Coupling of Surface Electronic States through the W{001} Phase Transition

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Angle-resolved photoemission spectra obtained from the W{001}-(1×1) structure are compared with spectra from the cooled $(\sqrt{2} \times \sqrt{2})R\,45°$ surface structure, providing the first experimental evidence for the coupling of surface states at the Fermi energy on formation of the latter phase. Calculations of the surface density of states are in good agreement with experiment. A prominent new feature observed from the low-temperature phase (at the 1×1 $\bar{M}$ point) is attributable to an umklapp process.

The surface layer of W{001} undergoes a continuous, reversible displacive phase transition from 1×1 to $(\sqrt{2}×\sqrt{2})R\,45°$ on cooling below 370 K.[1,2] This transition has aroused considerable interest, which, despite a detailed structural characterization,[3-6] has produced several important points of controversy. It has been proposed[1,2,7,8] that the driving force for the phase transition is a two-dimensional Fermi-surface instability, with the surface periodic lattice displacement (PLD) opening up a gap in the surface states band at the Fermi energy, as in charge-density–wave systems. Later, it was suggested[9,10] that the surface atoms are unstable for arbitrary lateral displacements, with surface-state coupling marginally favoring the observed wave vector of the reconstruction. In order to see whether surface-state effects actually occur in the reconstruction, and to examine the tenability of these theories, we have carried out detailed photoemission experiments of both the clean 1×1 and $(\sqrt{2} ×\sqrt{2})R\,45°$ structures, backed up by calculations using the matching Green's-function method.[11]

Experiments were carried out in a VG Scientific Model ADES-400 electron spectrometer incorporating a rotatable energy analyzer with an acceptance half-angle of 2°. The crystal was cleaned by successive heating cycles in 10^{-6} Torr of oxygen to 1700 K with subsequent flashing *in vacuo* to 2500 K, until no traces of contamination were observable by Auger-electron spectroscopy. The state of cleanliness was checked by observation of the $\bar{\Gamma}$ surface state, which is very sensitive to contaminants.[12] The crystal could be cooled to 200 K in ~5 min after flashing to 2500 K; formation of the low-temperature phase and the crystal symmetry were checked by low-energy electron diffraction. A good vacuum is essential to the success of these experiments, given the known sensitivity of the low-temperature phase to impurities[13]; total background pressures (major

constituent: H_2) were $<3×10^{-11}$ Torr. Results presented here were obtained with use of photons of 16.8 eV (NeI) and 21.2 eV (HeI), and a polar incidence angle of 45°.

Figure 1 shows a comparison of the observed dispersion of the surface states or resonances with a self-consistent calculation of the electronic structure of W{001} by Posternak *et al.*[14] along the $\bar{\Sigma}$ symmetry line for the 1×1 surface. These states were experimentally defined as those which were removed by hydrogen adsorption. The
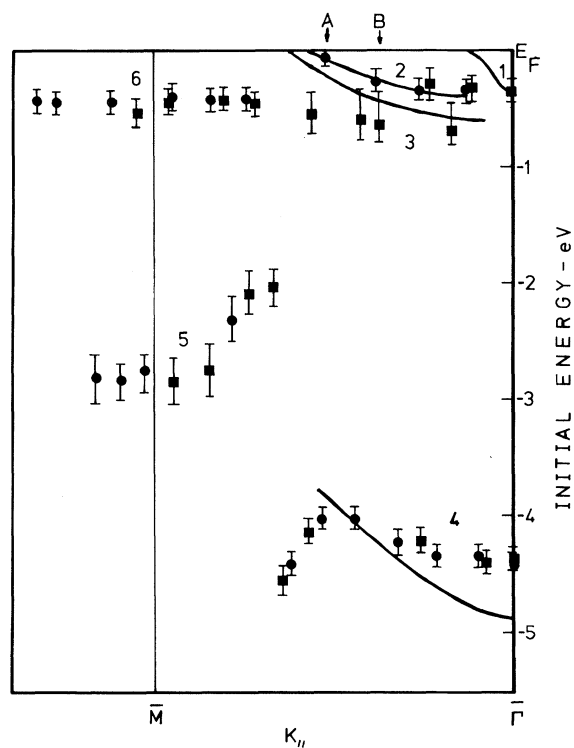

FIG. 1. Surface states and resonances observed on W{001}-(1×1) (points), compared with the calculations of Posternak *et al*. (Ref. 14) (lines). Data obtained with both HeI (solid circles) and NeI (solid squares).

