

## SURFACE PHASE TRANSITION AND KINETICS OF $\text{Cu}_3\text{Au}$ (111)

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**Résumé** - Nous avons analysé la transition ordre-désordre de  $\text{Cu}_3\text{Au}$  au voisinage de la surface (111) en utilisant la technique de diffusion de rayons X en incidence rasante. Le film de 5000 Å de  $\text{Cu}_3\text{Au}$  a été déposé par épitaxie sur du saphir ( $11\bar{2}0$ ) couvert par une couche tampon de Nb. Les expériences ont été conduites à la fois en fonction de la température et de l'angle d'incidence, ce dernier déterminant la profondeur de pénétration. Quand on approche de la température de désordre, les balayages radiaux de la réflexion ( $1\bar{1}0$ ) de surstructure présentent des profils non classiques qui consistent en la superposition de deux composantes gaussiennes. Ce profil indique qu'au voisinage de la surface de petits domaines désordonnés peuvent coexister avec des grands complètement ordonnés, ce qui est très différent du comportement du composé massif. De plus, des expériences de trempe faites à partir de températures supérieures à  $T_c$  montrent que le volume s'ordonne avant la surface et que le développement d'un profil à composante unique ou double dépend respectivement de la vitesse rapide, ou lente, de la trempe.

**Abstract** Using glancing angle x-ray scattering techniques we have investigated the order-disorder transition of  $\text{Cu}_3\text{Au}$  close to a (111) surface. The 5000Å thick  $\text{Cu}_3\text{Au}$  film was grown epitaxially on a sapphire ( $11\bar{2}0$ ) substrate with a Nb buffer layer. The experiments were made as a function of both temperature and angle of incidence, the latter determining the penetration depth. Upon approaching the disordering temperature, radial scans of the ( $1\bar{1}0$ ) superstructure reflection exhibit non-classical line shapes consisting of a superposition of two Gaussian components. This profile indicates that close to the surface small disordered clusters may coexist with larger ordered domains, which is much different from the bulk behavior. In addition, quenching experiments from above to various temperatures below the ordering temperature showed that the bulk orders before the surface does and that the development of a single or double component line shape depends on whether the quench is deep or shallow.

### 1-INTRODUCTION

$\text{Cu}_3\text{Au}$  is a prototypical ordering alloy with a high temperature fcc and a low temperature  $L1_2$  structure separated by a discontinuous transition at the bulk disordering temperature  $T_c = 663\text{K}$  /1/. A number of recent theoretical investigations /2-7/ and simulations /8,9/ have indicated that the order parameter depends on the atomic layer beneath the surface: at temperatures  $T < T_c$  the order parameter increases with the layer index towards the bulk value. In addition, it has been pointed out that a disordered layer may intervene between the surface and the bulk /5/. This has been referred to as a disordering surface layer wetting the ordered bulk phase /7/. The thickness of the wetting layers diverges at  $T_c$ , at which point the entire alloy becomes disordered. A number of surface /10-12/ and sub-surface experimental probes /13,14/ have recently been used to investigate the surface phase transition of  $\text{Cu}_3\text{Au}$ . Those investigations are, in general, in accord with the theoretical predictions. However, there has not been a thorough line shape analysis of the superstructure Bragg peaks for the test of correlation functions and fluctuations close to  $T_c$ . In this paper we present the results of a detailed study of the superstructure Bragg profiles using glancing angle x-ray scattering techniques. In addition, we present data from quenching experiments which demonstrate the time evolution of line shapes from a disordered state approaching an equilibrium state below the transition temperature.

