Surface-Induced Heterophase Fluctuation

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Using glancing-angle x-ray-scattering techniques we investigated the order-disorder transition of Cu_3Au near the (111) surface. Upon approaching the bulk disordering temperature, the superstructure reflections exhibit a very unusual double-Gaussian line shape. The narrow component is due to the usual long-range order, while the broad Gaussian component indicates that small disordered clusters of a well defined size of about 25 Å are present in the surface region. These clusters coexist with large ordered domains of about 5000 Å in size. We interpret the small clusters as surface heterophase fluctuations and discuss their implications.

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The investigation of surface effects on first-order phase transitions has gained much interest in recent years.[1-15] Theoretical work[1-10] predicts that the order parameter is no longer a constant in the material but varies as a function of depth. For example, near the surface the order parameter may exhibit a continuous temperature dependence while the bulk is undergoing a first-order phase transition. Upon approaching the bulk transition temperature from below, a disordered surface layer wets the ordered bulk phase and the average wetting layer thickness $\langle l \rangle$ increases with $\ln(1/t)$, where t is the reduced temperature. Cu_3Au is a system in which the first-order phase transition has been studied extensively with x rays, and attention has recently turned to a search for surface effects.[11-15] In particular, electron-scattering experiments showed that the order parameter at the surface is indeed a continuous function of the temperature for a (100) surface.[11,12] Recent x-ray results at this same surface have also been interpreted as a confirmation of the continuous transition.[15] Meanwhile, theoretical work on the order-parameter fluctuations revealed that the in-plane correlation length should diverge in the surface region when approaching the transition temperature T^* from below, implying that critical fluctuations should exist close to T^*.[2-7] Surface x-ray scattering has an important advantage over other surface-sensitive techniques, as one obtains line shapes which can be interpreted immediately in terms of correlation functions. We therefore investigated the surface fluctuations of the surface-induced disordering transition of Cu_3Au by this technique.

Bulk Cu_3Au exhibits an order-disorder phase transition at $T^* = 663$ K. The transition is intrinsically of first-order nature, since the $L1_2$ structure is isomorphic to an antiferromagnetic Ising system on fcc lattice sites with frustrated nearest-neighbor interaction. The phase transition has been extensively studied in the past by x-ray scattering.[16] Generally, in a first-order phase transition by crossing T^* from below, the order parameter η switches from a nonzero value to zero as one minimum in the Landau free energy replaces another.[17] Near T^*, fluctuations of the disfavored state should be thermally excited; in principle, either the ordered phase inside the disordered one or vice versa. The former "heterophase fluctuations" have been observed for Cu_3Au,[18] while the opposite situation of disordered fluctuations inside an ordered phase has not been seen before,[19] possibly because the experiment is hard. Fluctuations should also play a major role in the surface transition.

In our experiments we used a 5000-Å-thick single-crystalline film of $Cu_3Au(111)$ epitaxially grown on a sapphire $(1\bar{1}20)$ substrate with a Nb(110) buffer layer. The growth was carried out in a PHI 430 growth chamber within the EpiCenter of the University of Illinois. We chose the [111] orientation of the Cu_3Au film because the (111) planes are the only ones exhibiting the same chemical composition in the ordered and disordered states. As a consequence, the (111) surface shows only a small amount of segregation.[20] The in-plane mosaicity of the Cu_3Au film was 0.7°. The experiment was carried out at the AT&T X16A beam line of the National Synchrotron Light Source located at the Brookhaven National Laboratory. The sample loading and handling in a UHV followed standard procedures and will be discussed elsewhere.[21] Scanning of the truncation rod from the surface to the fundamental $(3\bar{3}1)$ peak both below and above T^* showed that the sample surface was atomically flat during the entire experiment. In order to study the ordering transition at the surface, we used grazing-incidence diffraction geometry.[22] The wavelength of 1.4 Å was chosen to lie below the Cu $K\alpha$ edge to minimize the fluorescent background. The resolution was set by slits to 0.02 $Å^{-1}$ for the measurements reported. The incident and exit angles of the x-ray beam to the surface were kept equal: $\alpha_i = \alpha_f = \alpha$.[23] The critical wave vector K_c perpendicular to the surface for total reflection at Cu_3Au is 0.067 $Å^{-1}$ or 0.023 unit of the perpendicular [111] reciprocal-lattice vector (L).