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observed states agree rather well with the theory. Calculations show[14] that state 1 consists of d_{z^2} orbitals, with even symmetry, while state 2 is a mixture of d_{zx}, d_{zy}, and d_{xy} (even), and state 3 is a mixture of d_{zx}, d_{zy}, and $d_{x^2-y^2}$ (odd). Detailed experimental results obtained at different incident photon angles and at higher resolution[15] support this assignment; despite the unchanged even symmetry,[12] the orbital character changes in going from state 1 to state 2.[15] This contradicts the previous assignment of Weng, Plummer, and Gustafsson.

Two new surface states or resonances (labeled 5 and 6) are observed in the vicinity of $\overline{M}$, at ~0.3 eV and 2.5 eV below E_F. Neither of these features suffer any change as the sample under-

goes the phase transition; a discussion of their origin is postponed until a later paper.[15] Furthermore, the features 1, 2, and 3 (near $\overline{\Gamma}$) do not change through the transition, save for a possible attenuation ($\leq 20\%$) of the surface state at $\overline{\Gamma}$ (feature 1).

Two significant differences were noted in the photoemission spectra from the 1×1 and the $(\sqrt{2} \times \sqrt{2})R45°$ structures. On the 1×1 surface the states dispersing up through the Fermi level (features 2 and 3, Fig. 1) are still visible at $\vec{k}_\parallel = (\pi/2a, \pi 2a)$, and the state at 4 eV (feature 4, Fig. 1) is also present [Fig. 2(a)]. On *cooling to 200 K, features 2 and 3 are absent* [Figs. 2(b) and 2(c)]. As indicated in Figs. 2(d) and 2(e), the attenuation of this state only occurs at $\vec{k}_\parallel$ close to $(\pi/2a, \pi/2a)$. The 4 eV state, feature 4, is not affected by the phase transition. The results clearly suggest an important role for features 2 and 3 in the phase transition.

Calculations show that the surface state/resonances at $\vec{k}_\parallel = (\pi/2a, \pi/2a)$ are coupled by formation of the displacive phase at 200 K to equivalent states at $\vec{k} = -(\pi/2a, \pi/2a)$ (Fig. 3)[16]; this splits
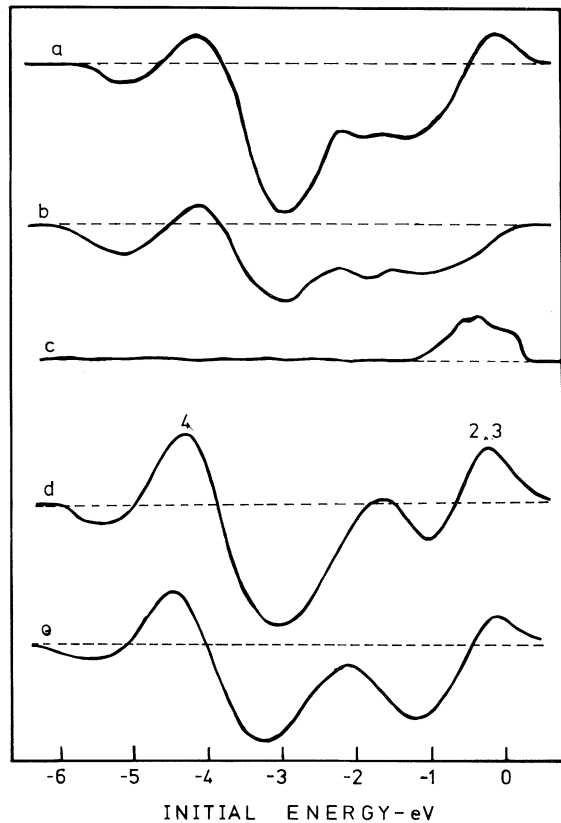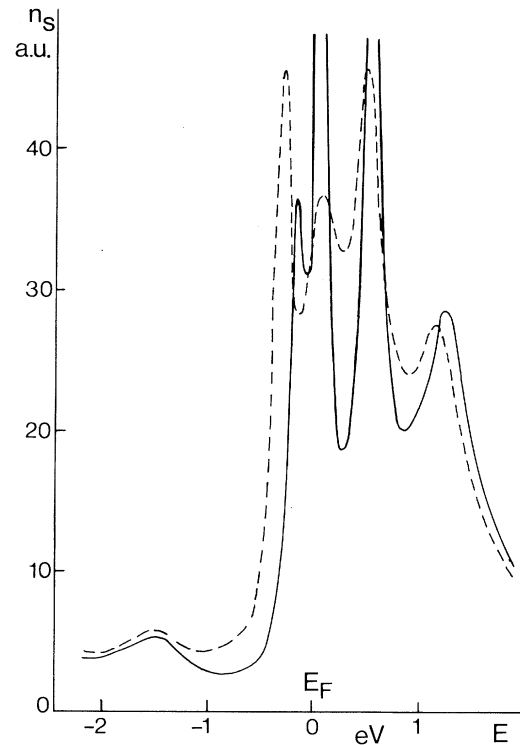

