[12]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).
[13]C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. 137, A583 (1965).
[14]C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1962), Sect. 8-b.
[15]P. C. Gibbons, J. J. Ritsko, and S. E. Schnatterly, Phys. Rev. B 10, 5017 (1974).
[16]S. P. Kowalczyk, F. R. McFeely, L. Ley, R. A. Pollak, and D. A. Shirley, Phys. Rev. B 9, 3573 (1974).
[17]C. Gout and F. Pradal, J. Phys. Chem. Solids 29, 581 (1968).
[18]R. Girlanda, M. Parrinello, and E. Tosatti, Phys. Rev. Lett. 36, 1386 (1976).

Surface Resonances on the (100) Plane of Molybdenum

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Surface resonances on Mo(100) have been confirmed and studied in detail experimentally by field-emission energy distributions and theoretically by a linear-combination-of-atomic-orbitals calculation of the $\vec{k}_{\parallel}$-resolved surface local density of states. The experimental results in conjunction with the calculations have provided evidence of band-structure effects in field-emission energy distributions. The calculated results have also explained the angle-resolved photoemission results on W(100) and provided a clear picture as to the origin of these resonances.

The discovery[1] of an "anomalous structure" in the field-emission energy distributions (FEED) on W(100) and Mo(100) surfaces has stimulated intensive investigations into the origin and properties of this feature. Experimentally, this strongly surface-sensitive feature has been widely studied by FEED[2,3] and photoemission-energy-distributions (PED)[4-11] experiments. Theoretically, it has been attributed to a surface state with $\vec{k}_{\parallel}=0$ ($\vec{k}_{\parallel}$ is the momentum parallel to the surface) located in the uppermost ("relative") d-band spin-orbit gap.[2,12] Later, it has been argued[13-15] that the observed peak was due to virtual surface states which exist in a large part of the surface Brillouin zone (SBZ), not just at $\vec{k}_{\parallel}=0$. More recently, an argument based on nonrelativistic time-dependent relaxation effects[9] has been used to suggest that the origin of this surface state is the "absolute" d-band spin-orbit gap at lower initial-state energies.

In this Letter, I report the results of an experimental FEED study of the surface resonance peak on Mo(100) in conjunction with a theoretical calculation of the $\vec{k}_{\parallel}$-resolved surface local density of states (SLDS) on the same surface. I have found in FEED that the resonance peak on Mo(100) shifts to a lower energy and broadens in width as the step edge of the (100) plane is approached. In conjunction with the theoretical calculations, these phenomena confirm a known effect and a yet to be proved theoretical argument, namely, (1) the surface resonances on Mo(100) and W(100) possess a dispersive nature, and (2) the experimental field-emission current from the (100) faces of Mo and W is actually contributed to mostly, if not completely, by the states of finite $\vec{k}_{\parallel}$ in the SBZ as has been suggested theoretically.[13] In order to support this conclusion more strongly, I have made a numerical calculation of the $\vec{k}_{\parallel}$-resolved SLDS on Mo(100) based on a nonrelativistic nine-band (s, p, and d) tight-binding Green's function method.

The calculated results show that, just below the Fermi energy (E_F), there is a band of surface resonances which exist in a large part of the SBZ, primarily in the range of $|\vec{k}_{\parallel}| \lesssim 0.6$ Å^{-1}. These resonances display dispersive characteristics. For example, in the vicinity of a major resonance ($k_x=0.2884$ Å^{-1}, $k_y=0.0111$ Å^{-1}) where the SLDS is extremely sharp and large at $\epsilon=-0.65$ eV, (a) the energy of the resonance decreases by 0.06 eV as k_y increases from 0.0111 to 0.122 Å^{-1}, and (b) the energy of the resonance increases by 0.4 eV as k_x increases from 0.15 to 0.45 Å^{-1}. The first result, (a), together with a necessary condition that the field-emission current is contributed mostly by the states of finite $\vec{k}_{\parallel}$ accounts for the observation in this FEED study. The second result, (b), together with the result that the SLDS of these resonances falls off dramatically as $|\vec{k}_{\parallel}| \gtrsim 0.6$ Å^{-1} accounts for the observations on W(100) by Willis, Feuerbacher, and Fitton.[9] Therefore this theo-