In x-ray- or neutron-scattering experiments, fluctuations give rise to a broad peak in addition to the narrow superstructure peak, the latter one being due to long-range order (LRO). The line shape of the broad component is given by the Fourier transform of the pair correlation function.[24] Near second-order phase transitions, the pair correlation function[25] is of the form $e^{-r/\xi}$, where ξ is the correlation length. The corresponding so-called short-range-order (SRO) diffuse scattering has a Lorentzian line shape with a strong temperature dependence and critical behavior.[24] In our case of a surface-induced bulk first-order transition, theoretical work (e.g., Ref. 7) has predicted that the pair correlation should have the form $e^{-r/\xi_\parallel}$ in the direction parallel to the surface and that it should exhibit a temperature behavior similar to second-order phase transitions. The corresponding fluctuations are attributed to fluctuations of the interface separating the disordered surface from the ordered bulk.

In our experiment we observe near T^* a $(1\bar{1}0)$ surface superstructure peak which exhibits a line shape with two Gaussian components [Fig. 1(a)] (see also Ref. 14). The narrow peak is expected from the LRO and its width reflects the separation of antiphase domains. Neither the line shape nor the temperature behavior of the broad component can be explained by critical fluctuations. First, for critical fluctuations, we expect a Lorentzian line shape. Instead, the Gaussian shape suggests the presence of domainlike small clusters.[26] Second, in the case of critical fluctuations, the peak height of the broad component should be proportional to the generalized susceptibility and should increase when approaching the transition temperature.[24] Figures 2 and 3 in Ref. 14 show, however, that the peak height of the broad component does not diverge upon approaching T^*. The peculiar double-Gaussian peak shape appears to be an equilibrium feature of the phase transition: The peaks in Fig. 2 have been recorded after quenching from $T > T^*$ to $T < T^*$ and annealing at the final temperature for about 10 h. Furthermore, the double-Gaussian peak shape is surface related: In a transmission scattering experiment on the same $(1\bar{1}0)$ peak using Mo $K\alpha$ radiation to penetrate the entire film [Fig. 1(a)], only the Bragg component corresponding to the LRO part is observed close to T^*.

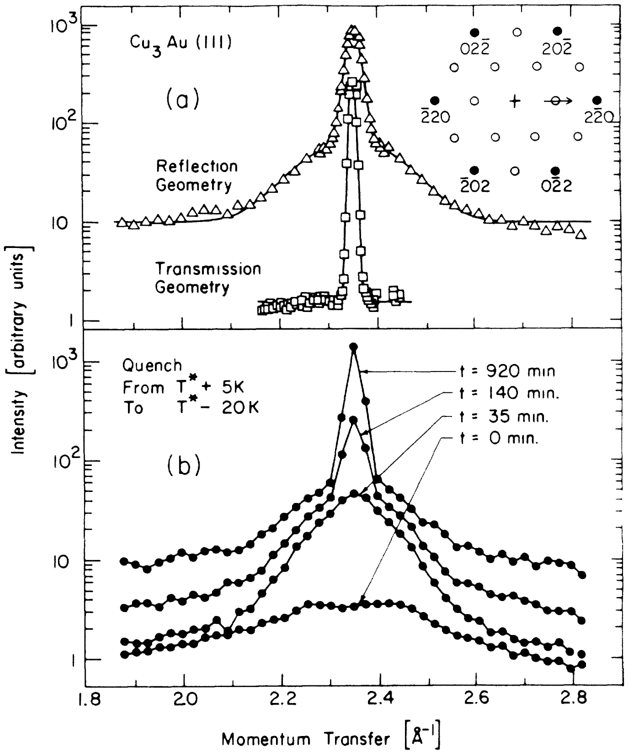

FIG. 1. (a) The upper trace reproduces a radial scan of the surface superstructure $(1\bar{1}0)$ peak for a scattering-vector component perpendicular to the surface of $L = 0.04$ (total reflection occurs at $L = 0.023$) and for a temperature of $T^* - 20$ K. The solid line is a fit by two Gaussians. The lower trace is the same scan in transmission geometry. The solid line is a fit by one Gaussian. Inset: Part of the reciprocal lattice with filled circles representing the fundamental reflections and open circles the superstructure peaks. The arrow shows the scan direction. (b) Sequence of radial scans after quenching from above T^* to $T^* - 20$ K, made at the same L as in (a). The first scan at $t = 0$ is taken before the quench above T^* and shows the SRO diffuse scattering only. Each subsequent scan is shifted 0.5 decade in the y direction.

