Absence of $2k_F$ Splitting in the Diffuse Scattering from Cu_3Au at the (001) Surface

H. Reichert,[1] O. Klein,[1] V. Bugaev,[1] O. Shchyglo,[1] A. Udyanskyy,[1] H. Dosch,[1,2] and K. F. Peters[3]

[1]*Max-Planck-Institut für Metallforschung, Heisenbergstrasse 3, D-70569 Stuttgart, Germany*

[2]*Institut für Theoretische und Angewandte Physik, Universität Stuttgart, D-70569 Stuttgart, Germany*

[3]*European Synchrotron Radiation Facility, F-38043 Grenoble, France*

(Received 8 December 2002; published 8 May 2003)

We report a new type of short-range order correlations at the (001) surface of Cu_3Au which no longer produces the $2k_F$-splitting characteristic for the bulk short-range order scattering. We present the temperature dependence of this phenomenon and a theoretical interpretation of its origin. We argue that this new surface effect is caused by a drastic change of the strain-induced interactions at the surface.

DOI: 10.1103/PhysRevLett.90.185504 PACS numbers: 61.10.Eq, 34.20.Cf, 61.66.Dk, 64.60.Cn

Binary alloys are model systems for the study of cooperative phenomena in condensed matter. As a function of temperature and composition (x), the prototypical phase diagram of such binary (A_xB_{1-x}) systems exhibits various ordered and disordered phases which are governed by the interplay between ordering and clustering tendencies. One of the principal scientific efforts has been to understand how the various long-range ordered and short-range ordered (SRO) structures are related to the details of the underlying interactions. An outstanding scientific controversy remains regarding the role of the long-ranging strain-induced interactions which originate in the atomic size mismatch between the two constituents A and B, and are controlled by the elastic response of the alloy crystal.

In recent years, the surface of binary alloys has moved into the focus of scientific interest, since the symmetry break at the surface has a fundamental influence on the balance between the different (bulk) contributions to the effective pairwise interactions. In fact, novel ordering and disordering phenomena which are absent in the bulk have been experimentally realized. Examples include surface-induced disordering in $Cu_3Au(001)$ [1], surface-induced oscillating segregation profiles in $Mo_{1-x}Re_x(001)$ [2] and $Cu_3Au(001)$ [3], surface-induced order in $Ni_{90}Al_{10}(110)$ [4], and surface-renormalized critical exponents as observed at FeAl(110) [5] and FeCo(001) [6] surfaces. While the generic conditions for the occurrence of these surface-induced phenomena are reasonably well understood [7], there is only poor microscopic understanding of the way in which the surface modifies the underlying effective pairwise interactions and how these changes affect or control surface phenomena. Disordered alloys with atomic size mismatch are particularly interesting in the near-surface region, since there the aforementioned strain-induced interactions must necessarily be altered by the additional mechanical degrees of freedom of the atoms permitted at the surface.

The only practical way to experimentally access the various contributions to the interactions in binary systems is by means of the SRO correlations which emerge in disordered phases and which give rise to a characteristic diffuse x-ray scattering distribution (''SRO diffuse scattering''). This smoothly varying SRO scattering has been studied quite extensively in the bulk [8]. Clearly, surface-modified interactions should be reflected in an associated redistribution of the SRO diffuse scattering at the surface and in the subsurface regime of the binary system. This rather weak surface scattering contribution has become experimentally accessible using the highly brilliant x-ray beams provided by 3rd generation synchrotron radiation facilities. Such experiments can now provide insight into this so far missing element in surface science.

