RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 43, NUMBER 2 15 JANUARY 1991-I

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Electronic structure of (1×1) H/Mo(001): Two-dimensional Fermi surfaces and nonadiabatic adsorbate vibrational damping

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(Received 17 July 1990)

The two-dimensional electronic structure of (1×1) H/Mo(001) has been measured using photoemission spectroscopy. A H-induced surface resonance is found that is suitable to participate in the recently observed nonadiabatic electronic damping of H vibrations on this surface. The full two-dimensional Fermi surface of this resonance was measured, and large-scale nesting was observed. This result is used to predict the existence of surface-phonon anomalies.

The (001) surfaces of Mo and W have been the subject of numerous investigations over the last two decades due to the plethora of electronic and structural phenomena they display. Among these phenomena are temperature-induced reconstructions,[1] adsorbate-induced reconstructions,[2–4] and nonadiabatic electronic damping of adsorbate vibrations.[5,6] Frustrating the goal of finding universal explanations for these phenomena is the occurrence of significant differences between the behavior of Mo(001) and W(001), despite these metals being isoelectronic, isosymmetric, and having almost identical lattice constants. Specifically, while W(001) reconstructs from a structure giving a (1×1) low-energy-electron diffraction (LEED) pattern at room temperature to a commensurate $c(2\times2)$ structure when cooled, Mo(001) reconstructs into an incommensurate $c(2.2\times2.2)$ structure.[1] Additionally, while a saturated coverage of H on both surfaces results in the formation of a (1×1) structure, there is clear evidence that at lower coverages H forms islands and incommensurate structures on Mo(001) while forming dispersed, homogeneous structures on W(001).[2] However, one point of agreement is the observation on both surfaces of nonadiabatic electronic damping of H vibrational modes via coupling to H-induced surface resonances close to the Fermi level (E_F).[5,6]

We present here the results of an angle-resolved photoemission study of the two-dimensional electronic structure of (1×1) H/Mo(001). The measured two-dimensional Fermi surface of (1×1) H/Mo(001) is found to differ radically from that of clean Mo(001),[7] and to display large-scale nesting along the high-symmetry directions in the surface Brillouin zone. We use this nesting to predict the existence of surface-phonon anomalies and compare these predictions to measurements using He atom scattering of the phonon-dispersion curves for H-saturated Mo(001).[8] We also discuss the role the H-induced surface resonance associated with this Fermi surface plays in the nonadiabatic damping of H vibrations.

The experimental procedure and apparatus has been described previously.[9,10] The Mo(001) surface was cleaned in the standard manner,[9] and remained clean for approximately 10 min in a vacuum of $<1.5\times10^{-10}$ Torr. H-covered surfaces were obtained by exposing a clean surface to H_2, admitted via a doser, for 5 min; the chamber pressure was 1×10^{-7} Torr H_2. H-covered surfaces were made every 30 min. All experiments were performed at the National Synchrotron Light Source using a hemispherical analyzer with resolution of less than 100 meV full width at half maximum and less than 1° full angular acceptance.[10]

Figure 1 presents a series of photoemission spectra taken from H-saturated Mo(001). The photon energy was 40 eV, and the light was incident at 65° along the (001) direction (the $\bar{\Delta}$ direction in the surface Brillouin zone). The analyzer was rotated perpendicular to the plane of incidence and thus states with momenta parallel to the surface ($k_\parallel$) along $\bar{\Delta}$ are detected.[11] The spectra in Fig. 1 reveal that a photoemission peak is observed close to E_F along most of $\bar{\Delta}$. This peak appears at approximately 0.11 Å^{-1} and disperses above E_F at approximately 0.68 Å^{-1}; the peak shows virtually no dispersion while below E_F and has a binding energy of approximately 0.2 eV. Since this peak shows such little dispersion, the usual problem of determining the exact value of $k_\parallel$ where a peak crosses E_F is exacerbated. Careful examination of the spectra in Fig. 1 makes us confident that the disappearance of the peak at 0.68 Å^{-1} is due to the associated state dispersing above E_F. There is some evidence for a very weak peak in spectra for $k_\parallel<0.11$ Å^{-1} but we consider that the associated state has probably crossed (or is at) E_F. The peak also shows little or no dispersion with changes in photon energy, indicating that the associated state is primarily of

