

Electronic structure of NiO

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A comparison of photoemission and inverse photoemission results on NiO and NiS shows that the optical gap in NiO can consistently be interpreted as a $p \rightarrow d$ transition.

The understanding of the electronic structure of transition-metal compounds is a long-standing problem and NiO has played the role of a prototype material for this question.¹ The present discussion deals with the question of whether this material is an insulator because of its large $d-d$ correlation energy (U)² or because of an exchange splitting in the d electron band.³

A combined photoemission (PES) and inverse photoemission (BIS) spectroscopy study of NiO in the uv regime⁴ and the x-ray regime⁵ showed that the charge transfer gap in this material is of the $p \rightarrow d$ type and that the experimental data are in agreement with a localized cluster calculation⁶ but less so with a band-structure calculation.³ The $d-d$ correlation energy deduced from these experiments was of the order of 10 eV.⁷ The interpretation of the BIS and PES data has been discussed by two recent publications.^{8,9}

Merlin concludes that the optical gap in NiO is a transition of the type $2d^8 \rightarrow d^8L^{-1} + d^9$.¹⁰ This means that the transition involves two Ni ions. The first ion loses an electron where the hole is screened out by a ligand-to-metal charge transfer and the second ion gains the electron. Williams, Kübler, and Terakura⁹ disagree with this view and interpret the optical absorption gap at 4 eV as a $p \rightarrow d$ transition (a transition that involves only one Ni ion) stating, however, that the experiment of Sawatzky and Allen⁵ is inconsistent with this interpretation. However, the data of Sawatzky and Allen⁵ and of Hüfner, Osterwalder, Riesterer, and Hulliger⁴ are basically in agreement, and the latter authors use them to interpret the optical gap as a $p \rightarrow d$ transition (one-ion transition). Thus, the optical absorption gap is given two different interpretations with respect to the number of Ni ions that are involved in it. In addition, electron spectroscopy and inverse electron spectroscopy data are said to support a $2d^8 \rightarrow d^8L^{-1} + d^9$ transition⁸ which contradicts the theories⁹ and are used to assign the optical gap in NiO to a $p \rightarrow d$ transition.⁴

The origin of this inconsistency is twofold. First, the meaning of the notations used seems misleading, and second, Hüfner *et al.*⁴ and Sawatzky and Allen⁵ incorrectly placed the optical gap in their measured spectra. Since these two problems are intimately connected with each other they will be dealt with in common. The difficulties can be outlined with respect to the data in Fig. 1, which show a combined PES and BIS spectrum of NiO. It is tempting to place the optical gap transition between the first peaks below and above the Fermi energy roughly of the half heights of the peaks.^{4,5} This means, however, that if the interpretation of the peaks is taken seriously, the gap energy corresponds to a $2d^8 \rightarrow d^8L^{-1} + d^9$ transition as implied, e.g., by Merlin.⁸

The state d^8L^{-1} , however, is a localized hole state (a screened hole in the d state) and therefore is lowered with respect to the Fermi energy, which is at the top of the valence band. The analysis of Hüfner *et al.* shows that this binding energy is 2 eV (Ref. 11) (from a comparison of PES and Auger energies), which agrees very well with the peak energy for the d^8L^{-1} state observed in the PES experiments (see Fig. 1).

At this point the use of the term Fermi energy in a material like NiO has to be inspected more closely. In an insulator this energy is in the middle of the gap. However, transition-metal oxides are defect structures with excess oxygen, which have Ni^{3+} ions that act as acceptors, pinning the Fermi energy at the top of the valence band,¹²⁻¹⁴ which is the oxygen $2p$ band. In the samples used in the experiment, namely thin NiO films on Ni, charging problems do not occur. The problem can be made more evident by a comparison of NiO and NiS, where NiS is a metal at room temperature. The spectrum of NiS clearly shows the Fermi energy (Fig. 2), and also indicates that it is at the top of the S $2p$ band. The d^8 final-state structure, namely, $3d^8L^{-1}$, is sitting on the valence band with its center more than 1 eV below E_F . If in metallic NiS the localized hole state has a binding energy of more than 1 eV, then in insulating NiO the binding energy must be even larger, and therefore a

