Observation of a double-step–single-step phase transition on a vicinal surface of $Cu_{83}Pd_{17}(110)$

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The $Cu_{83}Pd_{17}$ alloy is known to be chemically ordered (fcc $L1_2$) at low temperature and to exhibit a disordering transition at $T_c = 778$ K. Using thermal-energy atom scattering, a vicinal surface of $Cu_{83}Pd_{17}(110)$ (miscut 1.8°) was found to undergo a single-step–double-step morphological transition when crossing the bulk critical temperature.

Metal alloys present properties of fundamental interest in surface science and of technological importance. Indeed such systems often exhibit unusual catalytic properties. Moreover the formation of surface alloys is to be controlled when growing multilayers, which find a large number of applications, e.g., as sensors or as x-ray optical components. Previous studies of alloys were mainly devoted to determining the chemical composition and order of surface layers for singular surfaces. In the same way the stability of vicinal surfaces of pure metals or semiconductors has also attracted much attention whereas vicinals of alloys remain largely unexplored. Our paper is intended to be a contribution to the understanding of the mutual influence between bulk chemical order and surface morphology.

We focus here on alloys that undergo order-disorder transitions on a fixed lattice, i.e., where the chemical order only is modified by the transition. Among those, many binary alloys of the fcc A_3B type exhibit a first-order $L1_2$-disorder transition. In the low-T, $L1_2$ phase, A atoms occupy the centers of the faces of the fcc unit cell and B atoms are located at the corners. In such a structure the (100) and (110) planes are alternately pure A and AB mixed. Then two types of unequivalent terminal planes are *a priori* possible and it is the surface tension which determines which one effectively exists. For instance it was observed that the surface mixed plane (B segregation) is preferential for $Cu_3Au(100)$,[1] $Ni_3Al(100)$, $Ni_3Al(110)$,[2] and $Pt_3Sn(100)$.[3] In contrast, a pure A terminal plane (A segregation) was observed on $Cu_{85}Pd_{15}(110)$ (Refs. 4 and 5) and $Pt_3Ti(100)$.[6] In the presence of monatomic steps the termination of bulk order would make adjacent terraces unequivalent. On vicinal surfaces various structures can then possibly be formed such as antiphase boundaries parallel to the surface,[7] or perpendicular to the surface and pinned at single steps. The surface could also exhibit double steps with all the terraces of the low-energy type. Experimentally double steps were reported for the nominal $Pt_3Sn(100)$ surface[3] as well as for NiAl(111) ($B2$ type crys-

tal)[8] while some indications that all terraces have the same composition were found for $Pt_3Ti(510)$.[9] We have chosen to study a vicinal surface of $Cu_{83}Pd_{17}(110)$ since the singular $Cu_{85}Pd_{15}(110)$ has been widely studied.[4,5] The precise composition of our alloy corresponds to the congruent point of the bulk phase diagram and allows us to avoid the long period bulk structures which appear when the Pd (molar) composition is above 18%. The shift from the $Cu_{75}Pd_{25}$ stoichiometry brings about a small amount of chemical disorder in the mixed planes which are Cu enriched. The bulk properties of this alloy are well known from the work of Ricolleau *et al.*[10] and we used their method for elaborating the sample.

The morphology of vicinal surfaces of such crystals can be followed conveniently as a function of sample temperature by using thermal-energy atom scattering (TEAS). The crystal was oriented by the Laue technique and spark cut. The samples were successively mechanically and electrochemically polished. After a few cleaning cycles (Ar^+ bombardment and annealing) in ultrahigh vacuum (UHV) a reproducible He diffraction pattern was obtained. For our study only vicinal surfaces with a miscut plane azimuthally oriented 35° off the [$1\bar{1}0$] crystallographic axis were available. Consequently the steps on our sample have geometrical kinks, the presence of which presumably does not influence our main conclusions.

