SURFACE STATES ON d-BAND METALS

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Electron surface states on d-band metals are investigated by the method of matching the crystal wave function at the surface to the solution outside. On a (100) surface of an fcc metal such a state is found at an energy corresponding to 4-5 eV below the Fermi level E_F in Ni and 5-6 eV below E_F in Cu. This state explains peaks in the density of states seen in photoemission from Ni and Cu.

A recent study of the density of states of nickel by photoemission spectroscopy[1] showed that a large maximum at 4.5 eV below E_F is strongly related to surface properties. It was claimed that the surface monitored by the low-energy electron diffraction was clean so that adsorbates could not be responsible for the high emission current. There is also evidence of such a peak in earlier work on Ni and Cu.[2-6] The calculations reported here show that an intrinsic surface state on the clean nickel surface exists at the energy of the observed peak. It is believed that these are the first fundamental calculations of surface states on transition metals.

The method used here involves matching the wave function inside the crystal to the solutions of the Schrödinger equation in the vacuum outside the surface.[7,8] In this way the energy of the surface state is obtained relative to some well-established band-structure calculations. Thus it suffices to treat a model d-band metal in which the $l=2$ scattering phase shift of an atom has the form of a resonance,[9] $\tan\eta_2 = \Gamma/(E_d - E)$, and other phase shifts are neglected.

The energy region where one may expect a surface state is the band gap DE of Fig. 1, resulting from hybridization of the plane wave or sp band with the d band of the same symmetry. The calculation was carried out for the (100) surface of an fcc metal. Inside the crystal the wave function is a series of Bloch waves with complex $\vec{k}$ components normal to the surface. Therefore

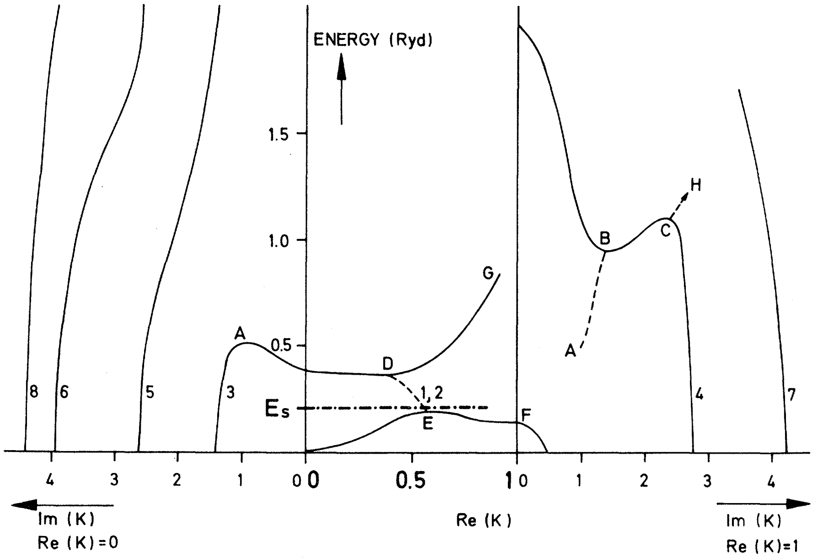

FIG. 1. Complex band structure in the (100) direction of an fcc transition metal, showing only bands of symmetry Δ_1. k is measured in units of $2\pi/a$. The center panel is the ordinary real band structure ($\mathrm{Im}k = 0$), with the nearly-free-electron band $OEDG$ hybridizing with the d band $ADEF$. The left and right panels show the bands with complex k joining onto the real band structure at $k = (0,0,0)$ and $(1,0,0)$, respectively. The bands along DE, BA, and CH depart from these planes and are shown schematically as broken lines. E_s is the energy of the surface state.

one needs as a first step in the calculation the complex band structure in the direction normal to the surface, the ΓX direction, as shown in Fig. 1.

The complex band structure associated with a resonance is rather more complicated than in the situation of a simple nearly-free-electron band gap found in semiconductors,[7,8] as discussed elsewhere.[10] Evanescent Bloch waves from all the bands 1 to 8 (Fig. 1) were included in the representation of the wave function in the metal, which was then matched in amplitude and derivative to the solution outside, namely a Fourier series. The corresponding eigenvalue equation yielded the surface-state energy E_s indicated in Fig. 1. Details of the calculation are given elsewhere.[11]

The results of the calculations may be summarized as follows: On the (100) surface of an fcc transition metal there exists a surface state close to the lower edge of the band gap formed by the hybridization of the *sp* band and the *d* band. Calculations for states with a nonzero component of $\vec{k}$ parallel to the surface and for other surface orientations are somewhat more complicated but are in progress. Since other directions show a similar band gap, the results are expected to be similar, i.e., we expect a narrow band of surface states with one state (of each spin) per surface atom. The wave function of the resultant surface state was mainly confined to the two topmost atomic layers.