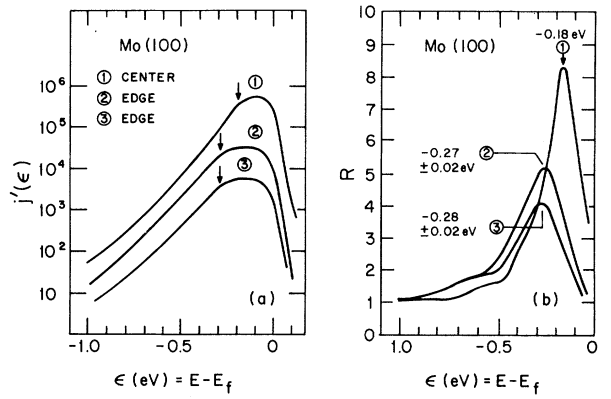

FIG. 1. (a) FEED at the center (curve 1) and two other positions of the (100) plane near its step edge. (Curve 3 is the one nearest to the edge.) (b) The corresponding enhancement factors $R(\epsilon) = j'(\epsilon)/j_0'(\epsilon)$, where $j'(\epsilon)$ is the measured FEED and $j_0'(\epsilon)$ is the free-electron FEED. The number associated with each arrow indicates the energy position of each peak in the units of eV. Data are taken at 78 K.

retical model calculation is capable of explaining the experimental results from two quite different experiments: FEED and angle-resolved PED.

The field-emitted electrons from a thermally cleaned molybdenum tip were retarded and energy-analyzed by a 135° spherical-deflection energy analyzer[2] of about 0.02-eV resolution. Effects of the proximity of the step edge of the (100) plane on the FEED spectroscopy are studied by probing the electrons coming from the center of (100) plane and from the area near the edge of the same plane.

Figure 1(a) shows the experimental FEED at three consecutive positions of the (100) plane. Figure 1(b) displays the same results in terms of the enhancement factor[2] $R(\epsilon)$, arbitrarily normalized to 1 at $\epsilon = -1$ eV. Near the plane edge, two significant phenomena are observed. (1) The resonance peak gets broadened; and (2) the position in energy of the resonance decreases by about a tenth of an eV. These effects shall be referred to as the "edge proximity effects." They will be explained by combining the following arguments with the predictions from the theoretical calculation. We know that in the vicinity of the step edge the periodicity along the surface plane is destroyed. This would give rise to (1) a short mean free path of the electron and (2) the destruction of two-dimensional long-range order in the vicinity of the plane edge. The first result leads to a "lifetime broadening." The second result invalidates k_y (assume it is perpendicular to the edge) as good quantum numbers for any electronic states near an edge. Both effects would result in a broadened resonance peak. Furthermore, the states of any k_y would get mixed with states of nearby values of k_y leading to a smearing out of the SLDS. If the resonance peaks found in FEED on Mo(100) and W(100) were a consequence of a single resonance with a specific $\vec{k}_{\parallel}$, the effects discussed above would not result in a shift in the peak position. Therefore the following conclusions must be a consequence of the present results: (1) The field-emission current is contributed by "many" states of finite $\vec{k}_{\parallel}$, thus giving the most recent FEED theory[13,15] strong direct support. (2) The resonances which contribute to this resonance peak have a definite dispersive character, which has already been confirmed by angle-resolved PED. (3) The dispersion of the resonances near a major resonance behaves in such a way that, for a given k_x (it is assumed that k_x is a good quantum number), the resonance energy decreases as (a) k_y increases in cases for which the major resonance has a very small k_y; or (b) k_y decreases in cases for which the major resonance has a very large k_y. In both cases, the mixing of k_y would cause the FEED peak near a plane edge to shift to a lower energy position.

In order to demonstrate the above references a Green's-function calculation of the $\vec{k}_{\parallel}$-resolved SLDS for the (100) plane of bcc metals, based on a nine-band nonrelativistic linear-combination-of-atomic-orbitals (LCAO) scheme[16] and calculated using a theory proposed by Kalkstein and Soven,[17] has been studied in detail. The results are generally in good agreement with the conclusions deduced from the FEED results. More strikingly, the calculated results can also account for the angle-resolved photoemission results on W(100).

Figure 2 shows the numerical results of the total SLDS and bulk density of states of Mo(100).[18] The most pronounced resonance peak, located at 0.65 eV below E_F, is identified with the observed peak in both FEED and angle-resolved PED. This resonance peak results from many resonances which exist in most of the SBZ but decay rapidly when $|\vec{k}_{\parallel}| \gtrsim 0.6$ Å^{-1}. This calculated result provides a basis to account for the observations on W(100).[9] Furthermore, the finite width of the resonance peak is caused by the dispersion of the composite resonances. An example is shown in Fig. 3, which shows the dispersion of resonances along two directions, both of which are very close to the [10] and [11] directions, respectively, in the SBZ. This result is also in good agreement with the observations on W(100).[9]

