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Mo(001) Surface: A Self-Consistent Calculation of the Electronic Structure

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A self-consistent pseudopotential calculation for an unrelaxed Mo(001) surface reveals strong surface states and resonances. The results are used to interpret the sharp peak structure near the Fermi level and other structures measured by recent angle-resolved photoemission experiments. The structure is attributed uniquely to surface states and resonances. Contrary to other proposals, relativistic, many-body, and surface-contraction effects are not necessary to explain the observed spectra.

Recent photoemission experiments applied to the (001) face of molybdenum[1-4] reveal two sharp peaks which are located around 0.3 and 3 eV below the Fermi level. Their large sensitivity to surface contamination[1-3] suggests that their origin is due to surface resonances or surface states. Moreover, angle-resolved photoemission experiments reveal that the peak near the Fermi level has its maximum for normal emission, but does not disappear when the emission angle is increased. In addition a second peak appears slightly below the high-lying resonance for larger emission angles.[4]

Theoretically, there has been some controversy about the origin and interpretation of the sharp structures as surface states or resonances. Noguera *et al.*[3] identified the upper peak due to normal emission as a combination of a surface resonance and a d-band edge around the Γ point of the two-dimensional Brillouin zone. In order to place the energy of this resonance at the energy of the experimental peak they had to include a 10% to 13% inward relaxation of the surface layer.

Using a nonrelativistic tight-binding Green's-function method Weng and co-workers.[2,4] predicted the occurrence and the dispersion of three occupied surface resonances away from normal emission in satisfactory agreement with the experimental results; however, they were not able to explain the existence of a strong resonance at normal emission.[5] They argued that it might be due to relativistic effects. It should be stressed that none of the above theoretical calculations treated the redistribution of the electrons at the surface self-consistently. Noguera, Spanjaard, and Jepsen[6] argued from the similarity of the total charge density at the surface as compared to the bulk charge density that self-consistency plays a minor role at transition-metal surfaces. They therefore used screened muffin-tin potentials obtained from a self-consistent bulk calculation also for the surface atoms. We have found that for self-consistency the screened potential around a surface atom must differ considerably from the corresponding potential around a bulk atom which demonstrates the important effect of self-consistency at a transition-metal surface.

In this Letter we report the results of a self-consistent nonrelativistic calculation of the electronic structure of an unrelaxed Mo(001) surface. Our method uses self-consistent pseudopotentials which give good results for the bulk band structure. The details will be presented in a longer paper. The essence of the method which is discussed at length by Louie and Cohen[7] consists of describing the surface of the semi-infinite system by either of the two surfaces of a thin slab which are exposed to a finite number of "empty space layers." Periodicity is artifically retained perpendicular to the slab by repeating this arrangement throughout all space, thus permitting the use of standard band-structure techniques. The charge density in the slab is practically identical to the bulk charge density two layers below the surface. This result was recently obtained from a similar calculation for a nine-layer Nb(001) slab.[8] Similarly a five-layer Mo slab exposed to three layers of vacuum on each side gives a reasonable representation of the surface electronic structure as far as the d character of the wave functions around the surface atoms is concerned. Using three special $\vec{k}$ points in the irreducible part ($\frac{1}{8}$) of the two-dimensional Brillouin zone,[9] iteration was continued until the potential was stable within 0.01 Ry. For the final self-consistent potential, we included a regular mesh of fifteen $\vec{k}$ points in the irreducible part of the Brillouin zone.

Since most of the surface states exist in the gaps of the projected bulk band structure (PBS), we have calculated the PBS self-consistently from the same potential used for the surface calculation. The result along certain symmetry lines of the two-dimensional Brillouin zone is shown in Fig. 1. Most of the true surface states occur in the absolute gaps of the PBS which are labeled by G_1 to G_4. Surface resonances can exist throughout the whole two-dimensional Brillouin zone. We identify a state as a true surface state if its charge density is completely confined to the surface layer with almost no contribution extending into the slab. A surface resonance state has most of its charge accumulated at the surface, but has usually a nonnegligible amount of charge in the slab interior.

