Structure of Valence and Conduction Levels in NiO

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Photoemission measurements on cleaved NiO(100) identify both the O $2p\ \pi$ valence orbitals and the previously undetected O $2p\ \sigma$ orbitals. An upper limit of 0.8 ± 0.1 eV is set on the width of the Ni $3d\ t_{2g}\downarrow$ emission. A large maximum in the empty density of states is detected in the secondary-electron spectrum, explaining previously debated photoabsorption data. We conclude from the available data that NiO is not a conventional band-gap insulator, as has been suggested recently, but is in fact a Mott insulator.

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The electronic structure of the valence and conduction levels of the antiferromagnetic, insulating, rocksalt transition-metal oxides NiO, CoO, and MnO has been the subject of controversy for many years. Of these compounds, NiO has received by far the greatest amount of attention, prompted by a remarkable range of motivations. A considerable body of experimental and theoretical literature has been generated simply in an attempt to understand basic parameters such as the energy position, width, and spectral features of the O $2p$ and Ni $3d$ valence levels.[1-7] There is disagreement in the current literature on the identification of the excitations leading to the Ni $3d$ emission and its satellite in photoemission spectra.[8,9] Also, surface studies of adsorption and catalysis on NiO are beginning to reveal the extremely interesting role of defects on this otherwise inert surface.[10] Finally, NiO is the "original" Mott insulator.[11] The majority of calculations and semiempirical descriptions of the electronic structure of NiO since Mott's pioneering work conform to the Mott insulator model, and an intra-atomic Coulomb potential, U, of 6 eV or greater has been proposed to effectively separate the occupied from the unoccupied Ni $3d$ levels.[3,12] However, recent experimental and theoretical work suggests a smaller separation between these levels,[4,13] and very recently Terakura *et al.*[6] have stated that NiO's insulating nature is determined not by U, as in Mott's picture, but by a conventional band gap created by exchange and crystal-field splittings.[4]

Photoemission[1,2,7] and photoabsorption[14-16] experiments provide nearly all of the information currently available on the NiO valence and conduction structure. Yet photoemission data prior to this study have resulted in an erroneous interpretation of the O $2p$ band structure and width,[1] and there has been no photoemission study in which the experimental resolution was significantly smaller than the observed widths of the Ni $3d$ levels. Also, there is no consensus on the origin of any of the peaks observed in the photoabsorption spectrum of NiO.

We have performed ultraviolet photoemission (UPS), electron-energy-loss (EELS), and secondary-electron spectroscopy measurements on nearly perfect, ultrahigh-vacuum (UHV) cleaved NiO(100) samples in order to clarify the nature of the valence electronic structure. Previous misunderstandings of the structure and width of the O $2p$ bands are corrected, showing the presence of both π and σ bonding orbitals, and a new upper limit on the width of the filled Ni $3d$ bands is set which is 40% narrower than previously measured values. The largest features in the photoabsorption spectrum are explained in terms of an empty band having primarily Ni $4p$ character that is centered 6.9 eV above the vacuum level. It is concluded that the insulating nature of NiO is not due to the presence of a conventional band gap, but is the result of correlation effects—i.e., that NiO is in fact a Mott insulator.

Single crystals of NiO were oriented and cut into cleavage rods of 4×4-mm^2 cross section having the (100) face normal to the rod axis. The samples were cleaved in an UHV surface-analysis system at a base pressure of less than 1×10^{-10} Torr. The (100) cleavage faces exhibited excellent (1×1) LEED patterns, and no impurities could be detected by either Auger or x-ray-photoelectron spectroscopy (XPS). The energy resolution of the spectrometer was 240 meV for UPS. Coarse but useful angular resolution of UPS spectra was obtained by simply masking the front of the cylindrical mirror energy analyzer (CMA) leaving an aperature of ± 6 degrees in polar angle and ± 30 degrees in azimuthal angle. The angle between the incident photons and the collected electrons was 117° in a {100} plane of the crystal. The vacuum level was determined from the onset of secondary electrons in the photoemission spectrum of samples which exhibited no charging. Although stoichiometric NiO is a very good insulator, it was possible to obtain pho-

toemission spectra which were free of charging effects by Ar-ion bombardment of the crystal prior to cleaving and by reduction of the photon flux.

