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Photoemission Final-State Spectroscopy Applied to KCl†

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A new method of taking uv photoemission data, employing synchrotron radiation, is described. The method has significant advantages for investigating final-state properties of interband transitions and for investigating many-body effects. Applying it to KCl, strong peaks in the conduction-band density of states are located at 9.7 and 12.6 eV. The data also suggest a probable interpretation of an optical-reflectance peak ($h\nu \approx 13$ eV) whose origin has been a matter of doubt.

This Letter reports a new mode of performing ultraviolet photoemission spectroscopy (UPS) with synchrotron radiation which conveniently provides data bearing directly on the final-state properties of interband transitions. Previously, UPS studies have obtained final-state properties by measuring sets of energy distribution curves (EDC's) and then analyzing peak amplitudes or peak positions as a function of photon energy $h\nu$.^{1,2} In principle, all the information available from an ordinary photoemission investigation of a substance is implicit in a family of EDC's measured at closely spaced $h\nu$ values. In practice, however, detailed amplitude differences in adjacent EDC's are difficult or impossible to determine, so that final-state UPS studies have been restricted in scope. As a result, the typical photoemission experiment has emphasized the initial-state properties of optical excitations.

The above limitations are ultimately traceable to constraints imposed by the nature of the radiation source: i.e., a narrow or discontinuous spectrum. Synchrotron radiation, however, possesses a broad smooth spectrum and it has been possible to exploit this quality in certain experimental adaptations, as described below, which render the desired information much more accessible and conspicuous.

The alkali halide KCl is selected for discussion because it has very strong final-state properties, making the relation between the new mode and the more familiar EDC mode easy to recognize. Further, KCl provides a good example of the utility of the new mode for studying certain many-body effects. The data are examined for evidence of the two-electron excitation mechanism proposed

by DeVreese *et al.*,³ and no evidence is found to support the proposal. The data do, however, show a feature which may be due to an excitonic resonance associated with the very strong d -like states in the conduction bands.

The emission data are obtained from KCl films deposited on Au in ultrahigh vacuum—about 270 Å thick for the data shown. The experimental arrangement is outlined by Baer and Lapeyre⁴ and Lapeyre *et al.*⁴ Synchrotron radiation from the University of Wisconsin storage ring was used as the excitation source, and the spectral dependence of its intensity was obtained from sodium salicylate fluorescence measurements.

To introduce the new mode of performing UPS experiments, we first present a set of EDC's in Fig. 1,⁵ arranged to demonstrate that the number of electrons photoemitted with final-state energy E_f is a two-variable function $N(E_f, h\nu)$ which can be viewed in three dimensions as a surface—the emission surface. The reference energy is the valence-band maximum and the threshold (vacuum level) is 8.6 ± 0.2 eV. In this picture the EDC corresponds to a scan along a constant- $h\nu$ line and is denoted by $N(E_f; h\nu \text{ fixed})$. Measurement of a family of EDC's is the classic mode for determining the properties of the emission surface. The peak which occurs at the far right of each curve is due to electrons emitted from the valence bands (VB) without energy loss—the VB primaries—and the width of the peak represents the width of the VB's (2.5 ± 0.2 eV). The balance of the electrons, emitted at lower energies, form the secondaries.

The new mode scans along a different section of the emission surface corresponding to the

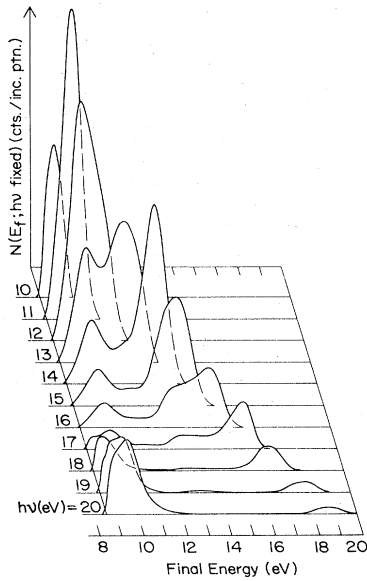


FIG. 1. A family of KCl EDC's plotted against final energy (referenced to VB maximum) and arranged according to $h\nu$ so as to approximate the emission surface $N(E_f, h\nu)$. The vertical axis units are the number of emitted electrons (counts) per incident photon; the scale is arbitrary.

