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Transition Probabilities and Overlap-Covalency Effects in the X-Ray Photoemission Spectra of Transition-Metal Compounds: ReO_3

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Differences in photoelectric transition probabilities have an important effect on the interpretation of x-ray photoemission spectra of transition-metal compounds with pronounced overlap-covalency effects. It is shown that the apparent discrepancy between the x-ray–photoemission valence-band data for ReO_3 and the theoretical density-of-states curve is resolved if one considers only the 5*d* component of the density of states.

It is shown in this communication that valence-band spectra of transition-metal compounds obtained by x-ray photoemission spectroscopy (XPS) may be grossly distorted by transition-probability effects. These effects are so severe that erroneous conclusions can be drawn from straightforward comparisons between XPS data and theoretical density-of-states curves. The fact that, for example, the strength of a rare-earth 4*f*-electron signal is strongly photon-energy dependent is, of course, well known. Similarly, it has been suggested that the small discrepancies which are found between theoretical and experimental band structures of the noble metals are due to increasing *s* admixture into the lower part of the *d* band.[1] As an example of rather more drastic effects we consider ReO_3.

The electronic structure of this cubic, metallic compound[2] has been the subject of a number of investigations.[3-6] In Fig. 1 we show the ReO_3 density of states from Ref. 3, smoothed by a 0.55-eV Gaussian, which corresponds to the resolution function of the spectrometer used to obtain the XPS data discussed below. This band structure successfully accounts for both the optical properties and the Fermi-surface dimen-

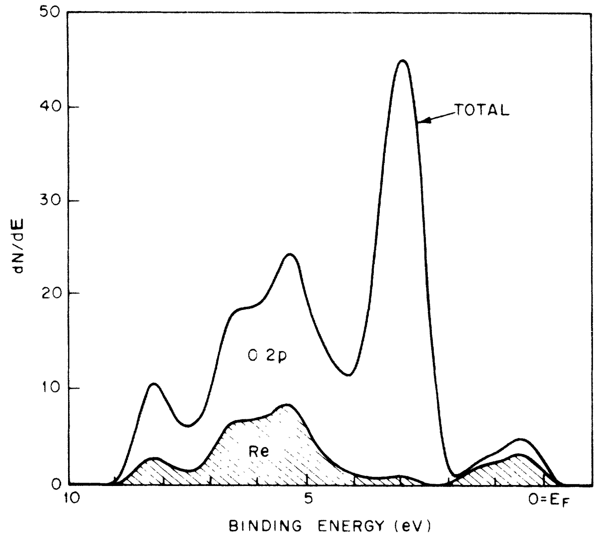

FIG. 1. Calculated density of states of ReO_3 from Ref. 3 smoothed by a 0.55-eV Gaussian. The shaded area indicates the Re 5*d* contribution.

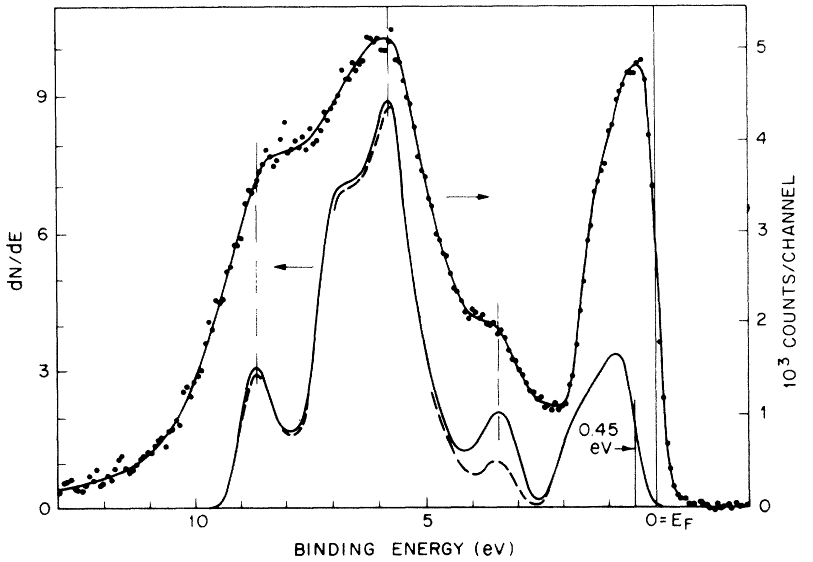

FIG. 2. Comparison of XPS data on vacuum cleaved ReO_3 with the Re 5*d* component of the density of states (dashed line), and a composite density of states containing the 5*d* and 2.5% of the oxygen 2*p* component (solid line).

sions and topology, as deduced from the de Haas–van Alphen effect. It is then distressing to find[7] that the XPS valence-band data appear to be in conflict with it. The problem becomes apparent from a preliminary look at the present XPS data in Fig. 2 where the most prominent peak in the density of states near 3 eV in Fig. 1 is largely absent.

