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Spin-Electron Interactions and the Band Structure of NiO*

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Recent theories of the band structure of NiO tend to emphasize the important role played by the coulomb correlation energy as originally suggested by Mott (*Proc. Phys. Soc. (London)* **A62**, 416 (1949)) many years ago. Electron and optical spectroscopic studies of the occupied valence bands have so far failed to identify evidence in the band structure which clearly define effects due to the correlation energy. While electron energy loss and soft X-ray absorption spectra reveal excitations from core levels to the empty $3d$ bands, it is impossible to determine the energy of these bands relative to the occupied d bands because of the strong core hole–electron binding energy. Nevertheless, a number of spectroscopic experiments have been performed which can be interpreted in terms of a Hubbard Model near the atomic limit. Multiple magnon scattering observed in Raman experiments suggests that the hopping matrix element t for d electrons is of the order of 1 eV or larger. Multiple magnon emission observed in inelastic tunneling in Ni–NiO–Pb junctions demonstrates spin-polaron formation with a mean coupling constant of at least 2. Both types of experiments suggest that the important conduction occurs in the $3d\ e_g$ band.

I. Experimental Evidence for the Band Structure of NiO

Over the past two decades a considerable amount of effort has been devoted to investigations of the electronic energy band structure of transition metal compounds such as NiO, with the basic aim of determining why they are metals or, as with NiO, insulators.

As is well known, the important difference between NiO and ordinary ionic semiconductors or insulators such as ZnO or MgO is that the cation, Ni^{2+}, contains a partially filled $3d$ shell, in this case eight electrons or two holes. Most recent investigators agree with Mott (*1*) that the reason NiO is not a metal is that the empty $3d$ states are split off from the filled $3d$ band by the coulomb correlation energy U (which is the repulsive energy when two electrons are found on the same site), resulting in an effective band gap of several volts.

Since the correlation energy is difficult to include in realistic band structure calculations, it is often ignored with the result that such calculations predict metallic behavior (*2*). The alternative is to attempt to use oversimplified but solvable models based on the Hubbard Hamiltonian to predict order of magnitude estimates of band widths, activation energies, and mobilities. Such an approach has been made by Brinkham and Rice (*3*) which gives considerable insight to systems such as NiO that are in the atomic limit of narrow, half-filled d bands. The object of this paper is to review recent experiments which bear on the effects of the correlation energy on the band structure and its consequences for d-band conduction in NiO.

(*a*) *Occupied Bands*

In Fig. 1 we show some recent XPS data of Wertheim and Hüfner (*4*) measured on a NiO film grown epitaxially on a single crystal of Ni. The two sharp peaks may be associated with the d-band density of states, while the peak at 21 eV may be assigned unambiguously to the O $2s$ band. The broad band at 9 V may belong to O $2p$, but Hüfner and Wertheim

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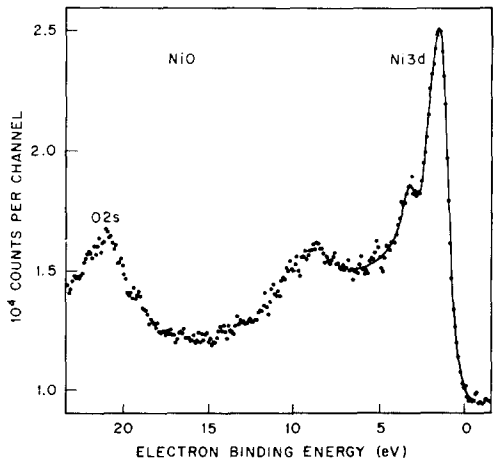

FIG. 1. The X-ray photoemission spectrum of NiO in the region of the valence bands (*4*).

(*5*) have discussed other possibilities. The resolution in this experiment was about 0.5 eV, appreciably smaller than the width of the sharp peak. As expected from transport properties, the Fermi level lies in a region of low density of states.

As has been pointed out by Hüfner and Wertheim (*5*) the energies of the assigned structure in the photoemission experiment are in good agreement with the corresponding Madelung energies, and are therefore likely to agree with calculated one-electron band structures, as they in fact do. A more crucial test would be to locate the empty 3*d* state density.

(*b*) *Unoccupied Bands*

Unfortunately, it is difficult to observe transitions from the filled to the empty 3*d* bands directly in the visible or uv absorption spectra, since these would be dipole forbidden. Furthermore, the low energy part of the spectrum is complicated by the numerous intrasite Frenkel excitons. Nevertheless, Adler and Feinleib (*6*) have suggested that a shoulder in the uv absorption coefficient at 14 eV corresponds to such an excitation, while a strong peak near 18 eV corresponds to an excitation from the oxygen 2*p* to the nickel empty 3*d* band. The basis for these assignments lay in estimates for the "relaxed" U being ~13 eV. However, in our view these assignments must be regarded as speculative since strong multielectron peaks are also seen in the electron energy loss spectrum in the same spectral region of Ni metal (*7*) for which U is small, and there are no O 2*p* states.