FIG. 2. Difference photoemission spectra (clean −hydrogen covered) from W{001} with Ne I at points A and B in the surface Brouillouin zone (FIG. 1): Curve a, at A, 1×1 structure; curve b, at A, $(\sqrt{2} \times \sqrt{2})R45°$ structure; curve c, at B, 1×1 structure; and curve e, at B, $(\sqrt{2} \times \sqrt{2})R45°$ structure. Clean surface features are labeled as in Fig. 1. Curve c is the difference spectrum between clean W{001}-(1×1) and W{001}-($\sqrt{2} \times \sqrt{2}$)$R45°$ at point A in the surface Brillouin zone, confirming the attenuation of the states close to E_F on cooling.

FIG. 3. Surface density of states n_s (E) at $\vec{k}_\parallel$ = $(\pi/2a, \pi/2a)$ calculated for Mo{001} (Ref. 16). Solid line, 1×1; dashed line, $(\sqrt{2} \times \sqrt{2})R45°$ with Debe-King model (Ref. 3).

the peak in the surface density of states, reducing the photoemission intensity of features 2 and 3 [Fig. 2(a)] in the $(\sqrt{2} \times \sqrt{2})R45°$ surface. Away from $\vec{k}_{\parallel} = (\pi/2a, \pi/2a)$, say point B, Fig. 1, surface states with the same energy are no longer coupled, and so there is little change in photoemission upon reconstruction [Figs. 2(d) and 2(e)]. As the surface states at $\vec{k}_{\parallel} = (\pi/2a, \pi/2a)$ lie almost at the Fermi energy, opening up an energy gap on the new Brillouin-zone boundary lowers the total one-electron energy of the system and stabilizes the PLD.[7,8,17] The well-defined surface state peak in the 1×1 phase suggests that it is well-defined surface state peak in the 1×1 phase suggests that it is well ordered, as randomization of atomic displacements would smear out the peak in the surface density of states by at least as much as the PLD-induced splitting.

On forming the $(\sqrt{2} \times \sqrt{2})R45°$ structure a prominent new feature appears at $\vec{k}_{\parallel} = (\pi/a, \pi/a)$ (the 1×1 $\overline{M}$ point), at 1.4 eV below E_F. This is shown in Fig. 4 where (a) is the energy distribution
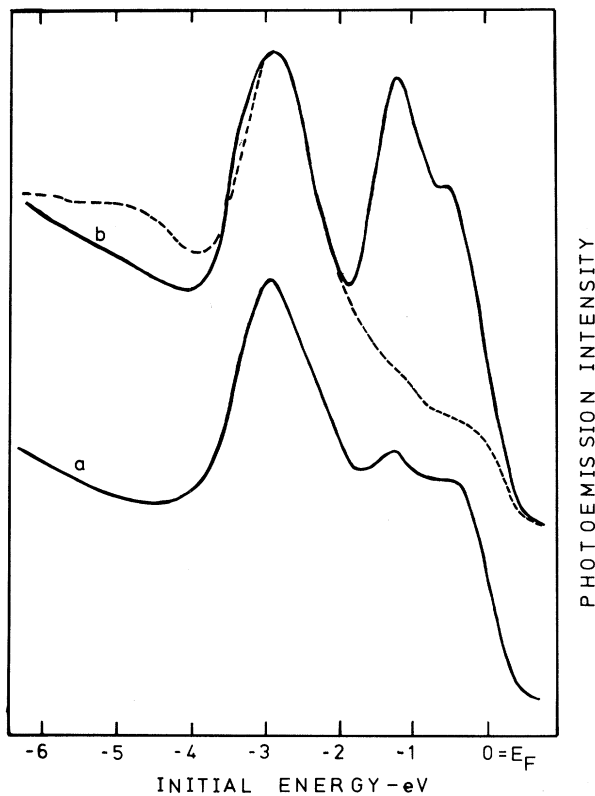

FIG. 4. Photoemission energy distribution curves obtained at a polar photoemission angle of 55°, corresponding to $\vec{k}_{\parallel} \sim (\pi/a, \pi/a)$, for the 1×1 structure (curve a) and the $(\sqrt{2} \times \sqrt{2})R45°$ structure (curve b).

curve (EDC) obtained from the sample in the 1×1 structure, and (b) is the EDC obtained after formation of the $(\sqrt{2} \times \sqrt{2})R45°$ structure. The dashed line represents the EDC obtained after the surface has adsorbed enough hydrogen to revert to the 1×1 structure,[18] illustrating that features 4 and 6 in Fig. 1, as well as the peak obtained after reconstruction, have been removed.

