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## Bulk-plasmon-enhanced photoemission from Nb(100) surface resonances

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The electronic properties of Nb(100) are studied using angle-resolved photoemission. Several bulk electronic states and surface resonances are identified. One surface resonance exhibits significant enhancement of its photoemission cross section at the *bulk* plasma energy. This phenomenon suggests a novel probe of the spatial extent of surface-state and surface-resonance wave functions that are not localized at the surface.

We report the observation of enhanced photoemission from Nb(100) *surface* resonances at photon energies near the *bulk* plasma frequency. This effect offers a sensitive direct probe of the spatial extent of the wave functions of surface states and surface resonances at metal surfaces in cases where the charge density is not confined to the surface. A related enhancement effect has been recently reported by Drube and Himpsel[1] for inverse photoemission. Enhanced photoemission cross sections associated with surface states, which arise form final-state effects, have also been observed on Ag(111) (Ref. 2) and Cu(111) (Ref. 3) surfaces. However, these enhancements in photoelectron cross section are produced by a distinctly different mechanism from the one described in this paper.

Our experiments were performed at the Synchrotron Radiation Center, Stoughton, Wisconsin, using a photoelectron spectrometer which has been described previously.[4] The single-crystal samples were prepared using conventional methods[4,5] and characterized using Auger spectroscopy and low-energy electron diffraction (LEED). Figure 1 displays selected angle-resolved energy distribution curves (EDC's) for Nb(100) obtained using normal emission geometry defined by $k_{\parallel}=0$, where $k_{\parallel}$ is the parallel component of the emitted-electron wave vector. Light was incident at $\theta_I=45°$ with polarization vector $E$ along a [10] crystal axis. Three prominent structures in the EDC's are designated by $\Delta_1$, $\bar{\Delta}_1$, and $\bar{\Delta}_1'$. We first establish the origin of these peaks, and obtain an accurate set of bulk Nb bands because our new result depends on this information.

Peak binding energy shifts in EDC's as a function of photon energy at fixed $k_{\parallel}$ are characteristic of direct transitions between bulk electronic states.[6] The peak labeled $\Delta_1$ is produced by emission from the lower $\Delta_1$ symmetry bulk band of Nb. Figure 2 illustrates the bulk band structure of Nb calculated by Louie, Ho, and Cohen.[7] Final bands lying more than 6 eV above the Fermi energy, $E_F$, have been adapted from the calculated band structure of Mo (Ref. 8). Energy bands and critical-point energies of the final bands above $E_F$ have been adjusted to fit our experimental results for the upper $\Delta_1$ symmetry band. These adjustments yield final bands in good agreement with photoemission data from Smith *et al.*[9] and inverse photoemission data from Johnson[10] for Nb(110). It is clear from Fig. 2 that the peaks labeled $\Delta_1$ originate from the lower $\Delta_1$ bulk band. All of the presently available experimental data (both photoemission and inverse photoemission) appears to be consistent with the band model of Fig. 2. We, therefore, judge this model to be an accurate representation of the excitation energies of bulk states in Nb.

The other two structures labeled $\bar{\Delta}_1$ and $\bar{\Delta}_1'$ are attributed to surface resonances. The binding energies of these two structures do not vary with photon energy. This is a necessary, but not sufficient, condition to demonstrate that they are surface states or surface resonances.[6] *Both peaks* are more sensitive to hydrogen adsorption than the bulk state feature as shown by EDC's taken after exposing the clean Nb(100) surface to 1-2 L (1 L = 1 langmuir = $1\times10^{-6}$ Torr sec) of $H_2$ (refer to the lower EDC of Fig. 1 and to Ref. 4). This property also supports assigning the peaks of surface states or surface resonances.

Finally, if the peaks labeled $\bar{\Delta}_1$ and $\bar{\Delta}_1'$ result from surface states or surface resonances, their binding energies must lie in real gaps or symmetry gaps of the projected bulk states, and there should be some evidence from surface electronic structure calculations that surface states corresponding to the peaks exist in the gaps. Figure 3 illustrates Louie, Ho, Chelikowsky, and Cohen's[11] calculated surface bands and projected bulk bands for Nb(100). At $\bar{\Gamma}$, of the two-dimensional Brillouin zone, a surface state of $d_{3z^2-r^2}$ character is predicted to exist in a $\bar{\Gamma}_1$ symmetry gap 0.2 eV above $E_F$. Also predicted near $E_F$ is an