The interaction of the helium atoms with the surface is poorly sensitive to the chemical nature of surface atoms, and even if one can take advantage of its high sensitivity to the details of the surface corrugation, extra information on the surface chemical composition is needed. From previous experiments by x-ray photoelectron spectroscopy, medium-energy ion scattering,[4] or by CO adsorption,[5] it was widely concluded that at low T the terminal plane of $Cu_{85}Pd_{15}(110)$ is constituted only by Cu atoms and that the second plane is a mixed Cu-Pd ordered one. During surface preparation in UHV, Pd segregation was observed while upon subsequent annealing the Cu surface concentration increases as Pd atoms

dissolve into the bulk.[4,5]

For purpose of verification and in order to know whether similar conclusions can be reached for our vicinal surface we have performed a study of its composition using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). We found that upon sputtering the surface Pd concentration increases while the LEED pattern becomes 1×1. When annealing the sample during 10 min at increasingly high temperatures, we found that Pd begins to dissolve at 533 K. In the same time, fractional-order diffraction peaks that reflect the (2×1) chemical ordering in the second layer become visible. In the 533–700-K annealing temperature range the Pd concentration decreases further whereas the half-order peaks become sharper and more intense. Annealing at 700 K and above does not change the surface composition anymore. Our sample thus behaves quite similarly to $Cu_{85}Pd_{15}(110)$.[4,5] So the terminal plane of our vicinal $Cu_{83}Pd_{17}(110)$ surface is undoubtedly Cu rich and presumably almost pure Cu.

TEAS diffraction spectra were recorded with a cooled beam (energy 21 meV, wave vector $k_i = 6.4$ Å^{-1}). The apparatus has been described in detail elsewhere.[11] The incidence angle θ_i is measured with respect to the surface normal. As the corrugation of the He solid potential on the (110) terraces is only measurable perpendicular to the dense rows ([$1\bar{1}0$] direction) we obtain a one-dimensional terrace diffraction pattern. The crystal was oriented in order to have the incident plane perpendicular to the average step direction. The diffraction from a stepped surface obeys simple rules concerning the width and the intensities of the peaks. The vicinal surface can be seen as the juxtaposition of adjacent terraces of width L_0 separated by steps of height h so that the step-step distance is $L = \sqrt{L_0^2 + h^2}$. The scattered intensity in the incidence plane and in the vicinity of the direction specular to the terraces can be approximated by

$$I(\Delta K_{\parallel}) = \left[|A(\Delta K_{\parallel t})|^2 \frac{\sin^2(\Delta K_{\parallel t} L_0 / 2)}{(\Delta K_{\parallel t}/2)^2} \right] P(\Delta K_{\parallel}), \quad (1)$$

$$P(\Delta K_{\parallel}) = \sum_{n_x} \delta \left[\Delta K_{\parallel} - n_x \frac{2\pi}{L} \right], \quad (2)$$

where A is the form factor of the (110) unit cell, $\Delta K_{\parallel t}$ and $\Delta K_{\parallel}$ are, respectively, the components of the momentum transfer parallel to the terrace plane and parallel to the surface plane. The term in square brackets is the terrace form factor. The last sum is the interference factor of the step lattice; it shows that terrace diffraction peaks are split into several surface diffraction peaks, the intensity of which is modulated by the terrace form factor. Throughout the paper the index of the surface diffraction peaks $(n_x, 0)_s$ is given in $2\pi/L$ units. The same splitting is expected for every terrace diffraction peak. As the azimuthal direction of the miscut is not aligned on the terrace crystallographic axis, it is more convenient to focus on surface peaks $(n_x, 0)_s$ around the specular direction to the terraces $(0,0)_t$. By changing the incidence angle θ_i it is possible to displace the surface diffraction peaks with respect to the $(0,0)_t$ direction. In

the presence of step disorder, the surface diffraction peaks broaden depending on their position with respect to the $(0,0)_t$. When in coincidence with the $(0,0)_t$ direction ($\Delta K_{\parallel t} = 0$), a surface peak remains narrow as steps meander parallel to the terraces.