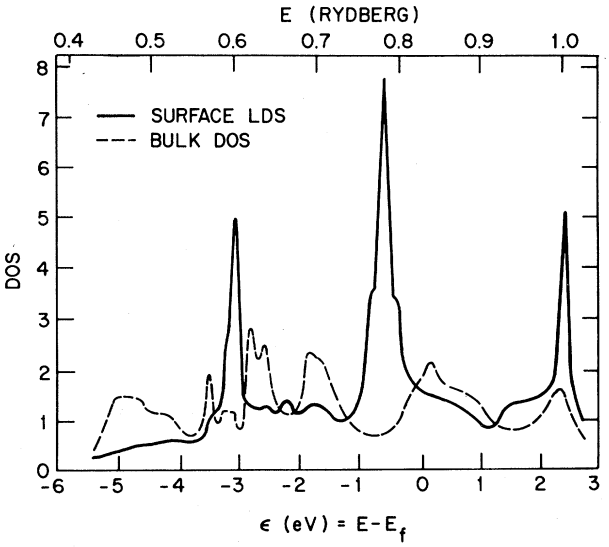

FIG. 2. Total SLDS and bulk DOS of Mo(100) calculated in LCAO model predict two resonance peaks below E_F. The most pronounced one is identified with the observed resonance peak. The densities are in arbitrary units.

In order to explain the FEED results, another dispersion feature has also been calculated. The result is shown in Fig. 4. It demonstrates that, in the vicinity of a major resonance ($k_x = 0.2884$ Å^{-1}, $k_y = 0.0111$ Å^{-1}), the energy of the resonance decreases as k_y increases. This feature explains why the mixing of k_y states, which are not good quantum numbers near an edge, causes *the resultant peak position in FEED to occur at lower energies*. The SLDS of the above mentioned major resonance is shown in the right-hand side of Fig. 5. It is found that this resonance state is

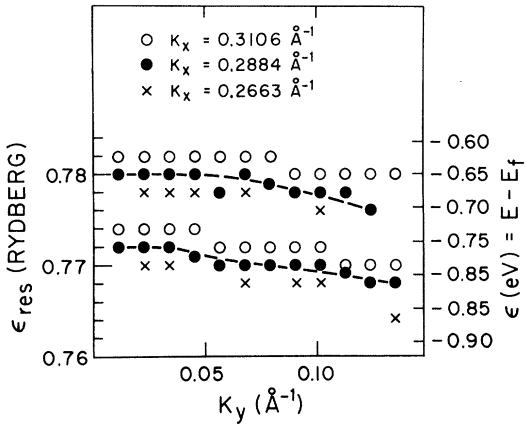

FIG. 4. The dispersion of resonances on Mo(100) as calculated along k_y for some fixed k_x.

composed of two resonances which have an energetic difference of about 0.14 eV. The contribution from each orbital to the SLDS of this state is tabulated in the left-hand side of Fig. 5. In comparison with the corresponding bulk band structures at $\vec{k}_{\parallel} = 0$ and at this resonance, the results shown in Fig. 5 provide a clear answer to the question of the origin of the resonance. The calculated results show that the resonances on the (100) surfaces of Mo and W are mainly made up of d_{zx}, $d_{x^2-y^2}$, and s orbitals. Each resonance is located in a hybridization gap in its associated bulk band structure. *This gap,* when traced back to the bulk band structure of $\vec{k}_{\parallel} = 0$, *is found to be related to the crossover of* Δ_2 *and* Δ_5 *bands.* Obviously, all the arguments based on $\vec{k}_{\parallel} = 0$ or time-dependent relaxation effects are not necessary for the interpretation of this observed resonance

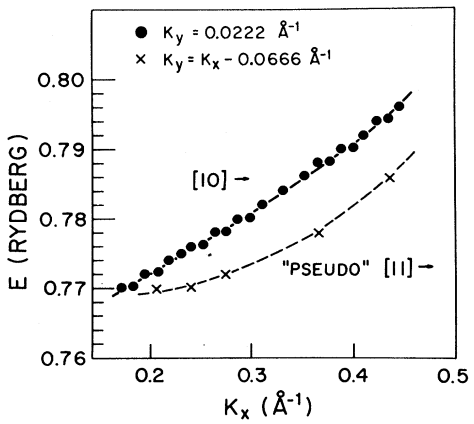

FIG. 3. The dispersion of resonances of Mo(100) as calculated along two directions which are very close to the [10] and [11] directions.

	BULK DOS	SURFACE LDS
S	0	546.
P_X	0	12
P_Y	1.4	1.1
P_Z	0	6.7
d_{XY}	14.0	16.0
d_{YZ}	20.0	80.0
d_{ZX}	0.1	17490.
$d_{X^2-Y^2}$	0	11327.
$d_{3Z^2-r^2}$	0	199.

