Magnitude and Origin of the Band Gap in NiO

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Photoemission and bremsstrahlung-isochromat-spectroscopy data on a cleaved NiO single crystal are presented and compared to band- and cluster-theory predictions. In contrast to band-theory predictions the band gap is found to be large but not determined solely by the even larger d-d Coulomb interactions so that NiO is not a Mott-Hubbard insulator in the simplest sense. A large d-d interaction need not prevent NiS from being a metal.

After four decades of intense experimental and theoretical investigations the electronic structure of transition-metal compounds remains highly controversial. This is evidenced by recent presentations[1,2] of sophisticated versions of the two extreme points of view, which have existed since 1949,[3] concerning the electronic structure of NiO. The two approaches make clear predictions concerning the structures which should be observed in electron ionization (photoelectron) and electron affinity (inverse photoelectron) spectra, as well as in the electron-conserving optical spectroscopies. The most striking difference between the two approaches concerns the magnitude of the charge-transport or conductivity gap. Density-functional theory[1] predicts a gap of 0.3 eV, whereas the local-cluster[2] approach including configuration interaction predicts a gap of 5 eV. The main reason for the differing results is that the effective one-electron potential of the density-functional theory utilizes the charge distribution of the ground state in determining the energies of all excited states. This procedure then assumes at the outset that there is no change in the d-d Coulomb repulsion energy for the charge distributions of the unbound hole-electron pair excitations required for d-charge transport, whereas in the cluster approach an extra d electron at one site and a missing d electron at another site give an increase in the energy equal to U_{dd}, the Coulomb repulsion between pairs of d electrons on a site. The importance of a large Coulomb interaction U_{dd} is implicit in the now commonly accepted Anderson superexchange theory,[4,5] and is fundamental to the concept of the Mott-Hubbard insulator.[3,6]

In this Letter we report combined x-ray–photoemission (XPS) and bremsstrahlung-isochromat-spectroscopy (BIS) measurements of cleaved single crystals of NiO. We show experimentally that the above mentioned gap is 4.3 eV with no detectable structure in the gap. We also locate the positions of the $4s$ and $4p$ bands as well as a high-energy Ni-$3d$–related peak (18 eV) predicted by the local-cluster theory and a comparison is made with optical data. From the data presented and the cluster-approach identification of the structure seen in XPS and BIS we argue that NiO is not a Mott-Hubbard insulator in the simplest sense but that rather the large band gap is indirectly caused by a large d-d Coulomb interaction in combination with one-electron energies involving the O $2p$ as well as the Ni $3d$ states. This forces the recognition that a large d-d correlation energy is a necessary but not a sufficient condition for obtaining a large band gap in a transition-metal compound.

A highly stoichiometric single crystal of NiO obtained from Keem, Honig, and van Zandt[7] was cleaved in a vaccum of 7×10^{-11} Torr, exposing a (100) face, and transferred under the same vacuum conditions to the measurement chamber of a VG ESCALAB electron spectrometer. The surface so obtained was found (by means of XPS) to be void of any trace of carbon or of an extra oxygen peak.[8] The surface remained unchanged during the course of the XPS and BIS measurements and remained free of any detectable change for several days after the measurement. LEED studies[9] of the (100) surface have also demonstrated the extreme stability of the surface and have shown it to be very close to a simple termination of the bulk crystal structure.

In the BIS experiment the highly insulating sample charged by an amount which decreased exponentially with increasing temperature, suggesting a temperature-activated electron mobility ($E_A \sim 0.20$ eV).[10] By measurement of the BIS peak positions at 200 °C for sample currents ranging from 10 to 125 μA, and then extrapolation of the linear dependence to zero current, the BIS spectrum was fully corrected for charging. In the XPS experiment charging did not occur, as shown by variation of the x-ray intensity and by comparison of the O $1s$ and Ni $2p$ binding energies to those obtained on thin oxidized Ni films.[11]

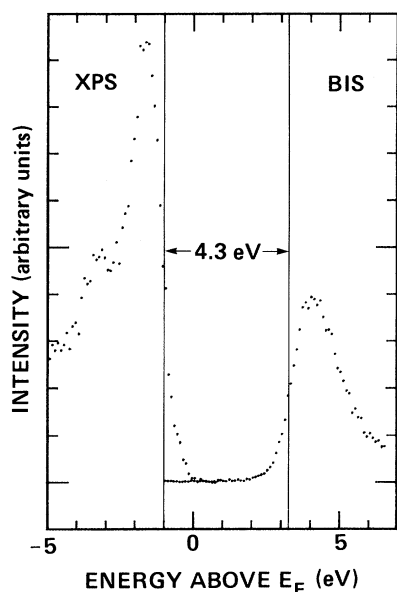The combined XPS-BIS spectra in the gap region

