Photoemission Partial State Densities of Overlapping p and d States for NiO, CoO, FeO, MnO, and Cr_2O_3†

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(Received 20 June 1974)

We report partial densities of states of overlapping bandlike p states and localized d states in several insulating transition-metal oxides which have been determined from frequency-dependent photoemission spectra taken in the range 5–90 eV. We observe that p-band features become weak relative to d-state and satellite features at high frequencies, i.e., at x-ray photoemission frequencies. Partial d-state densities together with a ligand-field description are reported which give a basis for evaluating recent theoretical descriptions of transition-metal oxides.

While the electronic properties of insulating transition-metal oxides containing partially filled $3d^n$ shells have been the subject of many theoretical,[1-4] x-ray photoemission,[5-7] and optical studies,[8,9] and are of current interest in surface adsorption and/or oxidation studies,[3] such basic parameters as the energy separations of the localized $3d$ states from the $2p$ bands as well as the spectral features and level widths of the overlapping $3d$ states and p bands have not been determined. X-ray photoemission measurements have been reported which clearly see d-state features[5-7] (but cannot usually see p-band features), and the suggestion has been made[6] that such features can be identified with the crystal-field-split states of the $3d^{n-1}$ final states.

In this Letter, we report photoemission-derived partial densities of states for $3d$ states and $2p$ bands in insulating NiO, CoO, Fe_xO ($x \simeq 0.9$–0.95), MnO, and Cr_2O_3, which typically show overlapping p- and d-state densities. These partial state densities are determined from photoemission energy distributions (PED's) measured in the energy range $5 \lesssim \hbar\omega \lesssim 90$ eV using synchrotron radiation. For these compounds, we observe partial d-state emission spectra characteristic of localized (~1–1.5 eV wide) d orbitals which can be well described using a ligand-field-theory description of the localized $3d^{n-1}$ final state. Also, significant $\hbar\omega$-dependent trends in the PED's are seen, with p-band emission becoming very small at x-ray frequencies while multielectron-satellite emission features become very strong. Thus care must be exercised when interpreting x-ray-photoemission spectra for such compounds. Also, several recent theoretical descriptions[1-4] are described in light of our data.

PED's were measured in the range $5 \lesssim \hbar\omega \lesssim 90$ eV using synchrotron radiation and a previously described photoemission-spectrometer system.[10] Single NaCl-type crystals of NiO, CoO, Fe_xO ($x \simeq 0.9$–0.95), and MnO of area ~4 mm^2 were cleaved [(100) face] and measured *in situ* at pressures of $\sim 2\times10^{-10}$ Torr.[11]

Several PED's for NiO(100) are shown in Fig. 1 together with an x-ray PED[5] in order to illustrate our method for separating the photoemission partial p- and d-state emission intensities, which is based on the characteristically different $\hbar\omega$-dependent photoemission intensities of p and d states in the range ~10–90 eV.[12] Recently, $\hbar\omega$-dependent photoemission measurements (employing Ne and He resonance lamps and Al x rays) have been used to study the hybridization of closed-shell p and d levels (which are close in energy) in several Cu and Ag halides.[13]

For the total primary valence-electron emission $N_T(E, \omega)$, we can in general write $N_T(E, \omega) = N_p(E, \omega) + N_d(E, \omega)$, where N_p and N_d are the (overlapping) p-band and d-state emission spectra and E is the electron energy. Also, at sufficiently high photon energies ($\hbar\omega \gtrsim 20$ eV for NiO, etc), we can approximately factor N_d and N_p into $\hbar\omega$-independent spectral shapes $\overline{N}_d(E)$ and $\overline{N}_p(E)$ and $\hbar\omega$-dependent intensity factors $C_d(\omega)$ and $C_p(\omega)$. That is, we assume[14] $N_T(E, \omega) \sim C_d(\omega)\overline{N}_d(E) + C_p(\omega)\overline{N}_p(E)$.

A prescription for determining $\overline{N}_d$ and $\overline{N}_p$ for NiO is as follows. Primary emission is first determined by subtracting inelastically scattered secondary emission[10] (and multielectron satellite emission) as shown for the $\hbar\omega = 30$ eV PED. Based on the overall $\hbar\omega$ dependence seen in Fig. 1 and model calculations,[1-4] the highest occupied peak at 0 eV is essentially a pure d-like peak while the ~3-eV peak (pronounced for $\hbar\omega \lesssim 25$ eV, e.g., see PED for 20 eV) is primarily a p-band peak. We then determine $\overline{N}_d$ by taking a weighted

