

Large Surface-State/Surface-Resonance Density on Copper (100)

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The electronic structure of the Cu(100) surface has been calculated self-consistently. The calculation predicts a strong surface-state/surface-resonance band near the top of the bulk Cu d band which has not been observed in previous calculations. The large attenuation in the experimental photoemission signal at the top of the d band which is independent of photon energy and which occurs when various species are chemisorbed on Cu(100) is attributed to disturbance of this surface-state band by the chemisorbed atoms.

Recent photoemission spectra¹⁻³ for copper with various species chemisorbed on the surface show a large attenuation near the upper edge of the d band upon adsorption of nitrogen, oxygen, or sulfur. This attenuation is essentially the same for all adsorbate species and for all photon energies used. We have recently completed an elaborate self-consistent electronic structure calculation for a nine-layer Cu slab with (100) surfaces. A number of surface-state/surface-resonance bands are found including a hitherto unreported set of bands located at the upper edge of the d band. This set of bands is present over a large fraction of the two-dimensional Brillouin zone of the slab and is responsible for the most prominent structure in the theoretical density of states in the surface region. We propose that the large reduction in photoemission signal near the upper edge of the d band is a consequence of disturbance of these bands by the chemisorbed atoms.

Previous electronic-structure calculations on Cu(100) show no evidence for a large surface-state/surface-resonance density near the top of the d band. Gurman and Pendry⁴ find a single surface-state band well below the top of the d -band edge. Kasowski⁵ finds no surface states on Cu(100). The most sophisticated existing surface-state calculations for Cu(100)⁶⁻⁸ predict a number of surface-state bands but no concentration of these at the top of the d band. The calculations of Refs. 6-8 actually show a lessening of the surface density of states relative to bulk near the top of the d band. It is likely that the above calculations fail to predict a large surface-state density near the top of the d band because they are not self-consistent. Our earlier calculation⁹ for Cu(100) is self-consistent, but uses a three-layer-thick film, which is not thick enough to make apparent the localization of a state in the surface. Appelbaum and Hamann¹⁰ have carried out a self-consistent calculation for the Cu(111) surface which uses a fitting procedure for achieving self-consistency that is different from our

Fourier-space technique (see below). The calculation is for eleven-layer slab so that surface localization can be observed. They report no localized states near the top of the d band which suggests that the new bands we have found may be peculiar to Cu(100).

The calculational procedure used in the current nine-layer calculation is a refinement of that used in our earlier self-consistent calculations^{9,11} on metal surfaces. It is *ab initio* in the sense that no pseudopotentials or other empirical forms are used. The basis functions consist of the occupied core and valence atomic orbitals of Cu augmented by $4p$, $4d$, and $5s$ orbitals to provide additional variational freedom. A significant feature of the procedure is that the self-consistency corrections are computed entirely in Fourier space. As a consequence there are no constraints on the shape of the final self-consistent potential other than the inherent symmetry of the slab. The procedure and its application to Cu(100) are exhaustively described in a forthcoming publication.¹² As an indication of the quality of the calculation we note that it is self-consistent to within 50 meV everywhere in the slab and yields a work function of 4.5 eV, which compares well with the experimental value of 4.6 eV reported in a recent survey.¹³

Once the self-consistent Hamiltonian is determined by an iterative procedure, the electronic structure of the slab is developed by solving the Hamiltonian at 45 uniformly spaced points in the irreducible one-eighth of the two-dimensional Brillouin zone. These solutions are used to compute electronic densities of states and to display the energy bands of the slab.

There are a number of symmetry band gaps as well as absolute gaps in the projection of the bulk Cu bands onto the (100) surface.⁶⁻⁸ Many have portions lying below the Fermi level and can therefore accommodate occupied surface states. The three largest such absolute gaps are discernible in Fig. 1. The largest gap runs mainly along