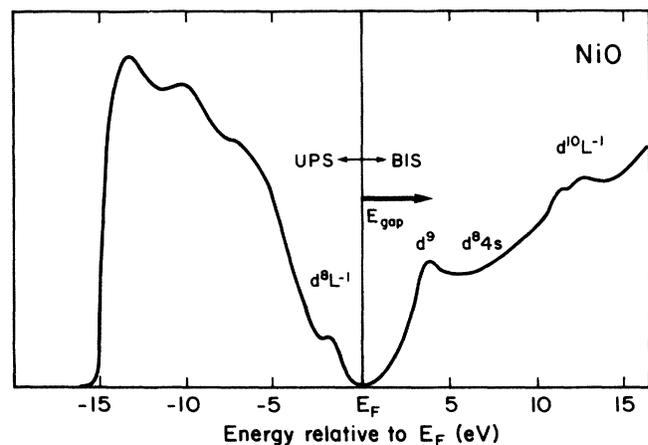


FIG. 1. Combined ultraviolet photoemission spectroscopy (UPS) (21.2-eV) and BIS (9.7-eV) spectra of NiO grown as a thin film on a bulk Ni sample. The Fermi energy is that of the Ni below the oxide layer. Since NiO is a p -type material, the Fermi energy will be close to the top of the oxygen valence band.

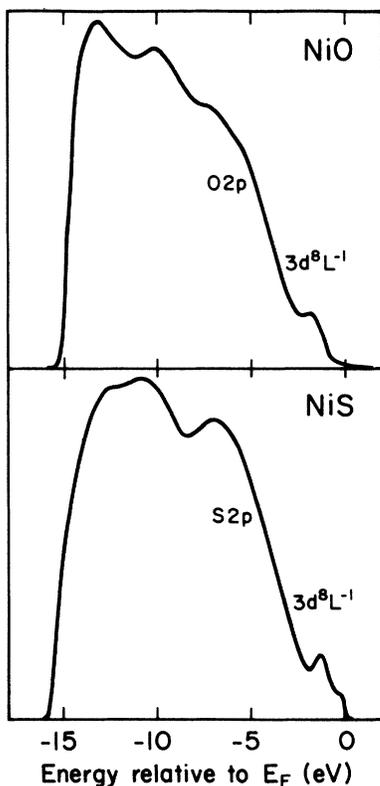


FIG. 2. Comparison of UPS (21.2-eV) spectra of NiS and NiO. In NiS the Fermi energy is clearly visible and the $3d^8L^{-1}$ final state is clearly below E_F , sitting on the $S2p$ valence band.

binding energy of 2 eV for the Ni hole states in NiO is not unreasonable.

A comparison of the BIS data of NiO and NiS (Fig. 3) further stresses the point. In NiS the d^9 state intersects the Fermi energy as expected. Note that a simple-minded comparison with the PES data of Fig. 2 would indicate a gap of 1 eV for NiS, namely, if it is assumed to be of the type $2d^8 \rightarrow d^8L^{-1} + d^9$. In NiO the d^9 state is at 4 eV above E_F . In the BIS experiment an intense current of electrons impinges on the sample. Thus if the NiO sample used were of good insulating nature, the Fermi energy in this experiment would be shifted to the bottom of the conduction band, and therefore also in this experiment the d^9 state would intersect the Fermi energy as in NiS. The fact that this obviously does not happen shows that the NiO samples used were strong p -type materials.

From these data the following facts emerge. A hole in the d state screened by a ligand valence electron has a binding energy different from that of a hole in the valence band. In a p -type material like NiO the Fermi energy is close to the top of the valence band, which is the oxygen $2p$ band. Thus, in Fig. 1 the gap energy is not the transition between the d^8L^{-1} PES final state and the d^9 BIS final state, but rather a transition from the top of the oxygen valence band (situated near the zero of the energy) and the BIS d^9 final state, which also gives the correct energy of 4 eV. The optical gap in NiO can thus properly be termed a $p \rightarrow d$ transition.

