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Electrical and Optical Properties of Narrow-Band Materials

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The electrical and optical properties of materials which are characterized by narrow bands in the vicinity of the Fermi energy are discussed. For such materials, electronic correlations and the electron-phonon coupling must be considered explicitly. Correlations in f bands and in extremely narrow d bands can be handled in the ionic limit of the Hubbard Hamiltonian. It is shown that free carriers in such bands form small polarons which contribute to conduction only by means of thermally activated hopping. Wider bands may also exist near the Fermi energy. Carriers in these bands may form large polarons and give a bandlike contribution to conductivity. A model is proposed for determining the density of states of pure stoichiometric crystals, beginning with the free-ion energy levels, and taking into account the Madelung potential, screening and covalency effects, crystalline-field stabilizations, and overlap effects. Exciton states are considered explicitly. The Franck-Condon principle necessitates the construction of different densities of states for electrical conductivity and optical absorption. Because of the bulk of experimental data presently available, the model is applied primarily to NiO. The many-particle density of states of pure stoichiometric NiO is calculated and is shown to be in agreement with the available experimental data. When impurities are present or nonstoichiometry exists, additional transitions must be discussed from first principles. The case of Li-doped NiO is discussed in detail. The calculations are consistent with the large mass of experimental information on this material. It is concluded that the predominant mechanism for conduction between 200 and 1000 °K is the transport of hole-like large polarons in the oxygen $2p$ band. A method for representing the many-particle density of states on an effective one-electron diagram is discussed. It is shown that if correlations are important, donor or acceptor levels cannot be drawn as localized levels in the energy gap when multiple conduction or valence bands are present. This result comes about because extrinsic ionization energies of two correlated bands differ by an energy which bears no simple relation to the difference in energies of the intrinsic excitations, which are conventionally used to determine the relative positions of the bands.

I. INTRODUCTION

Transition-metal and rare-earth compounds are characterized by d and f bands in the vicinity of the Fermi energy. Since the spatial extent of these electrons away from their ion cores is relatively small compared to outer s and p electrons, the d and f states on nearest-neighboring ions overlap only slightly and thus ordinarily form very narrow bands. It might be asked whether there is any meaning in referring to these somewhat spread out levels as bands rather than localized states, since they are certainly not one-electron bands in the or-

dinary sense. However, long-range magnetic order is the rule rather than the exception in these materials, and so the effective overlap must be finite.

These materials can be either insulating or metallic.¹ However, for a large class, e.g., CoO, band theory appears to fail. In these compounds, it can be shown by symmetry arguments that a partially filled band must exist, and yet they are excellent insulators. Although attempts at modifying band theory to explain the insulating behavior have been made,² and these have succeeded in reducing the number of materials in the class,³ it does not appear likely that a pure Hartree-Fock approach

will *consistently* account for the electrical behavior of all the transition-metal compounds.^{1,4} An explanation for this failure of band theory was first suggested by Mott,⁵ who brought attention to the importance of electronic correlations, neglected in a Hartree-Fock approach, in the case of an extremely narrow band. Mott pointed out the fact that any material with an integral number of electrons per primitive cell must be an insulator in the "atomic limit," or the limit where the lattice parameter becomes sufficiently large that overlap between nearest-neighbor electronic wave functions is negligible. In this limit of zero-width bands, the electrons are localized around their ion cores, just as a core electron. Mott further presented reasons why the transition from this insulating region to the region where band theory is appropriate must be sharp.⁶ The existence of a "correlation gap" in a simple model, consisting of a single *s* band with a δ -function interaction between electrons, was verified by Hubbard.⁷

Once it is concluded that a material is a "Mott insulator," it becomes important to explain the semiconduction which exists. There are many possibilities. Intrinsic conduction from excitation across the correlation gap can be observable at high temperatures if this gap is not too large. Furthermore, there can be intrinsic conduction due to excitation of a localized electron to an unoccupied state in a wide band or to excitation of an electron from a filled wide-band state to an unoccupied localized state above the correlation gap. However, since the materials under investigation have not yet been prepared as pure stoichiometric single crystals, extrinsic conduction always dominates at ordinary temperatures.¹ Once impurities and vacancies are present, the lowest-energy excitation is often one which creates a carrier in the narrow band, either a hole below the correlation gap or an electron above the gap. However, such a carrier should be quite localized, since the bandwidth is very small. Under these conditions, it can be shown that the carrier will induce a lattice distortion in which it becomes trapped.⁸ In such a case, it is more appropriate to consider not electronic states but states of the electron together with its associated lattice deformation, a quasiparticle known as a polaron. In the narrow-bandwidth limit, as must be the case in these materials, the distortion extends only to the immediate vicinity of the carrier, and the quasiparticle is called a small polaron. It can be shown theoretically⁹ that small polarons can conduct in a bandlike manner at low temperatures, although there has not yet been any unambiguous experimental demonstration of this regime. At high temperatures, small polarons contribute to conduction by thermally activated hopping, a

