PHYSICAL REVIEW B VOLUME 27, NUMBER 4 15 FEBRUARY 1983

Brief Reports

Brief Reports are short papers which report on completed research which, while meeting the usual **Physical Review** *standards of scientific quality, does not warrant a regular article. (Addenda to papers previously published in the* **Physical Review** *by the same authors are included in Brief Reports.) A Brief Report may be no longer than 3½ printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Image-potential states and energy-loss satellites in inverse photoemission spectra

P. D. Johnson and N. V. Smith
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 1 September 1982)

k-resolved inverse photoemission spectra taken on Ni(001) and Cu(001) show a weak peak at an apparent energy within a bulk band gap and close to the vacuum level. Comparisons with the energy-loss function $|\mathrm{Im}(1/\epsilon)|$ show that it may be due to an energy-loss satellite. Surface states associated with the long-range nature of the image potential are also expected to occur at the observed energies, and may therefore also be responsible.

This report is an addendum to a previous paper[1] which described the development of *k*-resolved inverse photoemission spectroscopy (KRIPES) and its application to band-mapping studies on Cu(001), Ni(001), and Ni(110). In the cases of Cu(001) and Ni(001), the energies E of the strong peaks in the spectra and their dispersion as a function of parallel wave vector $k_{\parallel}$ could be interpreted adequately in terms of direct transitions within the bulk band structure. Some weaker features were observed in the spectra, however, whose origin was left for further investigation. There are two main interpretations for these features; they are due to either surface states or energy-loss processes. Consideration of the surface-state possibility leads us into a discussion of the class of additional surface states which arise through the long-range nature of the image potential. The available information at present does not permit a definitive conclusion. We shall therefore simply list the arguments for and against both interpretations.

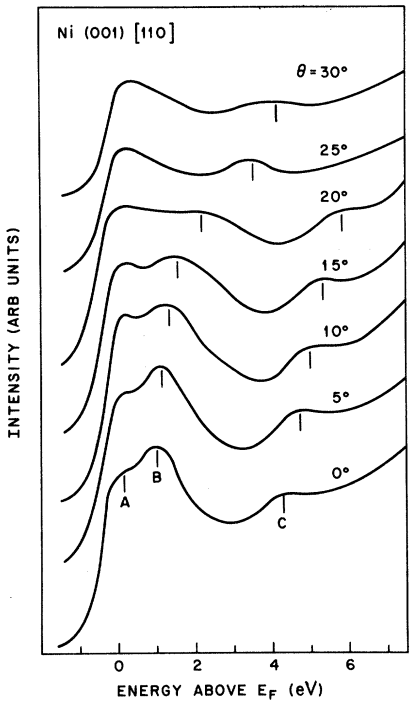

FIG. 1. Variation with angle of electron incidence θ of the KRIPES data on Ni(001) at the photon energy $\hbar\omega = 9.7$ eV.

For convenience we repeat in Fig. 1 the KRIPES data for Ni(001) from Ref. 1. Three features *A*, *B*, and *C* are seen. Feature *A* is associated with the unoccupied part of the Ni *d*-band density of states. Peak *B* and its dispersion to higher energies with increasing angle of incidence θ can be understood in terms of direct transitions into the unoccupied *s,p* band. Peak *C* is the feature which we shall be concerned with in this report. It also shows dispersion with θ. Measurements on Cu(001) show a similar feature.[1]

SURFACE-STATE HYPOTHESIS

The energy of feature *C* falls in an absolute gap of the bulk band structure projected onto the two-dimensional Brillouin zone, as illustrated in Fig. 2. This is very suggestive of a surface state. Counterarguments to the surface-state interpretation, however, are that the sensitivity of peak *C* to surface contamination is about the same as that for features *A* and *B* and also that available theoretical calculations[2,3] place

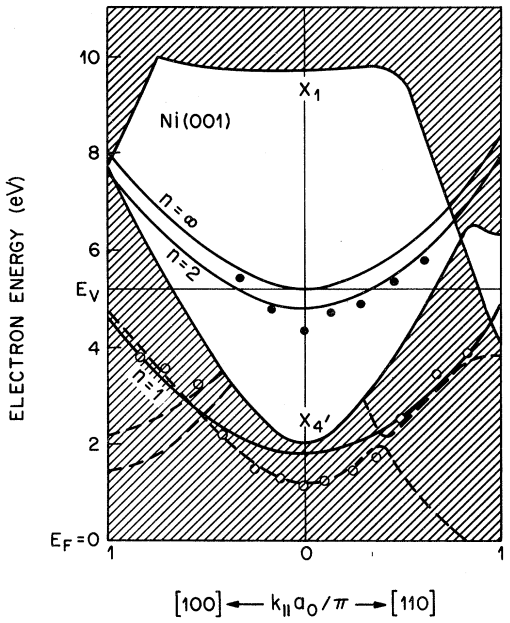

FIG. 2. Experimental $E(k_{\parallel})$ dispersion relations for peaks C and B (full and open circles, respectively) compared with the theoretical predictions for the image-potential states (full curves). The dashed curves are the predictions for direct transitions within the bulk band structure. The hatched area represents the projection of the bulk band states onto the two-dimensional surface Brillouin zone.

the surface states just above the lower edge of the band gap rather than at midgap as observed.