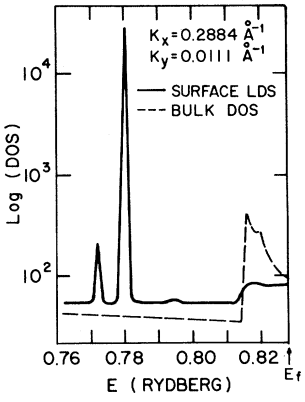

FIG. 5. The calculated SLDS of one major surface resonance (right). The table gives the contribution from all nine bands to the SLDS of this resonance. The densities are in arbitrary units.

peak.

In summary, four major conclusions are reported in this Letter. (1) In conjunction with a theoretical calculation of the $\vec{k}_{\parallel}$-resolved SLDS, the edge proximity effects, which result from the dispersion of the resonances, have provided experimental evidence for the band-structure effects in FEED.[13,15] (2) The present theoretical model calculation of the $\vec{k}_{\parallel}$-resolved SLDS has been shown to be successful in explaining the observations in both FEED and angle-resolved PED. (3) This FEED study on Mo(100) confirms the existence of surface resonances and also reveals their dispersive characteristics. Published results for angle-resolved PED from Mo(100)[11] do not definitely demonstrate the existence of a surface resonance peak.[19] (4) The present calculation shows that the resonance on (100) surfaces of Mo and W are mainly made up of d_{zx}, $d_{x^2-y^2}$, and s orbitals. Each resonance is located in a hybridization gap which, when traced back to the bulk band structure at $\vec{k}_{\parallel}=0$, is found to be related to the crossover of Δ_2 and Δ_5 bands.

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[1]L. W. Swanson and L. C. Crouser, Phys. Rev. Lett. 16, 389 (1966), and 19, 1179 (1967).

[2]E. W. Plummer and J. W. Gadzuk, Phys. Rev. Lett. 25, 1493 (1970), and Rev. Mod. Phys. 45, 487 (1973).

[3]C. Lea and R. Gomer, J. Chem. Phys. 54, 3349 (1971).

[4]B. J. Waclawski and E. W. Plummer, Phys. Rev. Lett. 29, 783 (1972).

[5]B. Feuerbacher and B. Fitton, Phys. Rev. Lett. 29, 786 (1972).

[6]E. Al Khouri Nemeh, R. C. Cinti, and J. B. Hudson, J. Phys. (Paris), Lett. 35, L179 (1974).

[7]B. Feuerbacher and N. Egede Christensen, Phys. Rev. B 10, 2373 (1974).

[8]W. F. Egelhoff, J. W. Linnett, and D. L. Perry, Phys. Rev. Lett. 36, 98 (1976).

[9]R. F. Willis, B. Feuerbacher, and B. Fitton, Solid State Commun. 18, 1315 (1976).

[10]B. Feuerbacher and R. F. Willis, Phys. Rev. Lett. 37, 446 (1976).

[11]J. Lecante *et al.*, in *Proceedings of the European Space Agency Meeting, Noordwijk, The Netherlands, September, 1976* (European Space Agency, Neuilly-sur-Seine, France); P. O. Gartland, *ibid.*

[12]R. Feder and K. Sturm, Phys. Rev. B 12, 537 (1975), and Solid State Commun. 14, 1317 (1974).

[13]N. Nicolaou and A. Modinos, Phys. Rev. B 11, 3687 (1975), and 13, 1536 (1975).

[14]M. C. Desjonqueres and F. Cyrot-Lackmann, J. Phys. B 6, 567 (1976).

[15]P. Soven, E. W. Plummer, and N. Kar, Crit. Rev. Solid State Sci. 6, 111 (1976).

[16]J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

[17]D. Kalkstein and Paul Soven, Surf. Sci. 26, 85 (1971).

[18]For the Slater-Koster parameters for molybdenum, see R. J. Iverson and L. Hodges, Phys. Rev. B 8, 1429 (1973).

[19]S. L. Weng and E. W. Plummer, to be published. Recent angle-resolved as well as angle-integrated PED measurements on Mo(100) in our own laboratory at 16.8 and 21.2 eV clearly show the existence of this resonance peak.

Electron–Molecular-Vibration Coupling in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)

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We comment on the feasibility of a recent suggestion by Carneiro that the Kohn anomaly in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) occurs in the C-H stretch molecular modes.

In a recent Letter discussing the inelastic-neutron-scattering studies[1,2] of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), Carneiro[3] has made the interesting point that the inelastic-neutron-scattering intensities from protonated TTF-TCNQ and deuterated TTF-TCNQ (D) can be quite different for particular molecular-vibrational modes. His suggestion that the Kohn anomaly and related Peierls distortion in TTF-TCNQ arises *specifically* from the coupling of the con-