In spite of the number of studies of NiO in the literature,[1,2,7] the width and orbital features of the O $2p$ levels have not previously been correctly determined. Angle-integrated UPS spectra of NiO(100), taken with a CMA whose axis was oriented approximately 45° to the surface normal, have led to the identification of what is actually only the poorly resolved π contribution as being the entire O $2p$ valence band.[1] (When our sample normal is positioned 45° from the CMA axis, we obtain spectra which are similar to those of the previous work.) Figure 1 displays angle-integrated UPS spectra taken with both 21.2- and 40.8-eV photons and with the CMA axis parallel to the surface normal. Initial-state energies are referenced to the peak having the lowest binding energy. The first two peaks, centered at 0 and 1.6 eV, represent Ni $3d$ emission, and the second two peaks, centered at 3 and 5.2 eV, represent emission from the O $2p$ π and σ orbitals, respectively; the same structure is seen in both spectra. In order to obtain a consistent method for describing bandwidths, each UPS spectrum was deconvoluted into four Gaussians superimposed on a secondary background. The entire O $2p$ band exhibits a full width at half maximum (FWHM) of 3.8 ± 0.2 eV.

Figure 2 displays angle-resolved UPS spectra in which the Ni $3d$ levels are clearly differentiated from the O $2p$ bands, both by the resolution of the separate peaks and by the strong angular dependence of the intensity of the O $2p$ emission as compared to the relatively angle-independent intensity of the Ni $3d$ emission. The angle between the incoming photons and the analyzer aperature is fixed, yielding a constant $\langle(\vec{A}\cdot\vec{p})^2\rangle$. The amplitudes of emission from the O $2p$ σ and π orbitals vary roughly as $\sin^2 2\theta$ and $\cos^2 2\theta$, respectively.

The ground-state symmetry of the $3d^8$ Ni^{2+} ion in NiO is $^3A_{2g}$ in a $t_{2g}^3\uparrow e_g^2\uparrow t_{2g}^3\downarrow$ configuration. Thus the conduction levels consist of empty Ni $3d$ $e_g\downarrow$ states. The emission from the localized Ni $3d$ levels can be understood in terms of a ligand-field–theory description of the $3d^7$ final states[7] or, as suggested by very recent configuration-interaction calculations, in terms of these same $3d^7$ final states as screened by a ligand $\rightarrow$ Ni-$3d$ charge transfer.[9] Three final states can result from emission of a Ni $3d$ electron.[17] The largest peak in the spectrum, at 0 eV, represents the $^4T_1$ final state and the second peak, at 1.6 eV, the $^2T_1$ final state.[7] The ^2E state, which results from an $e_g\uparrow$ excitation, is not visible as a separate peak; it is possible that ^2E is degenerate with $^4T_1$.[7]

A central element in Hubbard's treatment of correlation effects,[18] and in any discussion of conduction mechanisms in NiO and other narrow-band materials, is the $3d$ bandwidth. Various authors have estimated widths for the Ni $3d$ levels ranging from 2 eV to a few hundredths of an electronvolt.[3] The best previous photoemission spectra exhibit a $^4T_1$ peak of approximately 1.4 eV FWHM.[1] From

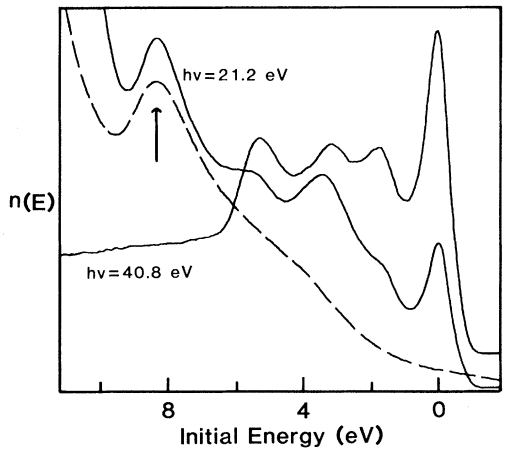

FIG. 1. Angle-integrated He I and He II photoemission spectra of the NiO valence levels (solid curves) and an electron-beam–induced secondary-electron spectrum (dashed curve; $E_p = 100$ eV).

