Image-Potential States Observed by Inverse Photoemission

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Momentum-resolved photoemission spectra from Cu(100) exhibit structure at 4 eV above the Fermi energy in a bulk band gap. This emission is pinned to the vacuum level and shows a free-electron-like dispersion. It is polarized with electric vector normal to the surface. The emission intensity is independent of the sample temperature unlike that of a simultaneously observed bulk direct transition. These properties identify the observed phenomenon as transitions into image-potential surface states.

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The charge of an electron approaching a metal surface is screened by the conduction electrons of the metal. The screening can be described in terms of a positive image charge inside the metal. This leads to an attractive potential between the electron and its positive image inside the metal. The experimentally observed trapping of electrons at the surface of liquid helium[1] has been explained by Cole and Cohen[2] in terms of bound states in the image potential. Image-potential bound states have also been invoked to explain the rapid variations in the specular reflectance of low-energy electrons at energies just below the threshold for the emergence of new low-energy electron-diffraction (LEED) beams. An extensive discussion of this topic has been given by McRae.[3] The relevance of image-potential states to the observed fine structure has subsequently been questioned and alternative explanations in terms of interference effects have been forwarded.[4,5] Johnson and Smith[6] have revived the discussion on image-potential surface states. They point out that these states are potentially observable by angle-resolved inverse photoemission but inaccessible by other methods. In an attempt to interpret an unexpected emission feature in angle-resolved inverse photoemission spectra from Ni(100), they propose either image-potential states or a momentum-conserving energy loss or surface contamination as the origin of this feature.

In this Letter, we present the first conclusive experimental evidence for image-potential bound states by polarization-dependent angle-resolved inverse photoemission. Solid dots in Fig. 1 indicate the bremsstrahlung isochromat spectrum from Cu(100) at a quantum energy of 9.7 eV slightly above room temperature excited by normally incident electrons.[7] The strong emission just above the Fermi level is due to a direct radiative transition between bands 6 and 7 in bulk copper. A second steplike emission feature is observed near 4 eV above the Fermi level. The experimentally determined energy-versus-momentum dispersion of this step feature is shown as open circles in a projected band structure of copper in Fig. 2. The emission falls in a gap of the bulk band structure. This suggests an explanation in terms of surface states. The alternative hypothesis of a momentum-conserving energy loss leading to a replica of the bulk direct transition[6] has been ruled out by measurements at different temperatures. Sample data from this series corresponding to a crystal temperature of 900 K are shown as the dashed line in Fig. 1. The bulk direct transition is attenuated by 30% while the steplike emission does not show any intensity

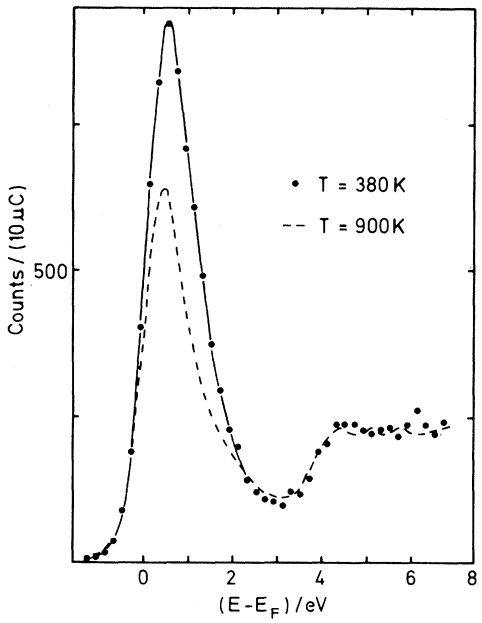

FIG. 1. Bremsstrahlung isochromat spectra at a photon energy of 9.7 eV from Cu(100) for normally incident electrons. The bulk direct transition at 0.5 eV is attenuated at elevated temperatures, whereas the steplike emission feature at 4 eV due to image-potential bound states remains unaffected.