A less ambiguous assignment of excitations to the empty 3*d* state density can be made to features observed in the soft X-ray absorption (SXA) and electron energy loss spectra (ELS). Excitations from $3p \rightarrow 3d$ have been observed in both SXA (*8*) and ELS (*9*), and from $3s \rightarrow 3d$ in ELS (*9*). Since the energy difference between the occupied 3*d* and 3*p* or 3*s* levels may be obtained from XPS measurements (*4*), the difference in energy between the centroids of the filled and empty *d* bands, which we will call U, may be estimated by subtracting the XPS energy difference from the corresponding ELS or SXA excitation energy. The resulting energy difference is not actually U but rather $U-V$ where V is a measure of the coulomb binding energy of the conduction electron–core hole pair. Values for $U-V$ are summarized in Table I for NiO and, as a comparison, for Ni metal. The uncertainty in measuring $U-V$ is about 0.5 eV.

These values of $U-V$ are useful in estimating U only if $U \gg V$, or if V is known. Unfortunately V is as difficult to estimate as U, and atomic calculations (neglecting interatomic relaxation and covalency effects) indicate that, in fact, both U and V are large, of the order of 20 eV. Thus it appears that exciton effects will prevent an assessment of U when using core-level spectroscopies. Although the exciton binding energy may be somewhat smaller when the hole is mobile too, as when it is created in the *d* band, one will have the

TABLE I

TRANSITION ENERGIES FROM CORE LEVEL SPECTROSCOPIES WHICH ESTABLISH THE EFFECTIVE SPLITTING U BETWEEN OCCUPIED AND UNOCCUPIED 3*d* BANDS

	XPS (*4*)	ELS (*9*)	$U-V$
Ni: $3s \rightarrow 3d$	109.5	111.5	2.0 eV
$3p \rightarrow 3d$	65.0	66.1	1.1
NiO: $3s \rightarrow 3d$	110.0	111.5	1.5
$3p \rightarrow 3d$	65.4	65.6	0.2

additional, difficult problem of identifying the empty d-band spectral density, as discussed above.

Hüfner and Wertheim (*10*) have obtained estimates of U for several transition metal oxides on the basis of XPS data. These estimates suggest that U is an order of magnitude smaller than the atomic estimate of 20 eV given above, presumably as a result of covalency of various relaxation processes. However, we point out that some of their estimates were based on the interpretation of XPS satellite peaks which must be complicated by similar exciton corrections as discussed above for ELS and SXA measurements.

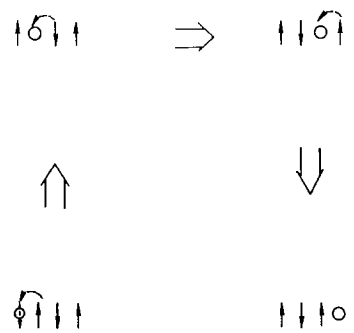

FIG. 2. The creation of spin deviations as a consequence of the propagation of a hole through a lattice of localized spins in the antiferromagnetic ground state.

II. Interaction between Localized Spins and Conduction Electrons

The basis for understanding the strong interaction between conduction particles and localized spins is most easily seen from a consideration of the Hubbard Hamiltonian:

$$\mathcal{H} = \sum_{ij\sigma} t_{ij} c_{i\sigma}^{+} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow},$$

where $c_{i\sigma}^{+}$ and $c_{j\sigma}$ denote, respectively, the creation and annihilation operators for an electron in a Wannier orbital at site i with spin σ, and $n_{i\sigma} \equiv c_{i\sigma}^{+} c_{i\sigma}$ is the number operator. The first term represents the hopping of electrons from site j to i with a hopping integral t_{ij} which we will consider to be nonzero only when i and j are nearest neighbors.

In the case of a ferromagnet, the fully occupied and empty d bands will each have a band width of $2zt$, where z is the number of nearest neighbors, and, since all of the spins are aligned, the motion of a conduction particle (hole or electron) will be unimpeded by the localized spins.

On the other hand, if we start from the ground state of an antiferromagnet, where the spins are aligned antiparallel on neighboring sites, then, as Brinkman and Rice have shown (*3*), the conduction particle scatters at every site with the consequence that the conduction band is somewhat narrowed from the $2zt$ value, and the mobility is significantly diminished. In Fig. 2, we show a portion of a linear antiferromagnet, each site containing one spin, and with a hole introduced on the first site. The hole is propagated by allowing the electron to hop into it from an adjacent site. As demonstrated in Fig. 2 each hop creates a spin deviation, thus suggesting that the interaction of the conduction particle with the lattice of spins should be thought of in terms of a large polaron.