In other words, the gap transition is a transition out of

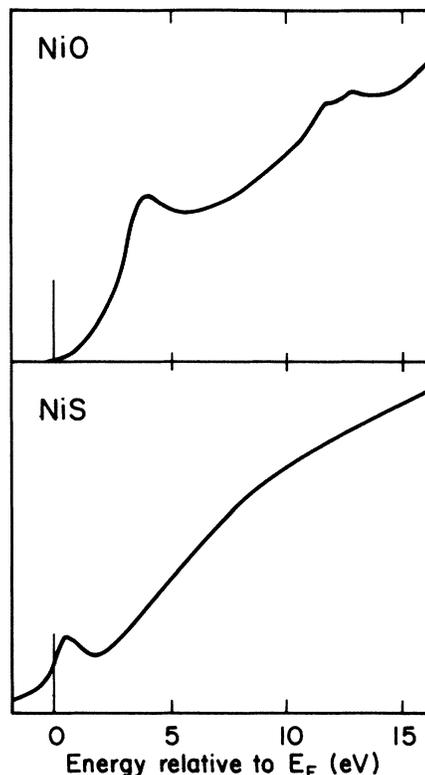


FIG. 3. Comparison of BIS spectra (9.7 eV) of NiS and NiO.

the oxygen valence band, leading to a final state which consists of a hole in the valence band, screened by other oxygen valence electrons yielding a small final-state energy. On the other hand, a transition out of the d^8 manifold can lead to a final state which consists of a d hole screened by a ligand-to-metal charge transfer and which is written in the

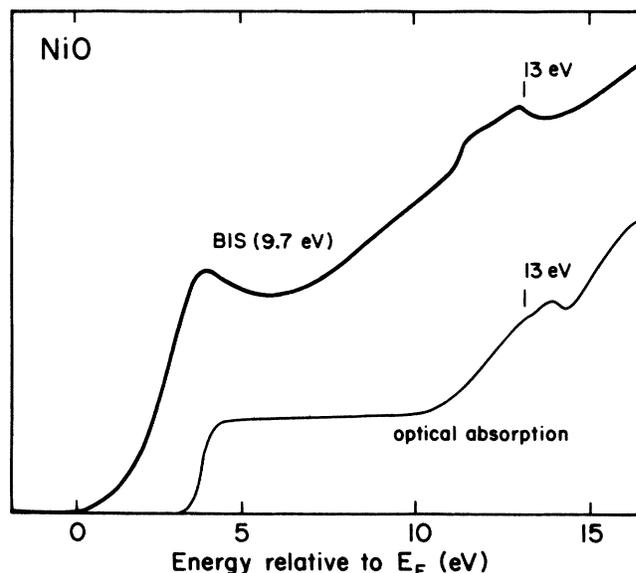


Fig. 4. BIS spectrum (9.7 eV) and absorption coefficient of NiO (Ref. 16).

cluster language as d^8L^{-1} . This state has, however, as shown above¹¹ a binding energy of ~ 2 eV relative to the Fermi energy. Thus, the two transitions $p \rightarrow d$ (charge transfer, one ion) and $2d^8 \rightarrow d^8L^{-1} + d^9$ (two ions) differ by ~ 2 eV in energy. This is the energy difference (see Fig. 1) of the transition from the Fermi energy to the first peak in the BIS spectrum, and that between the first peak in the photoemission and the BIS spectrum.

The reasoning is, in general, in agreement with the results from cluster calculations,⁶ and also in part with the band-structure calculations³ as far as the position of the energy bands goes. However, the comparison between the NiO and the NiS data makes it especially difficult to assign an insulating gap of ~ 0.5 eV produced by the e_g exchange splitting to NiO. The data as they stand rather favor a mechanism in which there is a competition between hybridization (which

tends to destroy insulation) and correlation between the d electrons (which tends to produce insulation).¹⁵

Finally, we show in Fig. 4 an interesting comparison between the 9.7-eV BIS spectrum of NiO and its optical absorption.¹⁶ The data are quite similar and seem to indicate that in the energy range shown, the optical absorption is dominated by transitions out of the p -like valence band into the conduction band in NiO.

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¹⁰The description of a hole state, produced in a PES experiment

varies. Recently, the notation \underline{L} , for a hole in a ligand state has come into use. This is, however, misleading because in printing it leads often to a bold L , and sometimes the bar is forgotten. Other authors have used the notation L for a ligand hole which can be confused with a filled ligand state. We therefore adopt the notation L^{-1} for a hole in the ligand state.

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