quantity $N(E_f; (E_f - h\nu) \text{ fixed})$. The measurement is accomplished by sweeping over a continuous range of $h\nu$, while scanning E_f , the electron analyzer "window," simultaneously and by the same energy increments so as to maintain $E_f - h\nu$ constant. Since $E_f - h\nu \equiv E_i$, the initial-state energy, the resulting curves are referred to as "constant initial-state-energy spectra" (CIS's). In concept, as $h\nu$ increases, one monitors the primary emission from initial states at a single selected energy to a continuous range of final-state energies. A family of CIS's are obtained by scanning $h\nu$ and E_f for different initial energy values E_i , and E_i becomes the parameter that identifies a given CIS.

The structures observed in the CIS data generally divide into two types: (1) Peaks occurring at the same value of final-state energy for each curve. They are most readily recognized when the CIS curves are plotted against E_f as in Fig. 2 because then those peaks line up vertically. (2) Peaks which occur at the same $h\nu$ value for each curve. These line up vertically when the CIS curves are plotted with respect to $h\nu$ as in Fig. 3. Each bears a particular significance in terms of the electronic properties of the material and are discussed in turn.

Fixed- E_f structures.—If such a peak occurs for

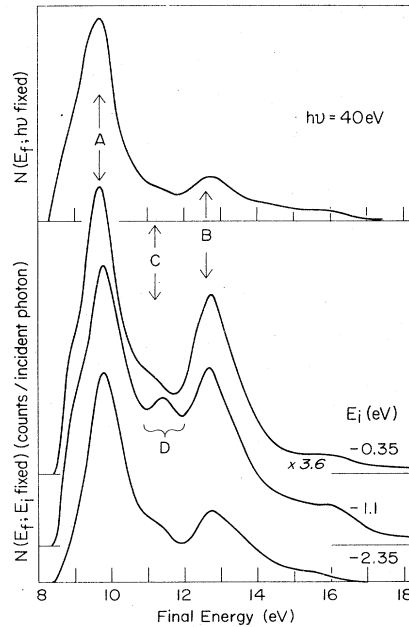


FIG. 2. Bottom: a set of CIS's for KCl taken at several initial energies E_i plotted against the final energy. Top: portion of an EDC containing inelastically scattered electrons (secondaries). Peaks A and B, common to both types of curves, demonstrate peaks in the pure CB density of states.

each member of a set of CIS's that spans the VB, it can generally be attributed to the properties of the conduction-band (CB) states. There is a degree of equivalence between this method of identification and the EDC method where persistent enhancement in the primary emission occur-

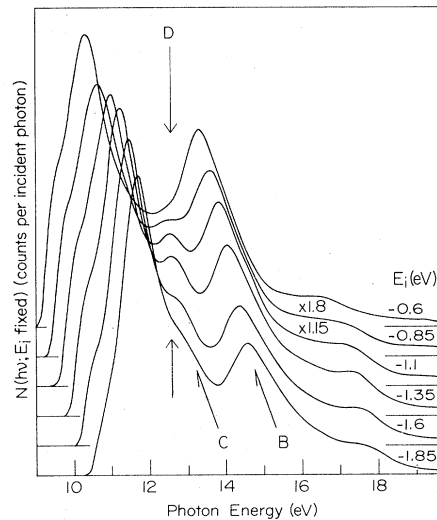


FIG. 3. A set of CIS's for KCl plotted against $h\nu$ energy.

