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Surface States on the (001) Surface of Nb†

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The electronic structure of the (001) ideal surface of niobium is calculated using a self-consistent pseudopotential method. Surface states are identified and analyzed throughout the two-dimensional Brillouin zone. Charge densities and the local density of states near the surface are presented and discussed. Our calculations predict strong surface features in the density of states in the range 0–2 eV above the Fermi energy. Occupied surface states are also discussed.

A self-consistent pseudopotential calculation[1] is presented for the (001) ideal surface of Nb. To our knowledge, this is the first fully self-consistent calculation for a transition-metal surface. The band structure and real space distribution of the electrons near the surface are determined. Surface states of different angular-momentum character are found to exist over a wide range of energies and over different portions of the two-dimensional (2D) Brillouin zone. Our calculations predict strong surface features in the density of states in the range 0–2 eV above the Fermi energy.

Although previous calculations[2-6] have provided useful information about band narrowing and some properties of surface states, their limitations have motivated us to attempt the present calculation. Using a self-consistent pseudopotential method,[1,7] we further take into account the important effects of screening and dehybridization of orbitals at the surface and obtain additional information about surface bands and their $\vec{k}$-space distribution.

In the present calculation, a nine-layer slab of Nb with the (001) surfaces exposed on both sides is used to simulate two noninteracting surfaces. The slab is placed in a periodic superlattice with the slabs separated by a distance equivalent to 6 atomic layers of Nb. Screening is achieved using a Hartree potential derived via Poisson's equation and a Slater-type exchange potential. The only input to the calculation consists of the structure (i.e., the atomic positions) and a fixed ionic pseudopotential for the Nb^{+5} ion cores. The Nb^{+5} ionic potential used here is an l-dependent nonlocal pseudopotential of the form

$$V_p = V(r) + \sum_{l=1}^{2} f_l(r) P_l \,, \qquad (1)$$

where P_l are projection operators for the various angular-momentum components. This potential was obtained by fitting the spectroscopic term values of the Nb^{+4} ion (i.e., the Nb^{+5} plus one-electron system).[8] In addition, we demanded that when V_p was used to calculate the Nb neutral atom self-consistently, it would reproduce the eigenvalues and the positions of the wave-function maxima calculated by Herman and Skillman.[9]

Self-consistent bulk energy-band calculations were carried out to test the Nb^{+5} potential. Plane waves with a maximum reciprocal-lattice vector corresponding to an energy of 10.2 Ry were used in the basis set. This corresponds to about eighty plane waves in the expansion of the eigenfunctions; another eighty plane waves were included by second-order perturbation theory. Since $V_{\rm Hartree}$ and $V_{\rm exchange}$ die quickly in q space, it does not make a significant difference whether the second group of plane waves is used or not in the self-consistency. We do not include these. The s and p levels converge to within 0.01 eV. The d levels shift by at most 0.2 eV if the matrix size is doubled. Good agreement was obtained with previous calculations on bulk Nb.[10] Figure 1 shows the calculated density of states (DOS) evaluated using 112 $\vec{k}$ points in the irreducible part (1/48) of the bcc Brillouin zone together with the DOS from Mattheiss's augmented-plane-wave (APW) calculation.[10] The two curves are in agree-

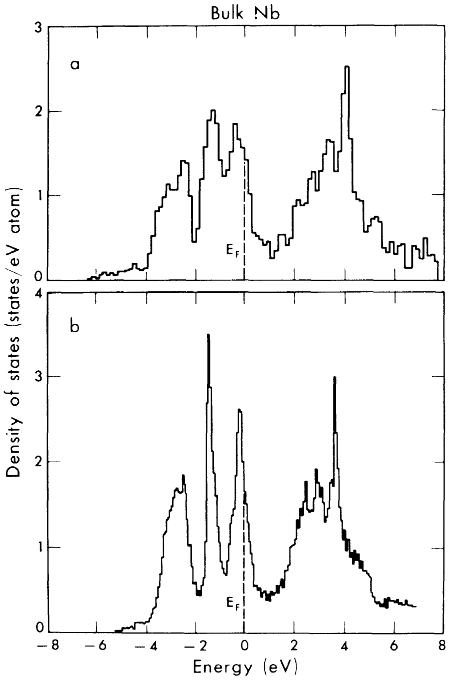

FIG. 1. Density of states for bulk Nb. (a) Present calculation and (b) APW calculation by Mattheiss from Ref. 10.