process which is characterized by a mobility which exponentially increases with increasing temperature.⁹ This hopping conductivity has been observed in many materials.¹⁰ For many years, this process was taken to be the dominant one in all the insulating transition-metal compounds.¹¹ However, the situation is now in doubt, since the discovery that the Hall mobility of NiO is not thermally activated.^{12,13} We have recently suggested that extrinsic conduction by excitation from a donor or acceptor to a wide band can be the most important conduction process in these materials at ordinary temperatures.¹⁴ On the other hand, Austin and Mott¹⁵ have cited this material as an example of conduction in a small-polaron band regime. It is important also to consider the possibility of conduction by thermally activated hopping within the impurity or vacancy levels themselves, a process which is usually called impurity conduction,¹⁶ and is important in partially compensated semiconductors at low temperatures.

In this paper, we formally analyze these possible conduction processes and indicate how to distinguish between them. In Sec. II, we review in detail the experimental results, concentrating in particular on NiO, the material for which the most information is presently available. In Sec. III, we present a model which we believe is more consistent with the data on NiO than is the small-polaron model, and which can be adapted to account for the properties of other narrow-band materials as well. The many-electron densities of states of pure and doped NiO are estimated, starting with the free-ion energies. Electronic correlations, screening, covalency, exciton and polaron formation, overlap effects, and crystalline-field stabilization are all taken into account explicitly. It is shown that ordinary one-electron techniques fail qualitatively to account for the effects of doping in narrow-band materials. In Sec. IV, we discuss a method for analyzing the electrical and optical properties of these materials in terms of an effective pseudoparticle density-of-states diagram.¹⁷ Finally, in Sec. V, we discuss the implications of our model and compare it to the other models currently cited.

II. SUMMARY OF EXPERIMENTAL RESULTS ON NiO

We shall discuss the available data on NiO in detail, since this is the material most exhaustively investigated. At the end of this section we shall note some of the results on other semiconducting transition-metal oxides which may indicate that small differences do exist among these similar materials.

Nominally pure stoichiometric NiO crystals are excellent insulators, with a room-temperature re-

sistivity in excess of $10^{13} \Omega \text{ cm}$.¹⁸ Since different samples have vastly different conductivities, this conduction is undoubtedly dominated by the effects of random impurities or lattice defects, which are always present in even the best crystals presently being grown. Because of this, NiO is usually doped with known amounts of Li, which goes in substitutionally for Ni. Since the second ionization potential of Li is much larger than the third ionization potential of Ni, the Li exists in the lattice as Li^+ . For charge neutrality, one Ni^{3+} should be formed for every Li^+ introduced. This need not, however, be the case. One O^{2-} vacancy, for example, can compensate for two Li^+ ions. Since a Ni^{3+} ion is a Ni^{2+} ion with an extra hole, Li^+ impurities act as acceptors, and the conduction is p type. In undoped samples, conduction is usually also p type, indicating that monovalent impurities or nickel vacancies are responsible. Occasionally, n -type material has been obtained¹⁹; in these samples, it can be assumed that trivalent metallic impurities or oxygen vacancies dominate.

