COMMENTS AND ADDENDA

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Lack of Evidence for Intrinsic Surface States in Ni and Cu

D. E. Eastman
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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Surface states on d-band metals have recently been studied by Forstmann and co-workers. They have reported that such intrinsic surface states explain peaks in the density of states seen in photoemission from Ni and Cu. We summarize recent photoemission and ion-neutralization data which indicate that no evidence for such states has as yet been found experimentally.

In recent papers, Forstmann and Heine[1] and Forstmann and Pendry[2] have investigated electron surface states on d-band metals and have reported that such states explain peaks in the density of states seen in photoemission at 4–5 eV below the Fermi level E_F in Ni,[3–6] and 5–6 eV below E_F in Cu.[4,7] We wish to summarize recent experimental evidence which indicates that the above-mentioned peaks are due to extrinsic contamination effects and should not be taken as evidence for intrinsic surface states on d-band metals. Also, we present high-energy photoemission data ($h\nu = 21.2$ eV) for clean Ni, which shows no structure at ~5 eV below E_F, and for oxygen-exposed Ni, which shows a strong oxygen peak about 3 eV wide centered at ~5.4 eV below E_F. These results, which were not available to the above authors,[1,2] are in good agreement with ion-neutralization studies (INS) of clean Ni and oxygen-covered Ni.[8]

For Cu, two recent photoemission studies show that the structure reported[4,7] at 5–6 eV below E_F is not intrinsic. Photoemission measurements of Cu at 16.8 and 21.2 eV have been reported which show no structure at 5–6 eV below E_F.[9] A broad peak ~2–3 eV wide at ~6 eV below E_F was observed for a Cu surface subjected to contamination.[9] The earlier measurement of a peak at 5–6 eV below E_F was made using a cesiated Cu cathode in a sealed-off glass phototube.[10] Smith[11] has recently reported photoemission measurements on cesiated Cu in ultrahigh vacuum and did not find the 5–6-eV structure reported earlier.

For Ni, the strong peak at ~5 eV below E_F reported in early work[4–6] has been shown to be mainly an extrinsic contamination effect.[12] In the photoemission work reported in Ref. 3, the limited photon energy range ($h\nu \leq 10.2$ eV) did not permit the probing of structure deeper than ~4 eV below E_F because of the large work function of Ni. Strong peaks were observed at $\simeq 4$, 4.5, and 5.4 eV below

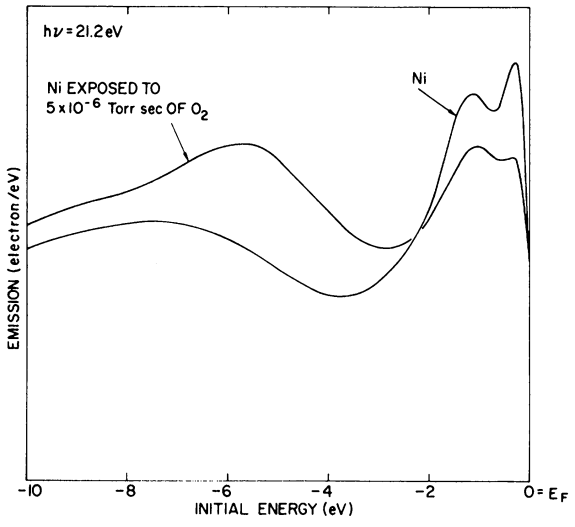

FIG. 1. Photoemission from Ni and oxygen-exposed Ni for $h\nu = 21.2$ eV. Energies are measured relative to the Fermi level E_F.

E_F for cesiated Ni, but were strongly dependent on the cesium treatment.[3]

We have recently measured photoemission from a Ni film at photon energies of 16.8, 21.2, 26.9, and 40.8 eV and find no structure at ~5 eV below E_F indicative of surface states. The energy distribution curve (EDC) for $h\nu = 21.2$ eV is shown in Fig. 1. The energy positions of peaks associated with Ni d bands (at $\simeq -0.25$ and -1.1 eV) are different from those observed for $h\nu \leq 11.6$ eV.[12] This result indicates that, as with the noble metals,[9] the nondirect-transition model[4,6,10] is inadequate for describing photoemission from Ni.

Because the escape depth for photoemitted electrons in Ni is very short ($\lesssim 5$ monolayers[12]), photoemission is quite sensitive to the presence of foreign adsorbed atoms such as oxygen. This is shown in Fig. 1, where the EDC for a Ni film exposed to $\sim 5\times10^{-6}$ Torr sec of O_2 results in an intense emission peak ~3 eV wide centered at ~5.4 eV below E_F. This structure is very similar, both in width and energy position, to that observed by Hagstrum in INS for a monolayer of oxygen on a Ni surface.[8] Hagstrum's INS results for clean Ni and for an ordered monolayer of oxygen on a (100) Ni surface is shown in Fig. 2.[8] Clean Ni shows only a peak $\simeq 1$ eV below E_F, while Ni with a centered 2×2 oxygen structure shows an additional intense peak ~3 eV wide centered at ~5.5 eV below E_F.[8] The width and energy position of this peak associated with oxygen are in good agreement with a similar peak seen in photoemission (Fig. 1). The above results suggest that the previously observed structure[3-6] at 4–5 eV below E_F was possibly due to adsorbed oxygen. Other extrinsic contaminants could also have caused or contributed to the observed structure.

Forstmann and co-workers[1,2] have suggested that there exists a narrow band of surface states at the bottom of the d band containing two electron states

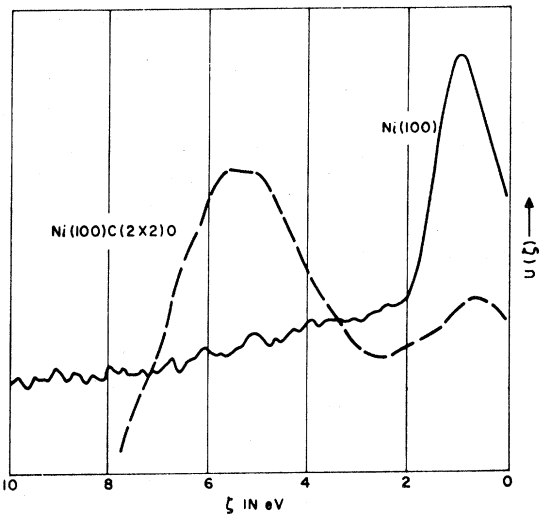

FIG. 2. Ion-neutralization transition density $U(\zeta)$ for a (100) Ni surface, clean and with an ordered c (2×2) oxygen structure upon it (after Ref. 8).

per surface atom in fcc transition metals. If such surface states existed in Ni and Cu, one would expect INS, which mainly probes the surface atoms,[13] to show corresponding emission peaks. Such peaks have not been observed as yet in Ni[8] or Cu.[14]

In summary, it is concluded that experimental evidence for intrinsic surface states on d-band metals as described by Forstmann and co-workers[1,2] has not yet been found experimentally. Earlier peaks seen in photoemission studies of Ni and Cu which were associated with such surface states were due to extrinsic effects, most likely adsorbed oxygen. Both INS and photoemission spectroscopy show a broad peak ~5.5 eV below E_F in Ni due to adsorbed oxygen.

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