When one adjusts the surface-state energy to a detailed band structure, one finds it at 4-5 eV below E_F in Ni,[12] and at 5-6 eV below E_F in Cu.[13,14] These are just the positions where a lot of photoemission spectra show an additional peak in the density of states for Ni[1,2] and Cu.[3,5] In both materials this peak appears at essentially the same distance from the main *d*-band peaks,[5] as one would expect from a rigid-band model.

Although optical absorption occurs to a depth of several hundred angstroms, the electrons excited near the surface have a much higher probability of escaping and being observed in the photoemission experiment. It is therefore not unreasonable to suggest that a surface state could contribute a measurable peak in the photoemission spectrum. Moreover the surface state would be sensitive to adsorbed contamination, as the peak in nickel was found to be.[1] Of course the additional peak in the density of states has already evoked a series of explanations (see references in Refs. 1 and 11), and one of the most important points to settle experimentally is whether it is a feature of the clean surface.

The surface state suggested by our calculation may also be relevant to other phenomena. For example, some ion neutralization spectra of Ni[15] and Cu[16] show low-lying maxima. The optical constants of Cu, too, indicate a strong absorption at 5 eV[17,18] which might arise partly from the surface states since a remarkably thin layer at the surface can make a substantial contribution to reflectivity measurements.[19] Only the low-energy end at 4.3 eV of that absorption peak in Cu could be attributed to a critical-point transition $L_{2'}(E_\mathrm{F}) \rightarrow L_1$[18,20] while the piezoreflectance behavior of the main part of the maximum at 5 eV is consistent with $\vec{k}$-nonconserving transitions.

Finally, the surface states could affect the magnetic properties of nickel at the surface. The 3*d* electron density that goes into the surface states must be subtraced from the bulk bands whose Bloch states suffer a reduction in amplitude over the last two atomic layers. This could reduce the exchange energy between them and hence might be responsible for the lack of magnetic moment[21] apparently observed in the surface atomic layers.[22]

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OPTICAL ABSORPTION AND VACUUM-ULTRAVIOLET REFLECTANCE OF GaN THIN FILMS

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Optical absorption of GaN thin films shows previously unreported structure at 3.8 eV, which is interpreted as the excitonic "knee" due to transitions across the fundamental direct energy gap previously thought to occur at an energy of about 3.4 eV. We also give the first report of the specular reflectance of GaN; peaks were observed at 6.8, 9.5, and 10.7 eV.

Until very recently, there have been no published optical-absorption or specular-reflectivity data on GaN, largely because no macroscopic single crystals could be made. Early values for the energy of the fundamental edge, ranging from 3.25 to 3.4 eV, have been obtained or inferred from diffuse reflectivity on GaN powder, from the highest-energy light emitted in photoluminescence or cathodoluminescence, and from photoconductivity on very small GaN crystals.[1] Recently work was reported of absorption measurements made on thick (50-100 μm) layers of GaN single-crystal films deposited pryolytically on Al_2O_3 or SiC substrates.[2] In this work, the authors fitted a curve of the type $(E-E_g)^n$ to their experimental data, obtained $E_g = 3.39$ eV, $n = 0.62$ as the best fit, and used this as evidence for a direct energy gap ($n = \frac{1}{2}$ in the simple one-electron model). However, the analytical function used to fit the absorption data neglects electron-hole interaction commonly needed to explain the shape of direct-gap absorption edges.[3]

The films used in this work for absorption and visible reflectance measurements were grown epitaxially on Al_2O_3 substrates by evaporating Ga in the presence of nitrogen activated by a microwave discharge.[4] In all these samples, the hexagonal GaN c axis was oriented perpendicular to the substrate, and essentially parallel to the direction of the incident light. A value of 2.03 ± 0.05 for the index of refraction was obtained at 1.6 eV for a thick sample from the ratio of the transmittance at an interference maximum to that of an adjacent minimum, knowing the index of refraction of the Al_2O_3 substrate.[5] From this value, the thicknesses of all films were obtained from measured interference fringes.

The transmittance in the absorption-edge region was measured, and using the known thickness the dependence of the absorption coefficient on photon energy was determined for each film. The reflectance was assumed constant for the wavelength range of this measurement, and the absorption coefficient was taken as $\alpha(\omega) = -(1/d) \ln t/t_0$, where t was the measured transmittance and t_0 the average transmittance in the visible part of the spectrum, where the film was transparent. For each film, the smallest α plotted was $\alpha \approx 0.25/d$, since smaller values are subject to considerable error. The results of these measurements are shown in Fig. 1. A shoulder appears in the absorption curves at about 3.8 eV for all the films measured.

In Fig. 1 we show also an absorption curve due to Vlasenko[6] for a polycrystalline thin film of cubic ZnS. This material is known to have a direct energy gap at 3.8 eV.[7] The strong resemblance between the shape of the ZnS and GaN absorption curves suggests that the shoulder in the GaN curve is caused by a direct energy-gap absorption, occurring at about 3.8 eV. Structure such as shown in the absorption curves of Fig. 1 is of a form which can be interpreted as due to a transition across a direct energy-gap minimum under conditions that the exciton peak is broadened and no peak is resolved. The analytic form