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Observation of an order-disorder phase transition on the Pd(110) surface

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The diffractive scattering of thermal He atoms has been used, for the first time, to investigate a phase transition ($T_c = 230$ K) on the clean Pd(110) surface. This transition has not previously been reported. Consideration of the beam profiles, over a range of incidence energies, suggests an order-disorder transition involving lateral displacements of the surface Pd atoms.

Thermal He atoms are ideal probes of surface order because of their extreme surface sensitivity. The repulsive potential between the surface atoms and the closed-shell He atoms is strong because of the Pauli exclusion principle, and the classical turning point for atoms of 60 meV occurs some 3–4 Å from the surface ion cores.[1,2] There is no surface penetration as in low-energy electron diffraction (LEED). As yet, however, scattering of monochromatic He beams has been restricted to crystallographic studies of well-ordered systems,[3,4] fundamental studies of the He-metal interaction potentials,[5] and some investigations of inelastic effects.[6,7] Surface-roughening transitions on some Cu surfaces have also been investigated.[8,9]

Reconstruction of several metal surfaces has been reported, principally on the basis of LEED data,[10–12] but also from diffractive atom scattering[13] and nondiffractive techniques.[14,15] Some of these surfaces exhibit transitions from a low-temperature phase, which has reduced symmetry relative to the corresponding bulk plane, to a high-temperature phase which shows (1×1) periodicity.[10,12] The high-temperature phase may be disordered, as in the case of the Au(110) $(1\times2)\rightarrow(1\times1)$ second-order transition ($T_c = 650$ K).[12] The W(100) surface exhibits a phase transition between 200 and 400 K, in which the low-temperature *p2mg* structure involves small (0.16 Å) lateral displacements of the surface tungsten atoms to produce zigzag chains parallel to the ⟨110⟩ directions in two orthogonal domains.[10] The high-temperature surface is believed, on the basis of LEED evidence, to be ordered with surface atoms in bulk termination sites and giving a (1×1) LEED pattern.[10]

This is the first reported observation of a Pd(110) surface phase transition. The transition, which occurs at 230 ± 5 K, differs from those of W(100) and Au(110) in that the surface periodicity remains (1×1) across the transition and simply involves a disordering process. Atomic diffraction techniques are highly suited to this study, for which there are no fractional order beams, because the integral order beams are "undiluted" by information from subsurface layers.

Experiments were carried out in an ultrahigh vacuum (UHV) chamber (base pressure 6×10^{-11} mbar) using 82-meV He atoms produced from a supersonic nozzle beam source. The relevant instrument parameters are the velocity resolution (4.5%) and angular resolution (1.5°). Most of the experiments described here were performed with the He beam incident at 50° to the surface normal and scattering in the incident plane. The Pd crystal, cut to expose the (110) face, polished and then cleaned *in situ* by standard Ar^+ bombardment and annealing techniques, was aligned such that the scattering plane was perpendicular to the close-packed rows of surface atoms. Crystal temperature control was achieved by circulation of liquid N_2 in the manipulator and resistive heating while the temperature was monitored with a chromel-alumel thermocouple attached to the back of the Pd crystal.

Figure 1 shows the Pd(110) bulk termination plane, the scattering geometry, and a typical in-plane diffraction scan with 82-meV He atoms obtained at a surface temperature of 180 K. Analysis of this, and results obtained at other incident energies (63–120 meV) and incident angles (30°–70°), enabled a corrugation of 0.23 Å to be determined for the equipotential surface corresponding to the turning point for normally incident 34-meV He atoms or 82-meV atoms incident at 50° to the normal. These results are in good agreement with the published results.[16]

Figure 2 shows the variation of the intensity I of the (1,0) diffracted beam, measured at the peak maximum, as a function of the surface temperature T while the sample was heated ($0.45\ \mathrm{K\,s^{-1}}$). The onset of a phase transition at 230 ± 5 K is clearly apparent. The data are presented as $\ln I$ vs T to facilitate the identification of thermal diffuse scattering by a Debye-Waller analysis. The slope of the curve below 230 K corresponds to a surface Debye temperature of 263 K to be compared with the bulk value of 275 K.

