

Surface states on *d*-band metals

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Fully self-consistent surface electronic-structure calculations predict unexpectedly high densities of surface states on the (100) surfaces of Cu, Ni, Ag, Pd, and Rh. The number of surface states correlates with the upward shift of certain surface core levels from their bulk values.

The concept of electrons localized at solid surfaces in surface states and resonances is well established.¹⁻⁵ Surface localized bands have been readily identified both theoretically and experimentally for semiconductors.^{2,3} There is much less information on electrons localized on metal surfaces, however. Localized states on *d*-band metals are particularly elusive experimentally because their spectra are often adjacent to or immersed within the high density-of-states (DOS) region of the bulk *d* bands. From a theoretical standpoint the existence of surface-localized electrons depends sensitively on self-consistency of the potential. It is only recently that fully self-consistent calculations have been possible. As a result, surface-localized electrons are usually not brought forward in explaining physical and chemical phenomena at transition-metal surfaces.

We have recently completed a series of fully self-consistent calculations of the electronic structure of the (100) surfaces of copper, nickel, silver, palladium, and rhodium. In the first of these calculations we found^{6,7} a large density of surface states or resonances on Cu(100). This correlates with the correspondingly large attenuation in photoemission signal near the top of the *d* band seen in chemisorption experiments.^{8,9} This density includes an unambiguous surface-state band which rises well clear of the bulk *d* bands around the *M* point in the two-dimensional Brillouin zone. The presence of this band was subsequently observed experimentally.⁵ The high surface-state density is apparently the consequence of subtlety in the self-consistent Cu(100) potential since earlier non-self-consistent but otherwise sophisticated calculations¹⁰⁻¹² predict no significant surface-state density at the top of the *d* band. In fact we find that 36% of the electrons in the surface layer of a seven-plane Cu(100) slab are in states which have at least 80% of their charge density in the surface layer and the next layer beneath it.

The surprisingly large density of surface-localized states on Cu(100) stimulated us to calculate the surface electronic structure of a num-

ber of *d*-band metals. In all cases we found significant numbers of surface states. We present here the results of such calculations on the (100) surfaces of Cu, Ni, Ag, Pd, and Rh.

The self-consistent local orbital (SCLO) method used in these calculations has been fully described.^{7,13} The Cu and Ni films were nine atomic layers thick, while the Ag, Pd, and Rh crystals were seven layers thick. We found virtually identical results for seven- and nine-layer crystals of Cu, and therefore used seven-layer films subsequently.

Table I shows the electron work functions for the five metals. In every case where there are experimental values, there is rather good agreement between theory and experiment. We found that the work function is very sensitive indeed to self-consistency. The good agreement is therefore a measure of the quality of the results, and shows that we have in fact achieved the desired self-consistency.

Figure 1 shows the results calculated for these five metals. For each metal, the first panel shows the projected density of states (PDOS) for the

TABLE I. Electron work functions.

Metal surface	Theory	Experiment
Ni(100)	5.1 eV	5.2 ^a 4.95 ^b
Pd(100)	5.0	5.3 ^c
Cu(100)	4.5	4.58 ^d 4.76 ^e 4.59 ^f
Rh(100)	4.8	
Ag(100)	4.2	4.2 ^g 4.6 ^h

^aReference 14.^bReference 15.^cReference 16.^dReference 17.^eReference 8.^fReference 18.^gReference 19.^hReference 20.

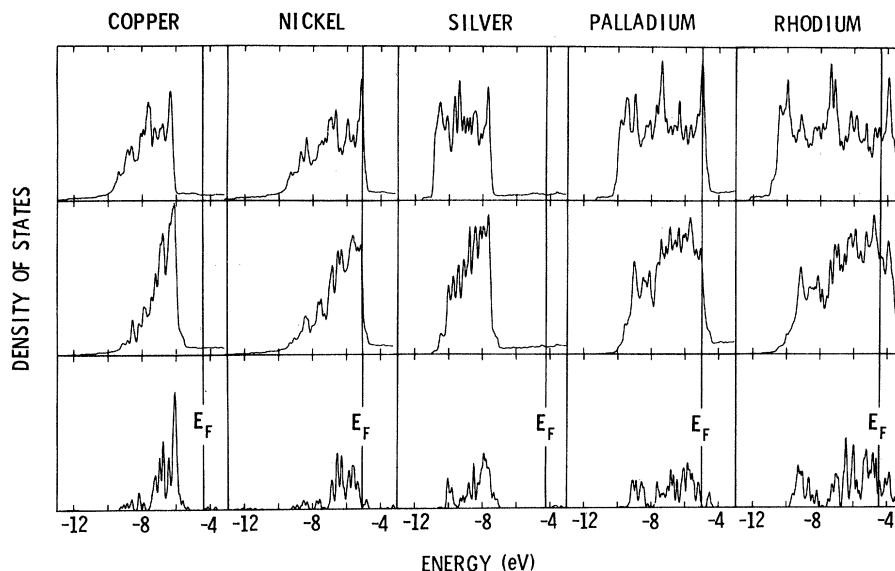


FIG. 1. Projected densities of electronic states: top panel—central atomic plane; middle panel—surface plane; bottom panel—surface states in surface plane. DOS scales are the same for all three panels of a given metal, but vary from metal to metal. Relative surface-state percentages in the surface layer are given in Table II.