The creation of multiple spin deviations by the motion of a conduction particle has been observed in two different types of spectroscopic experiments on NiO: Raman scattering and electron tunneling.

(*a*) *Multiple Magnons Created by Raman Scattering*

Very strong second order (*11*) and fourth order (*12*) excitation of magnons in NiO have been observed by Raman scattering. (Three magnons may not be created by Raman scattering since the electric vector of the light may not change the spin quantum number.) The second order scattering, shown in Fig. 3, has been fitted with an $S = 1$ simple cubic two-magnon Green's function, yielding the exchange integral $J_2 = 148$ cm^{-1}, in excellent agreement with the value $J_2 = 153$ cm^{-1} determined by neutron scattering (*13*). The significance of the simple cubic (SC) Green's function is that J_2 connects Ni^{2+} ions at the corners of the cube in the rock salt lattice. Neglecting the exchange interactions J_1 connecting first neighbors, which neutron scattering has determined to be small and ferromagnetic, the rock salt lattice breaks

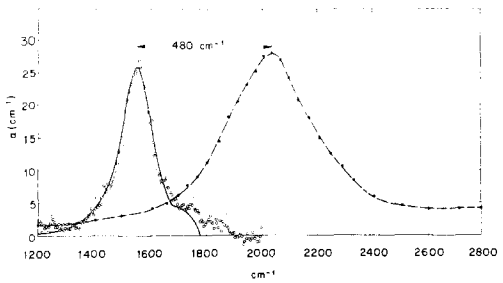

FIG. 3. Two-magnon Raman scattering in NiO. The open circles are data taken at 1.4°K using an argon laser. The solid line represents a fit to the data of a $S = 1$, simple-cubic, interacting, 2 magnon Green's function ($J_2 = 148$ cm^{-1}). The dashed line shows ir absorption (20.3°K) of the third-order process consisting of the simultaneous excitation of two magnons and one optic phonon (*11*).

up into four SC lattices, each of which behaves rather independently from a magnetic point of view. If the two magnons are created on the *same* SC lattice, then they may interact strongly via J_2, and the beautiful fit to the interacting SC Green's function ensues. Were the spin deviations created on different SC lattices, then a peak would instead be observed in the spectral density at twice the peak energy of the one-magnon density of states, or 1800 cm^{-1}.

A similar interpretation may be made of the four-magnon scattering data which is shown in Fig. 4 for NiO and $KNiF_3$. The observed four-magnon peak energy is likewise significantly lower than the value of 3600 cm^{-1} expected for four noninteracting magnons. In fact, as shown in the inset of Fig. 4a, if the two-magnon Green's function is scaled by 20/11, which is the ratio of the four- to two-magnon Ising energies, a good fit to the four-magnon data is obtained.

A visualization of the relationship between these optical results and the propagation of a conduction particle is depicted in Fig. 5. Starting with the lower left-hand corner, we represent a linear crystal of NiO of four sites, each occupied by 2 e_g electrons. The electric field of an incoming photon ε_i excites one of the e_g electrons up into a band of p character. (This could be the s–p antibonding band; alternatively, an electron from the bonding 0 $2p$ band could be excited into one of the e_g holes. Because of the symmetry between holes and electrons in the half-filled e_g band it is not possible at the present to distinguish between the consequences of these two processes.) The holes and electrons are allowed to hop as in Fig. 2, except that we assume that the electron in the p band moves with d hole because of their coulomb attraction. Each hop may be considered as an additional order of perturbation which adds a factor of $t/(E-W)$ to the scattering matrix element (E is the photon energy and W is the $d \rightarrow p$ excitation

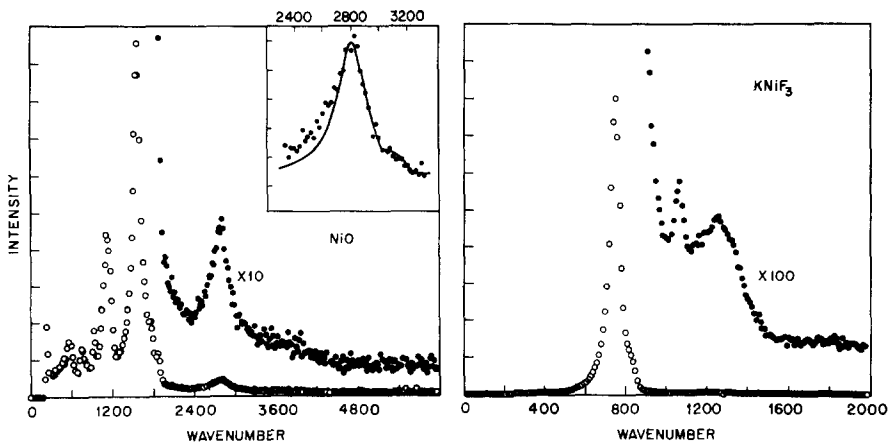

FIG. 4. Raman scattering in NiO and $KNiF_3$ (*12*). Scattering by four magnons is observed near 2800 cm^{-1} in NiO and near 1300 cm^{-1} in $KNiF_3$. The strongly scattering peaks in NiO at 1550 cm^{-1} and in $KNiF_3$ at 750 cm^{-1} are due to two-magnon processes. The other peaks arise from second-order phonon scattering.