The data shown in Fig. 2 were obtained from a single crystal of ReO_3 grown by iodine-vapor transport,[8] cleaved in a vacuum of 7×10^{-9} Torr, and immediately transferred without exposure to air into the spectrometer where the pressure is characteristically less than 10^{-9} Torr. (Data taken on material exposed to the atmosphere are quite different in character.) An HP 5950A spectrometer, employing monochromatized Al *Kα* radiation and achieving a resolution of 0.55 eV full width at half-maximum, was used. The sample was oriented with a [110] axis toward the entrance slit of the electron spectrometer. As an index of the success of the surface preparation we monitored the oxygen 1*s* and rhenium 4*f* lines. They were symmetrical and had widths of 1.02 and 0.78 eV, respectively. The 4*f* spin-orbit splitting was 2.46 eV. Each line was accompanied by a broad energy-loss satellite at 2.1 eV, the plasmon energy.

The photoemission spectrum in Fig. 2 consists of two parts. The 2-eV-wide component just below the Fermi energy is the Re 5*d*-derived conduction band. The shape of the cutoff at the Fermi energy is almost entirely determined by the resolution function. The structure between 3 and 10 eV is generally thought of as the oxygen 2*p*-derived valence band. It is characteristic of XPS valence-band spectra that the lower part of the band exhibits a tail-out suggestive of lifetime broadening. It must be recognized, however, that there is some distortion due to excitation of the 2.1-eV plasmon.

This separation into an O 2*p* and a Re 5*d* band is of course oversimplified because it ignores the effects of covalency, which are substantial in this material.[9] The shaded area in Fig. 1 represents the Re 5*d* contribution to the density of states. A most interesting observation is the fact that the prominent peak at 3 eV in the total density of states has almost negligible 5*d* content. This suggests that we compare the experimental XPS data with the 5*d* contribution alone rather than with the total density of states.[10] This is done in Fig. 2, where we have enlarged the theoretical density of states scale by a factor of 5. Two theoretical curves are shown, a dashed curve corresponding to the 5*d* density, and a solid curve resulting from the addition of 2.5% of the 2*p* density. The theoretical density of states has been shifted toward lower energy by 0.45 eV, which appears to bring the *p*-band features into optimum coincidence. The overall agreement between theory and experiment is gratifying.

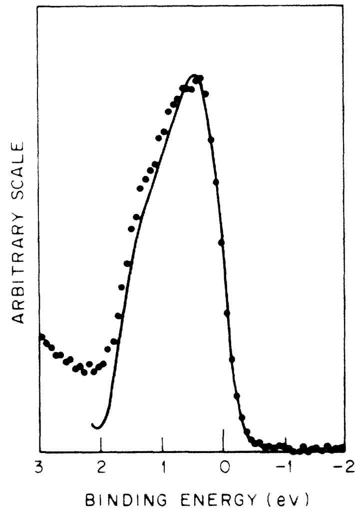

FIG. 3. Comparison of XPS data with the smoothed density of states for the ReO_3 conduction band.

A direct comparison between the theoretical and experimental d-band curves is shown in Fig. 3. The only adjustable parameter is the amplitude. (The 0.45-eV shift is of course not used here.) The band-structure results clearly reproduce the width and shape of the experimental data with gratifying accuracy. These comparisons suggest that the $2p$-$5d$ band gap is about 0.45 eV larger than originally estimated. Since this feature of the ReO_3 band structure was adjusted to fit optical data of relatively low definition, this discrepancy is not of serious concern.

One major question is whether it is reasonable to expect that the oxygen p electrons would make such a small contribution to the x-ray photoemission spectrum. Part of the answer is found by comparing the relative strength of the signal from the oxygen $2s$ and $2p$ electrons in various compounds. In ReO_3 the areas under the curves for these states are quite comparable. On the other hand, in MgO, where there is clearly no d admixture, the $2p$ signal is much weaker. This immediately confirms that a major part of the p-band signal in ReO_3 is due to d admixture. The data suggest that the $5d$ cross section is 20 to 40 times larger than the $2p$ cross section. This may, however, be an overestimate. Similar effects of d admixture are also apparent in the valence-band spectra of other transition-metal compounds, and will require a reconsideration of some previous work.

The difficulty encountered in the interpretation of the XPS valence band of ReO_3 does not in any real sense make such spectra less useful for the study of band structures. It should rather be viewed as a unique opportunity for investigating overlap-covalency effects in transition-metal compounds and alloys. This may ultimately further our understanding of collective magnetic effects in these materials. It also indicates the need for better information on photoelectron cross sections of outer electrons.

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