

## Is the Observed Photoemission Peak near the Fermi Level on the (100) Face of Mo a Surface State?

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By use of synchrotron radiation in the range 12 to 40 eV, angle-resolved photoemission spectra of the (100) Mo surface have been observed which exhibit a sharp peak near the Fermi Level. This structure points strongly in the normal direction, it is very sensitive to surface contamination, and its position does not change with photon energy. A similar peak has been attributed in the past to a surface state. We show that it is most likely due to a combination of a surface resonance and a *d*-band edge on both experimental and theoretical grounds.

In this Letter we report the results of an angle-resolved photoemission experiment on the (100) face of molybdenum and of a complete photoemission calculation. Molybdenum has a band structure very similar to that of W for which a large amount of theoretical and experimental work exists, but to our knowledge no calculation of the angle-resolved photoemission has been made. The (100) face of those two metals, studied by field emission<sup>1,2</sup> or photoemission,<sup>3,4</sup> presents the following common feature: The energy distribution of the photoelectrons is dominated by an intense peak near the Fermi level.

We have studied both the (100) and (110) faces of molybdenum by angle-resolved photoemission but we shall restrict ourselves here to the study of this sharp structure near the Fermi level on the (100) face. This structure has been attributed in the past to a surface state but in fact appears from our calculation to be due most likely to a combination of a band edge and a surface resonance.

The experimental setup is described elsewhere.<sup>5</sup> We merely recall that the photon source is the synchrotron radiation of the Orsay storage ring (ACO). The electron analyzer is of the cylindrical type (at 127°) and can be moved in a horizontal plane. Its angular resolution is about 1° in the horizontal and 3° in the vertical plane. The energy resolution is 150 meV. The analyzer rotation is referenced by the polar angle  $\theta$  between the surface normal and the direction of the analyzer. The azimuthal angle  $\varphi$  determines the sample rotation around an axis normal to its surface. The surfaces are cleaned in vacuum by oxi-

dation<sup>5</sup> and characterized by a low-energy-electron-diffraction-Auger system. Figure 1(a) shows the high-energy part of the photoemission spectra from the Mo (100) face for a photon energy of 16 eV and for  $\theta = 0^\circ$ ,  $10^\circ$ , and  $20^\circ$  and  $\varphi = 0$ . The  $\varphi = 0$  axis corresponds to the plane containing the (100) direction. We observe a sharp structure at 0.6 eV below the Fermi level, for the entire photon energy range investigated ( $12 \text{ eV} \leq h\nu \leq 35 \text{ eV}$ ). This peak is very sensitive to contamination; an adsorption of less than one half of an oxygen monolayer considerably reduces its intensity. There is also a shoulder at 0.7 eV below the main peak which proves to be less sensitive to surface contamination.

The analogous structure on the (100) face of W has been attributed to a surface state according to the following criteria:

(1) The sensitivity of a surface-state peak to contamination.<sup>1,3</sup>

(2) The fixed position of the structure in the electron distribution spectrum, independent of the photon energy.<sup>6,7</sup>

(3) The sensitivity of the peak intensity to the polarization of the light.<sup>8</sup>

These criteria are in fact insufficient to characterize a surface state for they apply equally well to a band edge or to a resonance state. First, as mentioned by Pendry,<sup>9</sup> a band edge or a resonance state will be sensitive to contamination because of the small electron mean free path. Furthermore we have experimentally verified that all the structure (surface or bulk) observed at given  $\theta$  and  $\varphi$  were modified for small coverages of CO or O. Second, the fact that the peak posi-

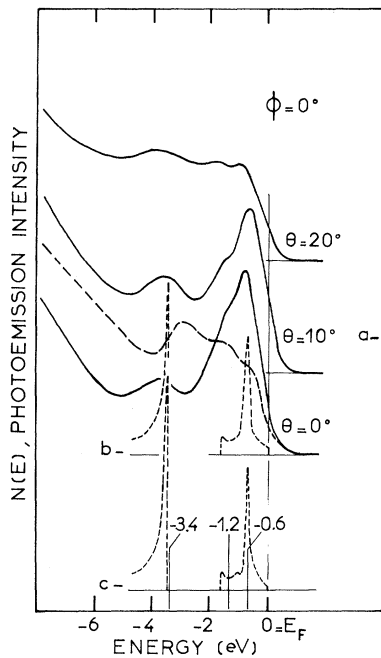


FIG. 1. (a) Energy distribution curves (EDC) of the (100) face of molybdenum obtained at  $h\nu = 16$  eV for different polar angles  $\theta$ . The dashed curve corresponds for  $\theta = 0^\circ$  to an adsorption of 5 liters of oxygen. Calculated EDC of the (100) face of molybdenum for a photon energy of 16 eV and a polar angle  $\theta = 2^\circ$ , (b) taking into account an inward normal relaxation of 13%, and (c) taking into account an inward normal relaxation of 10% and an upward shift of the potential of the first layer of 0.6 eV. Because our photoemission computations handle surface resonances and not surface states we have chosen a polar angle  $\theta = 2^\circ$  rather than  $\theta = 0^\circ$  because the corresponding EDC shows a strong surface resonance near  $E_F$  which would become a true surface state at  $\theta = 0^\circ$ .

tion does not move with the photon energy is an argument which can also be used in favor of a band edge or a resonance. Third, it has been shown on theoretical grounds<sup>10</sup> and experimentally<sup>11</sup> that the light polarization affects both bulk and surface structures.