The conductivity almost always increases exponentially with increasing temperature but the activation energy depends on the sample and the temperature range. For undoped samples, between 200 and 500 °K, the activation energy is approximately 0.9 eV^{13,20}; above the Néel temperature, 523 °K, the activation energy drops to 0.6 eV.²⁰ At very high temperatures, above 1000 °K, the activation energy increases to approximately 1.0 eV,²¹⁻²⁴ although higher values (1.8–1.9 eV) have also been measured.^{25,26} At very low temperatures, 10–100 °K, activation energies in the vicinity of 0.004 eV are observed.^{15,27,28}

Doping with Li does not affect the activation energy for electrical conductivity at either very high²⁴ or very low²⁷ temperatures. However, in the intermediate temperature range, moderate doping ($\sim 1\%$ Li) induces a drop in activation energy from 0.9 to approximately 0.3 eV below 500 °K and from 0.6 to approximately 0.2 eV above 500 °K.²⁰ Heavy doping (5–10% Li) results in a further decrease of activation energy to 0.18 eV below 500 °K and 0.14 eV above 500 °K.^{20,29}

The Hall mobility of both undoped and doped NiO has now been measured many times.^{12,13,24,28,30-32} The mobility is approximately $0.5 \text{ cm}^2/\text{V sec}$ at 200 °K; the sign indicates that the predominant carriers are holes. There is no striking temperature variation of mobility between 200 and 400 °K, but the mobility gradually decreases with increasing temperature. An empirical approximation describing the temperature behavior of the Hall mobility in this range is^{28,30,31}

$$\mu_H = (0.01 \text{ cm}^2/\text{V sec}) \exp(0.075 \text{ eV}/kT), \quad (1)$$

although the temperature range is sufficiently narrow so that an algebraic variation, such as $\alpha T^{3/2}$, cannot be eliminated. Above 400 °K, the Hall mobility begins to decrease more sharply, and at about 600 °K it reverses sign.²⁴

Thermoelectric power also has been often measured,^{12,15,19,22,28-30,33-36} but the results are not in as good agreement with each other as are those for the Hall mobility. It has been shown that some of these discrepancies are due to the effects of grain boundaries in polycrystalline samples of poor quality.^{35,36} When care is taken in preparing polycrystalline material, or when good single crystals are used, the thermoelectric power above 300 °K is proportional to the logarithm of the resistivity.^{28,30,36} The thermoelectric power has a maximum which is in the vicinity of 300 °K in undoped material, but which moves to 150 °K in Li-doped samples.^{30,36} Thermoelectric-power measurements on Li-doped material indicate primarily p -type conduction predominates, even above 600 °K, where the Hall effect is n type. This observation is difficult to account for theoretically, but we shall discuss a plausible explanation in Sec. III.

Thermoelectric-power measurements on single crystals of Li-doped NiO have been interpreted to give estimates of the effective mass of carriers ranging from less than 0.3^{28} to more than 30^{15} free-electron masses. We shall show in Sec. III that, if interpreted consistently, all the thermoelectric-power data are actually in agreement, and that the effective mass of the carriers in Li-doped NiO is approximately six free-electron masses. Our interpretation gives a value for the conductivity mobility of $5 \text{ cm}^2/\text{V sec}$ at 300 °K. This is a factor of 15 larger than both the room-temperature Hall mobility and the drift mobility as measured by a time-of-flight measurement.³⁷ However, the conductivity mobility is proportional to the Hall mobility from 200 to 500 °K.

The ac conductivity has been measured up to 24 GHz,^{18,19,28,38,39} and it has turned out to be an important method for distinguishing between several conduction processes. It is found in several investigations on various material that below 300 °K the conductivity obeys the relation

$$\sigma(\omega) - \sigma(0) \propto \omega^2 \tau / (1 + \omega^2 \tau^2), \quad (2)$$

with a single value of the staying time $\tau \sim 10^{-10} \text{ sec}$. The frequency-dependent conductivity is independent of temperature. Above 400 °K, the conductivity is independent of frequency. Figure 1 shows a typical result.

Optical-absorption experiments have been carried out from far-infrared through x-ray frequencies, and these measurements provide a strong basis for

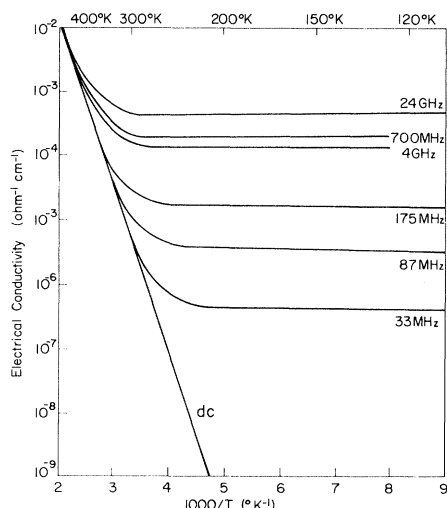


FIG. 1. The dc and ac conductivities as functions of reciprocal temperature for a single crystal of NiO doped with 0.001% Li⁺ (Kabashima and Kawakubo, Ref. 38).