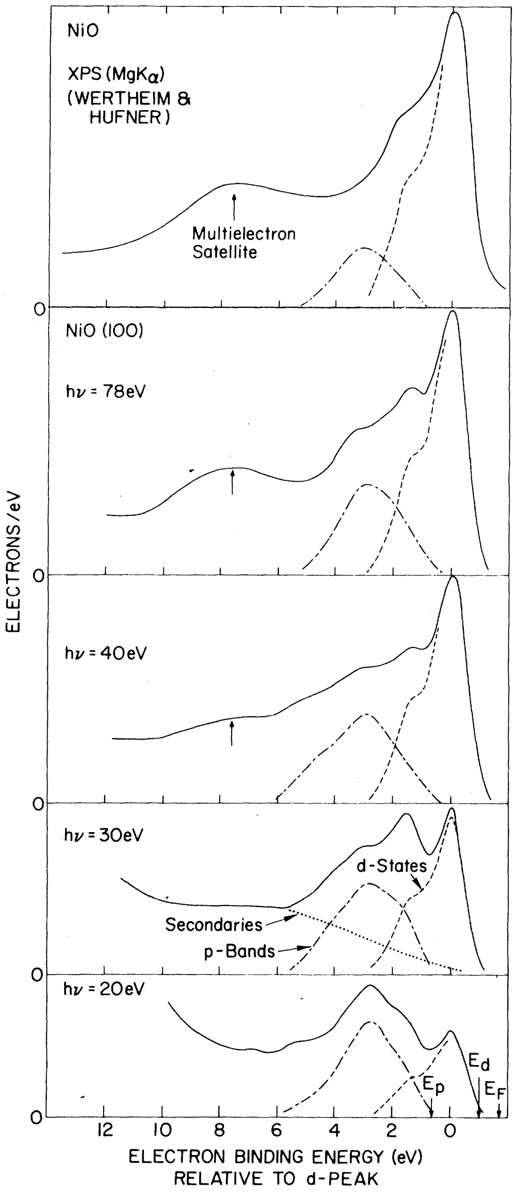

FIG. 1. PED's for NiO. The zero of energy is placed at the d-state peak and E_F, E_d, and E_p are the Fermi energy, d-state edge, and p-band edge. Partial d-state emission intensities (dashed lines) and p-band intensities (broken lines) are shown (see text).

difference of two PED's (e.g., for $\hbar\omega_1 = 20$ eV and $\hbar\omega_2 = 40$ eV) such that the p-band emission at $E \simeq 3$ eV vanishes. The resulting difference gives us the spectral shape $\overline{N}_d(E)$ of the d-state emission. N_d is determined by scaling $\overline{N}_d$ to the full amplitude of the first d-state peak at 0 eV in $N_T(E, \omega)$ and $N_p = N_T - N_d$ is then determined.

An important *consistency check* on this decomposition method for determining N_d and N_p is given by repeating the above procedure for several independent pairs of PED's over a wide range of $\hbar\omega$'s and comparing the resultant $\overline{N}_d$'s and $\overline{N}_p$'s. We have found this procedure to be self-consistent for the transition-metal oxides we have studied. A measure of this consistency is illustrated for NiO in Fig. 1. Namely, the d-state emission density $N_d(E, \omega)$ shown is proportional to the average $\overline{N}_d(E)$ determined from several pairs of PED's for $\hbar\omega = 20$, 30, 40, and 78 eV. We have subtracted this $N_d(E, \omega) = C_d(\omega)\overline{N}_d(E)$ from all four PED's, yielding four independent $N_p(E, \omega)$'s which are all quite similar, as shown.

Before leaving Fig. 1, we point out two important effects. The structure near 8 eV is identified as a multielectron satellite feature as previously suggested,[5] rather than a p-band feature,[3] since it has negligible intensity for $\hbar\omega \lesssim 30$ eV and slowly increases at higher energies. Conversely, the relative p-band emission intensity decreases with increasing $\hbar\omega$ and becomes quite small at Mg $K\alpha$ (~1253 eV), i.e., the main 3-eV p-band peak (estimated by our decomposition method) is essentially not seen in the x-ray spectrum in Fig. 1.

For CoO, FeO, MnO, and Cr_2O_3, a data analysis similar to that described for NiO has been made, and d- and p-state partial emission intensities are summarized in Fig. 2 for PED's at $\hbar\omega = 30$ eV (at 40.8 eV for Cr_2O_3). In all cases, we have placed the zero of energy at the center of the highest d-state feature and E_F, E_d, and E_p denote the Fermi energy, d-state emission edge, and p-band emission edge, respectively. All p-band spectra are about 3 eV wide [full width at half-maximum (FWHM)], with a p-band peak from ~3 to 5 eV below the highest d-state level ($\equiv 0$ eV).

