Electronic Structure of NiO

Three recent Letters[1-3] have addressed anew the problems posed by the determination of the electronic structure of NiO. These papers focus particularly on the questions of the origin of the $\sim$4-eV absorption edge, the magnitude of the correlation energy U_d, and the width W_d of the d band. The conclusions of the Letters are markedly different. The band-structure calculation of Terakura *et al.*[1,4] predicts $U_d \sim W_d \sim 1$–2 eV and a 0.3-eV gap separating occupied from empty d states. The $\sim$4-eV edge is ascribed to transitions out of the oxygen $2p$ states into the d band.[1,4] Sawatzky and Allen[2] find experimentally that the intrinsic charge-transfer gap in NiO is 4.3 eV. They also show their results to be consistent with local-cluster theory[5] giving $U_d \sim 7$–9 eV and an identification of the gap in terms of predominantly $d^8 + d^8 \rightarrow d^8L + d^9$ intercluster transitions (L denotes a ligand $2p$ hole).[2] McKay and Henrich[3] *implicitly* assign the $\sim$4-eV gap to $d^8 + d^8 \rightarrow d^7 + d^9$ excitations in the course of determining $U_d \cong 2.7$ eV and $U_d/W_d > 3$.

To support the contention that U_d is in the range 1–2 eV, Terakura *et al.*[1,4] recall earlier data[6] suggesting the presence of empty states within the gap in oxidized Ni, and also results[7] of resonant Raman scattering (RRS) by two-phonon and two-magnon excitations in NiO. McKay and Henrich[3] also refer to these works[6,7] as providing evidence against large values of U_d. The reported[6] structure in the gap was recently shown not to be intrinsic to NiO.[2] In this Comment, I show that the link between the RRS data and $U_d \sim 1$–3 eV does not actually exist. The correct interpretation of RRS leads rather to agreement with local-cluster calculations[5] which put U_d in the range 7–9 eV.[2,5] The available evidence provides a definitive answer to the question of the nature of the $\sim$4-eV gap.

In the $\sim$1.9–3.8-eV range of photon energies, the RRS spectra of NiO show a factor of $\sim$100 enhancement of all two-phonon features and a flat response of the two-magnon peak.[7] Two-magnon RRS in transition-metal compounds probes the contribution of d orbitals to the initial state of an allowed optical transition.[7] Accordingly, the absence of a two-magnon resonance indicates that the gap is due to largely $2p \rightarrow 3d$ excitations,[7] i.e., either $d^8 \rightarrow d^9L$ or $d^8 + d^8 \rightarrow d^8L + d^9$. This identification is the main and *only* conclusion that can be drawn from the RRS data. Contrary to what is indicated in Refs. 1, 3, and 4, RRS does not bear on the question of the presence of empty d states close to the top of the valence band in NiO.

At the time the RRS experiments were reported, they appeared to be in conflict with the then widely accepted assignment of the photoemission peaks at $\sim$2 and $\sim$3.5 eV below the Fermi level to final states of the d^7 configuration.[8] This situation might have led to the belief[1,3,4] that the RRS data imply $U_d \sim 1$–3 eV. In fact, the most recent photoemission work[2,8] is consistent with the RRS results. All the evidence together strongly point to a predominantly $d^8 + d^8 \rightarrow d^8L + d^9$ character of the $\sim$4-eV gap.

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