If we explain the broad peak by the physical picture that small disordered clusters are embedded in large ordered domains, both the line shape and the temperature behavior agree with the experimental results. We expect the scattering intensity due to domains to be proportional to $N\eta^2$, whereas the intensity due to the LRO part is proportional to η^2, where N is number of disordered domains. Therefore, the ratio of the intensities of the broad and narrow peaks reflects the number of clusters. The intensity behavior of the peaks shown in Figs. 2(a) and 2(b) can be interpreted qualitatively as an increase in the total number of clusters with temperature. We speculate that upon approaching T^*, small heterophase domains start to appear at the surface and that their concentration increases with increasing temperature. From the intensities we estimate[27] that at $T^* - 10$ K, 15% of the surface area is occupied by those clusters, whereas at $T^* - 3$ K the occupation is on the order of 70%.

We will now discuss the perpendicular distribution of the cluster size. This size distribution is given by the out-of-plane (L) dependence of the intensity of the broad component as shown by the solid squares in Fig. 3. The solid curve (b) is calculated by assuming that all the microdomains are located close to the surface with an average size $\bar{d} = 25$ Å. For comparison, the L dependence of the sharp component is also shown as open squares in Fig. 3 (curve a) which is due to the LRO including instrumental resolution effects. The solid line is a guide to the eye. Also shown in Fig. 3 by open circles (curve c) is the L scan for the SRO diffuse scattering above T^*, which exhibits a characteristic long diffuse tail at large L

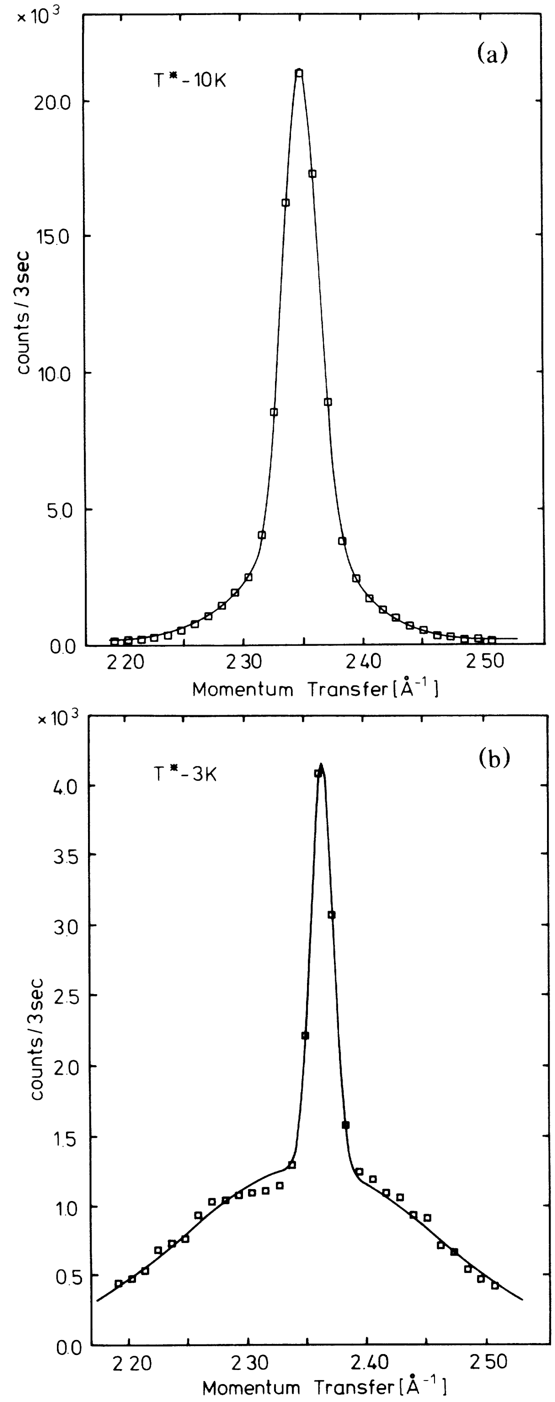

FIG. 2. Radial scans of the surface superstructure $(1\bar{1}0)$ peak at (a) T^*-10 K and (b) T^*-3 K. In both scans the perpendicular component of the scattering vector was fixed to $L=0.03$. The solid lines are best fits to the data points using a double-Gaussian line shape.