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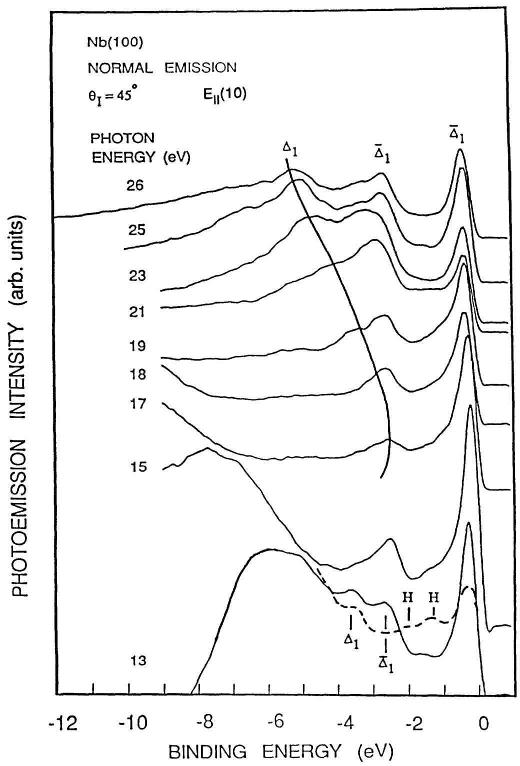


FIG. 1. Normal-emission ($k_{\|} = 0$) electron energy distribution curves for Nb(100). The solid line labeled $\Delta_1$ shows the dispersion of the lower $\Delta_1$ bulk state. The peaks labeled $\bar{\Delta}_1$ and $\bar{\Delta}_1'$ are produced by surface resonances at $\bar{\Gamma}$. Lower curve (dashed line) illustrates the effect of 2.2 L $H_2$ on Nb(100) at $h\nu = 13$ eV.

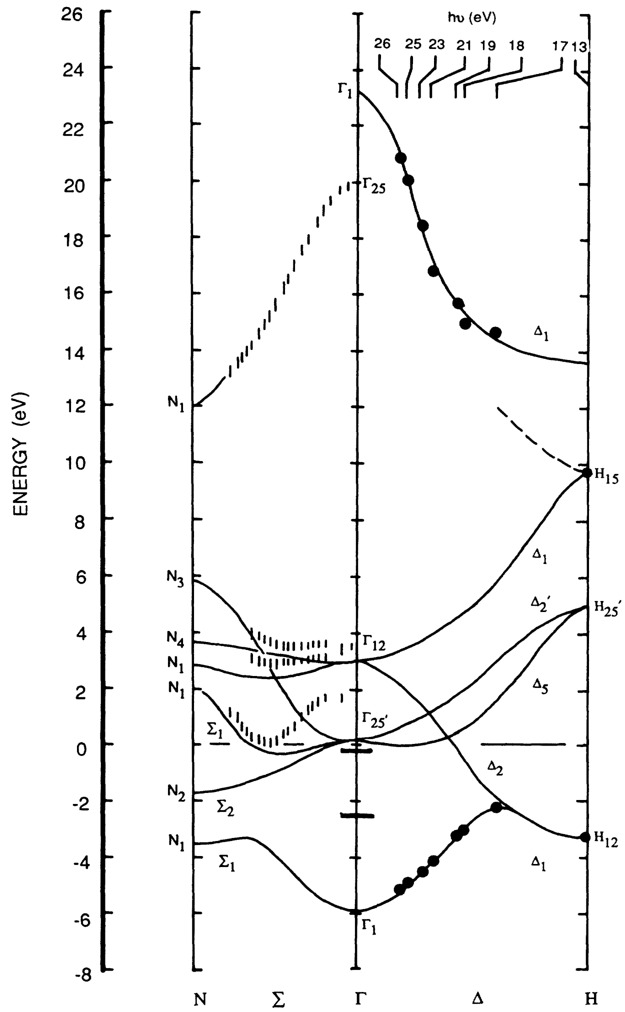


FIG. 2. Bulk band structure of Nb calculated by Louie, Ho, and Cohen (Ref. 7). Filled circles illustrate peak positions of the lower $\Delta_1$ state established by experimental data of Fig. 1, and the corresponding $\Delta_1$ symmetry final-state energies. Vertical bars along the $\Sigma$ direction show final bands above $E_F$ established by inverse photoemission (Ref. 10). Bars at $-0.2$ eV and $-2.3$ eV ($\Gamma$ point) show location of upper (lower) surface resonance.