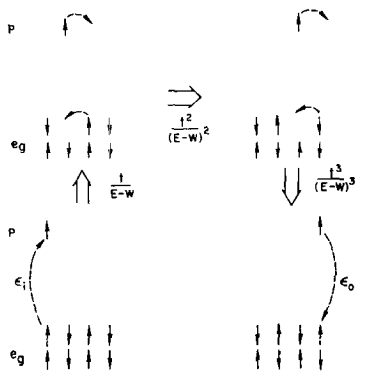

FIG. 5. A model for the multiple scattering of magnons by light (*12*).

energy). One or two hops create a two-magnon excitation, while three hops create four magnons. Finally, the hole-electron pair are recombined via the electric field of the scattered photon.

The relative probabilities of four-magnon to two- magnon scattering from the above model is $\sim(t/(E-W))^4$. Experimentally the ratio is about 1/16 in NiO and less than 1/100 in $KNiF_3$. Since in NiO $E \sim 2$ eV, $W > 4$ eV, we find $t > 1$ eV. Because of the energy considerations discussed above, we emphasize that t refers to conduction within a SC lattice. Apparently the t appropriate to hopping between different SC lattices is much smaller than the one determined above.

Another process which may lead to the creation of four magnons, combines the type of hopping process discussed above with the intraatomic or Hund's Rule exchange, J, between the p and $3d$ electrons. The lowest order of such processes will create one, two, and one spin deviations on three adjacent sites. The ratio of scattering probabilities of such a four-magnon process to the two-magnon process is then $(tJ)^2/(E-W)^4$. Assuming that J is no larger than 1 eV, which is the value of J for d electrons, then we again obtain a lower limit for t of about 1 eV.

(*b*) *Multiple Magnon Scattering by Electron Tunneling*

As a final example of the strong scattering of a conduction particle by localized spins, we show in Fig. 6 the results (*14*) of a tunneling experiment where the conductance G was measured as a function of bias applied to a junction formed from a single crystal (100) surface of Ni, on which was grown an epitaxial layer of NiO, 50 A thick, and the latter covered by a layer of Pb. The voltage derivative of the even part of the conductance is plotted vs the applied bias in Fig. 6, which gives the density of states function for the NiO. Below is the one-magnon density of states function (solid line) as determined from neutron scattering (*13*); the noninteracting two-magnon state density (dashed line) determined by convoluting the one-magnon state density with itself, and finally, the noninteracting three-magnon state density (dotted line) determined by convoluting the two-magnon density with the one-magnon density.

Three important conclusions may be drawn from these data: (1) The scattering by magnons is much stronger than by phonons (scattering by the phonons occurs below 50 meV). (2) If we neglect the fact that the magnons are not harmonic, and assume that they are excited according to a Poisson distribution, $I(n) = (e^{-S}S^n)/n!$, then the coupling constant is estimated to be at least $S \sim 2$. (3) The peaks in the spectral density corresponding to the simultaneous emission of two and three magnons have increasing energy deficits when compared to the corresponding joint densities for noninteracting magnons. In fact, the peak energies agree quite well with the peak energies indicated at the top of the figure: $2M$ indicates the two-magnon Raman

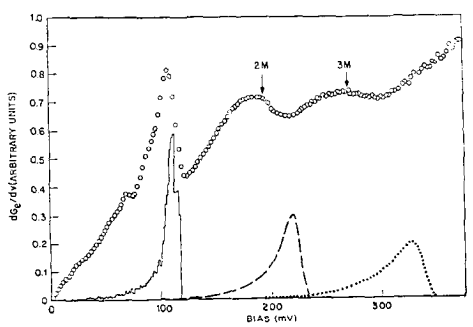

FIG. 6. Multiple emission of magnons by tunneling in NiO at 1.5°K (*14*).

peak, while $3M$ indicates a linear interpolation between the $2M$ and the $4M$ Raman peaks. As in the Raman scattering, the magnons created in the tunneling process all seem to be created on a single SC lattice, suggesting that the important transport is in the e_g bands. However, since hopping without the creation of spin deviations may occur between those first neighbors which have parallel spins, it is impossible to gauge the importance of that mode relative to the conduction in the e_g bands.[1]

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[1] I am indebted to B. H. Brandow for pointing this out to me.