The above counterarguments are not insuperable if one considers the class of surface states associated with the long-range nature of the image potential which have been reviewed recently by McRae.[4] The bound states of the image potential constitute a Rydberg series converging on the vacuum level E_V. In fact it was the proximity of peak C to E_V that provoked this particular hypothesis. In one theoretical approximation, the energies and $k_{\parallel}$ dispersion of the bound states are given by[4,5]

$$E(k_{\parallel}) = E_V + e_n + \hbar^2 k_{\parallel}^2/2m \ , \tag{1}$$

where the binding energy (in rydbergs) is

$$-e_n = 1/[16(n+a)^2], \qquad n = 1, 2, \ldots , \tag{2}$$

and the "quantum-defect" parameter a may take values between $-\frac{1}{2}$ and $+\frac{1}{2}$. Some theoretical curves are shown in Fig. 2 for the case $a = -\frac{1}{2}$; this gives $-e_1 = 3.4$ eV, close to the experimental value of 3.5 eV obtained for Ni(001) by McRae *et al.* using elastic electron scattering.[6] In this approach, we interpret peak C as the unresolved composite of the $n = 2$ and higher components of the Rydberg series. The wave functions of these higher components have their highest amplitudes well removed from the surface plane. The lack of sensitivity to surface contamination is therefore not a serious embarrassment.

The lack of agreement with typical surface-state calculations[2,3] is also no longer a problem. The surface state near the bottom of the band gap predicted by those calculations can be loosely identified with the $n = 1$ state of the present discussion. The $n = 2$ and higher Rydberg components, however, are a consequence of the *long-range* nature of the image potential and cannot therefore be reproduced in essentially short-range theories such as those of Refs. 2 and 3. The curve for the $n = 1$ component falls close to the experimental points corresponding to peak B. However, we have discussed in Ref. 1 how the dispersion of peak B can be adequately explained in terms of direct transitions within the bulk band structure (dashed curves in Fig. 2). It would be desirable to perform experiments at a different photon energy in an attempt to remove this near degeneracy between the bulk and surface predictions.

The strongest argument against the surface-state hypothesis arises because of its generality. Since the existence of the Ryberg series arises through the long-range nature of the image potential and the presence of a bulk band gap, we would expect to see such states on many metals. KRIPES measurements on various faces of Pd, Pt, Au having such band gaps[7] performed after those reported in Ref. 1 do *not* indicate the existence of a general feature just below E_V at $k_{\parallel} = 0$.

ENERGY-LOSS SATELLITES

Inverse photoemission spectra have an inelastic background of "secondary photons" which arise as shown in Fig. 3. The incoming electron decays nonradiatively, losing energy Δ, and then emits a detectable photon. If there is a particularly strong radiative transition between energies E_i and E_f, and if the energy-loss process through energy Δ is also strong, we expect to see a satellite at an apparent final energy $E_f + \Delta$.

The well-known energy-loss function is written

$$\left| \mathrm{Im} \frac{1}{\epsilon(q,\omega)} \right| = \frac{\epsilon_2}{\epsilon_1^2 + \epsilon_2^2} \ , \tag{3}$$

where $\epsilon \equiv \epsilon_1 + i\epsilon_2$ is the dielectric function. In the long-wavelength limit $q = 0$, we may use tabulated optical values[8] for ϵ_1 and ϵ_2. The resulting energy-loss functions for Cu and Ni are compared with the experimental KRIPES data for $k_{\parallel} = 0$ in Fig. 4. The zero of the energy-loss scale has been set at the maximum of peak B. In both Cu and Ni, the feature C occurring in the 4–5-eV range above E_F matches very well with a feature in $|\mathrm{Im}(1/\epsilon)|$.

The structures in $|\mathrm{Im}(1/\epsilon)|$ are not plasmons (i.e.,

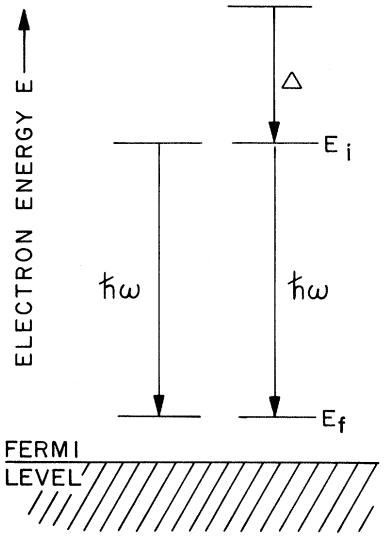

FIG. 3. Transitions contributing to the inverse photoemission spectrum. The inelastic background or secondary photon spectrum is due to transitions such as those on the right, where the radiative decay is preceded by a nonradiative transition due to electron-electron scattering.