unoccupied surface band in a $\bar{\Delta}_1$ symmetry gap, and an occupied band of strong surface resonances lying just below $E_F$. The experimental data of Fig. 1 are consistent with these predictions. Off-normal spectra for Nb(100) (not shown) exhibit splitting of the high-lying peak near $E_F$ that we attribute to a pair of surface resonances.[4] The projected bulk bands (Fig. 3) show that the even-state symmetry gap at $\bar{\Gamma}$ extends from near $E_F$ to approximately 2.5 eV below $E_F$. Although no strong surface resonances were predicted by Louie *et al.*[11] 2.5 eV below $E_F$ at $\bar{\Gamma}$, the gap permits a $\bar{\Delta}_1$ symmetry surface resonance to exist at $\bar{\Gamma}$ as our data suggest.

The above discussion serves to establish the origin of the three primary peaks in our EDC's. The discussion also shows that the peak assignments are consistent with available calculations and related experimental results for Nb. Our results are also in general agreement with corresponding experimental data[12] for Mo(100) and W(100): These experiments also found three occupied surface-resonance bands. The resonance are located at approximately 0.2, 0.6, and 3.3 eV (0.3, 0.8, and 4.2 eV) below $E_F$ for Mo (W). In normal emission geometry, only one of the two higher-lying resonances and the low-lying resonance are observed on both Mo(100) and W(100). The symmetry of both states observed at $k_{\|} = 0$ is $\Delta_1$ ($d_{z^2}$). The $k_{\|}$ dispersion of all three surface resonances is small (less than 0.3 eV). Two higher-lying states are observed on both Mo(100) and W(100) for $k_{\|} \neq 0$. The two higher-lying resonances have different character based on the cross-section dependence on polarization. Thus, we find that both the bulk and surface electronic properties of Nb(100) are very similar to corresponding properties of W(100) and Mo(100). We now turn to the photoemission enhancement of the lower surface-resonance cross section.

Examination of Fig. 1 reveals that the lower $\bar{\Delta}_1$ surface-resonance cross section is a maximum for $h\nu \cong 23$ eV. This enhanced cross section (resonance) cannot be attributed to a final-state effect.[2] Resonances in the surface-state photoemission cross section can occur at photon energies corresponding to direct transitions from the surface state to regions of final bulk bands described by Bloch states[2,3] that exhibit a high density of states (i.e., at the zone center or at zone boundaries). It is important to note that models that account for this type of final-state

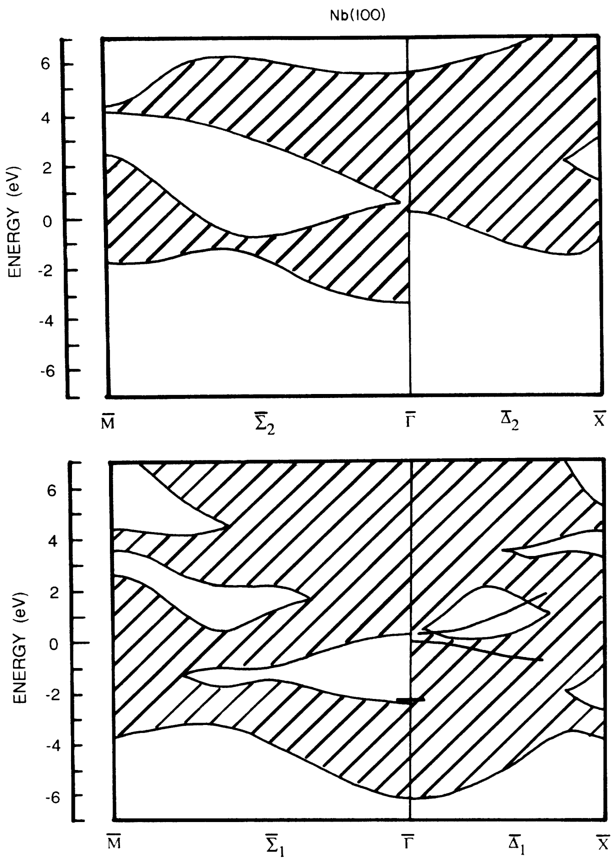


FIG. 3. Projected bulk bands of Nb(100) from Louie *et al.* (Ref. 11). The lower surface resonance lies near the (even-state) symmetry gap at $\bar{\Gamma}$ of the two-dimensional Brillouin zone.