In this Letter we present an x-ray scattering study of the surface effects on the SRO correlations in Cu_3Au. This model alloy exhibits a pronounced short-range order for temperatures above the $L1_2 - A2$ order-disorder transition temperature $T_o = 663$ K. The ordering is described by a four-component order parameter (OP) $\mathbf{\Psi}$, where Ψ_1, Ψ_2, and Ψ_3 denote orthogonal concentration waves along the $\{1, 0, 0\}$ directions (Ψ_4 is associated with the concentration of component B of the alloy) [3]. Because of the large size mismatch between the Cu and Au atoms, the strain-induced interaction is expected to be quite pronounced in this system [9]. The bulk SRO has also been studied in great detail [10] showing diffuse scattering maxima at the $\{1, 0, 0\}$ type wave vectors. More detailed diffuse scattering studies unraveled a fine structure with a fourfold peak splitting which is commonly attributed to Fermi surface nesting effects ($2k_F$ splitting) (see Ref. [11] and references therein). Figure 1 shows a sketch of the topology of the diffuse scattering maxima in reciprocal space in the $(h, k, 0)$ plane together with a typical scan along the $(h, 1, 0)$ direction. Notice that in real space this scattering distribution corresponds to local order fluctuations which are correlated in space over a medium range distance $L \approx 10$ nm as deduced from the observed peak splitting $\Delta k = 2\pi/L$ [11]. The effect of a free surface on this peculiar fine structure is the main thrust of this Letter.

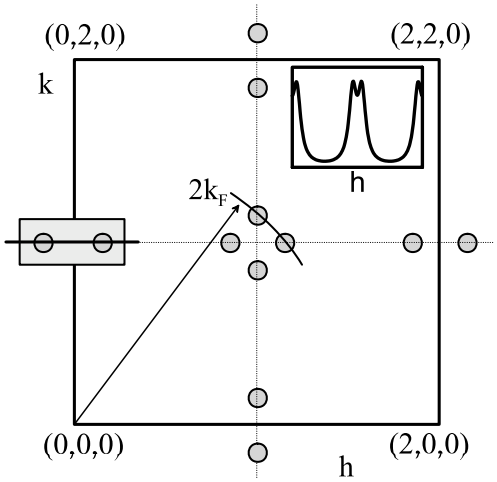

FIG. 1. Topology of the bulk SRO in the $(h, k, 0)$ plane of Cu_3Au. The inset sketches a line scan along the $(h, 1, 0)$ direction. The surface measurements in reciprocal space are indicated by the grey box and the thick line through the $(0, 1, 0)$ superstructure position.

The x-ray scattering experiments have been performed at the beam line ID3 of the European Synchrotron Radiation Facility on a well characterized $Cu_3Au(001)$ surface which has previously been used to study order parameter and surface segregation profiles [3,12]. Prior to the scattering experiments the sample surface was prepared using a standard sputter and annealing procedure. We achieve surface sensitivity by applying the grazing angle scattering geometry [13] which permits a restriction of the scattering depth to values as small as 18 Å at incidence and exit angles $\alpha_i = \alpha_f = 0.5\alpha_c$, where $\alpha_c = 0.21°$ denotes the critical angle for total external reflection at an x-ray wavelength of $\lambda = 0.7256$ Å. Figure 1 summarizes the experimental conditions together with the scans performed in reciprocal space. At the (100) and (010) superstructure position we determine in the grazing angle geometry the pure in-plane short-range order correlations testing the fluctuations of the in-plane OP components Ψ_1, Ψ_2. In a bulk sensitive mode we recorded the diffuse scattering around the (101) superstructure position.

Figure 2 shows the bulk diffuse scattering around the (101) reciprocal lattice vector. It confirms the aforementioned bulk split peak structure around the superstructure positions in reciprocal space (see Fig. 1). By way of example Fig. 2(a) depicts the intensity contours measured in the $(1 + \Delta h, \Delta k, 1)$ plane at a temperature $T = T_o + 45$ K. The temperature dependence of this structure is shown in Fig. 2(b). The asymmetry in the line shape is caused by the distortions due to the size mismatch [8].