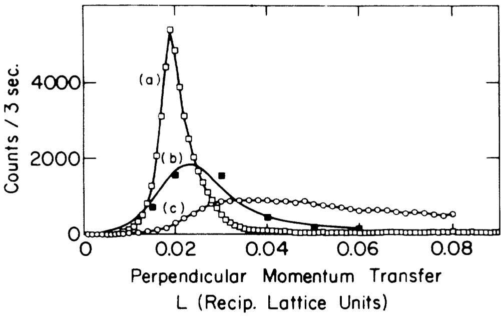

FIG. 3. The scattering intensities of the $(1\bar{1}0)$ peak for T^*-20 K as a function of perpendicular momentum transfer L for the narrow component (curve a) and the broad-peak component (curve b). Curve c is the SRO diffuse intensity above T^*. The intensity of a is scaled by a factor of 0.05 for better visibility. The solid line in curve b is the calculated intensity for an average disordered domain size of $\bar{d}=25$ Å. All other solid lines are guides to the eye.

due to the short correlation length. The profile of the broad component lies between that of the LRO and the SRO above T^* just as it does in the parallel direction. The corresponding domain size is therefore in a range intermediate between the long- and the short-range-order correlation lengths in the direction perpendicular to the surface.

What we can say about these clusters is their size (25 Å both parallel and perpendicular to the surface), with its Gaussian distribution, and their preferential location in the surface region. Another question concerns their internal structure. Indeed it is entirely possible that they consist of antiphase domains rather than heterophase domains. Note, however, that for clusters of such a small size it is not possible to distinguish anymore between an antiphase domain and its disordered antiphase domain wall. If we assume that the domain-wall thickness is of the order of 5 Å with a tendency to increase upon approaching T^* as is found in the bulk,[28] the domain wall contains more atoms than the antiphase domain itself.

A kinetic characteristic of the heterophase fluctuations is their time dependence after a sudden temperature change. We performed a quenching experiment which carried the metastable phase into the stable phase as shown in Fig. 1(b). For $T>T^*$, the LRO component disappears completely and a broad weak component due to the SRO correlations remains. We have found that the SRO peak above T^* exhibits a rather peculiar shape in that it has two straight wings with a flat top. This is shown in Fig. 1(b) as the first scan before the quench. After quenching to T^*-20 K, the broad peak first rises in intensity then subsequently diminishes slowly with time as the ordered central peak appears.

Now we shall discuss in more detail the physical origin of the heterophase fluctuations. For a first-order phase transition, when the temperature is sufficiently close to T^*, the Landau free energy has two minima and yields a metastable phase. According to Ref. 26, the energy needed to create a microdomain of the metastable phase with size d has a volume and an area term: $E=\Delta d^3+\sigma d^2$, with $\Delta \equiv f(\eta_m)-f(\eta_s)$. Here η_m and η_s are the order parameters of the metastable and the stable phases, respectively, while $f(\eta_i)$ are their corresponding free energies per volume; σ is the interfacial energy between these two phases. At the transition temperature, the volume term vanishes and the interfacial term dominates.

When a surface is present, the order parameter predicted for the ordered phase is no longer uniform but becomes a function of depth: $\eta_s(z)$. The metastable phase is the disordered phase: $\eta_m(z)=0$. The energy needed to create a disordered microdomain is also a function of z as $E(z)=\Delta(z)d^3+\sigma(z)d^2$, with $\Delta(z)\equiv f(\eta_m(z))-f(\eta_s(z))$. The depth dependence of $E(z)$ implies that the creation of microdomains at different depths takes different amounts of energy. It is reasonable to argue that $\Delta(z)$ as well as $\sigma(z)$ decreases towards the surface. $\Delta(z)$ should decrease for $z\rightarrow 0$ because of the reduced coordination number at the surface as compared to the bulk, and since the difference between an ordered and a disordered domain diminishes by approaching the surface and so does the interfacial energy or domain-wall energy $\sigma(z)$ separating these domains. Heterophase fluctuations are therefore likely to be strong at the surface.

We believe that heterophase fluctuations and critical fluctuations cannot coexist close to the transition temperature. Critical fluctuations require a rather long correlation length to be developed, which, however, may be disrupted when heterophase fluctuations become thermally excited. Therefore, a metastable phase may always suppress critical order-parameter fluctuations.