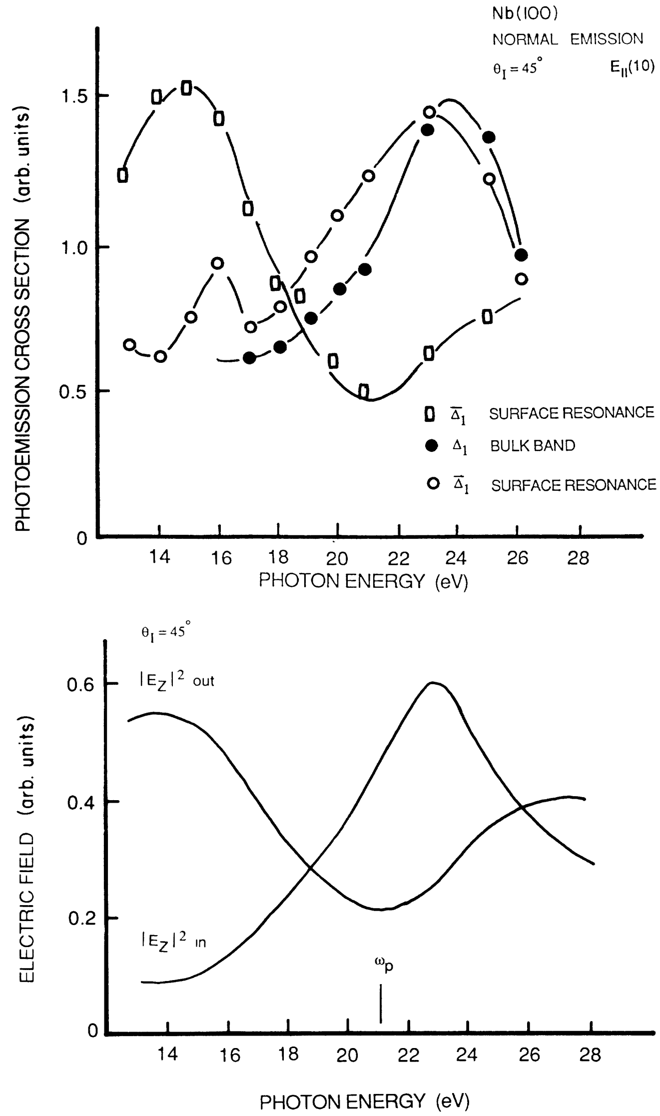


FIG. 4. Upper panel: energy dependence of the photoemission cross section for the bulk state ($\Delta_1$) and the two $\bar{\Delta}_1$ symmetry surface resonances. Lower panel: calculated electric field strength normal to the surface just above ($|E_{\parallel}|^2$ out) and just below ($|E_{\parallel}|^2$ in) the surface for light incident at 45° from the surface normal direction.

resonance require the decay length of the surface state or surface resonance into the bulk to be long compared with the crystal interlayer spacing. According to Fig. 2, final-state resonances for the lower $\bar{\Delta}_1$ state could be expected to occur at photon energies corresponding to transitions to the upper $\Gamma_1$ state ($h\nu = 25.8$ eV) or to the upper $H_{12}$ state ($h\nu = 16$ eV). The observed maximum in the $\bar{\Delta}_1$ surface-resonance cross section occurs between these photon energies (at $h\nu \cong 23$ eV). Note that the bulk $\Delta_1$ state cross section is also maximum at $h\nu \simeq 23$ eV, and final-state resonances for this band should occur at $h\nu \simeq 29.5$ eV ($\Gamma$) or $h\nu = 26.7$ eV ($H$). We, therefore, cannot attribute the enhancement in cross section of the $\bar{\Delta}_1$ surface-resonance emission or the $\Delta_1$ bulk state emission to a final-state resonance. The bulk plasma resonance for Nb occurs at $h\nu \cong 23$ eV, and below we present a mechanism that accounts for the cross-section enhancement of both states based on this resonance.