The diffuse x-ray scattering in the surface sensitive mode is summarized in Fig. 3. The intensity contours measured in the $(\Delta h, 1 + \Delta k, 0)$ plane at a temperature $T = T_o + 45$ K are shown in Fig. 3(a), while the temperature dependence of this structure is demonstrated in line scans $(\Delta h, 1, 0)$ [see Fig. 3(b)]. Interestingly, we find a more complex line shape pointing to a strong surface effect onto the local order fluctuations.

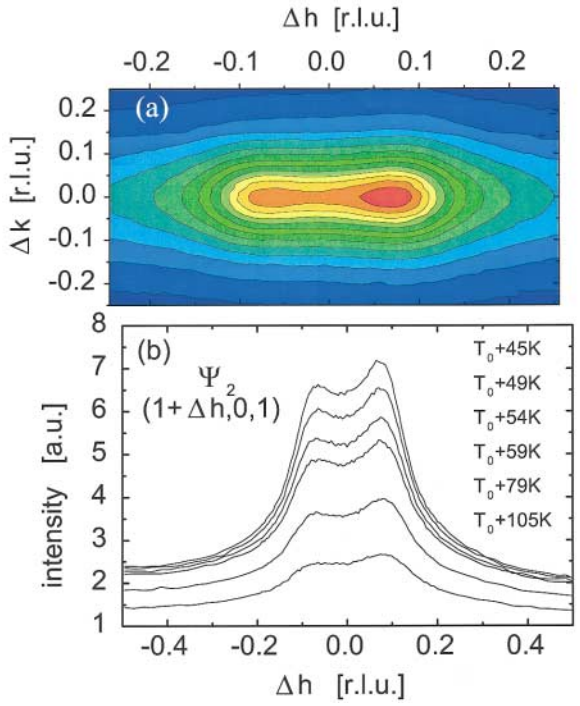

FIG. 2 (color). (a) Contour plot of the bulk diffuse scattering of Cu_3Au in the $(1 + \Delta h, \Delta k, 1)$ plane at $T = T_o + 45$ K. (b) Temperature dependence of the line shape along the line $(1 + \Delta h, 0, 1)$.

In order to understand the striking difference between the diffuse scattering profiles of Figs. 2 and 3, and to extract the pure surface contribution, one has to consider in detail the various contributions to the evanescent x-ray wave field which decays exponentially with depth with a scattering depth of $\Lambda = 18$ Å, thereby producing a sum of surface-related and bulk diffuse scattering contributions. This is depicted schematically in the inset of Fig. 4(a). The surface and subsurface regime which shows a new SRO distribution is shown as the grey area. Its thickness should be close to the intrinsic (temperature dependent) SRO correlation length ξ with $\xi = 5$ Å for $T = T_o + 54$ K. Thus, we expect a noticeable bulk SRO contribution in the evanescent signal. In fact, closer inspection of the evanescent scattering profiles [see Fig. 3(b)] reveals clearly the existence of symmetric shoulders in the profile along the line $(1 + \Delta h, 1, 0)$. Using the symmetric part of the diffuse scattering derived from the bulk profiles shown in Fig. 2(b) (corrected for asymmetric linear size-effect contribution), we have separated the surface contribution from the measured diffuse scattering. Figure 4(a) demonstrates this procedure for $T = T_o + 54$ K. By this, a surface-modified contribution to the diffuse scattering is retrieved as a function of temperature $T = T_o + \Delta T$ in Fig. 4(b). At first sight we find a