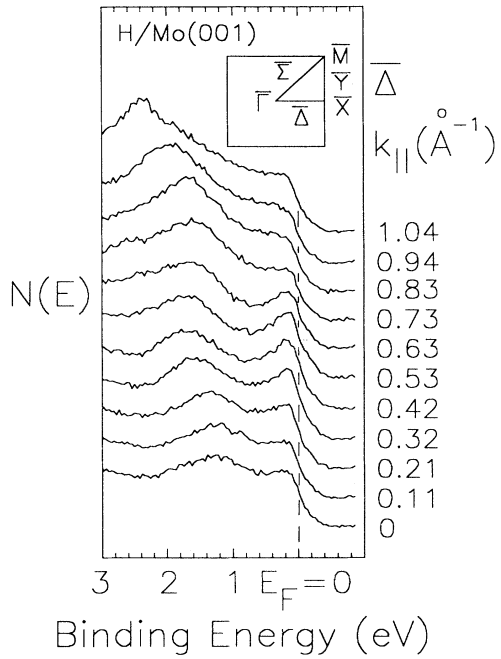

FIG. 1. Photoemission spectra taken from H/Mo(001). Light was incident at 65° in the (001) plane and the detector rotated perpendicular to this plane. $h\nu$=40 eV. The surface Brillouin zone is also shown.

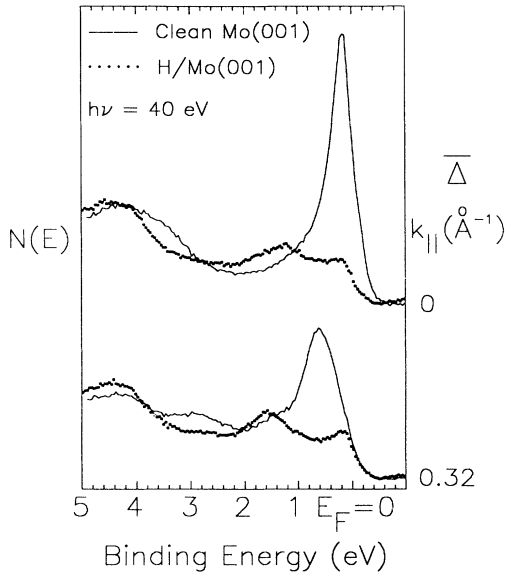

FIG. 2. Photoemission spectra from Mo(001) and H/Mo(001). Light was incident at 65° in the (001) plane and the detector moved in this plane. $h\nu$=40 eV.

two-dimensional character.[11] The peak is observed clearly with the light incident along both the $\bar{\Delta}$ and $\bar{\Sigma}$ axes, and when the detector is rotated either in or out of the plane of incidence; thus the state is of even symmetry with respect to both the (100) and (110) mirror planes.[11] This suggests that along $\bar{\Delta}$ the associated state is primarily of $d_{x^2-y^2}$ character while along $\bar{\Sigma}$ it is primarily of d_{xy} character. However, the state is most likely hybridized with the H 1s orbital (which is of even parity throughout the zone) and labeling the state by the character of simple Mo d orbitals may not be relevant. The state is, in fact, a resonance in large parts of the zone given the absence of band gaps along the $\bar{\Delta}$ direction for clean Mo(001).[12]

That this resonance is induced by the H overlayer is revealed by the data in Fig. 2, which presents spectra taken from both H-saturated and clean Mo(001). For both data sets the experimental parameters were as detailed for Fig. 1, except that the analyzer was rotated in the plane of incidence. Spectra are shown for $k_{||}$=0 Å^{-1} and $k_{||}$=0.32 Å^{-1}. The clean surface spectra are dominated by an intense peak close to E_F. This is emission from a surface resonance of clean Mo(001).[7,13] At $k_{||}$=0 Å^{-1}, this emission is quenched when the surface is exposed to H. This result contrasts with that of an earlier photoemission study,[14] where the emission from the clean surface resonance only fell to 50% of its original intensity at $\bar{\Gamma}$. We believe this difference is due both to photon energy and angular resolution differences and to the difficulty in obtaining a truly H saturated surface. Figure 2 shows that the peak that exists close to E_F (away from $\bar{\Gamma}$) on the H-covered surface is clearly distinct in binding energy from the clean surface resonance.

