ and an average Au concentration oscillating without noticeable decay between $c_{\mathrm{Au}}(n) = 0.44$ for n even and $c_{\mathrm{Au}}(n) = 0.04$ for n odd. Since the distribution of the rod intensities around $L = 1$ is smooth and symmetric, the influence of surface relaxation phenomena turned out to be small and is therefore neglected in Eq. (1).

In the least squares fit of the $(20L)$ rods at $T > T_c$, which is shown as full lines in Fig. 2(b), we assumed that the ratio $\langle u_S^2\rangle/\langle u_B^2\rangle = 1.15$ is constant in our temperature range and that the roughness parameter β is increasing linearly, with temperature taking the slope as a free parameter. A temperature independent segregation amplitude Δc_{Au} (top layer Au excess concentration) has been taken as a further free fitting parameter. When allowed to float with temperature, it displayed only a small statistical variation around Δc_{Au} (in apparent agreement with the LEIS results [3]). The decay length Λ has been allowed to float free with temperature. The final results disclose that the roughness parameter β increases with temperature from $\beta = 0.17$ at $T = T_c + 1$ K to $\beta = 0.3$ at $T = T_c + 216$ K and that a top layer gold excess concentration of $\Delta c_{\mathrm{Au}} = 0.2$ is present. Figure 3 shows, for three selected temperatures, the layer dependent excess gold concentration $\Delta c_{\mathrm{Au}}(n) = c_{\mathrm{Au}}(T,n) - c_{\mathrm{Au},B}$ disclosing a pronounced oscillatory behavior that decays exponentially versus depth with a decay length Λ. The exponential decay length decreases distinctly upon heating, as Fig. 4 shows.

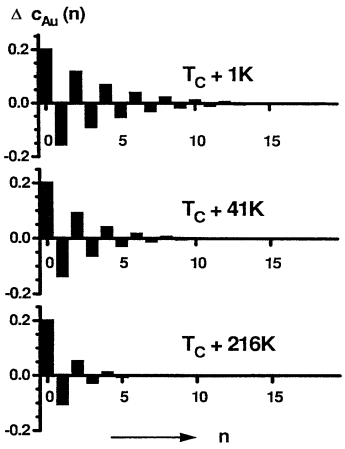

FIG. 3. The decay of the segregation profile with temperature versus layer number n for selected temperatures. The vertical axis denotes the layer dependent excess Au concentration. The profiles are decaying to the average bulk value $c_{\mathrm{Au},B}$.

Since the crystal is in the disordered state the only length scale provided by the system is the correlation length ξ_b that governs the decay of the SRO correlation function. In the bulk these correlations of the order parameter fluctuations (average order parameter $m = 0$) give rise to a temperature dependent diffuse scattering. A careful analysis [14,15] of this scattering shows that $I_{\mathrm{diff}} = t^{-\gamma}$, with $\gamma = 1.0$ and $t = T - T_{\mathrm{SP}}/T$ being the reduced temperature. T_{SP} denotes the spinodal temperature for continuous ordering. This implies that in the temperature range of our experiment a continuous ordering takes place in the bulk, whereby the temperature dependence of the order parameter fluctuations is governed by mean field theory ($\gamma = 1.0$). In turn the correlation length should follow the relation $\xi_b \sim t^{-\nu}$ with $\nu = \gamma/2 = 0.5$. As a test of whether the exponential decay of the segregation profile is governed by ξ_b, we plot Λ versus t on a double logarithmic scale (inset of Fig. 4), thereby using $T_{\mathrm{SP}} = T_c - 34$ K, which is the most accurate value up to now. By this we obtain a power-law exponent $\nu = 0.49 \pm 0.04$ [16], in remarkable agreement with the bulk mean field value $\nu = 0.5$. We conclude that the thermodynamic behavior of the surface segregation at $Cu_3Au(001)$ is governed by the power-law behavior of the bulk correlation length ξ_b and by the spinodal temperature T_{SP} of the system. This finding is fully confirmed by a mean field calculation [17].

As one knows the correlation length ξ_b governs the SRO correlations in the disordered state, that is, ξ_b is associated with a so-called two point function. The crystal truncation rod scattering (or asymptotic Bragg scattering) is, as Bragg scattering itself, always associated with a one point function (average quantity). Thus, the appearance of ξ_b in the crystal truncation rod scattering is somewhat unexpected and apparently puzzling. The truncation of translational symmetry at the surface that induces the projection of a feature of the two point function onto

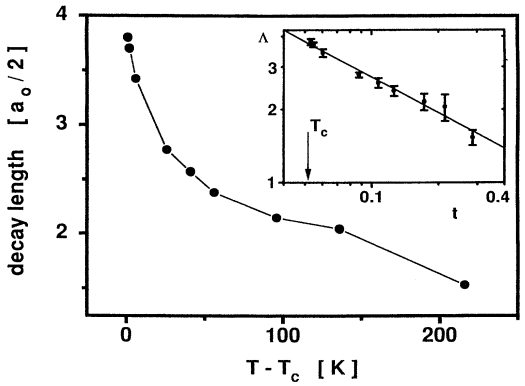

FIG. 4. The temperature dependence of the decay length Λ. The inset shows Λ versus the reduced temperature $t = (T - T_{SP})/T$ on a double logarithmic plot disclosing a power-law behavior with exponent $\nu = 0.49 \pm 0.04$ (straight line).

the one point function is, however, quite universal and may be understood by considering the analog of a liquid in contact with a structureless wall [18]. The liquid shows the well-known liquid SRO correlations (two point function) in the bulk as well as parallel to the structureless wall. The symmetry break at the wall, however, induces an oscillating average liquid density (one point function) normal to the wall that decays like the liquid correlations. By identifying the average liquid density profile as the segregation profile in our system, we arrive at a remarkable conclusion: Since the presence of the surface gives rise to a segregation profile reflecting the decay of the SRO correlations in the bulk, this segregation profile can be viewed as a real space projection of the bulk correlations. The accuracy in the profile determination may allow a more detailed access to the underlying interactions.