FIG. 1. XPS and BIS spectra of NiO showing the 4.3-eV band gap. Both were collected with a photon energy of 1486.6 eV.
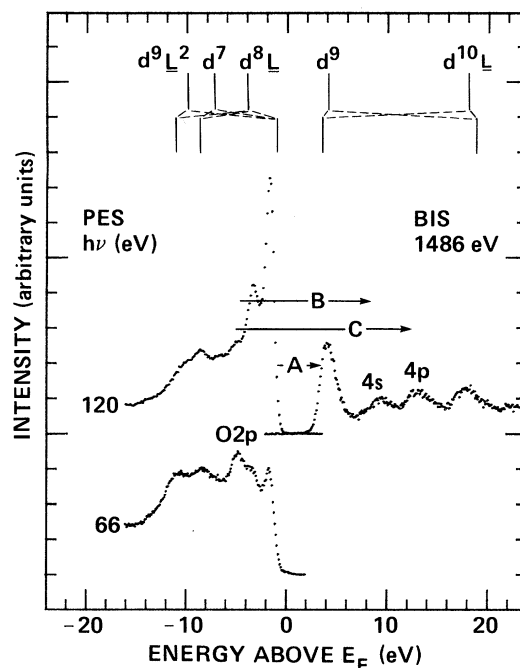

FIG. 2. Complete valence-band structure of NiO. The bar diagram shows the assignments of the peaks according to the local-cluster calculation. Also indicated are the positions of the 4s and 4p bands. The arrows indicate the expected energies of the nonexcitonic optical transitions.

are shown in Fig. 1. The spectra were scaled in intensity according to the nominally expected ratio of d electrons to d holes of 8:2. Since the edge structure in both XPS and BIS exhibits a width corresponding to the experimental resolution of 0.6 eV full width at half maximum, determined from Ag Fermi edge spectra, both the valence- and conduction-band edges must have extremely sharp cutoffs. On this assumption the band gap is 4.3 eV, measured as indicated in Fig. 1.[12] The BIS peak at 4 eV above the Fermi level is identical in position to the major peak observed in oxidized Ni crystals.[13] However, except for tailing into the band gap caused by the experimental resolution, there is no detectable structure in the gap, which shows that structure found nearer the Fermi level in oxidized Ni[13,14] is not intrinsic to NiO. Such structure appeared only after intense argon-ion bombardment and was accompanied by the appearance of an extra O 1s structure and a change in the Ni 2p line shapes, suggesting defect formation. Thus the measured intrinsic gap of NiO has nearly the value predicted by the local-cluster approach, and is an order of magnitude larger than predicted by the band theory.

In Fig. 2 we combine BIS and previously published[15] resonant photoemission spectra from the same sample to show the complete valence-band structure. The bar diagram at the top is a qualitative picture of the structure expected from a local-

cluster model for NiO, as proposed by Fujimori and Minami.[2,16,17] In this approach a $(NiO_6)^{10-}$ cluster is treated as a separable unit and its electronic structure is described by configuration interaction. Although translational symmetry is ignored, local interactions can be treated explicitly. The most important interactions included are the d-d Coulomb interactions and the O $2p$–Ni $3d$ hybridization. This is done by consideration of the two-hole configurations contributing to the ground state (d^8, d^9L and $d^{10}L^2$), the one-hole states contributing to the electron-affinity (BIS) spectrum (d^9 and $d^{10}L$), and the three-hole states contributing to the ionization (XPS) spectrum (d^7, d^8L, d^9L^2, and $d^{10}L^3$). Holes are defined relative to filled $3d$ and ligand (O $2p$) states and L denotes a ligand hole. The conductivity gap is then given by the minimum energy required to remove an electron from one such cluster plus the minimum energy required to add it to another such cluster. The optical spectrum includes, in addition to the intercluster transitions, also the intracluster transitions given by various possible two-hole states of a cluster. These latter transitions will be highly localized (excitonic) provided their energies lie inside the conductivity gap.