ring at constant E_f appears in contiguous EDC's. This is because in both cases the same region of the emission surface is sampled. However, the EDC method does—and the CIS method does not—suffer from the necessity of mentally or otherwise folding out the rather large structure imposed by the initial-state density in the VB. The peaks *A* and *B* at $E_f = 9.7 \pm 0.2$ and 12.6 ± 0.2 eV in Fig. 2 are taken to be high densities of states in CB, and they are attributed to crystal states derived from the *d* states of the constituent atoms. The weak shoulder *C* at ~ 11.2 eV has the same character. The effects of these CB states are so strong that their presence can be easily observed as they modulate the amplitude of the primaries in the EDC's; see Fig. 1.⁶

The observation that a CB density of states can impose its structure on the energy distribution of secondary electrons has recently been reported.^{1, 4, 6} Figure 2 contains an EDC, taken at $h\nu = 40$ eV, which demonstrates this. The emission consists wholly of low-energy scattered electrons and the primaries are off scale to the right. The EDC's of Fig. 1 also show how the CB density of states affects the higher-energy secondaries—those VB primaries that lose a relatively smaller amount of energy.⁴ These are the humps on the low-energy side of the VB primaries. In all cases, concentration of CB states at 9.7 and 12.6 eV are clearly delineated.

The secondary-distribution methods and the CIS method of locating CB structure are independent of each other, firstly, in the sense that they sample different regions of the emission surface, and secondly, because entirely different quantum processes are responsible for producing the emission. Therefore, the rather firm conclusion can be drawn that strong structures in the "simple" density of states occur at CB energies noted by *A* and *B*. Combining this result with the VB density of states determined from the primary emission in the EDC's, strong structures in the one-particle joint density of states can be determined. To a first approximation, suppressing matrix elements, etc., the mean interband-transition energy for peaks *A* and *B* is given by the final energy for *A* and *B* plus half the VB width which gives values of 10.9 and 13.8 eV, respectively. The resultant transition energies do not correlate with the main peaks in the optical spectra (reflectance or ϵ_2).^{3, 5, 7} Not all structure in the CIS's with fixed E_f values can be simply interpreted in the above manner. The drop in emission above $E_f = 16$ eV, for instance, represents

the attenuation of the primary emission which results when the primaries can lose energy by scattering events which produce VB excitations.^{4, 8}

Fixed- $h\nu$ features.—In Fig. 2 there is a peak *D* which, when examined in a large set of CIS's, occurs at a different E_f value for each curve. It does, however, occur at a constant $h\nu$ value of 12.6 ± 0.2 eV as illustrated in Fig. 3. We propose that the $h\nu$ peak may be due to an excitonic state associated with the very strong *d*-like conduction bands at *B* ($E_f = 12.6$ eV), that is, a resonance state just below a strong interband transition. The emission of electrons comes about as the exciton decays via the configuration interaction (or nonradiative direct recombination) promoting a VB electron up into the continuum.^{4, 7} An alternative, but improbable, interpretation for the $h\nu = 12.6$ eV feature exists. For one-electron direct transitions in the band picture an $h\nu$ feature would mean $\Delta E_i = \Delta E_f$ —that is, transitions between parallel bands. However, the presence of the peak for E_i values, which essentially span the full width of the VB's, would require the bands to be parallel over the whole Brillouin zone, an unlikely event.

The CIS phenomena which have been presented provide a probable interpretation for the strong structure near 13 eV in the optical spectra.^{3, 7} That is, the structure is a composite made up of an excitonic resonance followed at high energies by a shoulder due to structure in the joint density of states. The CIS method further provides a means for directly examining another interpretation of the optical peak by DeVreese *et al.*³ in which the peak is attributed to a double excitation, involving the formation of two excitons at the interband threshold. The consequences of this process would be a transfer of oscillator strength away from the interband transitions as this additional process "turns on." As a result, one ought to see a dip in the amplitude of the VB primaries when $h\nu$ is equal to the excitation energy. The curves in Fig. 3 show no trace of such an effect so we conclude that the process is too weak to be observed by this method. The null result is consistent with a calculation by Herman⁹ which predicts an extremely small strength for the double excitation.

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