### 2-EXPERIMENTAL PROCEDURE

We used a thin film of  $\text{Cu}_3\text{Au}$  which was grown by MBE in a PHI 425 growth chamber within the Epi-Center of the University of Illinois. The 5000Å thick  $\text{Cu}_3\text{Au}(111)$  single crystal was grown at a rate of 0.5Å/sec on a  $\text{Al}_2\text{O}_3(11\bar{2}0)$  substrate with a  $\text{Nb}(110)$  buffer layer at 325°C. The in-plane mosaicity of the  $\text{Cu}_3\text{Au}$  film was 0.7° and the in-plane  $(2\bar{2}0)$  fundamental reflection had a width of  $\Delta Q = 0.048\text{Å}^{-1}$ , limited by instrumental resolution in the radial direction. The position and width of the fundamental peaks showed no indication of coherency strain. The surface x-ray 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 was loaded into a surface chamber equipped with  $\text{Ar}^+$  sputtering gun, LEED, and Auger probes for surface preparation and analysis, as well as a Be window for x-ray scattering. Careful Auger intensity analysis showed no change (< 5%) in the ratio of Cu KLL to Au LVV lines over the range of temperatures considered. Thus dramatic evidence of segregation is not found, although the limit of detectability is rather inadequate in this regard. For more details of the surface x-ray chamber we refer to Ref. /15/. After loading, the chamber was baked at 180°C and the sample was sputtered with 940eV  $\text{Ar}^+$  ions for one minute. Subsequently, a LEED pattern with superstructure spots was observed. The cleaning and analysis procedure was repeated several times during the course of the 11 day experiment. The wavelength and wavevector used in the experiment were 1.4Å and  $4.4864\text{Å}^{-1}$ , respectively, chosen to lie below the Cu  $K_\alpha$  edge to minimise fluorescent background. In all scans the incident and exit angles of the x-ray beam to the surface were kept identical:  $\alpha_i = \alpha_f = \alpha/16$ . The critical wave-vector  $K_c$  perpendicular to the surface for total reflection at  $\text{Cu}_3\text{Au}$  is  $0.067\text{Å}^{-1}$  or 0.023 in units of the  $[111]$  reciprocal lattice vector ( $L$ ) perpendicular to the surface. All scans were carried out in an angle dispersive step fashion.

### 3-EXPERIMENTAL RESULTS

We have found that in angle-dispersive surface measurements on small mosaic single crystals the determination of equilibrium order parameters from Bragg intensities is exceedingly difficult. This is because the superstructure reflections slowly change their shape upon annihilation/creation of antiphase domain boundaries, in particular close to  $T_c$ . We have therefore focused our attention on Bragg profiles of superstructure peaks as they develop following a quench from temperatures above to temperatures below  $T_c$ . Preceding the quenches, the sample was annealed at about 20K above  $T_c$  until the long range order (LRO) completely relaxed and only short range order (SRO) diffuse intensity was detected in radial as well as in rod scans. Then the sample was cooled to 5K above  $T_c$  and quenched to desired temperatures below  $T_c$ . The quenching time was on the order of 5 minutes which is acceptable for the investigation of the intermediate to late stage development. Radial scans required about 2 to 3 minutes. Fig. 1(a) shows a typical time sequence of radial  $(1\bar{1}0)$  scans after a deep quench of 20K below  $T_c$ . All scans were taken with the constant perpendicular wavevector  $L=0.02$ . The first scan in this sequence 3 minutes into the quench is essentially identical to a scan above  $T_c$  and is due to SRO diffuse scattering. In subsequent scans the peak heights increase dramatically while their widths decrease, yielding a single component line shape in the late stage of the development. This single component line shape is due to the LRO, and the width reflects the domain size. This deep quench experiment exhibits the normal nucleation and domain growth behavior which is also observed in the bulk. The width follows the usual power law in time  $\Delta Q \propto t^{-a}$  /17/. We find in this surface experiment an exponent  $a = 0.4 \pm 0.1$ , which is essentially identical to the exponent which we find in bulk experiments on the same sample, in agreement with values which have recently been reported /18/. The line widths from both our surface and bulk experiments as a function of time after quench are compared in Fig. 2.

The time evolution of the line shapes after shallow quenches is much different than that after deep quenches, as is demonstrated in Fig. 1(b). Following a quench to 10K below  $T_c$ , we observe a rather long incubation time of about one hour during which only the broad component gains some intensity. Finally, a sharp component starts to appear on top of the broad component, and while the former grows with time, the latter remains unchanged. The final line shape consists of two components, a broad and a narrow one, both having Gaussian line shapes. This double line shape in radial  $(1\bar{1}0)$  scans has been observed previously/13/, but the present quench experiments confirm, for the first time, that the broad component is an equilibrium feature of the ordering in a narrow temperature range below  $T_c$ . We have also observed these two components in radial scans of other surface superstructure reflections, as well as in transverse scans but not in bulk measurements on the same sample. We therefore attribute the broad component to fluctuations of micro-clusters of disordered phase which are generated close to the surface upon approaching  $T_c$ . The micro-clusters or heterophase fluctuations of the ordered phase embedded in the disordered phase