Our approach has been to make a careful comparison between experiment and theory: We have computed both the electronic structure of Mo (surface and bulk) and the angle-resolved energy distribution of the photoelectrons. A self-consistent nonrelativistic Hartree-Fock-Slater potential of the muffin-tin type has been used. Relativistic effects have been shown to be small in tungsten,<sup>12</sup> and therefore it should be a reasonable assumption to neglect them in molybdenum.

Calculations of the electronic structure of the (100) face of molybdenum were made using a

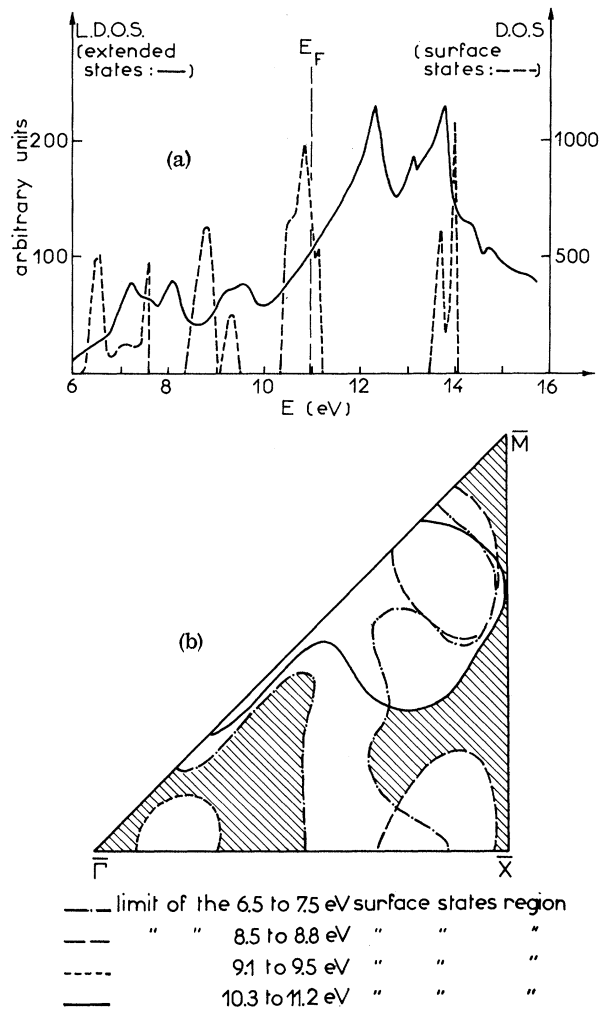


FIG. 2. (a) The solid line represents the local density of states calculated at the position of the surface barrier due to extended states. The dashed line represents the unweighted density of surface states, i.e.,  $\sum_n \delta(E - E_n)$ . (b) Localization of the surface states in the reduced Brillouin zone. The cross-hatched region does not have any surface states occupied.

method previously described<sup>13</sup> where the muffin-tin atoms are assumed to be the same in the surface layer as in the bulk. This method is essentially identical to that of Pendry and is closely related to the field-emission calculation of Modinos and Nicolaou.<sup>14</sup> Figure 2 shows the results of an initial computation in which the surface barrier is defined by a step potential placed midway between the planes of atoms.<sup>15</sup> No surface state is found at the  $\Gamma$  point. Therefore, under the assumption of conservation of the component of  $k$  parallel to the surface ( $k_{||}$ ) in the photoemission process, none of the surface states exhibited in

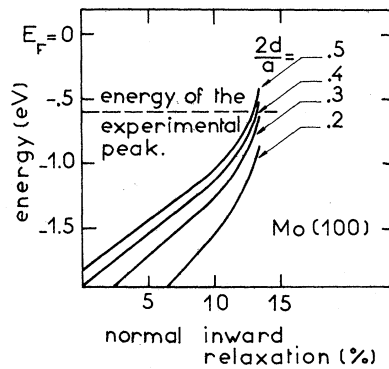


FIG. 3. Energy of the surface state found at the  $\Gamma$  point as a function of the normal inward relaxation and parameter  $d$  (slope of the surface potential).  $a$  is the lattice parameter.

Fig. 2 can account for the feature observed experimentally at normal incidence. However when the step potential is replaced by a gradual transition  $\{V = \frac{1}{2}V_0 [\tanh(z/2d) + 1]\}$ , a surface state with  $spd_{z^2}$  character appears at  $k_{\parallel} = 0$  which becomes a strong resonance around the  $\Gamma$  point.<sup>16</sup> Its energy position as a function of normal relaxation (normal displacement of the final layer of atoms) and parameter  $d$  (slope of the surface potential) is shown in Fig. 3. One sees that a 13% relaxation puts the resonance energy very near the experimental results for a large range of values of  $d$ .<sup>17</sup> We would like to point out that we need at least 21 beams to reproduce accurately the  $d$  band previously calculated elsewhere<sup>18</sup> for the same potential. In their field-emission work on tungsten, Nicolaou and Modinos used only nine beams and a step potential between the crystal and the vacuum; thus their structure cannot be the same as the one reported here.