the conclusion that the *d* electrons in NiO and related materials are extremely localized. The most significant energy range for optical absorption is from 0.1 to 20 eV.^{28, 40-47} There is a peak at 0.24 eV, which begins to broaden and decrease in energy above 400 °K and disappears above 600 °K.^{40, 46} It appears to be connected with antiferromagnetism, since it vanishes just above the Néel temperature and moves to lower energies with decrease in sublattice magnetization by either increase of temperature⁴⁰ or dilution with MnO or CoO.⁴⁸ In Li-doped samples only, there is a peak at 0.43 eV.^{28, 45} Between 1.0 and 3.7 eV there are a series of at least ten absorption peaks superimposed on a continuously rising background.^{40, 42, 43} These peaks are correlated within a few percent with those found in the absorption of dilute solutions of Ni²⁺ in MgO.⁴⁹ This correlation is shown in a most striking manner in Fig. 2, taken from the work of Reinen,⁴³ who measured the spectrum of Ni_xMg_(1-x)O from *x* = 0.05 through *x* = 1.0. The background absorption below 4 eV is much lower in the purer crystals of NiO grown by halide decomposition than in the samples prepared by flame fusion.⁴⁰

The main feature in the optical spectrum is an absorption edge at about 3.8 eV, the absorption coefficient rising rather sharply to approximately $6 \times 10^6 \text{ cm}^{-1}$.^{40, 44, 50, 51} There are several peaks in the 4–20-eV range, and the absorption increases significantly above 12 eV, as is shown in Fig. 3, taken from the work of Powell.⁴⁴ The edge at 3.8 eV has also been observed in electroreflectance measurements.⁵²

X-ray absorption spectra^{53, 54} show differences

between the *d* electrons in Ni metal and in NiO. While the *L*_{II} and *L*_{III} bands of NiO are centered around the same positions as those of metallic Ni, only the oxide bands showed structure in the form of subpeaks in the vicinity of +1 and -3 eV from the main peak.

Infrared absorption spectra^{30, 40, 42, 45, 55} have given information on the lattice potential in NiO, and are also useful for estimating the strength of the electron-phonon interaction. There are strong reststrahlen peaks in the vicinity of 0.05 eV, from which it can be deduced that the static dielectric constant of NiO has the large value $\kappa \sim 12$, the high-frequency dielectric constant is $\kappa_\infty \sim 5$, the energy of the transverse optical phonons is $\omega_{\text{TO}} \sim 0.05 \text{ eV}$, and the energy of the longitudinal optical phonons is $\omega_{\text{LO}} \sim 0.07 \text{ eV}$. These values for the dielectric constant are in agreement with direct measurements.^{56, 57} Multiphonon bands have been observed between 0.08 and 0.15 eV⁴² and phonon difference bands near 0.02 eV.^{30, 45} Finally, the antiferromagnetic resonance peak has been observed at 0.04 eV, below the Néel temperature.^{30, 45, 58, 59}

A photoconductivity edge has been observed in epitaxially grown crystals of NiO at about 3.8 eV.²⁵ This observation taken together with the strong absorption edge at this energy are the strongest evidence for intrinsic bandlike conduction in NiO. We shall show in Sec. III that this wide-band conductivity takes place in the band arising from the 4s

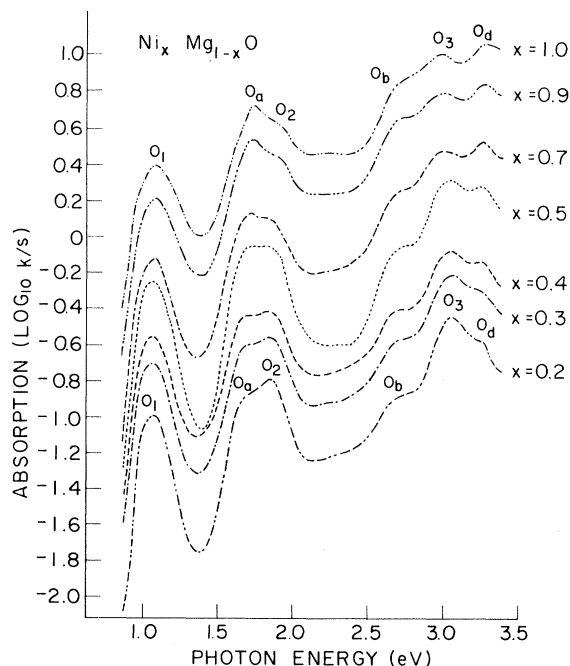


FIG. 2. Absorption spectrum of crystals of Ni_xMg_(1-x)O as a function of energy (Reinen, Ref. 43).