In summary, our surface scattering experiments of the order-disorder phase transition in Cu_3Au have revealed a double-Gaussian shape of the superstructure peak in the vicinity of the transition temperature, which has not been observed before in bulk measurements. We attribute this line shape to disordered clusters of an average size 20 to 25 Å embedded in the ordered matrix. These clusters are identified as heterophase fluctuations existing preferentially close to the surface. We have shown qualitatively why strong heterophase fluctuations should be expected near the surface. An immediate question which follows is whether a continuous transition is possible in the presence of strong heterophase fluctuation. Because, close to the transition temperature, a large proportion of the surface is in the form of small domains, the correlation length may not be able to diverge upon approaching T^*. Another problem is that in the theoretical calculations so far it was assumed that near the surface the ordering is uniform in the direction parallel to the surface while smoothly varying in depth. This domain-type fluctuation is so strong in the surface region close to T^* that this assumption may be invalid. We hope the present experimental paper will bring these issues into attention in the future.

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[1] K. Binder, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. Lebowitz (Academic, New York, 1983), Vol. 8.

[2] S. Dietrich, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. Lebowitz (Academic, New York, 1988), Vol. 12.

[3] R. Lipowsky, J. Appl. Phys. **55**, 15 (1982).

[4] R. Lipowsky and G. Gompper, Phys. Rev. B **29**, 5213 (1984).

[5] R. Lipowsky, D. M. Kroll, and R. K. P. Zia, Phys. Rev. B **27**, 4499 (1983).

[6] R. Lipowsky, Phys. Rev. Lett. **49**, 1575 (1982).

[7] R. Lipowsky, Z. Phys. B **55**, 335 (1984).

[8] F. Meijia-Lira, K. H. Benneman, and J. L. Moran-Lopez, Phys. Rev. B **32**, 5925 (1985).

[9] G. Gompper and D. M. Kroll, Phys. Rev. B **38**, 459 (1989).

[10] J. M. Sanchez and J. L. Moran-Lopez, Phys. Rev. B **32**, 3534 (1985).

[11] E. G. McRae and R. A. Malic, Surf. Sci. **148**, 551 (1984).

[12] K. D. Jamison, D. M. Lind, F. B. Dunning, and G. K. Walters, Surf. Sci. **159**, L451 (1985).

[13] S. F. Alvarado, M. Campagna, A. Fattah, and W. Uelhoff, Z. Phys. B **66**, 103 (1987).

[14] X-M. Zhu, R. Feidenhans'l, H. Zabel, J. Als-Nielsen, R. Du, C. P. Flynn, and F. Grey, Phys. Rev. B **37**, 7157 (1988).

[15] H. Dosch, L. Mailänder, A. Lied, J. Peisl, F. Grey, R. L. Johnson, and S. Krummacher, Phys. Rev. Lett. **60**, 2382 (1988).

[16] D. de Fontaine, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnball (Academic, New York, 1979), Vol. 34, p. 73; H. Chen, R. J. Comstock, and J. B. Cohen, Annu. Rev. Mater. Sci. **9**, 51 (1979).

[17] For a review, see K. Binder, Rep. Prog. Phys. **50**, 783 (1987).

[18] H. Chen, J. B. Cohen, and R. Ghosh, J. Phys. Chem. Solids **38**, 855–857 (1977).

[19] For example, B. W. Roberts and G. H. Vineyard, J. Appl. Phys. **27**, 203 (1956).

[20] C. G. Shaw and S. C. Fain, Jr., in *Proceedings of the Seventh International Vacuum Congress and Third International Conference on Solid Surfaces, Vienna, 1977,* edited by R. Dobrozemsky *et al.* (F. Berger & Söhne, Vienna, 1977), p. 2315.

[21] P. H. Fuoss and I. K. Robinson, Nucl. Instrum. Methods **171**, 222 (1984).

[22] R. Feidenhans'l, Surf. Sci. Rep. **10**, 105 (1989); J. Als-Nielsen, in *Structure and Dynamics of Surfaces II,* edited by W. Schommers and P. von Blanckenhagen, Topics in Current Physics Vol. 43 (Springer-Verlag, Berlin, 1987).

[23] I. K. Robinson, Rev. Sci. Instrum. **60**, 1541 (1989).

[24] J. Als-Nielsen and O. W. Dietrich, Phys. Rev. **153**, 706 (1963).

[25] H. E. Cook, M. Suezawa, T. Kajitani, and L. Rivaud, J. Phys. (Paris), Colloq. **38**, C7-430 (1977).

[26] J. Frenkel, *Kinetic Theory of Liquids,* (Oxford Univ. Press, New York, 1946).

[27] J. M. Cowley, *Diffraction Physics* (North-Holland, Amsterdam, 1984), p. 144ff.

[28] Ch. Leroux, A. Loiseau, M. C. Cadeville, and F. Ducastelle, Europhys. Lett. **12**, 155 (1990).