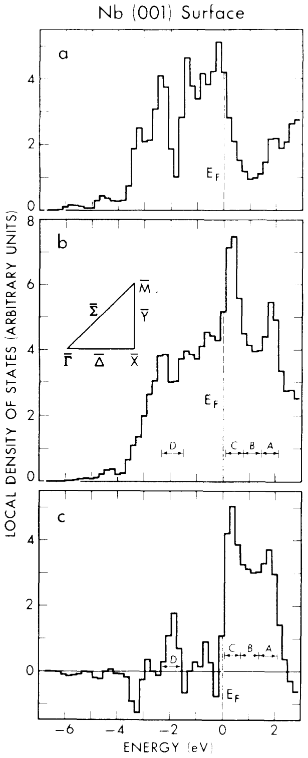

FIG. 2. Calculated local density of states for the Nb (001) ideal surface. (a) LDOS for the fifth layer from the surface. (b) LDOS for the surface layer (first layer). Inset, the irreducible part of the 2D surface Brillouin zone. (c) Difference curve (see text). The calculated work function is 3.6 eV; the measured value is 4.0 eV [(001) surface; from R. P. Leblanc *et al.*, Can. J. Phys. 52, 1589 (1974)].

ment and are consistent with photoemission data.[11]

For the surface calculations, we used the same convergence criteria as in the bulk calculation. The electronic wave functions were expaned in a basis set consisting of approximately 1000 plane waves; an additional 1000 plane waves were treated by second-order perturbation techniques. Using symmetry, the Hamiltonian matrix was reduced to two $\sim 500\times 500$ matrices since the central plane of the slab is a reflection plane.

The local density of states (LDOS)[7] curves are presented in Fig. 2. Figure 2(a) depicts the LDOS for layer 5 which is at the center of the slab. The LDOS for the surface layer (layer 1) is shown in Fig. 2(b). Fifteen $\vec{k}$ points in the irreducible part $(\frac{1}{8})$ of the 2D square Brillouin zone [shown in Fig. 2(b)] were used to calculate the LDOS. In addition, a difference curve obtained by subtracting the LDOS at the center of the slab from the LDOS at the surface is shown in Fig. 2(c).

Away from the surface in layer 5, the LDOS strongly resembles the bulk Nb spectrum given in Fig. 1(a); slight differences arise because of the use of a smaller number of $\vec{k}$ points. The observed changes at the surface layer are mostly due to surface states[12] and partly due to distortions of the bulk-state wave functions at the surface. Narrowing of the rms width of the LDOS is observed for the surface layer. The energy regions A, B, C, and D shown in Fig. 2 indicate the regions where some of the prominent surface bands are found.

The increase in the density of states at the surface layer in the energy range of 0 to 2 eV arises mainly from the contributions of three surface bands ($T1$, $T2$, and $T3$). These three surface bands occur in an absolute energy gap located just above the Fermi level in the 2D projected band structure (PBS). This gap encompasses nearly 70% of the irreducible zone extending from $\bar{M}$ to over $\frac{2}{3}$ of the way to $\bar{\Gamma}$ along the $\bar{\Sigma}$ direction and similarly to over $\frac{2}{3}$ of the way to $\bar{X}$ along the $\bar{Y}$ direction. The existence of these surface bands in the above gap is not very sensitive to the potential used. Their dispersion is ~2.5 eV for two of the bands ($T2$ and $T3$) and ~0.4 for the other

($T1$).

The $T2$ and $T3$ surface states yield similar charge distributions. These two bands follow each other closely in $\vec{k}$ space with a typical energy separation of ~ 0.5 eV which vanishes near $\bar{M}$. The character[12] of the two bands is for the most part $d_{zx,zy}$ with admixtures of d_{xy} and $d_{x^2-y^2}$, depending on the value of $\vec{k}$. The band $T1$, on the other hand, is almost solely of $d_{3z^2-r^2}$ character. In terms of spectral weights, the $T2$ and $T3$ states are mainly concentrated in energy regions B and C, whereas the $T1$ states are concentrated in region A.

A natural, but perhaps oversimplified interpretation of the above surface band is that the $T2$ and $T3$ surface states are states principally derived from the two bonding orbitals d_{zx} and d_{zy} of the surface atoms which are broken by the formation of the surface. They split off as two surface bands into the above-discussed band gap from the bonding and antibonding part of the spectrum. Similarly the $T1$ surface states are $d_{3z^2-r^2}$ orbitals which split off from the antibonding part of the spectrum and move down into the band gap to form one surface band. There are other surface states near the Fermi level E_{F}. For example, at $\bar{\Gamma}$ a surface state of $d_{3z^2-r^2}$ character is found at 0.2 eV. Also found near E_{F} is an unoccupied surface band in a symmetry gap[13] in the PBS along the $\bar{\Delta}$ direction. These states, however, do not contribute much to the LDOS.