A $d^{10}L$ peak is expected to occur at 18 eV in BIS

and to have 15–20% of the total BIS d weight. Such a peak is observed. The peaks labeled $4s$ and $4p$ appearing at 9.5 and 13.5 eV, respectively, are in the same energy region and have a splitting similar to that obtained from band-structure calculations.[18] The $h\nu = 120$ eV spectrum, which is dominated by Ni $3d$ emission,[19] exhibits a strong satellitelike structure which, in the cluster model, is assigned to d^9L^2 and d^7 final states. Especially the latter should show a strong resonant behavior at photon energies corresponding to the Ni $3p$ absorption edge, in agreement with experiment.[14,20] In the $h\nu = 66$ eV spectrum, where the d^8L peaks are resonantly depressed, the nonbonding and therefore predominantly O-$2p$-like states centered 4 eV below the Fermi level can easily be seen. The arrows A (4.3 eV), B (13.5 eV), and C (17.3 eV) in Fig. 2 correspond closely to structures found in the optical absorption spectrum,[21] although the strong absorption edge at 3.8 eV is well below our predicted conductivity gap. This and the fact that the 50% point of the photoconductivity edge[22] also occurs well above 3.8 eV indicate that the absorption edge has an excitonic nature. Because of configuration interaction the first ionization peak has much d weight even though the final state is of primarily d^8L character.[23] Since the first affinity structure is d^9 this optical transition is then of a mixed character,[2] predominantly charge transfer involving two Ni sites, but with the transition matrix element strongly mediated by the intervening ligand.

We note that although the density-functional calculation does badly for the fermion excitations of NiO, it provides an extremely good description of the ground state, even predicting its antiferromagnetic nature,[1] and also predicts low-energy excitations of the same type and in the same energy range (< 4 eV) as the Frenkel-exciton $d \rightarrow d$ transitions[24] which are observed in the optical spectrum and cause NiO to be green. We speculate that this is because the ground-state charge density is being used to determine the potential for describing excited states, a procedure which will be most accurate for states in which the density is little changed from the ground state, i.e., the localized excitonic $d \rightarrow d$ states. This view is rather radically opposite to that usually taken, namely, that band theory provides a good description of the delocalized rather than the excitonic excitations.

In the picture emerging from the spectroscopic results of Fig. 2, NiO is not a Mott-Hubbard insulator in the simplest sense. The d-d Coulomb interaction required to produce the predominantly d^7 (XPS) and d^9 (BIS) structures is about 7–9 eV.[25]

However, there are other states (d^8L) which fall *inside* this correlation gap, causing the charge-transport gap to be much smaller and in fact determined to a large extent by the electronegativity of the ligand. It is therefore quite possible to reduce this conductivity gap to zero even though the d-d Coulomb interaction remains large by the simple choice of a ligand with a smaller electronegativity, as in a sulfide, telluride, or selenide. The situation would then be identical to that commonly assumed for mixed-valent rare-earth chalcogenides,[26] except that the sharp state has penetrated the top of the valence band instead of the bottom of the conduction band, and would have all the well-known theoretical complexities of a lattice of large-U local orbitals degenerate with and hybridized to a continuum. In this case, of course, the local-cluster approach would not be able to describe the ground state and low-energy excitations.

In conclusion, we have found experimentally that the intrinsic charge-transfer gap in NiO is 4.3 eV. The Ni d-d Coulomb interaction is between 7 and 9 eV leading to a large correlation gap in the Ni d band. However, we have also found that O $2p$ hole states lie inside the d correlation gap so that NiO is not a Mott-Hubbard insulator in the simplest sense. This energy-level structure can then also qualitatively describe the metallic behavior of NiS even though the Ni d-d Coulomb interaction may be comparable to that in NiO.

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[25]The energy separation between the bare d^7 and d^9 states shown in Fig. 2 is $U + 2\Delta$, where Δ is the hybridization shift of the ground state due to Ni $3d$-O $2p$ mixing (labeled E_8 in Fig. 8 of Ref. 2). The uncertainty in U is due to the uncertainty in Δ, reasonable fits to the specturm being obtained for 1.0 eV $< \Delta <$ 1.5 eV and 8.5 eV $> U >$ 6.75 eV. $\Delta/2$ is also equal to the σ-bonding covalent contribution to the crystal-field splitting $(10Dq)_{cov}$ and hence, with Eq. (33) of Ref. 4, can be used to evaluate the superexchange interaction as $J_{eff} = 2(\Delta/6)^2 U^{-1}$, yielding 81 K $< J_{eff} <$ 220 K, which can be compared with $J_{eff} = 260$ K inferred from the experimental Néel temperature of 520 K with use of the molecular-field theory. If, as seems likely, the U appropriate to the superexchange calculation is the smallest ionization-energy/electron-affinity difference for the d electrons, i.e., the hybridization-screened (Ref. 23) U value given by the 4.3-eV gap, the range in Δ yields 160 K $< J_{eff} <$ 345 K.

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