Figure 4 displays the photon energy dependence of the emission cross sections for the bulk ($\Delta_1$) peak, and the two surface-resonance peaks ($\bar{\Delta}_1$ and $\bar{\Delta}_1'$). Note that the cross sections associated with the bulk peak and lower $\bar{\Delta}_1$ resonance are similar while the higher-lying $\bar{\Delta}_1'$ resonance cross section is qualitatively different. The cross-section energy dependence of all three states can be explained by considering the photon energy dependence of the normal component of the electric field $E_z$ just above and just below the surface (also illustrated in Fig. 4). Based on symmetry selection rules, it is the $Z$ component of the electric field that causes the $\Delta_1 \rightarrow \Delta_1$ bulk interband transitions and $\bar{\Delta}_1$ (even symmetry) transitions at $\bar{\Gamma}$ of the two-dimensional Brillouin zone. Optical constants from Weaver, Lynch, and Olsen[13] were used to calculate $E_Z$ just above the surface, and just below the surface, based on Fresnel formulas from Jackson.[14] The behavior, illustrated in Fig. 4, is similar to what Weng, Plummer, and Gustafsson[12] calculated for corresponding fields at surfaces of Mo and W, and is characteristic of all metals near the bulk plasma frequency: The normal component of the electric field just above the surface experiences a local minimum as $h\nu$ passes through the plasma frequency $\omega_p$.

The corresponding field inside the surface experiences a local maximum just above $\omega_p$. Based on this effect, bulk states and surfaces resonances which have charge density extending beyond the surface into the bulk should experience enhanced cross sections just above $\omega_p$. True surface (top layer) resonances can be expected to experience suppressed cross sections at photon energies just below $\omega_p$ as shown by the calculated results in Fig. 4, and the spectra for the $\bar{\Delta}_1'$ surface resonance.

In discussing their calculations of the surface resonances on Nb(100) Louie *et al.*[11] noted that several of the surface-resonance bands (the $T_5$ and $T_4$ bands in particular) exhibit a striking change in character over different regions of $k$ space. In some regions of $k$ space, the concentration of charge is shifted from the first (surface) layer to the second layer. Unfortunately, our experiments did not probe the line in $k$ space extending from $\bar{X}$ to $\bar{M}$ where these effects are predicted to exist. However, our results presented for states around $\bar{\Gamma}$ suggest that similar effects occur near $\bar{\Gamma}$. Our results also represent a reasonably good experimental test of the accuracy of the surface calculations as well as a demonstration of a novel probe of the depth that a surface state or surface resonance penetrates into the bulk based on bulk plasma assisted processes. The clear implication of our results is that the lower $\bar{\Delta}_1$ surface resonance extends into the bulk while the upper $\bar{\Delta}_1'$ resonance is highly localized at the surface. The latter conclusion is not unreasonable. If the $\Gamma_{25}'$ point lies above $E_F$ as predicted by first-principles calculations, the upper $\bar{\Delta}_1$ band may lie below the projected $\Sigma_1$ and $\Delta_5$ bulk bands, and can therefore be considered a true surface state.

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[1]W. Drube and F. J. Himpsel, Phys. Rev. Lett. **60**, 140 (1988).

[2]T. C. Hsieh, P. John, T. Miller, and T.-C. Chiang, Phys. Rev. B **35**, 3728 (1987).

[3]S. G. Louie, P. Thiry, R. Pinchaux, Y. Petroff, D. Chandesris, and J. Lecante, Phys. Rev. Lett. **44**, 549 (1980).

[4]B.-S. Fang, C. A. Ballentine, and J. L. Edskine, Phys. Rev. B **36**, 7360 (1987).

[5]Y. Li, J. L. Erskine, and A. C. Diebold, Phys. Rev. B **34**, 5951 (1986).

[6]E. W. Plummer and W. Eberhardt, Adv. Chem. Phys. **49**, 533 (1982); F. J. Himpsel, Adv. Phys. **32**, 1 (1983).

[7]S. G. Louie, K.-M. Ho, and M. L. Cohen, Phys. Rev. B **19**, 1774 (1979).

[8]A. Zunger, G. P. Kerker, and M. L. Cohen, Phys. Rev. B **20**, 581 (1979).

[9]R. J. Smith, G. P. Williams, J. Colbert, M. Sagurton, and G. J. Lapeyre, Phys. Rev. B **22**, 1584 (1980).

[10]P. D. Johnson (private communication).

[11]S. G. Louie, K.-M. Ho, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B **15**, 5622 (1977).

[12]S.-L. Weng, E. W. Plummer, and T. Gustafsson, Phys. Rev. B **18**, 1718 (1978).

[13]J. H. Weaver, D. W. Lynch, and C. G. Olsen, Phys. Rev. B **7**, 4311 (1973).

[14]J. D. Jackson, *Classical Electrodynamics,* 2nd ed. (Wiley, New York, 1975), p. 278.