Recent infrared (IR) spectroscopy measurements of the vibrational modes of H/Mo(001) have revealed evidence for the nonadiabatic damping of H vibrations on Mo(001).[6] Specifically, a mode at 161.2 meV is observed to have an asymmetric Fano line shape that is characteristic of the damping of a discrete adsorbate vibrational mode via coupling to the electron-hole pair continuum at E_F.[15] However, this explanation for the line shape is contingent on the existence of a H-induced state that has a binding energy close to E_F, shows little dispersion, has a large density of states (DOS), and, finally, has a symmetry suitable to couple to the vibrational mode. [These criteria were recently detailed in the context of a study of H/W(001).[16]] We show here that the observed H-induced resonance satisfies all of these criteria, and thus the explanation for the asymmetric line shape based on nonadiabatic electronic damping is valid.[6]

If a vibration with an energy of 161.2 meV is to excite an electron above E_F, the binding energy of the electronic state must be close to this value. As noted above, the observed H-induced peak (Fig. 1) never disperses more than 0.2 eV below E_F, and consequently this resonance has a suitable binding energy. Additionally, since the resonance is essentially dispersionless, the electrons in this resonance are very slow, leading to a strong breakdown of adiabaticity.[15] Furthermore, since this resonance is observed throughout a large region of k space, it has a very large two-dimensional DOS, which allows effective vibrational coupling.[15] Thus the resonance satisfies three of the four criteria listed above for a state to participate in nonadiabatic vibrational damping. Remaining to be determined is the suitability of the symmetry of the resonance. There is an ongoing debate concerning the identity of the vibrational mode observed to be nonadiabatically damped for both H/Mo(001) (Ref. 6) and H/W(001).[5] Essentially, the energy of the vibrational mode [161.2 meV for

H/Mo(001) and 159.5 meV for H/W(001)] is such that it can be energetically identified as either the asymmetric stretch or the first overtone of the wag vibration.[5,6,15] Since the asymmetric stretch vibration is parallel to the surface, the former assignment requires that the component of the incident electric field parallel to the surface be significant even though the experiments were performed at grazing incidence.[15] While assignment of the mode to the overtone of the wag does not require this assumption (since the overtone has a component perpendicular to the surface), it has been shown that effective coupling to this mode can only occur if the surface is disordered.[15] However, photoemission spectroscopy can provide a resolution of this problem.[16] Since both the initial and final electronic states, and the vibrational mode, all supposedly have some parity with respect to mirror planes of the surface, the product of these parities must be even for the coupling to be nonzero. In the case of H/W(001), a H-induced state was observed that was primarily of even symmetry with respect to (100), and thus the vibrational mode could be identified as the asymmetric stretch.[16] However, the H-induced resonance on Mo(001) is even with respect to *both* the (100) and (110) mirror planes. Thus the observed resonance could couple equally well to either the asymmetric stretch or the wag vibration, and our selection rule fails to clarify the situation. Indeed, the possibility that *both* modes are coupled to the surface electrons is an equally valid conclusion.

We now consider the two-dimensional Fermi surface of this resonance. The location in k space where a photoemission peak derived from a two-dimensional state crosses E_F defines an individual point on the two-dimensional Fermi surface for that state. A full discussion of the use of photoemission spectroscopy to measure two-dimensional Fermi surfaces is presented in Ref. 9. Due to the subjective determination of the k vector at which a peak crosses E_F, there is an error of approximately 0.025 Å^{-1} in the magnitude of any given Fermi-surface crossing. However, this error is systematic and while the area of a Fermi-surface structure may be inaccurate, its shape will be correct. The spectra in Fig. 1 show that a H-induced peak appears below E_F at approximately $k_\parallel = 0.11$ Å^{-1} along $\bar{\Delta}$ and remains close to E_F until approximately $k_\parallel = 0.68$ Å^{-1}, where it crosses above E_F. These two k vectors are points on the two-dimensional Fermi surface. In order to map out the entire Fermi surface, spectra must thus be taken along every direction in the irreducible zone. Figure 3 presents the measured two-dimensional Fermi surface for H-saturated Mo(001). Spectra were taken in half the zone and the full Fermi surface generated by folding the data points into the second half of the zone. The Fermi surface consists of two structures: a small hole pocket around $\bar{\Gamma}$ enclosing unoccupied electronic states, and a larger electron pocket, also around $\bar{\Gamma}$, enclosing occupied electronic states. (Note that the shape and size of the small hole pocket around $\bar{\Gamma}$ are very difficult to determine given the poor nature of this crossing, as discussed above.) This Fermi surface is radically different from that of clean Mo(001), which consists of hole pockets around the $\bar{M}$ points together with small electron structures along $\bar{\Gamma}$.[7] A Fermi surface is said to be