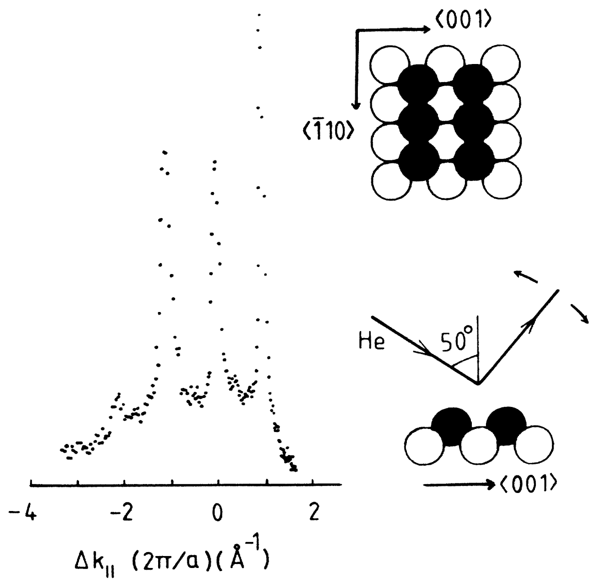

FIG. 1. The diffraction of 82-meV He atoms from a Pd(110) surface at 180 K, in the plane defined by the surface normal and the ⟨001⟩ direction.

Figure 2 shows the phase transition to be complete at 280 K, but for a higher heating rate (3 $\mathrm{K\,s^{-1}}$) this could be increased to 380 K while leaving the onset unchanged at 230 K. The equivalent experiment performed during sample cooling (0.5 $\mathrm{K\,s^{-1}}$) showed an onset at 230 ± 10 K. We conclude that the apparent temperature range and hysteresis are due to the kinetics of the phase transition itself and that the transition occurs over a narrow temperature range < 10 K and may possibly be first order.

Beam profiles for the (1,0) beam measured above and below the phase transition are shown in Fig. 3. At the lower temperature (200 K), the beam width is determined by instrumental parameters [full width at half maximum (FWHM) $\simeq 11\%$, of the surface Brillouin zone (SBZ)], while at the higher temperature (350 K) a marked broadening has occurred. The profile is that of a broad feature (FWHM $\simeq 40\%$ of SBZ) and a narrow central component whose width is also dictated by the instrumental resolution. The broad feature remains of constant width, corresponding to a surface length of 8–10 Å, during further heating. The intensity of the central component does not fall to zero above the transition, even to 550 K, and at no stage are fractional order beams ever observed. We believe that this dramatic temperature dependence of the beam profile is unlikely to arise from inelastic effects which only steadily become more important at higher surface temperatures.[17]

The low temperature of the transition precludes significant surface transport of atoms as, for example, in an island–lattice-gas transition. This contention is supported by measurements of the beam profiles above the transition temperature, as a function of incidence angle between 40° and 70°. If the surface were composed of small islands or narrow terraces, then oscillations in the beam width would occur corresponding to constructive and destructive interference conditions being met across an island or terrace edge.[18–20] Such oscillations are well documented in LEED.[18,20] For a step height determined by the (110) interplanar spacing (1.38 Å), the interval 40–70° should correspond to about two cycles through the oscillations. No variations of beam profile with incidence angle were observed.

We suggest that the surface Pd atoms have a small lateral displacement in the ⟨001⟩ direction within the unit cell defined by the second layer atoms. Even for an isolated Pd atom, such a displacement would not involve crossing the surface diffusion barrier. In the low-temperature phase, the direction of the displacement of neighboring surface atoms along the ⟨001⟩ direction is correlated. This leads to order at least within the transfer width (~ 50 Å). At the transition temperature disorder sets in such that the direction of displacement of atoms is correlated only within 2–3 unit cells. A model of the surface is shown in Fig. 4. Note that no information is available from these experiments on the

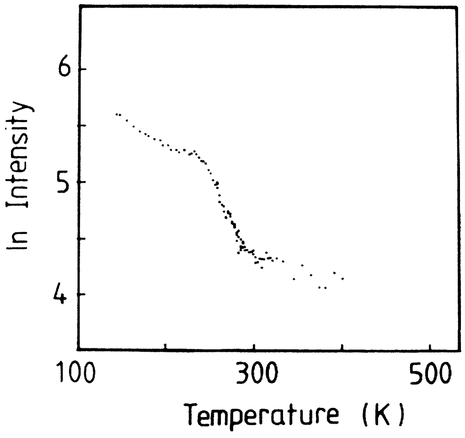

FIG. 2. The variation of the (1,0) diffracted beam intensity as a function of surface temperature during sample heating (0.45 $\mathrm{K\,s^{-1}}$).