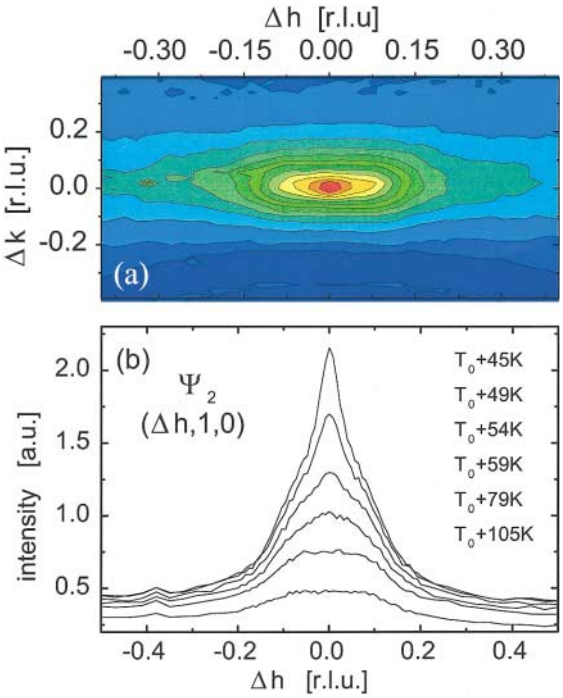

FIG. 3 (color). (a) Contour plot of the near-surface diffuse scattering of Cu_3Au in the $(\Delta h, 1 + \Delta k, 0)$ plane. (b) Temperature dependence of the line shape along the line $(\Delta h, 1, 0)$.

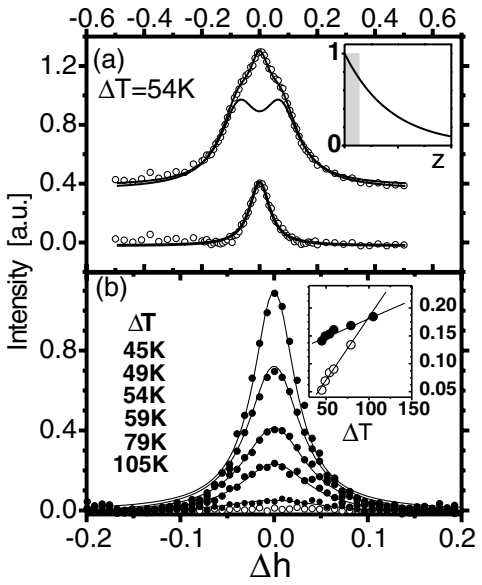

FIG. 4. (a) Surface contribution (lower curve) to the near-surface diffuse scattering at $T = T_o + 54$ K after subtraction of the bulk contribution. In the inset the exponential damping of the bulk contributions from deeper layers n is compared with the effective thickness of a surface-modified structure where n denotes the layer number. (b) Temperature dependence of the surface diffuse scattering profiles and (see inset) of the peak width in reciprocal lattice units (r.l.u.) of the surface (open circles) and the bulk (full circles) diffuse scattering.

rather surprising result: First of all, and this is our key observation, the $2k_F$ splitting is absent in the surface-related SRO diffuse scattering, in which we observe only a single Lorentzian line shape. Evidently, the presence of the free surface removes the $2k_F$ effect. The inset in Fig. 4(b) shows the temperature dependence of the peak width of the surface and the bulk contribution, where the bulk width is determined from the deconvoluted width of the separated satellites. The surface SRO fluctuations clearly occur on larger length scales $\xi_s^{\parallel}$ than in the bulk and are not correlated by strain fields.

In order to understand this unexpected experimental observation on a microscopic level we have to consider the elements which determine the detailed structure and the interactions at this surface. An apparent structural feature is the exponentially decaying concentration profile normal to the surface [3]. Consequently, the surface-related SRO fluctuations occur within a spatially inhomogeneous lattice. This, however, cannot explain our observations, since the *occurrence* of the $2k_F$ effect does not depend on concentration [3,14,15].

The occurrence of the split peaks in the bulk and their absence at the (001) surface must, therefore, be mediated by modification of the internal interactions at the surface. According to a hitherto accepted phenomenological description [16–18] the $2k_F$ splitting of the diffuse scattering maxima is caused by electronic screening singularities in the dielectric response function $\epsilon_{\vec{q}}$ caused by particular Fermi surface topologies. In this picture, the electronic screening acts only on the chemical interaction potential, $V_{\vec{q}}^{\mathrm{ch}} = v_{\vec{q}}/\epsilon_{\vec{q}}$, where $v_{\vec{q}}$ is the unscreened potential. Since such screening singularities get more pronounced in one or two dimensional systems [16,17], one might expect a surface enhancement of the tendency to form split maxima in the diffuse scattering which is in contradiction to our experimental observation. Evidently the situation is more involved. We will show in what follows that the microscopic understanding of our surface findings, in fact, requires us to revisit the entire bulk scenario.