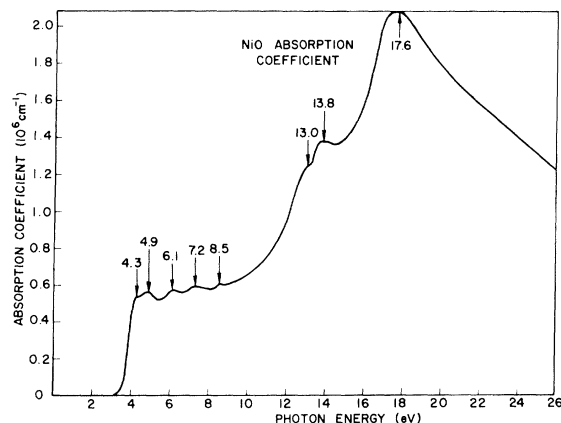


FIG. 3. Absorption spectrum of a crystal of NiO (Powell, Ref. 44).

states of the Ni^{2+} ions. Photoconductivity has also been found below 3 eV on vacuum-evaporated films.⁶⁰ A peak in photocurrent appeared at 0.24 eV, superimposed on a steadily increasing background. On the other hand, a crystal grown by flame fusion showed no evidence for any photoconductivity below 7 eV.⁴⁴

Photoemission experiments have also been carried out.^{44,61,62} These have been used by Powell,⁴⁴ in conjunction with absorption and reflectivity data, to obtain an optical density of states for NiO. As will be discussed in Secs. III and IV, the presence of significant many-body effects in the optical transitions makes such a one-electron density of states difficult to interpret.

None of the other semiconducting transition-metal compounds have been studied to the extent that NiO has. However, recent investigations of CoO ,^{63,64} MnO ,⁶⁵ and Fe_2O_3 ^{24,66} have indicated great similarities among all of these materials. A very few differences have been observed. Dielectric losses due to $\text{Li}^+\text{-Co}^{3+}$ dipoles have been found in CoO , indicating that bound holes hop around the vicinity of a Li^+ impurity, with a 0.20-eV activation energy necessary for motion.⁶⁷ This is in conflict with the results of such experiments on NiO, in which no such activation energy was found.^{68,69} Also, in epitaxially grown single crystals of MnO , photoconductivity has been observed, in addition to that in the intrinsic region, in the region 2–4 eV.⁷⁰ The peaks coincided almost exactly with the fairly sharp optical-absorption peaks^{42,71,72} in this range. Although NiO also has sharp structure in this region, no such photoconductivity has been observed in NiO.^{25,44,60} As we shall show in Sec. III, since these peaks in both NiO and MnO are connected with localized excitations of the d electrons, it is difficult to reconcile these different results.

III. MODEL FOR NARROW-BAND MATERIALS

In this section, we present a model which can be adapted to explain the electrical and optical properties of either pure, doped, or nonstoichiometric narrow-band crystals. We shall quantitatively apply the analysis to NiO, and show how it is consistent with all the experimental data presently available.

A. Optical Properties of Pure Stoichiometric Material

For simplicity, we begin with an analysis of the properties of perfect undoped stoichiometric crystals, despite the fact that really good material has not yet been prepared when judged by usual semiconductor standards. Since the materials under consideration are insulators, there are no free carriers in ideal crystals at $T=0$, and thus the lattice can be taken as completely periodic. In order to discuss the optical properties, we assume the Franck-Condon principle, which states that there can be no ionic displacements at optical frequencies. Consequently, for the considerations of this subsection, we do not have to introduce the electron-phonon interaction into the Hamiltonian.