In a first experiment we have recorded the intensity (I_{00t}) exactly in the $(0,0)_t$ direction versus the incidence angle θ_i and for various crystal temperatures. The intensities shown in Fig. 1 were corrected for thermal attenuation. As Salanon et al.[12] have found that the specular intensity weakly depends on θ_i for the nominal Cu(110) surface, $A(\Delta K_{\parallel t})$ can be taken constant in Eq. (1). The I_{00t} intensity variations can then be directly related to the step height: Indeed the intensity variations described by the relation (2) can be related to the phase $\varphi_h = \Delta k \cdot h$ where h is perpendicular to the terrace plane with a modulus h equal to the single step height ($h = 1.30$ Å) and $\Delta k = k_f - k_i$ is the total momentum transfer. φ_h is calculated for given incidence conditions and for k_f in the $(0,0)_t$ direction. A narrow and intense surface peak is expected in the $(0,0)_t$ direction, for $\varphi_h = 2n\pi$ (in-phase condition) whereas for $\varphi_h = (2n+1)\pi$ (out of phase) the intensity in the $(0,0)_t$ direction is expected to be weak as the two nearest surface peaks are symmetrically located on each side of the $(0,0)_t$ direction. At 762 K we have observed strong oscillations of the I_{00t} intensity while at 823 K the period of the intensity oscillations is doubled (Fig. 1). At 823 K the maxima correspond to $\varphi_h = 2n\pi$ which shows that single steps are present on the surface whereas at 762 K the maxima are for $\varphi_{2h} = \Delta k \cdot 2h = 2m\pi$ revealing a step height doubling.

By recording the diffraction pattern around the $(0,0)_t$ direction, at different incidence angles θ_i we have observed the evolution of the spectrum from an in-phase (with respect to h) to an out-of-phase position. The data of Fig. 2 were taken at a temperature of 793 K, i.e., in the single step phase. For $\theta_i = 69°$ the narrow $(-1,0)_s$ peak is dominant and in coincidence with the $(0,0)_t$ direction for which $\varphi_h = 2\pi$. By varying θ_i the peak moves away from the $(0,0)_t$ direction, decreases in intensity, and broadens, thus revealing that the steps meander. For
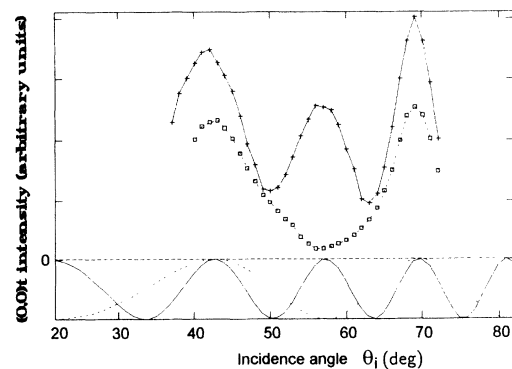

FIG. 1. Intensity in the direction specular to the terraces $(0,0)_t$ [(+) $T = 762$ K, (□) $T = 823$ K]. Lower curves show expected phase-antiphase oscillations cos(φ_h) for single (---) and cos(φ_{2h}) for double height steps (——). The incidence angles are measured with respect to the surface plane.
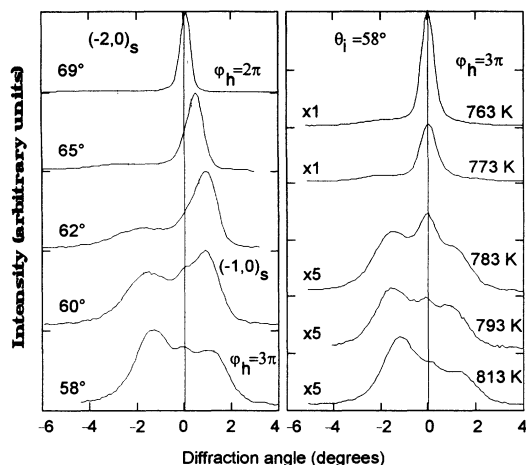
FIG. 2. Left: Diffraction spectrum at $T = 793$ K (single-step phase) for various incidence angles θ_i. The $(-1,0)_s$ and $(-2,0)_s$ peak positions are indicated by the dotted lines. Right: Evolution of the diffraction spectrum at $\theta_i = 58°$ ($\varphi_h = 3\pi$) from the low-T double-step phase to high-T single-step phase. The diffraction angles are measured with respect to the $(0,0)_t$ direction.