In Fig. 3, the charge densities of the states in regions A, B, and C are presented. These include both bulk and surface states. We note that the charge for all three regions are highly localized on the first layer, indicating that these regions are essentially composed of surface states. Since $T1$ states are dominant in region A, the charge-density plot for this region [Fig. 3(a)] shows a strong charge lobe protruding out into the vacuum region along the z direction perpendicular to the (001) surface. Although it cannot be seen from the plot, the charge density is completely symmetric about the z axis, giving the charge distribution a striking $d_{3z^2-r^2}$ character. In contrast, the charge densities for regions B and C have their maxima protruding out into the vacuum region at a 45° angle with respect to the normal; they are nearly symmetric with respect to the z axis. Therefore they are mostly of $d_{zx,zy}$ character with some admixture of d_{xy} and $d_{x^2-y^2}$ character.

Other prominent surface states found are two occupied surface bands in the energy region D. Similar to the $T1$, $T2$, and $T3$ states, they appear in an absolute gap in the PBS. But, unlike the former states, they are not dangling-bond-like. The $\vec{k}$-space extension of this lower gap consists of a strip extending from midway along the $\bar{\Sigma}$ line to the point $\bar{X}$. The surface-charge distributions for the states in the upper band are primarily d_{xy}-like, whereas the states in the lower band are primarily $d_{x^2-y^2}$-like. However, the charge distributions for these states do change significantly over different parts of $\vec{k}$ space. In some regions charge is shifted from the first layer to the second layer.

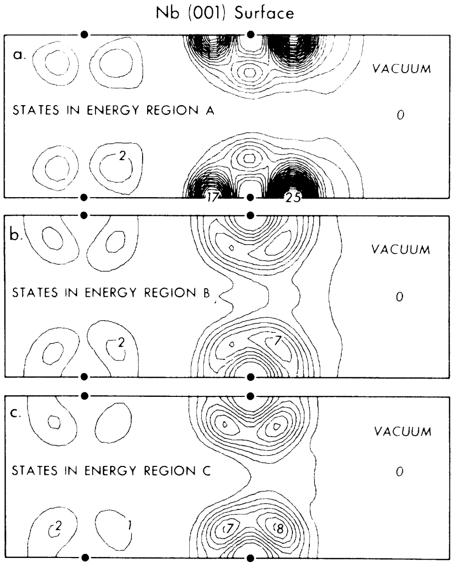

FIG. 3. Charge-density contour plots for the three energy regions (a) A, (b) B, (c) C. The charge density for each region is normalized to 1 electron per unit cell and is plotted for a (100) plane cutting the (001) surface. The Nb atoms are indicated by the dots.

Finally, to our knowledge there is no published experimental data on the (001) surface of Nb; measurements[14,15] have been done on the (001) surfaces of Mo and W. A rigid-band interpretation of our results can be made for Mo and W provided that screening at the surface does not significantly alter the energies of the surface states. We also note that spin-orbit interactions are not necessary for the existence of these states.[16]

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Spectroscopy of Excited Acceptor States in GaP

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Luminescence excitation spectroscopy of donor-acceptor pair recombination in GaP is reported. We observe *s* and *p* excited states of C, Mg, and Zn acceptors, and deduce acceptor binding energies and Luttinger valence-band parameters ($\gamma_1 = 4.04$, $\gamma_2 = 0.53$, and $\gamma_3 = 1.26$). Directly obtained information on the interaction between donors and acceptors characterizes the acceptor state and confirms observation of the $1S_{1/2}$ level.

This Letter reports a novel method to observe donor and acceptor excited states, and its application to C, Mg, and Zn acceptors in GaP. We evaluate valence-band parameters and ionization energies independently of other measurements, and resolve many uncertainties in the basic parameters characterizing GaP. Detailed information about the donor-acceptor (D-A) interaction is obtained more directly than with any other method.

We measure photoluminescence excitation spectra of D-A pair transition. The ground state of a D-A pair with separation R decays with luminescence energy[1]

$$\hbar\omega_L(R) = E_g - (E_D + E_A) + e^2/\epsilon R + J(R), \tag{1}$$

where E_D and E_A are the donor and acceptor binding energies, E_g is the band gap, and J is the interaction energy of a neutral-donor–neutral-acceptor pair. Luminescence from D-A pairs of a selected R is observed by choosing an appropriate $\hbar\omega_L$, and the emission intensity is recorded as a function of excitation energy $\hbar\omega_x$. A dye laser with linewidth 0.3 meV is used as excitation source.

A peak in the excitation spectrum corresponds