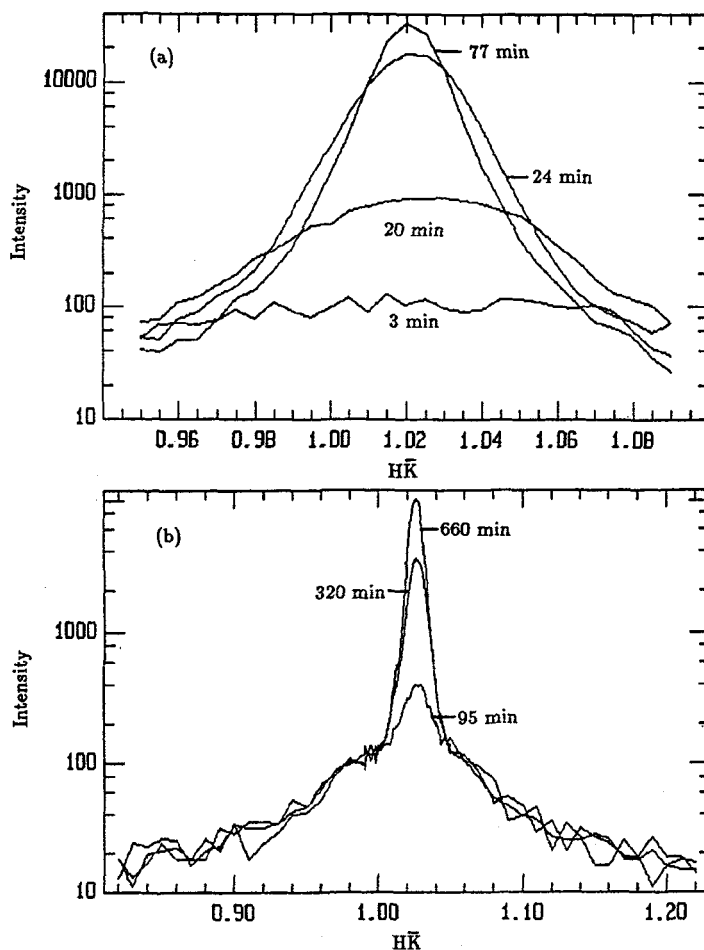


Fig. 1 - (a) Radial scans through the  $(1\bar{1}0)$  superstructure reflection at constant  $L = 0.02$  ( $\alpha_i = \alpha_f = \alpha$ ) and for several times after the quench from  $T_c + 5K$  to  $T_c - 20K$ . (b) same as in (a), only for a more shallow quench to  $T_c - 10K$ . The center of the peak position are at  $[1.02, -1.02, 0]$ .

may have been observed before in the  $Cu_3Au$  bulk crystal above  $T_c/19$ . In Fig. 3 we compare intensities of the radial scans taken at  $L = 0.02$  and  $0.01$  as a function of time after a quench to  $20K$  below  $T_c$ . The ratio goes through a maximum at short times and then drops continuously reaching a constant value of about 3.5 after 300 minutes. This remarkable time dependence demonstrates that the ordering starts in the bulk and induces the ordering of the layers closer to the surface. Thus the ordered regions in the bulk serve as a template for the surface ordering.

#### 4-DISCUSSION AND CONCLUSION

The experiment described above revealed two new features of the ordering transition in  $Cu_3Au$ . The first concerns the line shape of Bragg peaks from radial scans through surface superstructure reflections, which has been seen to depend sensitively on the temperature. Close to  $T_c$ , the superstructure Bragg peaks convert from a single component line shape to a two component line shape, both are well described by Gaussian profiles. The broad component can not simply be considered as classical SRO diffuse scattering, first because of the Gaussian instead of the usually observed Lorentzian line shape for SRO diffuse scattering, and second because the width of the broad peak does not change with temperature. We are therefore led to the assumption that close to  $T_c$  two types of domains with distinctively different length scales of about  $10-15\text{\AA}$  and of  $4000-6000\text{\AA}$  coexist in near surface layers. This is very different from the bulk behavior where nuclei

