

Comment on "X-Ray-Photoelectron Diffraction from a Free-Electron-Metal Valence Band: Evidence for Hole-State Localization"

In a recent Letter,¹ Osterwalder *et al.* (hereafter referred to as OGHS) presented some interesting data of x-ray-photoelectron diffraction (XPD) from Al. The XPD results from the core level and from the valence region are found to be strikingly similar; this prompted the authors to suggest that the hole state in the valence band following photoionization may be similarly localized as in the core level. Here we wish to point out that there is an alternate explanation for their experimental observations, without invoking hole-state localization in the valence-band photoionization.

The motivation to provide an alternative explanation stems from the experience that a large body of experimental evidence exists to indicate that the hole created by photoionization in the valence-band regions of metals, in general, is *not* localized. If the created hole state were indeed localized at an atomic site (i.e., "dehybridized"), one would then find sharp spectral features typical of such cases with multiplet structures. Examples of such cases are the $4f$ spectral signatures in the rare earths and the two-hole satellites in the valence-band regions in photoemission, as well as the two-hole states in the LVV Auger spectra of Ni and Cu. However, the valence-band photoemission spectra of most metals are reasonably well explained in terms of band-structure calculations, both in terms of band-dispersion measurements and in terms of angle-integrated density-of-states (DOS) measurements. This suggests that the hole state following photoionization is not localized.

In order to understand the results of Ref. 1 without invoking any valence-hole localization, we note that the first step of the photoemission process is the excitation of the electron to a high-lying continuum state, described *entirely* in terms of matrix elements coupling the initial state to the final state. If the initial state is a band state, it is given by a Bloch function with a summation over every lattice site. However, the crucial point here is to realize that at such high excitation energies (> 1200 eV) as employed in the study of Ref. 1, the resolution in k space is poor and a large part of the Brillouin zone is integrated in the signal in spite of the small angular acceptance of the analyzer. (This is one of the main reasons why band mapping is normally carried out with low photon energies.) Further averaging takes place when the total integrated valence-band DOS is used, as in Ref. 1. In the presence of k -space integration, the rapidly oscillating phase factor in the matrix elements ensures that only the local contributions are important, just as in a core-level excitation. This, in fact, forms the basis for the so-called local approximation for calculating the matrix elements in the photoemission process.²

While the matrix elements describing the photoexcitation process from the valence band as well as the core levels can be expressed by the local contributions in the matrix elements, resulting in similar XPD behaviors, it *does not imply* that the photoionization-created valence holes are *localized*.

OGHS have also put forward arguments in terms of intrinsic plasmon creation during valence-band photoemission in support of the suggestion of hole-state localization. The fact that similar strengths of intrinsic plasmon features have been found for the core-level spectra and the valence-band spectra is suggested as further evidence of valence-hole localization. In this context, we point out an early work³ where it was shown that similar plasmon intensities should indeed be expected in the valence-band and the core-level photoemission spectra. However, it was shown that different mechanisms are responsible in the two cases. Specifically, the intrinsic plasmon features accompanying the valence-band photoemission were shown³ to be due to correlation effects and *not* due to valence-hole localization at an atomic site.

We further point out that very similar physics is involved in the observation⁴ of the extended fine structure in bremsstrahlung isochromat spectroscopy (BIS), which can be viewed as the time-inverse process of photoemission. There it was found that the fine structure observed in BIS of Cu was very similar to the extended x-ray-absorption fine structure (EXAFS), though BIS represents transitions from extended continuum states to another extended state, while EXAFS is a transition from a localized to a continuum state. We believe that these observations from XPD to BIS justify the use of local approximations in estimating the transition probabilities and *do not establish localization of the valence-band hole state*.

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