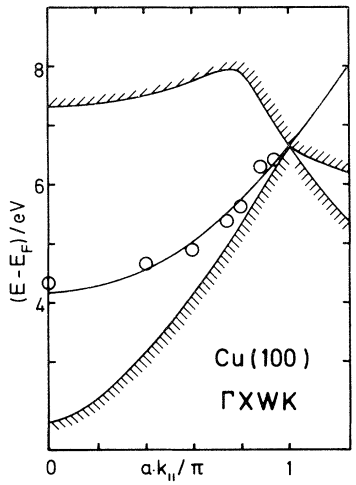

FIG. 2. The experimental energy-versus-momentum dispersion of the emission from radiative transitions into image-potential bound states (open circles) follows a free-electron-like parabola (solid line) with an effective mass $m^*/m = 1.2 \pm 0.2$. This surface emission exists only in a gap of the projected bulk band structure (shaded).

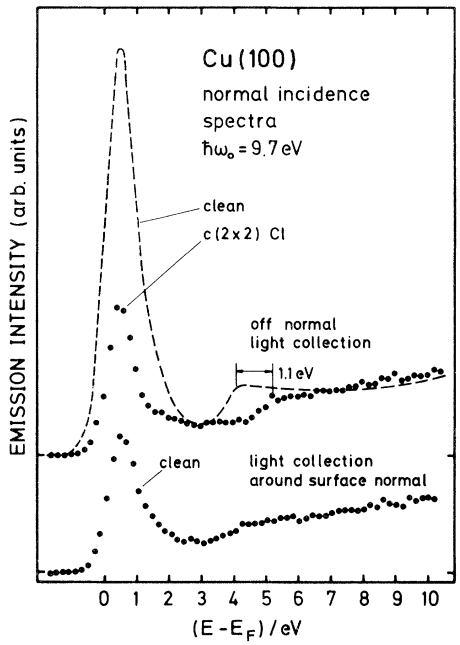

FIG. 3. A comparison of spectra from clean Cu(100) and Cu(100) with a $c(2\times2)$ chlorine overlayer shows that the emission from transitions into image-potential states is pinned to the vacuum level (upper curves). The lower dotted curve shows that the emission is polarized with electric vector normal to the surface.

change. The reduction of the bulk peak is due to enhanced electron-phonon interaction which randomizes the momentum of the incident electrons. The associated attenuation of bulk direct transitions is also well known in ordinary photoemission.[8] The fact that the step emission remains unchanged proves conclusively that it is not an energy-loss replica of the bulk transition. Furthermore, since surface Debye temperatures are lower than bulk, the insensitivity of the step emission to temperature variations suggests that the electronic states involved reside mainly outside the crystal surface in the vacuum. Shockley[9] has conceived the possible existence of such states quite early.

The energy of electrons trapped in the surface potential is

$$E(k_{\parallel}) = \hbar^2 k_{\parallel}^2/2m^* - \epsilon_n + e\phi, \quad (1)$$

where $k_{\parallel}$ is the component of momentum parallel to the metal surface, m^* the electron's effective mass, $e\phi$ the work function, and ϵ_n the binding energy of the bound state with quantum number n. In an oversimplified picture, where the surface potential is approximated by the image potential for all distances, the eigenvalues ϵ_n span a range of 850 meV. This is consistent with the work function of Cu of 4.5 eV[10] and the observed inflection point of the step at about 3.7 eV. Instrumental broadening of the radiative transitions into discrete bound states and the adjacent continuum is responsible for the steplike emission.