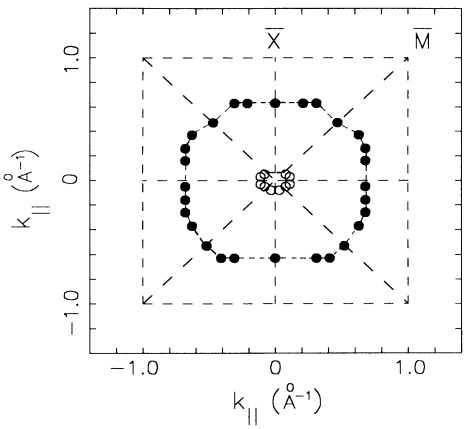

FIG. 3. Measured two-dimensional Fermi surface for (1×1) H/Mo(001).

nested if there exists regions of the surface in different parts of the zone that are flat and parallel. Here the electron pocket displays unusually large nesting along both $\bar{\Delta}$ and $\bar{\Sigma}$. The resonance crosses E_F at 0.68 Å^{-1} along $\bar{\Delta}$ and 0.47 Å^{-1} along $\bar{\Sigma}$ and thus the nesting vectors are 1.36 and 0.64 Å^{-1} along $\bar{\Delta}$ (i.e., $2k_F$ and $G-2k_F$, respectively; G represents a surface reciprocal-lattice vector) and 0.94 and 1.89 Å^{-1} along $\bar{\Sigma}$.

The existence in a solid of a heavily nested two-dimensional Fermi surface has many implications for the structure and dynamics of its surface. In particular, if a phonon wave vector spans heavily nested regions of Fermi surface, a large discontinuity in the generalized susceptibility can occur which in turn can lead to phonon mode anomalies and even periodic lattice distortions.[17] Reconstruction in such a material can thus be viewed as a two-dimensional periodic lattice distortion where a particular surface-phonon mode is frozen into the lattice.[18] This mechanism has been proposed as the origin for the clean surface reconstructions of both Mo(001) and W(001).[1] Recent measurements of phonon dispersion on these surfaces have revealed soft modes,[19] in agreement with theoretical predictions based on Fermi-surface nesting.[20] Using photoemission, we measured the two-dimensional Fermi surfaces of Mo(001) (Ref. 7) and W(001) (Ref. 21) and found significant nesting on both surfaces. However, the nesting observed on either Mo(001) or W(001) is markedly smaller than that displayed by H/Mo(001). Although the existence of a heavily nested Fermi surface is not in itself sufficient to drive a phonon mode to zero energy, this result indicates that there is the possibility of surface-phonon anomalies, and perhaps mode softening, for H/Mo(001) at wave vectors of 0.64 Å^{-1} along $\bar{\Delta}$ and 0.94 Å^{-1} along $\bar{\Sigma}$. However, a measurement of low-energy surface-phonon dispersion in this system shows no evidence for soft modes.[8] We suggest further phonon dispersion measurements be undertaken using both He scattering and high-resolution electron-energy-loss spectroscopy to look for the predicted phonon anomalies in the higher energy (optical) modes. The importance of nonadiabatic coupling to these adsorbate modes is clear from the IR data of Reutt, Chabal, and Christman.[6]

This work was supported by U.S. Department of Energy (DOE) Grant No. DE-FG06-86ER45275, and undertaken at the National Synchrotron Light Source, which is supported by the U.S. DOE, Divisions of Materials Sciences and Chemical Sciences. S.D.K. would like to acknowledge the National Science Foundation and A. P. Sloan Foundation for financial support.

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