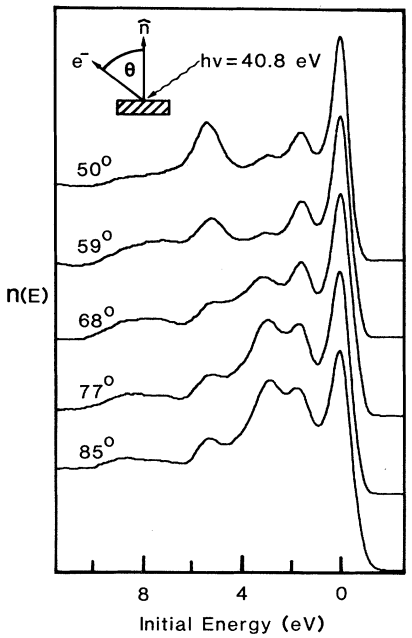

FIG. 2. Angle-resolved He II photoemission spectra of the NiO valence levels.

the data in Figs. 1 and 2, we place an upper limit of 0.8 ± 0.1 eV FWHM for the $^4T_1$ peak and 1.6 ± 0.1 eV FWHM for the $^2T_1$ peak.

The energy distribution of secondary electrons resulting from photon- or electron-induced primary excitations can reflect major features in the density of empty states above the vacuum level.[19,20] NiO provides a striking example of this phenomenon, as illustrated in Fig. 1. A large peak (indicated by an arrow), which is centered 6.9 eV above the vacuum level (E_v) and has a FWHM of 1.5 ± 0.1 eV, is visible both in the electron-beam–induced secondary-electron distribution (dashed line) and in the secondaries of the 21.2-eV UPS spectrum. (Note that this peak occurs at fixed kinetic energy.) A maximum is observed in the amplitude of this peak for emission 45° from the sample normal, and the intensity reduces to zero for either normal or grazing emission. The intensity of the peak is also dependent on the stoichiometry and perfection of the lattice; five minutes of inert-gas bombardment, which has little effect on filled levels in photoemission, reduces the amplitude of the secondary peak by one-half. The origin of this sensitivity is not understood and is currently being investigated. The intensity of this feature does not vary measurably with primary electron energy (E_p) in the range 13 to 100 eV. However, it does not appear for E_p below 13 eV, which is the minimum energy required to excite a transition from the highest filled Ni $3d$ valence level to this maximum in the empty density of states. This fact rules out processes such as Auger or plasmon decay as possible excitation mechanisms for this feature.[20] Since the energy for the Ni $3d \rightarrow$ Ni $4p$ transition is 13.7 eV in the free Ni^{2+} ion,[21] we expect this empty level to be of largely Ni $4p$ character.

Transitions to such a large maximum in the density of empty states should dominate the optical absorption spectrum. The UPS and secondary-electron emission data above show the maximum in the empty levels 6.9 eV above E_v, the Ni $3d$ levels centered 6.8 eV below E_v, and the O $2p$ band centered 10.1 eV below E_v. Therefore, in the photoabsorption spectrum, one expects structure around 13.7 eV due to transitions from Ni $3d$ levels to the empty level and a broad peak at 17 eV due to transitions from the O $2p$ band. This is in agreement with the photoabsorption spectrum of Powell and Spicer,[15] where the major peaks are observed at 13, 13.8, and 17.6 eV.

The theoretical model of the valence electronic structure of NiO which compares most satisfactorily with our photoemission data is the recent band calculation of Terakura *et al.*[4] However, those authors and others have suggested recently that NiO is a conventional band-gap insulator,[6,22] with the $t_{2g}\downarrow$ electrons forming the highest occupied valence band and the empty $e_{g}\downarrow$ states the conduction band.[6] This is not in agreement with the sum of the experimental data, which shows that the intra-atomic Coulomb energy, U, is well in excess of the bandwidth. U is determined as follows. In the usual Hubbard model one employs $E_g^{\text{eff}} = U - B$, where E_g^{eff} is the effective band gap for carrier creation and B is the bandwidth. As has been pointed out in several papers,[6,23] $U - B$ is not the only contribution to the energy needed for the interatomic $t_{2g}\downarrow \rightarrow e_g\downarrow$ transition in NiO since both optical absorption data[14] and EELS[24] show the intra-atomic $t_{2g}\downarrow \rightarrow e_g\downarrow$ transition centered at 1.1 eV. This is accounted for by modifying the equality to read $E_g^{\text{eff}} = U - B + 1.1$ eV. The $t_{2g}\downarrow$ valence level, as we have shown, has a FWHM of < 0.8 eV; the $e_g\downarrow$ conduction band should be of equal or smaller width.[6] The experimentally determined activation energy for conduction in stoichiometric NiO indicates an effective band gap of at least 3 eV.[14,22] This results in $U = 2.7$ eV, which is greater than three times the bandwidth of 0.8 eV. Nonmetallic behavior is therefore expected without considering the conventional band gap, and we conclude that NiO is in fact a Mott insulator.

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