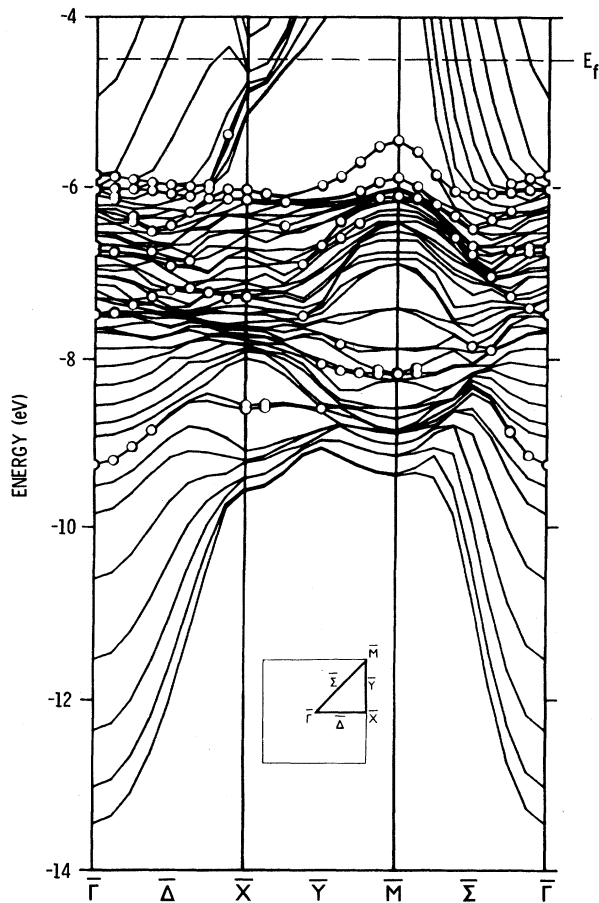


FIG. 1. Two-dimensional energy bands along high-symmetry directions for the nine-plane Cu(100) slab. The open circles represent states on a 45- k -point mesh (see text) which are highly localized in the surface of the slab.

the \bar{Y} direction and is bounded below by the d bands and above by the s - p band. Another perceptible gap opens around the \bar{X} point well within the d band at about -8.5 eV. A third absolute gap within the d band opens about the \bar{M} point. This gap may be only apparent, disappearing for very thick films, as discussed by Sohn *et al.*⁶

Operationally surface states may be defined as states that exist primarily on the outer planes of the slab and shun the central planes. Accordingly we use the following rule to select from the bands of Fig. 1 those portions which are surface-state/surface-resonance bands. An electronic state is deemed a surface state or resonance if more than 80% of its probability density is located on the outer two planes at each surface. The occupied states on the 45- k -point mesh which satisfy this rule and lie along the high-symmetry

directions are shown in Fig. 1 by the open circles. The selected states lying below about -6.5 eV correlate reasonably well with surface-state bands found in Refs. 6-8. However, the extensive group of states centered at about -6 eV which run along the top edge of the d bands have not been observed previously. We conclude that these edge bands which are predominately of d -electron character are a distinctive feature of the self-consistent Cu(100) potential.

The planar densities of states (PDS) arising from the surface plane, second plane, and central plane of the nine-plane slab are shown in Fig. 2, as well as the total density of states (DOS) for the slab. From the close resemblance of the central-plane PDS and the total DOS, it is apparent that the central region of the film is bulklike. But while the second plane in from the surface is very much like the central plane, there is a striking difference in the surface plane. There is a definite narrowing of the d band at the surface, with the second moment or mean-square width being reduced to only two-thirds of its value for the other planes.

The most interesting feature of Fig. 2 is the large enhancement of the surface PDS relative to the bulk (as exemplified by the central-plane PDS) in the approximately 1-eV range at and above the d -band edge. Clearly this is principally due to the surface states of Fig. 1, which are heavily concentrated in the region at -6 eV or just at the top edge of the d band.

We now discuss the experimental evidence for the existence of these surface edge bands in Cu(100). Several studies have been performed, which examined the changes in photoelectron spectra which occur when various atomic species are chemisorbed on Cu(100). The experiments have involved chemisorption of nitrogen,³ of nitrogen, oxygen, and sulfur,¹ and of oxygen.² A universal feature of the data from these experiments is that a sharp peak in the Cu(100) spectrum at the top edge of the band is substantially attenuated when the atomic species are chemisorbed. This is illustrated in Fig. 3, taken from Ref. 1, where the difference between the clean Cu(100) spectrum at 40.8-eV photon energy and the spectrum with fractional monolayers of nitrogen, oxygen, and sulfur are shown. The dominant feature in each difference spectrum is the sharp dip at the d -band edge which arises from attenuation of a large peak in the clean Cu(100) spectrum. In addition to appearing for all three adsorbates, the attenuation is also present in nitrogen chemisorp-

