BAND STRUCTURE AND ELECTRICAL CONDUCTIVITY OF NiO

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It is proposed that the dominant mechanism for electrical conduction in NiO and similar materials is by means of holes in the oxygen $2p$ band. A band-structure diagram which takes into account the primarily localized $3d$ states is suggested.

The recent optical, photoemission, transport, and Hall measurements on the well-characterized crystals of NiO that are now being grown have reopened the controversy on the mechanism of conduction in the insulating transition-metal oxides. A serious difficulty in correlating the results of the wide variety of experiments with the theoretical models has been the lack of a consistent energy-level diagram, the counterpart of the diagrams of one-electron band structure for more conventional semiconductors and metals. For the oxides, these models must show compatibility between apparently localized, crystal-field-like optical spectra on the one hand, and apparent bandlike conduction processes on the other. All previous models have attributed both the electrical conductivity and the optical absorption to the $3d$ electrons of the transition-metal ions.[1] We feel there is now sufficient available experimental evidence opposing the model of a conduction process in bandlike d levels. In this Letter, we propose a model in which the d electrons are essentially localized, the observed bandlike conduction taking place in the oxygen $2p$ bands. We shall show how the physics of the situation can be displayed on an energy-level diagram which combines one-electron band states with correlated many-body states by representing the primarily localized levels of the d electrons in terms of effective single-particle energies.

A model suitable for NiO and generally applicable to other insulating transition-metal oxides must explain the following observations:

(1) A relatively simple band model is useful for describing the d-band conduction and optical spectra of transition-metal oxides with only one or two outer $3d$ electrons per ion.[2] In contrast, without major empirical modifications for each material, ab initio band calculations do not give sufficient splittings in the energy spectrum of the d bands to obtain insulating behavior for the set of oxides MnO, FeO, CoO, and NiO, which have more than three $3d$ electrons per ion.[3]

(2) Optical-absorption measurements in the 1- to 4-eV range show a direct correspondence between the ligand-field spectrum of Ni^{2+} ions in MgO and that of NiO.[4] For the isolated ion, this spectrum consists of transitions among the many-electron, $3d^8$ multiplet states. This type of spectrum has not been demonstrated in simple band theory, since all of the localized ground and excited $3d^8$ states will have spread into a $3d$ band.

(3) The model of conduction by uncorrelated hopping of localized electrons or polarons between equivalent ionic sites requires a thermally activated mobility. This is not in agreement with recent data, which show that above 150°K thermoelectric power is proportional to $\ln\rho$,[5] indicating a relatively temperature-independent mobility. This is confirmed by many Hall-effect experiments, all of which imply that it is the carrier concentration rather than the mobility that is thermally activated.[6] The conduction above 150°K is p type.[6]

(4) Below 150°K, the evidence is very strong in favor of partial compensation of acceptors by random donors,[5,7] in agreement with an ordinary band model. At very low temperatures (20-50°K), the activation energy falls to 0.007 eV,[8] in conflict with a thermally activated hopping model but easily explainable in the language of band theory as a shallow acceptor level.

(5) High-frequency measurements indicate that at low temperatures (below 250°K) electrons hop among the sites surrounding an impurity or vacancy, but that this process does not require an activation energy.[9] However, it is found that the staying time, or time between hops, is $\sim 10^{-10}$

sec, which is much longer than lattice vibration or typical band frequencies.[9]

(6) There is an optical absorption edge at ~4 eV,[4,10] which agrees with both a photoconductivity edge at the same energy[11] and a very high temperature activation energy of 2 eV.[11] All three of these suggest that a conduction band exists 4 eV above the ground state.

(7) A change in sign of the Hall constant above 600°K,[6] if not an anomalous effect due to internal magnetic fields, could indicate the onset of a second mobile-carrier contribution—possibly electrons in the 4*s* band.

(8) NiO is antiferromagnetic below 523°K with a moment near the spin-only value.[2] This is consistent with a localized description for the *d* electrons, as is the fact that NiO remains insulating above the Néel temperature.

As suggested by (1) above, a simple band theory will not be useful to describe the insulating oxides, because the important correlations between the *d* electrons are largely neglected, permitting the overall *d* band to contain ten states and be partly filled in most cases, even when the full crystal symmetry and exchange splittings are considered. The problem of obtaining sufficient splittings is crucial in the conventional band-theory approach because polar states, those which contain one more or one fewer electrons on a site than the average, are closely spaced in energy and are therefore conducting unless the band is completely full or empty. The correlations in the atomic limit of small overlap can be taken into account by noting that if the band widths are sufficiently small, the states corresponding to having eight *d* electrons per atom will be widely separated in total energy from the states with seven or nine. In the example of pure NiO, therefore, with exactly eight $3d$ electrons per Ni^{2+} ion, the $3d^8$ levels are exactly filled at $T=0$, and NiO is an insulator.