central plane, the second panel shows that for the surface plane, and the last panel shows the portion of the surface PDOS which is due to surface states. For the seven-layer films, a state is designated a surface state if it has at least four times as much of its charge density in the surface layer and the next layer beneath it as it has in the interior layers. For nine-layer and thicker films, the corresponding minimum ratio of four is demanded between the outer two layers and the next two layers inward. This provides a thickness-independent definition which includes strong resonances as well as true surface states.

All the interior planes of the slab have PDOS very much like that of the central plane. Only the surface-plane PDOS is different. Fig. 1 shows that in every case the surface PDOS is narrower than the central PDOS, although the leading

(higher-energy) edges of the *d* bands in the two planes closely coincide.

In all five cases, there is a significant enhancement of the surface PDOS relative to the central-plane PDOS. In Cu and Ag, this is evident at the upper *d*-band edge and extends well below the edge; in Ni, Pd, and Rh it begins 0.5–2.0 eV below the Fermi energy and extends for 1–3 eV. The enhancement is caused mainly by the presence of surface states. These surface-state densities shown in the bottom panels are obviously a sizeable fraction of the surface PDOS. Table II summarizes the actual values involved. The fraction of surface-layer electrons in surface states ranges from a high of 36% for Cu to a low of 19% for palladium.

We are thus compelled to conclude that surface states are a prominent feature in the electronic

TABLE II. Surface-state densities and core eigenvalue shifts.

3 <i>d</i> metal	4 <i>d</i> metal	Percent of surface- layer electrons in surface states	Surface core shifts		
			<i>s</i>	<i>p</i> _{<i>x,y</i>}	<i>p</i> _{<i>z</i>}
Cu(100)		36	0.66 eV	0.63	0.73
Ni(100)		23	0.38	0.23	0.51
	Rh(100)	27	0.75	0.76	0.81
	Ag(100)	22	0.51	0.49	0.58
	Pd(100)	19	0.41	0.30	0.40

structure of d -band metals in general. This role has not been recognized previously, but can no longer be ignored by anyone seeking to understand the behavior and properties of these metals.

At this point it is natural to wonder how to explain the variations of surface-state densities from metal to metal. Surface charging, for example, simply does not occur. The charge density readjusts in the presence of these very localized surface states, such that each atomic layer remains neutral (within 0.02 electrons per atom). We believe that the dominant contributor is the rise toward the vacuum level of the potential in the surface atomic layer. Because of this rise, the average potential in the surface atomic layer is less deep than it is in the central plane. The amount of this rise should provide a simple measure of the tendency to form surface states. As the potential varies rapidly with position within the layer, it is important to define a physically meaningful average of this rise. Since the surface states are predominantly of d symmetry, the appropriate average would be over the range of the d orbitals (see Fig. 10, Ref. 7). This rather localized average can be approximated by the variation of the eigenvalues of the highest core levels in each metal. These core levels shift between surface and central planes and so are a crude measure of the average potential shift. For the $3d$ metals (Cu, Ni) we examine the $3s$ and $3p$ core levels, while for the $4d$ metals the $4s$ and $4p$ core levels, which are the highest core levels. The core electron levels group according to row in the Periodic Table, as do the shapes of the valence electronic structures (top panels, Fig. 1).

The difference between the core eigenvalues in

the surface and central layers are shown in Table II, with $3d$ metals in the first group and $4d$ metals in the second. Within each group there is good correlation between these surface core shifts and the surface-state fraction. This suggests that the density of surface states is in fact determined by the upward shift of the surface potential relative to the bulk.

One might wish to inquire about the generality of the correlation. First, we find it only applies well to the highest core levels as listed in Table II. Deeper core levels sample different regions of the potential and therefore exhibit different surface eigenvalue shifts.²¹ We have examined the shifts in the on-site potential matrix elements (not only for the highest s and p levels, but also for the valence d levels); we find they bear out the correlation very well. Secondly, note that the five metals we have treated have filled or nearly filled d bands. Feibelman and Hamann²² have reported that their calculations indicate the surface potentials in the vicinities of the cores of Sc(0001) and Ti(0001) are *deeper* than the corresponding bulk values. These metals have relatively empty d bands, and thus there may be a dependence of the sign of the surface potential shift on d -band filling.²³

In summary, we have demonstrated that surface states are a significant feature of d -band metals. Their relative abundance is determined by the strength of the upward shift of the surface core eigenvalues²¹ relative to the bulk values. Henceforth surface states should always be considered in analyzing physical and chemical processes at solid surfaces.

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