not associated with the condition $\epsilon_1=0$), but are associated rather with interband transitions. In the case of Ni, the optical absorption $\omega\epsilon_2$ has a peak at $\hbar\omega=4.7$ eV which is due to direct interband transitions from states near the bottom of the Ni d band to states just above the d band. These occur primarily along the Σ line in $\vec{k}$ space.[9] In the case of Cu, $\omega\epsilon_2$ has a peak at about 5 eV which is a composite structure due partly to direct transitions from the bottom of Cu d band and partly to direct transitions between the s,p bands in the vicinity of the L gap.[10]

There are two arguments against the energy-loss interpretation. The first concerns the observed $E(k_\parallel)$ dispersion of feature C. In the energy-loss process which precedes the radiative transition, one would expect to lose memory of $k_\parallel$ for the incident electron, leading to a dispersionless satellite. Secondly, there are no indications from ordinary photoemission work on Cu and Ni for the existence of energy-loss satellites in the 4–5-eV region.

CONCLUDING REMARKS

Unfortunately, we cannot at this time conclude definitively in favor of either of the two main interpretations, image-potential surface states or energy-loss satellites. The surface-state interpretation is clearly the more interesting because of its novelty. Energy-loss phenomena, on the other hand, have been documented for many years. It would be desirable to demonstrate the existence of the image-potential states by some technique other than elastic electron scattering. Since the states are unoccupied and reside partly in the region below the vacuum level, the KRIPES technique is particularly well adapted to this purpose. It should be pointed out that recent studies[11] indicate that the threshold fluctuations in electron scattering are due not so much to resonances but to interference effects. KRIPES may therefore be the only unambiguous way of detecting the image-potential bound states. Further work, preferably at higher sensitivity and higher resolution, would be desirable to resolve this issue.

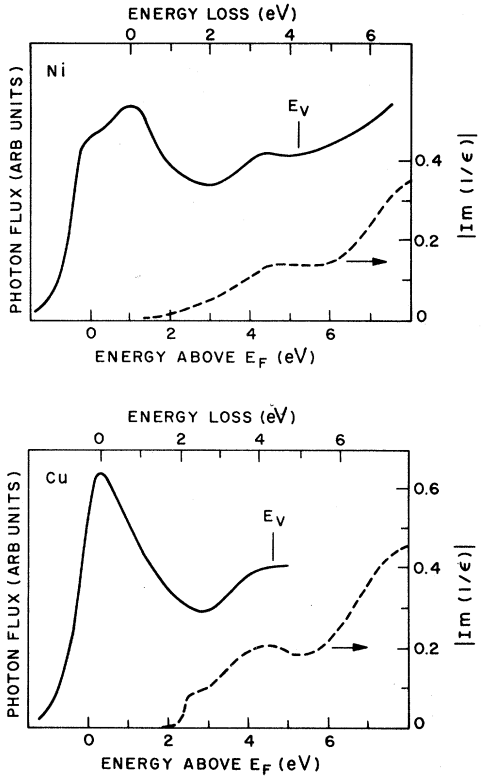

FIG. 4. Comparisons between the KRIPES data for Ni and Cu at $k_\parallel=0$ with the electron energy-loss function $|\mathrm{Im}(1/\epsilon)|$ (dashed curves). The zero of the energy-loss scale has been set at the maximum of the most prominent peak. E_V indicates the vacuum level.

ACKNOWLEDGMENTS

We are grateful to E. G. McRae and R. E. Dietz for instructive discussions.

[1]D. F. Woodruff, N. V. Smith, P. D. Johnson, and W. A. Royer, Phys. Rev. B 26, 2943 (1982).
[2]D. G. Dempsey, W. R. Grise, and L. Kleinman, Phys. Rev. B 18, 1270 (1978).
[3]D. G. Dempsey and L. Kleinman, Phys. Rev. B 16, 5356 (1977).
[4]E. G. McRae, Rev. Mod. Phys. 51, 541 (1979).
[5]In the terminology of Ref. 4, we adopt the specular (or 00) branch of the dispersion curves.
[6]E. G. McRae, D. Aberdam, R. Baudoing, and Y. Gauthier, Surf. Sci. 74, 285 (1978).
[7]P. D. Johnson and N. V. Smith, Phys. Rev. Lett. 49, 290 (1982), and unpublished results.
[8]J. H. Weaver, C. Krafka, D. W. Lynch, and E. E. Koch, in *Optical Properties of Metals* (Physics Data, Fachinformationszentrum, Karlsruhe, 1981).
[9]N. V. Smith, R. Lässer, and S. Chiang, Phys. Rev. B 25, 793 (1982); C. S. Wang and J. Callaway, *ibid.* 9, 4897 (1974).
[10]For a recent discussion, see R. Lässer, N. V. Smith, and R. L. Benbow, Phys. Rev. B 24, 1895 (1981).
[11]J. C. LeBosse, J. Lopez, C. Gauber, Y. Gauthier, and R. Baudoing, J. Phys. C 15, 3425 (1982); R. E. Dietz, E. G. McRae, and R. L. Campbell, Phys. Rev. Lett. 45, 1280 (1980).