In conclusion, we have shown how the analysis of CTR profiles has the potential to determine surface segregation profiles in binary alloys up to tens of layers with high accuracy and depth resolution. The application of this tool to the $Cu_3Au(001)$ surface disclosed an exponentially decaying, oscillatory segregation profile that exhibits a distinct temperature dependence. While the top layer Au concentration persists up to high temperatures, the decay length of the profile decreases distinctly upon heating. The decay length is found to scale with T in the same way as the bulk correlation length in mean field theory. In view of the current discussion of whether or not a surface does evoke a new length scale ("second length scale problem"), see e.g. [19], we present here an example where the surface phenomenon is apparently controlled by the bulk correlation length.

In summary, we arrive at the following picture of surface segregation in Cu_3Au which may be split into two parts. First, the Au concentration in the top layer is enhanced, as reported by [3], and decays only weakly with temperature. Second, the inherent bulk interactions lead to an oscillatory composition profile, as detected in the broad extra peak at $L = 1$ on the $(20L)$ CTR seen in our experiment. The decay length of this profile is strongly affected by the phase transition and its characteristic quantities, the bulk correlation length and the spinodal temperature.

Stimulating discussions with S. C. Moss (Houston) as well as S. Dietrich and K. Mecke (Wuppertal) are gratefully acknowledged. We thank S. Krummacher (Jülich) for the Cu_3Au crystal. We are grateful to R. Schuster (Urbana) for assistance with the measurements and to W. Fehr (München) for the microprobe analysis. We thank H. Peisl for support and the NSLS for the hospitality during our experimental campaign. The NSLS is supported by DOE under Grant No. DE-AC012-76CH00016. This work was also supported by the Bundesminister für Forschung und Technologie under Contract No. 03PE1LMU and by the University of Illinois Materials Research Laboratory under Grant No. DEFG02-91ER45439.

[1] For an early pioneering study, see K. Binder, D. Stauffer, and V. Wildpaner, Acta Metall. **23**, 1191 (1975).
[2] For review, see J. Du Plessis, in *Solid State Phenomena* (Sci-Tech Pub., Vaduz, 1990), Vol. 11; *Surface Segregation and Related Phenomena,* edited by P. A. Dowben and A. Miller (CRC Press, Boca Raton, 1990).
[3] T. M. Buck, G. H. Wheatley, and L. Marchut, Phys. Rev. Lett. **51**, 43 (1983).
[4] Y. Gauthier *et al.,* Surf. Sci. **276**, 1 (1992); E. G. McRae *et al.,* Surf. Sci. **238**, L481 (1990).
[5] R. Döll *et al.,* Surf. Sci. **307–309**, 434 (1994).
[6] H. Dosch, in *Critical Phenomena at Surfaces and Interfaces,* Springer Tracts in Modern Physics Vol. 126 (Springer, Berlin, 1992).
[7] J. M. Sanchez and J. L. Moran-Lopez, Surf. Sci. **157**, L297 (1985); Y. Teraoka and T. Seto, Surf. Sci. **255**, L579 (1991).
[8] I. K. Robinson, Phys. Rev. B **33**, 3830 (1986).
[9] B. E. Warren, *X-Ray Diffraction* (Dover, New York, 1990).
[10] H. Dosch, W. Beisler, and H. Reichert (unpublished).
[11] P. H. Fuoss and I. K. Robinson, Nucl. Instrum. Methods Phys. Res. **222**, 171 (1984).
[12] H. Dosch *et al.,* Phys. Rev. Lett. **60**, 2382 (1988); H. Dosch *et al.,* Phys. Rev. B **43**, 13 172 (1991).
[13] D. R. Chipman, J. Appl. Phys. **27**, 739 (1956).
[14] H. Chen, J. B. Cohen, and R. Ghosh, J. Phys. Solids **38**, 855 (1977); H. Chen and J. B. Cohen, Acta Metall. **27**, 603 (1979).
[15] K. F. Ludwig *et al.,* Phys. Rev. Lett. **61**, 1859 (1988); M. Asta, G. Ceder, and D. de Fontaine, Phys. Rev. Lett. **66**, 1798 (1991).
[16] The error bars for the decay length have been estimated by applying different models as described in the text. The error bar ± 0.04 for the slope ignores the uncertainty in T_{SP}. Using $T_{SP} = T_c - 24.4$ K, as published by Chen *et al.* [13], we find $\nu = 0.41$.
[17] H. Reichert, H. Dosch, K. Mecke, and S. Dietrich (to be published).
[18] S. Dietrich (private communication).
[19] K. Hirota, G. Shirane, P. M. Gehring, and C. F. Majkrzak, Phys. Rev. B **49**, 11 967 (1994).