As previously mentioned, we can describe the partial d-state densities $\overline{N}_d(E)$ for NiO, CoO, FeO, MnO, and Cr_2O_3 quite well using a ligand-field-theory description in terms of $3d^{n-1}$ final-state ionization potentials. Namely, a d electron is photoionized out of the sharp $3d^n$ ground state, leaving the $3d^{n-1}$ final state in one of several possible energy states. A fractional parentage method for determining the energies and relative transition intensities of these atomiclike localized final-state d-electron configurations is described by Sugano, Tanabe, and Kamimura.[8] In this limit one may show that allowed $3d^{n-1}$ final states differ from the $3d^n$ initial state by one $3d$-electron orbital and have relative transition inten-

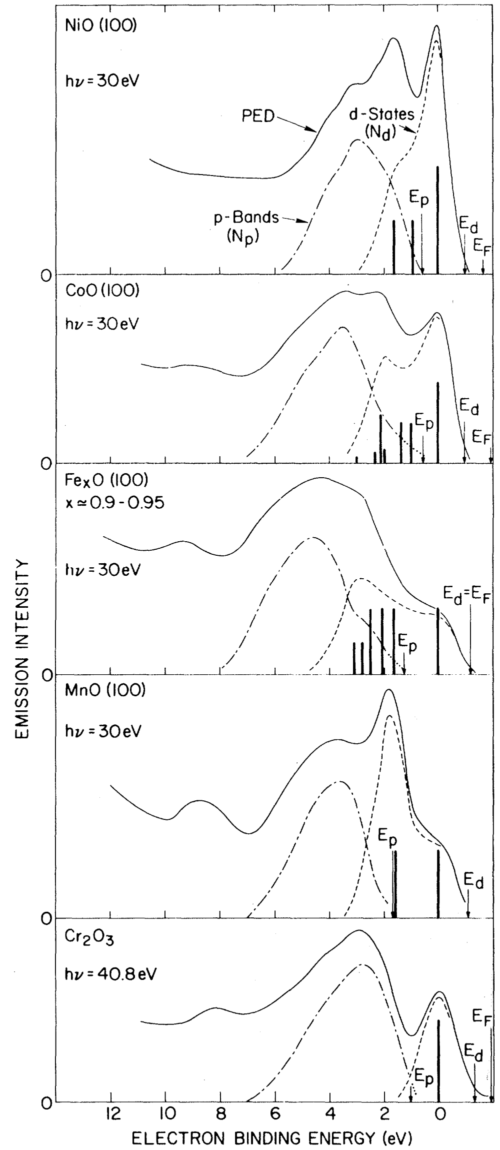

FIG. 2. PED's, partial d-state intensities $N_d(E)$, and p-band intensities $N_p(E)$ for NiO, CoO, Fe_xO, MnO, and Cr_2O_3. The vertical lines denote calculated $3d^{n-1}$ final-state ionization potentials (see text). The weak features near 8–10 eV for CoO, Fe_xO, MnO, and Cr_2O_3 are attributed to multielectron satellite peaks.

sities proportional to $(2S+1)C^2(f)$ where S is the spin and $C(f)$ the fractional parentage coefficient of the final state $|f\rangle$.[15]

We summarize ionization potentials (IP's) for $3d^{n-1}$ final states in Fig. 2 (where the heights of the heavy vertical lines are proportional to the calculated transition intensities)[16]. In our calculation, we have followed the nomenclature and description of Sugano, Tanabe, and Kamimura.[8] In summary, for NiO, CoO, FeO, MnO, and Cr_2O_3, respectively, $3d^n$ ground states are $Ni^{2+}(d^8; {}^3A_2)$; $Co^{2+}(d^7; {}^4T_1)$; $Fe^{2+}(d^6; {}^5T_2)$; $Mn^{2+}(d^5; {}^6A_1)$; $Cr^{3+}(d^3; {}^4A_2)$, and $3d^{n-1}$ final states are ${}^4T_1[\equiv 0\text{ eV}]$, ${}^2E^*[0.92]$, ${}^2_aT_1[1.64]$; ${}^5T_2[\equiv 0]$, ${}^3T_1^*[1.03]$, ${}^3T_2^*[1.42]$, ${}^3T_1[2.01]$, ${}^3T_2[2.11]$, ${}^3E[2.31]$, ${}^3A_2[3.04]$; ${}^6A_1[\equiv 0]$, ${}^4T_1^*[1.59]$, ${}^4T_2^*[2.06]$, ${}^4A_1[2.53]$, ${}^4E[2.53]$, ${}^4T_2[2.81]$, ${}^4T_1[3.13]$; ${}^5E^*[\equiv 0]$, ${}^5T_2[1.56]$; ${}^3T_1[\equiv 0]$, respectively. States with asterisks correspond to removal of an e_g electron. Final-state ionization potentials are given in square brackets; they were obtained using Racah exchange parameters B, for Ni^{3+} through Mn^{3+}, of ≈690, 660, 629, 598 cm^{-1}, respectively (i.e., ~67–70% that of the 2+ ion[17]), to obtain best overall agreement with experiment.[18] In Fig. 2, if a broadening of ~0.5–0.75 eV (FWHM) is ascribed to each calculated final-state IP, reasonably good agreement is observed with the experimental $N_d(E)$ spectra. The Mn^{3+} spectrum suggests a somewhat smaller (i.e., $\sim\times\frac{1}{2}$) emission intensity for e_g relative to t_{2g} electron excitations; if this is also true for NiO, CoO, and FeO, even better agreement occurs.