FIG. 3. Intensity of the $(-2,0)_s$ ($\times$) and $(-1.5,0)_s$ ($\square$) peaks vs temperature ($\theta_i = 58°$). The dotted line joining data points is for cooling and the continuous line is for heating.

$\theta_i = 58°$ the $(-1,0)_s$ and $(-2,0)_s$ peaks are broadened by step disorder and appear on each side of the $(0,0)_t$ direction ($\varphi_h = 3\pi$). The separation in reciprocal space between these surface diffraction peaks gives the average distance between single steps ($L = 41.5$ Å, miscut 1.8°). It is noteworthy that a component in the $(0,0)_t$ direction is always visible. One possible explanation of this observation is that some wide (110) flat areas devoid of steps exist on the surface. Below T_c, the same measurements show that the surface period is doubled. All these results show consistently that the surface exhibits a regular array of double steps between (110) terraces below T_c and of single steps above T_c.

In the double-step phase, one could have double steps with double terraces ($2L_0$), conversely the surface unit cell could be formed by two nonequivalent adjacent terraces of different sizes separated by a single step. To clarify this point we have measured the evolution of the diffraction spectrum versus temperature across the transition zone in the out-of-phase position ($\theta_i = 58°$). The data have been taken by increasing or decreasing slowly the temperature across the transition zone and after a few minutes equilibration (≈ 10 min). As explained here above we observe the splitting in the single step phase whereas below T_c the intense central half-order peak $(-1.5,0)_s$ dominates (Fig. 2). Moreover, upon cooling the intensity of the $(-1,0)_s$ and $(-2,0)_s$ peaks vanish. This behavior can be understood if the width associated with the terrace form factor in Eq. (2) is reduced (L_0 replaced by $2L_0$). In the high-T phase we have carefully checked that the remaining intensity in the $(0,0)_t$ direction does not belong to the $(-1.5,0)_s$ peak. Consequently one can assess that the terrace width is practically doubled in the low-T phase although the detailed structure of the double step itself cannot be easily determined.
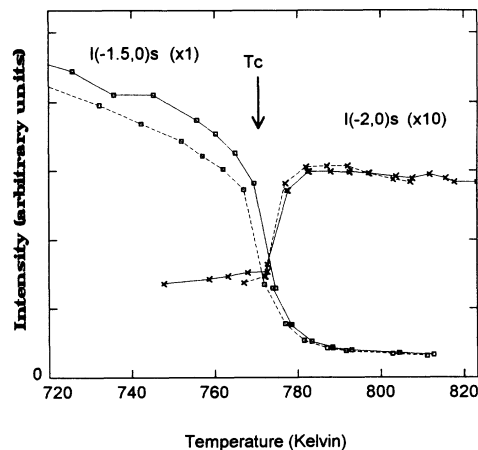
Across the transition, the width of the peaks remains constant and only the intensities change. In particular, the $(-1.5,0)_s$ peak, which is not sensitive to the step disorder, always has a width close to the instrumental resolution. So the size of double-step domains is larger than the transfer width of our apparatus (typically 300 Å) as long as the peak is visible. The $(-2,0)_s$ and $(-1,0)_s$ peaks are broadened by the step disorder and we have found no width variation with temperature.

In Fig. 3 we report the measured intensity of the central $(-1.5,0)_s$ peak and of the satellite $(-2,0)_s$ peak versus temperature. The data were corrected for thermal attenuation. For each temperature the intensities were measured until a stationary value (after ≈ 10 min) was obtained. We find that the transition is narrow around 770 K. Note that temperature inhomogeneities on our sample are of the order of 10 K which makes the difference between the known bulk critical temperature (778 K) and our measurement of 770 K not significant. The same intensity curves were obtained whether the crystal temperature is lowered or increased. The transition shows no clear hysteresis as long as the temperature variation rate is kept below $\cong 1$ K/min.

Nonetheless the transition is not instantaneous and its kinetics can be monitored in the transition zone. For this purpose the peak intensities ($\theta_i = 58°$) were recorded versus time at 772 K after a temperature jump of $+5$ K. The $(-1.5,0)_s$ intensity decays and the $(-2,0)_s$ intensity increases roughly exponentially with a time constant of 110 ± 10 s. An opposite variation with the same time constant was obtained for a temperature drop of 5 K from an initial temperature of 777 K.