Our calculation shows that the surface density of states of the 1×1 surface at $\overline{M}$ is featureless at -1.4 eV, where the new peak appears. However, formation of the displacive phase with $\vec{Q}$ $= (\pi/a, \pi/a)$ couples $\overline{M}$ to $\overline{\Gamma}$, where the surface and bulk densities of states show a prominent peak, associated with the Γ_{25}' band edge (with use of nonrelativistic bands). The best available band structure for W, obtained by Christensen and Feuerbach,[19] puts this very flat edge at -1.2 eV, close to the observed peak, which we conclude is photoemission at $\overline{\Gamma}$ umklapped to $\overline{M}$. The main components of this peak are d_{zx} and d_{zy} orbitals. Furthermore, the feature is observed in normal-photoemission spectra from the 1×1 phase, also at -1.4 eV.[12] Hydrogen adsorption to form a 1×1 structure removes the reciprocal-lattice vector required for the umklapp and hence the umklapp feature (Fig. 4).

In a calculation of the surface density of states for the PLD structure (using Mo potentials, which give essentially the same results as for W), we find no new surface states or resonances appearing at $\overline{\Gamma}$ or $\overline{M}$, supporting the notion that the new state observed at $\overline{M}$ is produced by a surface umklapp mechanism, analogous to the Ir{100}-(5×1) surface.[20]

To summarize, in mapping out and comparing the surface states or resonances on W{001} in the high-temperature 1×1 and the low-temperature $(\sqrt{2} \times \sqrt{2})R45°$ structures, two features have been found to be significantly altered:

(1) A surface state at E_F and midway between $\overline{\Gamma}$ and $\overline{M}$ in the surface Brillouin zone of the 1×1 structure is strongly attenuated in the low-temperature structure, when this point in k space lies on the new zone boundary of the low-temperature structure. The calculations for both structures show that this state is split and smeared out of formation of the low-temperature phase. This result provides the first direct experimental support for the coupling of surface states at the Fermi energy as a major factor in the formation of a displacive phase on W{001}.[1,2,7,8,17] Furthermore, it gives strong support to the low-energy electron-diffraction evidence[4] that the transition

is between ordered structures.

(2) A new surface feature is observed from the $(\sqrt{2} \times \sqrt{2})R45°$ structure, at $\vec{k}_\| = (\pi/a, \pi/a)$, 1.4 eV below E_F, which is attributed to umklapp and surface photoemission from a state associated with a bulk band edge at $\bar{\Gamma}$.

We acknowledge helpful discussions with N. V. Richardson, and the United Kingdom Science Research Council for financial support. We are also grateful to M. W. Holmes and T. Gustafsson for comments on the first draft of this paper.

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Do Metal Alloys Work as Substrates for Surface-Enhanced Raman Spectroscopy?

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Surface-enhanced Raman signals are reported from pyridine adsorbed onto $Ag_{1-x}Pd_x$ for $x \lesssim 0.04$. For $x \gtrsim 0.05$ the alloys do not support enhancement within our limit of detection. The quenching is due to the introduction of Pd d states which are involved in electron excitations that interfere with Ag's favorable free-electron–like behavior.

PACS numbers: 78.30.-j, 73.40.-c

The occurrence of an anomalously large Raman-scattering cross section associated with adsorbed molecules has been restricted to only a few metals. The relationship between the enhancement and substrate properties must be understood before surface-enhanced Raman scattering (SERS) can be exploited to study the vibrational structure of adsorbates. Previously, only Ag, Cu, and Au were reported[1] as unambiguously supporting the enhancement at a level which allows experimental detection.

We report here the first observation of SERS on an alloy surface. We have detected Raman scattering from pyridine adsorbed onto Ag-Pd alloys under electrochemical control with Pd concentration as high as 4% (0%, 1%, 2%, and 4%). The alloy surfaces provide a significantly improved catalytic function in hydrogen adsorption and are expected to affect many other reactions in a similar manner. Surface enhancement, if present, on Ag-Pd alloys with Pd > 5% (5%, 10%, 20%) is smaller than our ability to detect it by use of incident photon wavelengths of 4579, 4880, or 5145 Å. We attribute this quenching to the introduction of low-energy excitations which supply damping channels to the normally free-electron–