More commonly, transport measurements are made on crystals with Li doping or Ni vacancies. Here one or two Ni^{3+} ions per Li atom or Ni vacancy are formed to maintain charge neutrality, and each Ni^{3+} ion can be viewed as a Ni^{2+} ion with a hole on it. Conduction might then take place by ionizing the hole from the Li^{+}-Ni^{3+} acceptor and having it move with either a hopping mobility or a bandlike mobility through the $3d^8$ levels. The first of these is eliminated by (3) above. The latter process would be difficult to explain in view of the optical data of (2) and the results discussed in (5). From (2), we can conclude that overlap between $3d^8$ states is essentially negligible, since the lowest excited states correspond precisely to single-ion $3d^8$ crystal-field excitations. These excited states, which we call $3d^{8*}$ states, would normally be part of the $3d^8$-band continuum if such a band existed. Thus the $3d^8$ band is unlikely to be sufficiently wide to give the reasonably high, ~1-cm²/V sec, nonactivated bandlike mobilities observed.[5,7] This conclusion is confirmed by the results in (5) above, since the bandwidth corresponding to the observed staying time of a Ni^{3+} hole is several orders of magnitude too small to be consistent with the measured mobilities. Instead of attempting to modify the simple ideas of band theory to reconcile these localized aspects of the *d* electrons with the band-like conductivity, we here propose a more natural explanation, in which conduction occurs in the oxygen $2p$ band. The nickel $3d$ electrons are taken to be essentially localized, not far removed from the atomic limit.

Consider first the left-hand side of Fig. 1, which is a schematic density-of-states curve. We have drawn the oxygen $2p$ and Ni $4s$ states as normal one-electron bands. The $2p$ band is filled and the $4s$ band is empty at $T=0$. The $2p$-$4s$ splitting is placed at 4 eV to describe the optical absorption and photoconductivity edges

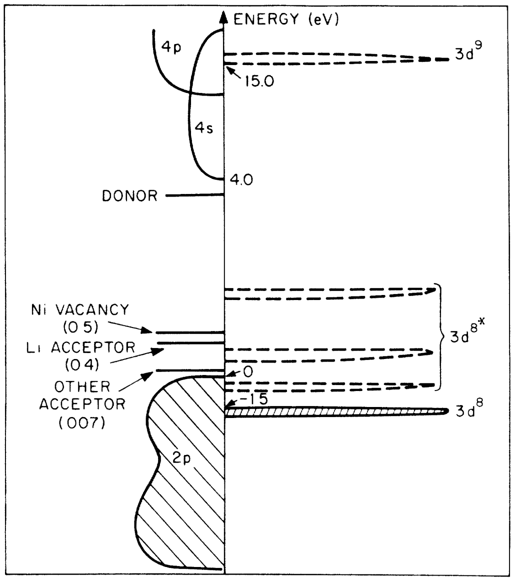

FIG. 1. Sketch of suggested density of pseudoparticle states for NiO. Conducting states are shown to the left of the vertical line, nonconducting states to the right. Shaded states are full at $T=0$; unshaded states are empty. A constant is added to all energies to set the top of the $2p$ valence band at 0.

mentioned in (6) above. Since the $3d^8$ states are filled and nonconducting, pure NiO is thus a semiconductor with an intrinsic energy gap of 4 eV.

Conduction in the doped crystal comes about as follows: Introduction of Li^+ creates a neighboring Ni^{3+} state and this complex acts as an acceptor for the $2p$ band. At low temperatures the Ni^{3+} hole can hop among the Ni^{2+} ions near the Li site and so contributes to the ac conduction, as observed in (5). At higher temperatures the acceptor is ionized, leaving a Ni^{2+} near the Li^+ and putting a hole in the oxygen $2p$ band. These holes will give the p-type band conduction which is observed at moderate temperatures (3). The measured mobility may be low because of the impurity of the material available. On the other hand, since the covalency between oxygen and Ni ions is small, as seen from the optical spectrum, the $2p$-band width would be correspondingly narrowed and should afford only low mobilities. The Li^+-Ni^{3+} acceptor ionization energy is set by the carrier activation energy, as well as by the optical ionization energy, to be 0.4 eV.[12] Other acceptor levels and donor levels will account for the variation in the carrier activation energy with doping and also the observed partial compensation mentioned in (4).

All the data cannot be described by the left-hand side of Fig. 1 alone, since we have completely neglected the d electrons. If we consider the Ni^{2+} ion to contain eight strongly interacting d electrons, then the ground state can be labeled $3d^8$ while the crystal-field excited states can be labeled $3d^8*$, as has been done on the right-hand side of the figure. These many-electron states are determined largely by the mutual repulsion of the electrons within the same ion and the perturbation of the crystal-field potential from neighboring ions. Optical excitations between these single-ion $3d^8$ spectral levels will appear as discrete structure, and those absorptions below 4 eV will be seen in the absorption spectrum of NiO before the onset of the strong 4-eV $2p$-$4s$ absorption edge. For simplicity, we have not included the fine structure due to antiferromagnetic ordering, such as the absorption peak at 0.24 eV,[4] which appears only below the Néel temperature. These are also $3d^8$ excitations and thus do not contribute to the electrical conductivity.