We then performed a single-step photoemission computation using the same potential for the bulk and for a 13% relaxed surface. This calculation assumes conservation of  $k_{\parallel}$  and includes multiple-scattering final-state damping due to inelastic scattering and matrix elements between the low-energy electron-diffraction outgoing waves and all possible initial Bloch states (these Bloch states and evanescent waves are properly matched at the surface). The method is described elsewhere<sup>10</sup> and has proved to give very good agreement with Nilsson's data on copper.<sup>19</sup> The results show a strong resonance near normal incidence 1 eV below the Fermi level, as expected, and a shoulder caused by a group of  $d$ -band edges coming into  $\Gamma$  in a very flat manner. Emission from a band edge is actually possible in moly-

bdenum in violation of the bulk selection rule ( $K_{zf} - K_{zi} = P$ ) because the relatively strong inelastic scattering of the electrons in the upper states limits the active region of transition to the immediate neighborhood of the surface (this is why we call it a surface effect). A typical curve is exhibited in Fig. 1(b). It appears that the resonance is more restricted to the normal direction than is the experimental peak. At  $\theta = 5^\circ$  it has essentially disappeared.<sup>20</sup>

Since it has been suggested<sup>21</sup> that the experimental resonance is actually the  $d$ -wave resonance of the surface atoms in a more vacuumlike environment, a calculation was made with the potential of the first layer shifted up by 6 eV. In this way one moves the calculated  $d$  resonance of the muffin-tin atoms to the energy of the observed peak. The photoemission spectrum obtained from this modified crystal, with 10% relaxation of the surface, shows a resonance at the experimental position but similarly restricted to the immediate neighborhood of normal incidence [Fig. 1(c)].

One could also argue that an inward relaxation of the surface increases the charge density, thus shifting down the potential of the first layer. A calculation with a shift  $\sim 0.6$  eV downwards does not move the resonance appreciably but changes its shape somewhat. Finally, a peak at  $-3.4$  eV can be seen on the experimental spectra. The photoemission computation also gives a peak at the same energy. Moreover the angular dependence of the theoretical peak is in good agreement with that of the experimental one. This peak is due to a vertical transition between a lower-running Bloch wave very near the  $spd_{z^2}$  band edge and an upper evanescent Bloch wave, i.e., a wave which would not propagate into the crystal even if no final-state damping due to inelastic scattering was included. Thus it is also a surface effect, and the experimental peak is indeed very sensitive to contamination [Fig. 1(a)].

To summarize: (1) The strong structure located near the Fermi level on the (100) face of Mo is due not only to a surface state (as previously claimed) but most likely to a combination of a surface resonance and a  $d$ -band edge. This could also explain the so-called asymmetry of the peak observed by Feuerbacher on W.<sup>22</sup> (2) A muffin-tin potential with suitable, although nonself-consistent, gradual matching to vacuum produces a surface resonance on the (100) face of molybdenum at the right energy position (and probably also in the tungsten case) if an inward relaxation is taken into account.<sup>23</sup> However, up to now the

calculations give this resonance in a narrower range of angle than seen experimentally. It is possible that surface roughness, phonon scattering, or correlation effects<sup>24</sup> make observation over wider angles possible.

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<sup>14</sup>A. Modinos and N. Nicolaou, Phys. Rev. B **13**, 1356 (1976).

<sup>15</sup>The density of states (DOS) shown on Fig. 2 is not averaged over the last atomic layer as in the tight-binding calculations (Ref. 12) but is the local DOS at the surface barrier.

<sup>16</sup>This surface state is also found by R. W. Kasowski, Solid State Commun. **17**, 179 (1975), although much lower in the *sp-d* gap. It does not belong to the surface-states band located near the Fermi level seen in Fig. 2 and also appearing in tight-binding calculations [see Ref. 12 and S. L. Weng, Phys. Rev. Lett. **38**, 434 (1977)]. We should like to point out that we disagree with Weng regarding the origin of the photoemission peak seen at  $\theta = 0$ ; this peak can only be due to a state located at the  $\Gamma$  point or in its neighborhood and cannot be due to states lying all over the Brillouin zone as in field-emission energy distributions. In addition it appears clear that the surface state we have found has a different orbital character from the ones described by Weng.

<sup>17</sup>A value of 11.5% was used to explain low-energy electron-diffraction [see A. Ignatiev, F. Jona, H. D. Shih, D. W. Jepsen, and P. M. Marcus, Phys. Rev. B **11**, 4787 (1975)]. In fact such a relaxation reduced interatomic distances near the surface by only 3.7%.

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<sup>20</sup>We have ignored the effect of the damping of the hole. Introducing a reasonably small imaginary part in the potential of the lower state to take it into account should broaden the calculated resonance peak to the experimental value.

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<sup>22</sup>B. Feuerbacher and R. F. Willis, Phys. Rev. Lett. **37**, 446 (1976).

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