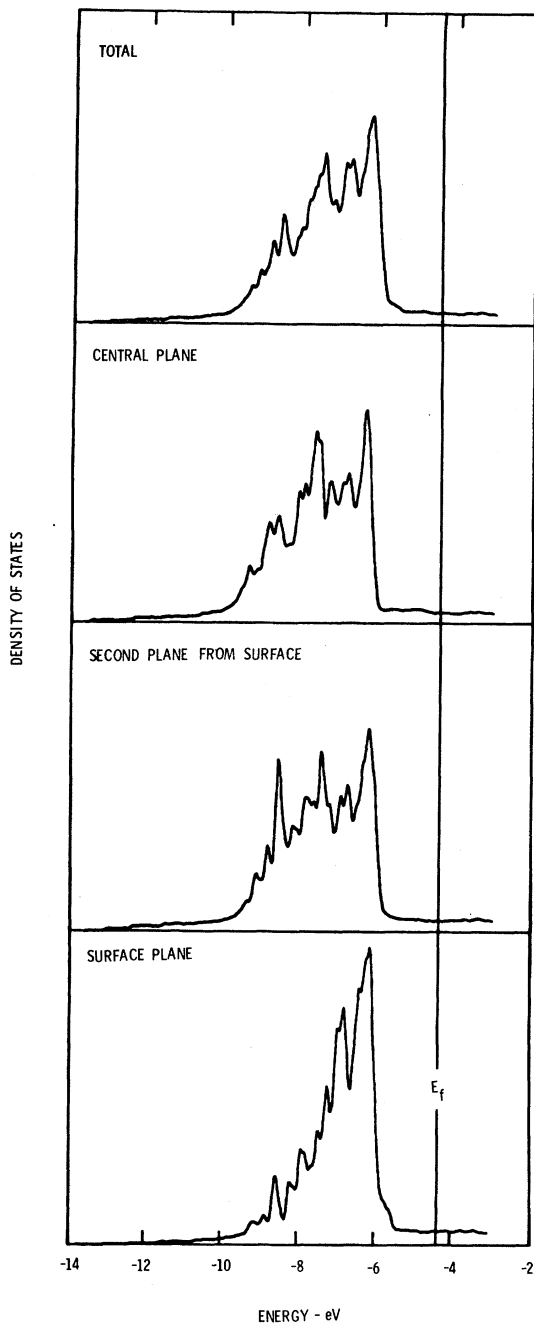


FIG. 2. Calculated density-of-states curves for the nine-plane Cu(100) slab.

tion experiments at 16.7 and 21.2 eV photon energy,³ and in angle-resolved oxygen chemisorption experiments at 13 and 19 eV.²

Figure 3 also shows the theoretical difference curve, the difference between the planar densities of states of the central and surface planes of our film. The correlation with the experimental

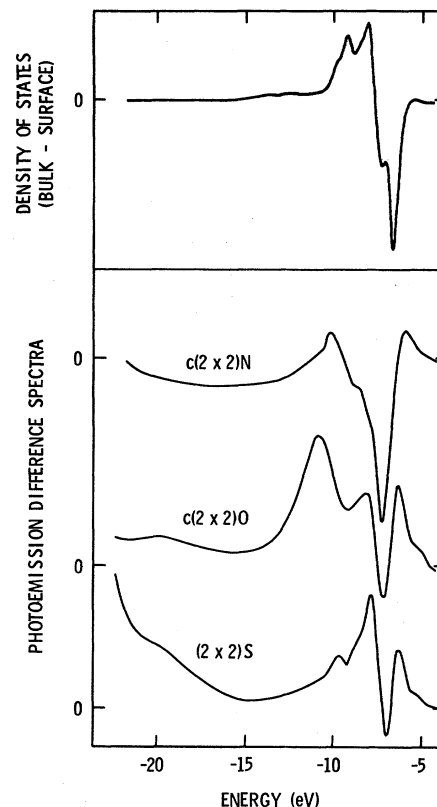


FIG. 3. Top panel, theoretical difference density of states between central and surface planes; bottom panel, experimental difference spectra for Cu(100) covered with partial monolayers of various adsorbates.

curves is striking. The fact that the large attenuation of the photoemission signal at the top of the *d* band is quite insensitive to photon energy and adsorbate is consistent with the explanation being found in the initial density of states of the clean Cu(100) surface as we propose. Our results indicate that this large attenuation must be due to a high density of surface states/resonances, which are disturbed on chemisorption due to their participation in the bonding with the chemisorbed species.

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Double Superconducting Transitions in Single Crystals of V_3Si

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Nearly stoichiometric V_3Si single crystal have been found to exhibit a double superconducting transition which in this instance is believed to be a fundamental physical feature representing an intermediate case between transforming and nontransforming material. A correlation between the existence and degree of the structural transformation and departure from stoichiometry in the Si-rich direction has also been observed.

V_3Si and several other members of the A15 structure class have been studied extensively because they undergo a lattice distortion from cubic to tetragonal symmetry at a sample-dependent temperature above T_c .¹ Not all samples exhibit structural transformations and the fundamental characteristics of a sample which determine whether it transforms are not really known, although model calculations give some plausible reasons for the differences between samples.² From various observations it is generally thought that the structural transformation in V_3Si is second order with the transformed phase consisting of macroscopic tetragonal domains. The superconducting transition temperature is found to be different in the cubic and tetragonal geometries. The reasons for this difference, which is usually not large, may provide fundamental insight into both the connection between superconductivity and the structural instability and the causes of the structural instability which is also believed to be of electronic origin.³⁻⁵

In this Letter we report measurements of the heat capacity, electrical conductivity, and mag-

netic susceptibility of single crystals of V_3Si which exhibit a "double" superconducting phase transition. The existence of two separate superconducting transitions in otherwise homogeneous specimens implies that domains with different transition temperatures of a characteristic size greater than the superconducting coherence lengths may coexist in these crystals. In composition the V_3Si crystals exhibiting a double transition are slightly Si rich. Crystals with a clear structural transformation are found to be more Si rich. Nontransforming crystals are less Si rich than those exhibiting a double transformation. Crystals with a double transition have a resistivity ratio of 12, in contrast with values in excess of 20 generally reported for transforming samples. These results imply that the microstructural disorder which lowers the resistivity ratio and which may be necessary to stabilize samples with compositions close to stoichiometry may not be the fundamental parameter in determining whether a crystal transforms.

The case for the double transitions being a genuine thermodynamic state of the crystal, ra-