An important consequence of (1) is that the energies of the image-potential bound states are pinned to the vacuum level. A change of the vacuum level with respect to the Fermi energy can be accomplished by adsorption of gases on the surface. We have chosen to adsorb chlorine in an ordered $c(2\times2)$ overlayer. This is known to produce a work-function increase of 1.1 eV.[11] Bremsstrahlung isochromat data from Cu(100) with an oriented $c(2\times2)$ chlorine overlayer are displayed as the upper dotted curve in Fig. 3. The effect of chlorine adsorption on the bulk direct transition will be discussed in a forthcoming paper. The important point in the present context is that the step emission is shifted to higher energies by 1.1 ± 0.2 eV in accord with the known work-function change. Note that this provides further evidence against the momentum-conserving energy-loss hypothesis.

Equation (1) predicts a free-electron-like dispersion of the image-potential states. A parabolic fit to the experimentally observed energy-versus-momentum dispersion is shown as the full line in Fig. 2. The fit results in an effective mass $m^*/m = 1.2 \pm 0.2$.

The wave function of an electron trapped in a

bound state n of the z-dependent surface potential can be written as

$$\Psi(\vec{\rho},z) = (1/2\pi)\exp(i\vec{k}_{\parallel}\cdot\vec{\rho})\Psi_n(z). \quad (2)$$

$\vec{\rho}$ is a vector parallel to the surface and z the coordinate normal to the surface. Since the surface potential depends on z only, the x and y components of the dipole-transition matrix element vanish. This predicts polarization of the emitted radiation with electric vector normal to the surface. The prediction was checked experimentally with two different light-collection geometries described in detail elsewhere.[9] The dashed curve in Fig. 3 represents the copper isochromat spectrum for off-normal light collection such that contributions from all three components of the vector potential are recorded with roughly equal sensitivity. The lower dotted curve was obtained when light collection was confined to a cone of 20° aperture around the surface normal. In this geometry, emission with electric vector normal to the surface is strongly attenuated. The bands involved in the bulk direct transition are both of Δ_1 symmetry, and consequently only A_z contributes to this emission. The experimentally observed intensity reduction in the lower dotted curve clearly confirms this prediction. Moreover, the steplike emission is hardly visible in these data indicating a polarization normal to the surface also as expected from the wave functions (2). This completes the experimental characterization of image-potential states.

Image-potential states should, of course, be observable on many metal surfaces since their existence depends only on the presence of a bulk band gap. Though we have not yet carried out a systematic search, emission features as on Cu(100) have so far been detected in our laboratory also on Ni(100) and Fe(110) slightly below the vacuum level. The absence of such a feature in our previous data[13] on Pt(100) is a natural consequence of the light-collection geometry in that experiment which was insensitive to light polarized normal to the surface.

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[1]W. T. Sommer, Phys. Rev. Lett. **12**, 271 (1964).

[2]M. W. Cole and M. H. Cohen, Phys. Rev. Lett. **23**, 1238 (1969).

[3]E. G. McRae, Rev. Mod. Phys. **51**, 541 (1979).

[4]R. E. Dietz, E. G. McRae, and R. L. Campbell, Phys. Rev. Lett. **45**, 1280 (1980).

[5]J. C. L. Bosse, J. Lopez, C. Gaubert, Y. Gauthier, and R. Baudoing, J. Phys. C **15**, 3425 (1982).

[6]P. D. Johnson and N. V. Smith, Phys. Rev. B **27**, 2527 (1983).

[7]W. Altmann, V. Dose, A. Goldmann, U. Kolac, and J. Rogozik, Phys. Rev. B **29**, 3015 (1984).

[8]R. S. Williams, P. S. Wehner, J. Stöhr, and D. A. Shirley, Phys. Rev. Lett. **39**, 302 (1977).

[9]W. Shockley, Phys. Rev. **56**, 317 (1939).

[10]P. O. Gartland, S. Berge, and B. J. Slagsvold, Phys. Norv. **7**, 39 (1973).

[11]D. Westphal and A. Goldmann, Surf. Sci. **131**, 113 (1983).

[12]K. Desinger, V. Dose, M. Glöbl, and H. Scheidt, to be published.

[13]G. Denninger, V. Dose, and H. P. Bonzel, Phys. Rev. Lett. **48**, 279 (1982).