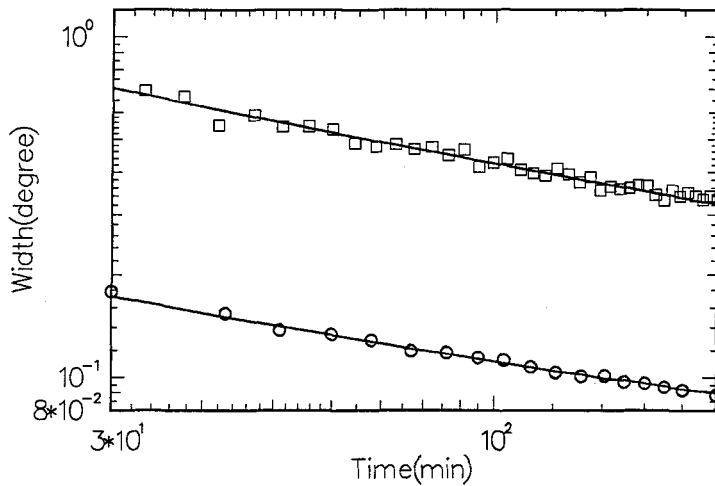


Fig. 2 - The width of the  $(1\bar{1}0)$  superstructure reflection as a function of time after quenches from  $T_c+5K$  to  $T_c-20K$ . The circles refer to a surface scattering experiment with  $L = 0.01$  ( $20\text{\AA}$  penetration depth), and the squares are from a bulk experiment on the same sample. In both cases the exponent  $a$  for the time dependence is  $0.4 \pm 0.1$ . The lower curve is shifted to better show its slope.

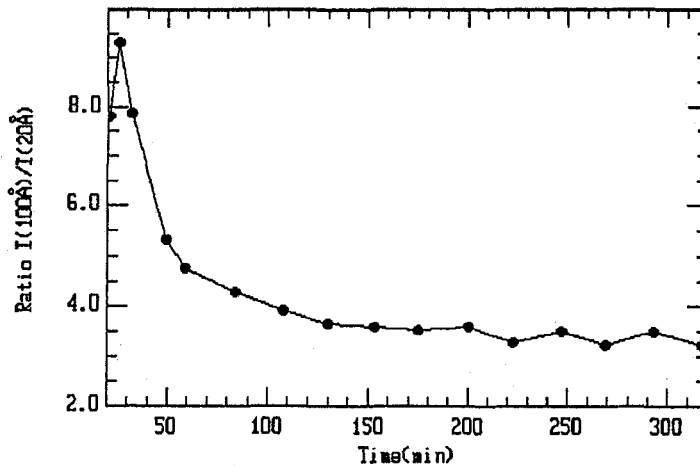


Fig. 3. Ratio of the intensities from radial scans of the  $(1\bar{1}0)$  reflection taken at the  $z$ -components  $L=0.01$  and  $0.02$ , which translate to a penetration depth of the  $x$ -ray to  $20\text{\AA}$  and  $100\text{\AA}$ , respectively. The ratio is plotted as a function of time after a quench from  $T_c+5K$  to  $T_c-20K$ . Integrated intensities and peak height intensities exhibit exactly the same time dependence.

of a critical size either grow or disappear such that only one average domain size survives, yielding a single component Bragg profile. Our theoretical estimates show that the free energy for the excitation of micro-clusters is considerably smaller in the surface region than in the bulk, favoring the coexistence of domains with different sizes. Current mean-field type theories of the first order phase transition have not predicted these non-classical fluctuations. The second new piece of information concerns the growth rate of surface and bulk regions. The data provide convincing evidence that the ordering and domain growth after a deep quench starts first in the bulk and subsequently proceeds to the surface layers in a template like fashion. Since both the integrated and the peak intensity show identical time dependencies, the observed intensity ratio must be due to a spatial gradient of the order parameter, which diminishes with time. From the present data we can not extract whether an order parameter gradient remains after equilibration. A more complete account on this work, including the relaxation of antiphase domain boundaries after quenches and surface truncation rods which are sensitive to the surface order, will be reported in forthcoming papers.

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