In a strongly size mismatched alloy such as Cu_3Au the effective pair interaction consists of two equally important parts,

$$V_{\vec{q}}^{\mathrm{eff}} = V_{\vec{q}}^{\mathrm{ch}} + V_{\vec{q}}^{\mathrm{s\text{-}i}}, \tag{1}$$

where $V_{\vec{q}}^{\mathrm{s\text{-}i}}$ denotes the strain-induced interaction in the system. We now argue that the observed $2k_F$ splitting in the Cu-Au system is caused by this strain-induced interaction. Because it is long ranged, it is an ideal candidate to be responsible for the spatial correlations between fluctuations which occur in the system Cu_3Au on a length scale L of a few nm. It has indeed been demonstrated experimentally that lattice distortions carry the signature of the $2k_F$ splitting [19]. This conjecture is confirmed by a calculation of the effective pair interactions which explicitly includes strain-induced many-body effects.

Based on the theory outlined in Ref. [20] we have calculated the SRO diffuse scattering pattern in the

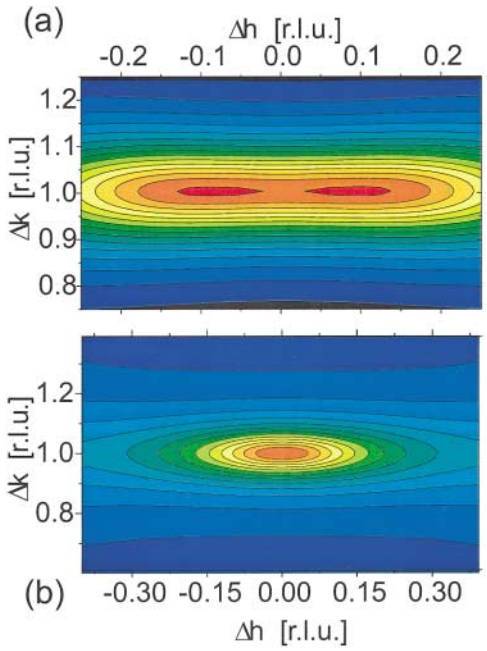

FIG. 5 (color). Calculation of the bulk SRO of Cu_3Au (a) including two-body strain-induced interactions and (b) without strain-induced interactions. Note that the bulk SRO scattering shows the $2k_F$ splitting that arises from the contribution of $V_{\vec{q}}^{\text{s-i}}$ to the symmetric intensity.

(001) plane. Most interestingly, it turns out that the existence of splitting in the SRO is not caused by the chemical interactions, but depends sensitively on the details of the strain-induced interactions [21]. Figure 5 shows the resulting bulk SRO patterns for two cases: (a) with strain-induced two-body interactions (including Kanzaki forces up to the second nearest neighbor shell), and (b) without strain-induced interactions. For the calculations we have deduced chemical interactions from the known values for the effective pair potential $V_{\vec{R}}^{\text{eff}}$ in Cu_3Au [10] subtracting from $V_{\vec{R}}^{\text{eff}}$ the strain-induced contribution $V_{\vec{R}}^{\text{s-i}}$ which was calculated using the elastic constants and the concentration dependence of the lattice constant [20]. The Kanzaki force parameter in the second coordination shell was the fitting parameter used to obtain agreement between the calculated SRO and our experimental data. Figure 5(a) demonstrates convincingly that the strain-induced interactions produce the observed splitting of the bulk SRO order maxima.