By a quench from 823 K to room temperature (10 K/s across the transition temperature down to 673 K) we could freeze the surface in the single-step phase. By annealing the sample at increasingly high temperatures during 10 min we found that the surface remains frozen below 673 K and that the double-step morphology is first recovered at 723 K. This narrow temperature interval (50 K) is an indication that the activation energy for the ordering process is of the order of a few eV (in the range of

bulk diffusion activation energy) rather than of a fraction of an eV (range of surface-diffusion activation energies). This strongly suggests that the surface morphology kinetics is controlled by processes in the underlying bulk. Moreover, bulk resistivity measurements on crystals quenched to room temperature in the disordered state show consistently that the system is frozen below 670 K while ordering is rapid above 720 K.[13]

Generally, in a system which undergoes a bulk first-order phase transition, specific transitions occur at the surface. For instance disordering at the surface can take place below T_c and extend further into the bulk via a wetting transition.[14] We have found here that the surface morphology itself can be modified by a bulk transition. Moreover unlike most surface transitions which are two dimensional and affect only the outermost surface layer, this transition appears to be linked to the chemical order beneath the surface. In an attempt to model the system we have imagined three possible surface structures below T_c. (1) *Single steps with alternate Cu and CuPd terraces.* The energy for one step (per unit step length) being $F1_{ss}$ and the excess energy per unit area of the CuPd terrace (relatively to the Cu terrace) being $F1_{tCuPd}$, the excess free energy per unit area associated to this configuration is $F1 = F1_{ss}/L_0 + F1_{tCuPd}/2$. (2) *Single steps with Cu terraces.* This configuration contains a diffuse (over a depth of several layers) antiphase boundary parallel to the terrace (APB∥) of energy per unit area $F2_{APB∥}$ beneath every other terrace.[7,15] One should also take into account two antiphase boundaries (APB⊥) perpendicular to the terraces upright to each step over the same depth, with an energy per unit step length $F2_{APB⊥}$. The excess free energy density is then in this case, $F2 = F2_{ss}/L_0 + F2_{APB∥}/2 + F2_{APB⊥}/L_0$. (3) *Double steps with Cu double terraces.* This configuration requires only the formation of double steps: $F3 = F3_{DS}/2L_0$.

The composition of the terraces in the disordered phase cannot be given by our AES or He experiment. However, for $Cu_3Au(100)$ which is also cfc $L1_2$ it was found that the low-T concentration in each of the first two planes (CuAu at the surface and pure Cu beneath) is maintained well above the transition temperature.[16,17] This shows that segregation is not dramatically altered by the transition. This behavior is presumably general[15] and rules out structure (1). Between structures (2) and (3) the free-energy difference is $\Delta F = F2 - F3 = F2_{ss}/L_0 - F3_{DS}/2L_0 + F2_{APB∥}/2 + F2_{APB⊥}/L_0$. The step free energies include the configurational entropy which can play an important role: first, the number of steps is divided by two at the transition, and second the roughening properties of single and double steps are presumably different. In the single-step phase the APB energies vanish and one has $F2_{ss}/L_0 - F3_{DS}/2L_0 < 0$. Below T_c the addition of the APB energies makes ΔF positive which explains the observation of the double-step phase. For less vicinal surfaces (i.e., with lower L_0), the weight of the costly term associated with the APB∥ is reduced. So above a critical miscut the single-step phase should be stabilized below T_c. Such a critical miscut between a single-step and a double-step phase was evidenced on vicinal surfaces of $Si(100)$.[11] For $Cu_{83}Pd_{17}$ the experimental observation of this critical miscut would be a strong evidence that it is the free energy of APB's (i.e., bulk chemical order) which drives the transition.

In conclusion, we have shown experimentally that a vicinal $Cu_{83}Pd_{17}(110)$ surface presents a dramatic morphological change at a temperature close to that of the bulk phase transition. Although the details of the underlying physical mechanism for this type of behavior are not yet completely understood, it is clear now that bulk chemical order influences surface morphology.

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