There are other possible transitions from the $3d^8$ ground state in which the number of d electrons on the Ni ions changes, e.g., the excitation of a $3d$ electron into the $4s$ band. To display these excitations on the same diagram as those involving the many-electron excitations of the $3d^8$ states, and include the interband transitions as well, requires that we relate the many-electron states on the right to the single-electron band states on the left. This can be done for the lowest few excitations by considering the many-electron $3d^8$ states to be equivalent to a set of pseudoparticle states. This pseudoparticle equivalence can be made as follows: We consider the NiO crystal to be made up of the ion "cores" O^{4+} and Ni^{3+}. Thus seven $3d$ electrons on each nickel ion are considered to be core electrons. The eighth $3d$ electron on the normal Ni^{2+} ion is then considered to take on energy values equal to the difference between the $3d^8$ many-body energies and the $3d^7$ core energy. Note that the excited states of this pseudoparticle are not simply those of a single electron in a fixed-core potential, but they are the true excited states of the correlated system. The internal transitions of the $3d$ electrons on a nickel ion are then those given by the right-hand side of the figure. We can now, however, indicate on the same diagram the transition from a $3d^8$ state to the $4s$ band by the difference in energy between the $3d^8$ level and the $4s$ band edge. From optical absorption[13] and photoemission[10] data this transition may be put at 5.5 eV. Similarly, a transition in which a $3d$ electron is transferred from one Ni^{2+} to another leaving a Ni^+ and a Ni^{3+} "core" can be indicated on the diagram by the energy difference between the levels labeled $3d^8$ and $3d^9$, and is estimated to be ~16 eV from x-ray[14] and optical data.[10] This scheme restricts our diagram to those transitions which leave a d^7 core as final state. For example, a transition involving a transfer of an electron from the $2p$ band to a $3d^8$, making it $3d^9$, does not leave a $3d^7$ core. Therefore this transition may have an energy greater or less than the indicated $2p$-$3d^9$ separation. However, most transitions likely to occur within the 16-eV range of our figure are simply displayed.

We must keep in mind, however, the additional rule that these single-particle states depend on occupation number. For example, if a particle is excited from a $3d^8$ ground state to a $3d^8*$ excited state, the $3d^8$ ground state becomes unavailable for occupation by another particle; i.e., the sum of occupied $3d^8$ and $3d^8*$ states must exactly equal the number of Ni ions. In this way, these excitations do not leave behind a hole to contribute to conduction or photoconduction. Another required rule is that no transitions are allowed from a solid band on the left to a dashed band on the right since this does not leave behind a $3d^7$ core state. Our single-particle representation of the many-electron states thus gives us a simple model for displaying the lowest excitations needed to describe both the localized optical spectrum and the bandlike conduction in NiO.

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SEARCH FOR MASSIVE PARTICLES IN THE COSMIC RADIATION AT SEA LEVEL*

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We have found no evidence for the existence of long-lived, massive particles in the cosmic radiation at sea leavel. The experimental limit for masses above 2 BeV/c^2 is 2.2×10^{-8} particles (cm^2 sr sec)$^{-1}$.

A search has been made at sea level for massive, long-lived particles that might be present in the cosmic radiation. The experiment, shown schematically in Fig. 1, consists of measuring the velocity of particles capable of traversing an aluminum absorber. For velocities measurably smaller than the speed of light, this corresponds to imposing a lower limit on the mass of the traversing particle. The velocity range accessible to our experiment is from 0.5 to 0.9c. The absorber is 195 g/cm^2 of aluminum which corresponds, for the above range of velocities, to a lower limit on the mass of 30 to 0.65 BeV/c^2.

The detectors are nine plastic scintillation counters each 36 in. long, 12 in. high, and 1 in. thick. Each counter is viewed by two RCA 7746 photomultipliers, one at each end. The counters are arranged vertically in banks of three giving detection areas of 36×36 in.^{2} and the banks are equally spaced at 14-ft intervals. The zenith angle for the central axis is 84°, and the solid angle subtended is 0.01 sr. A trigger is generated by the fast logic when there are signals from

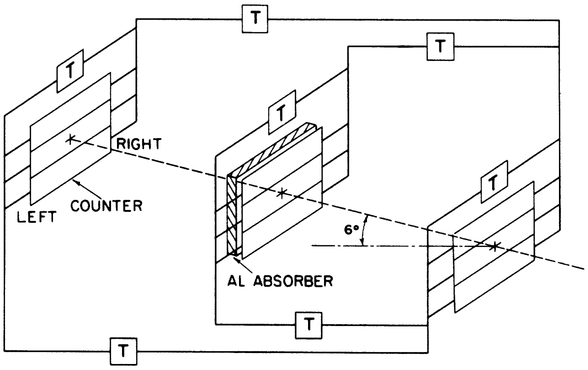

FIG. 1. Schematic of experimental setup and time-measurement arrangement. Each box labeled T indicates measurement of the time interval between the two signals entering the box.