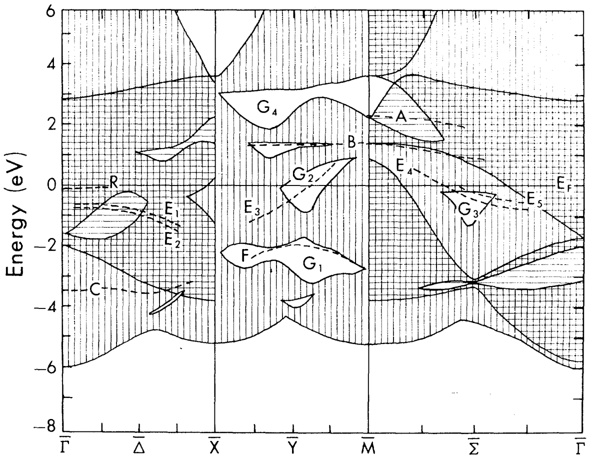

FIG. 1. The molybdenum projected band structure together with surface resonance bands (dashed lines). Vertical hatching is used for states with $\bar{\Delta}_1$, $\bar{Y}_1$, and $\bar{\Sigma}_1$ symmetry; horizontal hatching refers to states with $\bar{\Delta}_2$, $\bar{Y}_2$, and $\bar{\Sigma}_2$ symmetry. The PBS for the symmetry points $\bar{\Gamma}=(0,0)$, $\bar{X}=(\frac{1}{2},0)$, and $\bar{M}=(\frac{1}{2},\frac{1}{2})$ is not included. The various surface resonances are described in the text.

We found four major energy intervals in which surface states or resonances exist. A low-lying resonance band labeled by C appears at $\bar{\Gamma}$ and along the $\bar{\Delta}$ line at about −3.5 eV with fairly small dispersion of less than 0.5 eV. Looking at the charge density along the band one finds that its character is mainly $d_{3z^2-r^2}$ at $\bar{\Gamma}$ with an increasing admixture of $d_{x^2-y^2}$ away from $\bar{\Gamma}$. This resonance band can be clearly associated with the peak structure observed by photoemission at 3.3 eV below the Fermi energy E_F. Along the $\bar{Y}$ line we find a relatively weak resonance band in the gap G_1 with an average energy of −2.0 eV denoted by F. Its charge-density distribution shows primarily d_{xy} character.

Most of the surface features occur within 1 eV below E_F. Two strong double surface resonances E_1, E_2 and E_4, E_5 exist in a symmetry gap along $\bar{\Delta}$ and in the absolute gap G_3; a further resonance band E_3 occurs along $\bar{Y}$ in and near G_2. All E-type resonances have a charge-density distribution which is predominantly of $d_{xz,yz}$ type. In terms of a simple bond-orbital picture these resonances have their origin in the two bonding orbitals d_{xz} and d_{yz} of a surface atom which are broken once the surface is formed. They become true surface states whenever they lie in the absolute gaps G_2 or G_3.

Weng and Plummer[2] also found a double resonance along the [10] and [11] directions, but obtain the opposite dispersive behavior along [10]; their resonance energy increases towards E_F for increasing k_x, whereas the resonance bands E_1 and E_2 drop energetically when k_x increases.

These surface states or resonances have to be distinguished from a strong resonance R around the $\bar{\Gamma}$ point just below the Fermi level. In Fig. 2 we have plotted the charge density of R at $\bar{\Gamma}$ in a plane perpendicular to the surface. It has $d_{3z^2-r^2}$ character and can be considered to be a true surface state, because it decays farily rapidly into the slab interior. Looking at the PBS of the $\bar{\Gamma}$ point (not shown in Fig. 1), one finds that this state exists in the $\bar{\Gamma}_1$ symmetry gap of the corresponding bulk PBS. It is precisely this state which is probed by angle-resolved photoemission at normal direction. Along the [10] direction it can be traced as a strong resonance up to $\vec{k}_\parallel = (\frac{1}{8}, 0)$, and then it decays rapidly. It shows a very weak dispersion towards E_F for increasing k_x. One might argue how this state can be orthogonal to the low-lying surface resonance C at $\bar{\Gamma}$ which has the same symmetry. However, the C state decays much more slowly into the slab because it can couple to bulk or slab states of the same symmetry. The contributions to the wave function of the two states coming from inside the slab essentially guarantee orthogonality. Above the Fermi level two weakly dispersive resonance bands A and B are found around $\bar{M}$; A is a true surface state of $d_{x^2-y^2}$ character which exists in the gap G_4 at $\bar{M}$ and decays rapidly away from $\bar{M}$, and B is a nonbonding resonance band of distinct $d_{3z^2-r^2}$ type.

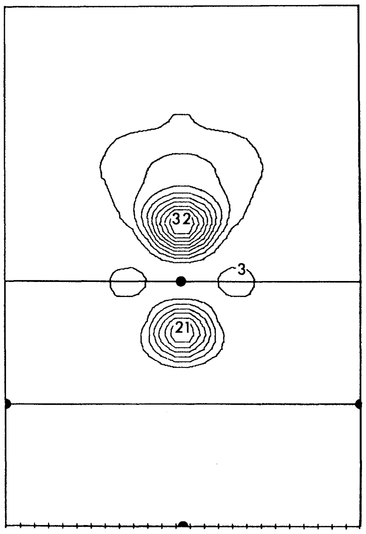

FIG. 2. Charge-density contour plot of the surface state at $\bar{\Gamma}$ at -0.2 eV. The contour plane is perpendicular to the surface, heavy lines represent atomic layers, and heavy dots indicate the atomic positions. The charge density is normalized to unity over the unit cell. Successive contours are separated by one tenth of the maximum density value given in the plot.