Many theoretical descriptions of NiO and other transition-metal oxides have been given [Refs. 1–4 and references therein]. We find our results consistent with the qualitative hybrid model of Adler and Feinleib.[1] Recently, this hybrid model[1] has been extended to consider various $3d \rightarrow 4s$, $2p \rightarrow 3d$, and interionic transitions.[4] However, comparison with our description indicates an error in the latter work[4] in that $3d^{n-1}$ final states are taken to be the crystal-field-split terms of the $3d^{n-1}$ ground state, rather than final states which are coupled to the ground state by the one-electron dipole operator as we have described.

A promising recent one-electron approach for studying transition metal compounds and surface complexes is the self-consistent-field X_α method.[3] However, comparison of our new results with the most recent cluster calculation[3] for NiO [actually for a $(NiO_6)^{-10}$ cluster] shows a p-d separation which is too large (~4.5 versus 2.9 eV measured) and an apparently incorrect ordering of the $3d$ final-state IP's, with the $e_{g\alpha}$ level ~0.6 eV above the $t_{2g\beta}$ level rather than at or below the $t_{2g\beta}$ level.

We wish to thank H. K. Bowen for FeO crystals.

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†Work supported in part by the Advanced Research Projects Agency and monitored by the U. S. Air Force Cambridge Research Laboratory under Contract No.

F192628-73-C-0006, the National Science Foundation under Grant No. GA35823, and the U. S. Atomic Energy Commission under Contract No. AT(11-1)3063.

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[11] Cr_2O_3 was prepared by evaporating a Cr film and oxidizing a thick surface layer to Cr_2O_3 at room temperature. Spectra for Cr_2O_3 were measured using He I (21.2 eV) and He II (40.8 eV) radiation.

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[14] This factorization is only approximate, of course, and we ignore certain p-d and s-d hybridization effects as well as possible $\hbar\omega$-dependent intensities for different p and d orbitals. We expect this partial state decomposition to be approximately valid for materials such as the transition-metal oxides.

[15] Previously (Ref. 6), transition intensities were taken to be proportional to the initial-state orbital degeneracy.

[16] This description is only approximate for at least two reasons: (1) The ratio B/C is apparently different from that used by Sugano for the ground state and this may modify his calculated energies; (2) configuration interaction between many-electron wave functions with the same $S\Gamma$ representation can alter relative intensities. However, the observed agreement (Fig. 2) suggests that the assumed model is a good first approximation.

[17] *Ab initio* calculations by P. Bagus (to be published) for ground state and ionized Ni in NiO imply $B^{3+}/B^{2+} \simeq 0.67$, consistent with our present results.

[18] Crystal-field parameters Dq appropriate for a divalent ion (Ref. 8) were used; overall widths were virtually unchanged (but e_g levels shifted slightly) by using a larger (e.g., 2.5 valent) Dq.

Surface Photoelectric Effect and Orbital Symmetry: Evidence for Anomalous Dielectric Properties

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(Received 23 September 1974)

Ultraviolet photoelectron spectra using He I resonance radiation and Ge(111) surfaces have been measured for both bonding and nonbonding orbitals. In all cases the partial photocurrent from a specific orbital is considerably enhanced for the macroscopic electric field normal to the surface independent of the orbital symmetry. This is interpreted in terms of an anomalous enhancement of the dielectric response due to surface polarization charge within the short electron escape depth ($\lambda_e \lesssim 10$ Å) at these energies.

The role of the surface in photoemission from a solid (i.e., the surface photoelectric effect) is an old topic which has been studied both experimentally[1] and theoretically[2] for more than four decades. Most experiments have concerned only the total yield which displays a strong vectorial photoeffect at low photon energy $\hbar\omega$ near threshold. Recent work has tended to concentrate on free-electron metals[3,4] but even for these materials the detailed mechanism of optical excitation is far from being completely understood[5] since both surface-plasmon effects and direct excitation are possible for $\hbar\omega \lesssim \hbar\omega_s$, the surface-plasmon energy. In contrast, high-energy photoemission ($\hbar\omega > \hbar\omega_p$) is expected[4] to exhibit a negligible surface photoeffect with optical selection rules determined by the symmetry properties of the photoelectron wave functions.[6-8] This paper reports the first systematic measurement of high-energy photoelectron energy spectra ($\hbar\omega > \hbar\omega_p$) as a function of angle of incidence for both bonding and nonbonding orbitals. The bonding orbitals