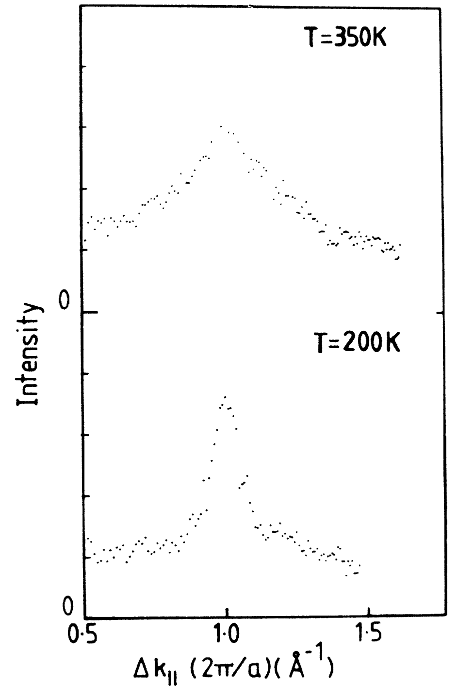

FIG. 3. Profiles of the (1,0) diffracted beam at 200 and 350 K.

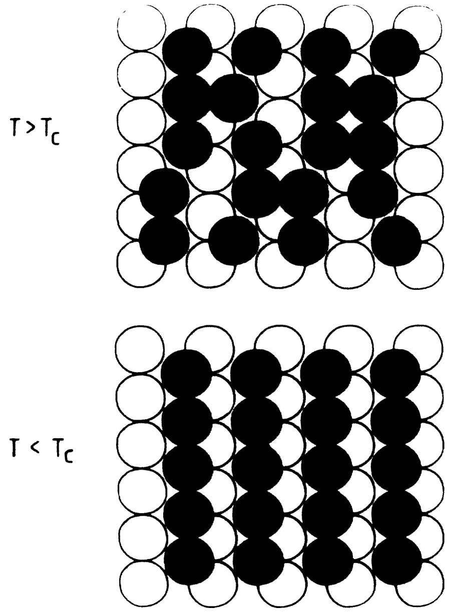

FIG. 4. Suggested model of the Pd(110) surface below and above the phase transition showing ⟨001⟩ lateral displacements. The experiment gives no information on the extent of disorder along ⟨$\bar{1}$10⟩.

ordering of surface atoms along the ⟨110⟩ direction.

The origin of such lateral displacements can be rationalized as follows. In a bulklike site, surface atoms are equidistant from four atoms in the second layer and one atom directly beneath in the third layer. The (110) surface of Pd exhibits, in common with many other relatively open metal surfaces, a relaxation with a contraction of 0.08 Å in the separation between the first and second layers.[21] Modeling this with hard spheres requires a 0.06-Å lateral shift of the surface atom in the ⟨001⟩ direction, in order to retain contact with at least two second-layer atoms. As in the case of W(001),[10] a hard-sphere model cannot account for the magnitude of the lateral shift as well as the surface relaxation since a shift of 0.06 Å or 1.5% of the unit-cell dimension (3.89 Å) could not account for the relatively high intensity found in the broad component above the transition. This intensity, or rather the residual intensity in the central component, leads to an estimate for the lateral displacement of 0.7 ±0.1 Å.

In conclusion, the unique properties of thermal He atoms have been exploited in the investigation of a hitherto unreported phase transition on the Pd(110) surface. The phase transition, at 230 ± 5 K, is suggested to involve disordering in the direction of the displacement of surface atoms along ⟨001⟩, relative to a low-temperature phase in which neighboring displacements are correlated.

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