The total self-consistent charge density at the surface has a stronger $d_{zx,zy}$ character than the corresponding charge density of Nb(001) because the $d_{zx,zy}$-type surface states become partially occupied in Mo whereas they are almost unoccupied in Nb.[8] The local density of states (LDOS) at a surface layer of the slab is shown in Fig. 3. As stated before, it is obtained by using fifteen $\vec{k}$ points in the irreducible part of the Brillouin zone. It is dominated by two sharp peaks at -0.2 and -3.3 eV caused by the surface resonance bands C, E, and R. The character of the charge density under the peak at E_F is mostly $d_{xz,yz}$ type; the contribution of the R is small, since it is only defined near $\bar{\Gamma}$ and does therefore not contribute very much to the LDOS.

Also shown in Fig. 3 is the surface "excess" density of states which is obtained by subtracting the LDOS at the center of the slab from the LDOS at the surface. The positive contributions represent an excess in electrons at the surface layer as compared to the innermost layer of the slab. All the major surface effects already discussed in terms of their $\vec{k}$-space behavior are displayed, and in addition we see a relatively intense peak labeled by D at 0.5 eV above E_F which is mainly due to the unoccupied parts of the resonance bands E_3 and E_4. Additional structure in the surface LDOS due to the finite slab thickness is ignored. We have not attempted to look for states which are localized on second-layer atoms.

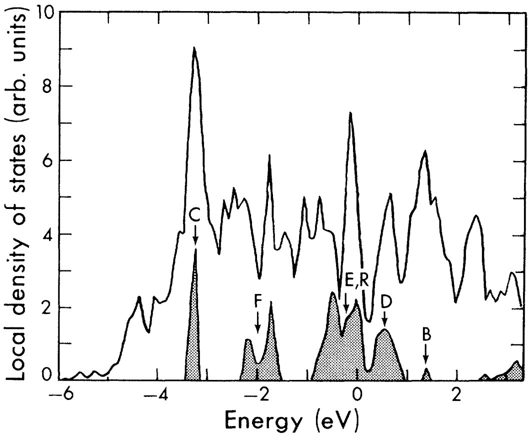

FIG. 3. The local density of states for the surface layer of the Mo(001) slab. The shaded areas refer to the excess density of states (see text). All energies are measured with respect to the Fermi level. The labeling of the surface states is according to Fig. 1.

In conclusion, we note the following: (1) For finite $\vec{k}_{\parallel}$, surface resonances and true surface states exist over a wide range of energies and in different portions of the two-dimensional Brillouin zone. They explain the experimentally measured double-peak structure 0.5 eV below the Fermi level and the single peak at 3.3 eV below E_F. (2) For $\vec{k}_{\parallel}=0$ a true surface state at -0.2 eV and a strong surface resonance at -3.4 eV occur causing the strong peaks observed by angle-resolved photoemission at these energies. (3) Neither relativistic nor many-body effects are necessary to explain the experimental data in our self-consistent method. Also, no surface contraction has to be included to obtain the characteristic electronic structure of this transition-metal surface.

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Numerical Study of the Conductivity in the Vicinity of Mobility Edges

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Energy-dependent conductivity is studied in the Anderson model of a disordered system by a direct simulation of particle diffusion on a two-dimensional square lattice. In the vicinity of the mobility edges, the results indicate a continuous variation of conductivity, consistent with classical percolation theory. Critical behavior of the participation ratio in the extended regime, which follows from this analysis, also supports this interpretation.

Since the introduction of mobility edges in the theory of disordered systems by Mott,[1] a large amount of information has been accumulated supporting this notion. It has also become apparent that the transition between the localized and the extended regime bears a relationship to the phase transition problem.[2-4] It is to a large extent the merit of numerical investigations[2,5-7] that the localized side of the transition is better understood at present. In the extended region, on the other hand, there are as yet no reliable results available[8,2,5] for critical quantities, i.e., conductivity, participation ratio, etc. Furthermore, the controversies about their behavior have recently led to some basic reconsiderations of the mobility-edge idea.[9]

In this Letter I present results obtained directly for the energy-dependent conductivity, which are for the first time accurate enough to discriminate between various theoretical proposals.[9] I study the Anderson Hamiltonian for the disordered system, where site energies ϵ_i are uniformly distributed within the interval $-\frac{1}{2}W<\epsilon_i<\frac{1}{2}W$, while the transfer integrals V are constant, connecting only nearest neighbors. The simulations are performed for the 2D (two-dimensional) square lattice. The central idea of the approach is to employ the relation between the energy-dependent diffusivity $D(E)$ and the conductivity in the noninteracting Fermi system, $\sigma(E)=2e^2D(E)N(E)$, which was pointed out for disordered systems by Butcher.[10] The method of the $D(E)$ calculation