This new insight into the origin of the $2k_F$ splitting in the bulk of Cu_3Au provides the explanation for our intriguing surface observations: due to the freedom of a surface to relax strain, the magnitude of the strain-induced interactions in the system should be noticeably decreased in the surface regime. The calculations displayed in Fig. 5 show that indeed the splitting of the surface SRO intensity should essentially disappear, as observed.

In conclusion, we have measured bulk and surface diffuse scattering in Cu_3Au and found a rather unexpected surface effect, namely, the absence of the well-known $2k_F$ splitting of the diffuse maxima. We demonstrate that the microscopic understanding of this surface phenomenon forces one to reconsider the origin of the $2k_F$ splitting in this system. Our observation can be explained if the underlying spatial correlations of the local order fluctuations are mediated by strain-induced interactions which in turn experience the electronic screening effects [16,17].

This work is a first model study of SRO at the surface of binary alloys demonstrating a significant surface effect. Since in nature any system is finite sized, the understanding of SRO in binary alloys is incomplete as long as such surface effects as described here are ignored. Furthermore, the study of the surface SRO is a very powerful way to access experimentally the effective atomic interaction potentials which govern the behavior of metallic alloys and related crystals in nanoconfinement.

[1] S. F. Alvarado *et al.*, Z. Phys. B **66**, 103 (1987); H. Dosch *et al.*, Phys. Rev. Lett. **60**, 2382 (1988).
[2] M. Kottcke *et al.*, Surf. Sci. **376**, 319 (1997).
[3] H. Reichert *et al.*, Phys. Rev. Lett. **74**, 2006 (1995); H. Reichert and H. Dosch, Surf. Sci. **345**, 27 (1996); H. Reichert *et al.*, Phys. Rev. Lett. **78**, 3475 (1997).
[4] R. Drautz *et al.*, Phys. Rev. Lett. **87**, 236102 (2001).
[5] L. Mailänder *et al.*, Phys. Rev. Lett. **64**, 2527 (1990).
[6] S. Krimmel *et al.*, Phys. Rev. Lett. **78**, 3880 (1997).
[7] K. Binder, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic Press, London, 1983), Vol. 8, p. 1.
[8] W. Schweika, *Disordered Alloys*, Springer Tracts in Modern Physics Vol. 141 (Springer, Berlin, 1998).
[9] C. Wolverton, V. Ozolins, and A. Zunger, Phys. Rev. B **57**, 4332 (1998).
[10] J. M. Cowley, J. Appl. Phys. **21**, 24 (1950); S. C. Moss, J. Appl. Phys. **35**, 3547 (1964); B. D. Butler and J. B. Cohen, J. Appl. Phys. **65**, 2214 (1989).
[11] H. Reichert, S. C. Moss, and K. S. Liang, Phys. Rev. Lett. **77**, 4382 (1996).
[12] H. Dosch *et al.*, Phys. Rev. B **43**, 13172 (1991).
[13] H. Dosch, *Critical Phenomena at Surfaces and Interfaces*, Springer Tracts in Modern Physics Vol. 126 (Springer, Berlin, 1992).
[14] O. Malis *et al.*, Phys. Rev. B **59**, 11105 (1999).
[15] K. Ohshima, J. Harada, and S. C. Moss, J. Appl. Crystallogr. **19**, 276 (1986).
[16] M. A. Krivoglaz, *Diffuse Scattering of X-Rays and Neutrons by Fluctuations* (Springer, Berlin, 1996).
[17] S. C. Moss, Phys. Rev. Lett. **22**, 1108 (1969); S. C. Moss and R. H. Walker, J. Appl. Crystallogr. **8**, 96 (1974).
[18] D. de Fontaine, Solid State Phys. **34**, 73 (1979).
[19] W. Schweika, in *Properties of Complex Inorganic Solids 2*, edited by A. Meike *et al.* (Kluwer Academic, Dordrecht, 2000).
[20] V. N. Bugaev *et al.*, Phys. Rev. B **65**, 180203 (2002).
[21] V. N. Bugaev *et al.* (to be published).