Let us, for example, consider an oxide of the iron group of the transition metals. We shall restrict ourselves to elementary excitations of, say, 20 eV or less. Since the covalency parameters for MnO and NiO have been shown to be less than 4%,⁷³ the effective charges on the ions are reduced by less than 10% from their maximum value. Thus, it is a reasonable assumption to begin with the electronic states of the fully ionized metal atom (e.g., Ni^{2+} in NiO) and the filled-shell O^{2-} ion. Since we have restricted ourselves to energies within 20 eV of the Fermi energy, only the $2p$ electrons of the oxygen ions and the $3d$ and $4s$ electrons of the metal ions need be considered. Consistent with the assumption of near total ionicity, the $2p$ band of the oxygen ions must be filled at $T=0$. Since the ionized metal atoms always lose their $4s$ electrons before any $3d$ electrons, it is reasonable to assume that the $4s$ band of the metal ions is empty at $T=0$. Outer p and s bands are generally accurately handled by means of ordinary one-electron theory, and this appears to be the case for the saturated transition-metal oxides such as SrTiO_3 .⁷⁴ Thus, we expect a normal $2p$ band below the Fermi energy and a normal $4s$ band above the Fermi energy of the material. Neither of these bands can overlap the Fermi energy, since the materials are insulators.

It is clear from the considerations of Secs. I and II that the $3d$ electrons cannot be treated by standard one-electron methods, and that a normal $3d$ band does not exist. The effects of correlation must be explicitly introduced in any calculation of

the $3d$ bands. A technique for doing this has been suggested by Hubbard,⁷ who considered an approximation in which two electrons interact only when they are in Wannier states centered on the same ion core. The Hamiltonian for a nondegenerate band in this approximation becomes

$$H = \sum_{i,j} \sum_{\sigma} T_{ij,\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_i n_{i\uparrow}, \quad (3)$$

where $c_{i\sigma}^{\dagger}$ is the creation operator for an electron in the Wannier state of spin σ centered around \vec{R}_i , U is the Coulomb repulsion between two electrons of opposite spin simultaneously located in state i , $T_{ij,\sigma}$ is the Fourier transform of the Bloch energies $\epsilon_{k\sigma}$ and $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ is the operator which counts the number of electrons in state i, σ . This Hamiltonian has the virtue of being exact in two opposing limits, the Bloch limit, in which $U=0$, and the zero-bandwidth limit, in which $T_{ij} = T_{ii}\delta_{ij}$. Hubbard,⁷⁵ in an approximate solution, found that ordinary band theory predicted the correct electrical behavior in the range where the ratio of the bandwidth Δ to U was large, but that near the opposite limit, when $\Delta \ll U$, the material was indeed a Mott insulator. Clearly, a Mott transition must then occur for a critical value of Δ/U . In Hubbard's approximation, the Mott transition comes at $\Delta/U \sim 1.16$. Hubbard's result for the pseudoparticle density of states as a function of Δ/U is shown in Fig. 4.

In order to extend this model to transition-metal oxides, we must complicate the problem considerably. We need to consider all bands arising from the $2p$ electrons of the O^{2-} ions and the $3d$ and $4s$ electrons of the metallic ions. Only the $4s$ band is nondegenerate. Hubbard⁷⁶ made an attempt at treating degenerate bands, but found that the problem was quantitatively prohibitive because

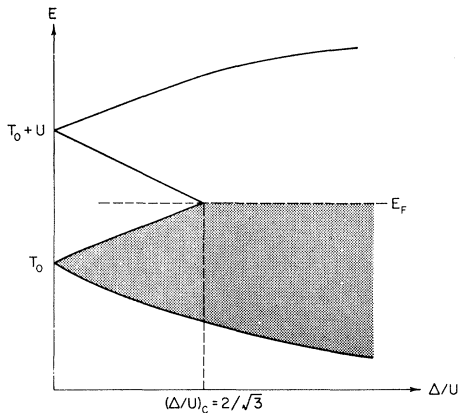


FIG. 4. Pseudoparticle band structure as a function of Δ/U for a single s band (Hubbard, Ref. 75).

of the proliferation of pseudoparticle bands. However, we can use the experimental results to simplify the problem considerably in any particular case. We can consider the spread of pseudoparticle bands from the atomic limit ($\Delta/U=0$; $1/a=0$, where a is the lattice parameter) to the Bloch limit ($\Delta/U \gg 1$; $1/a$ large) assuming that the qualitative behavior shown in Fig. 4 is maintained. From the previous discussion, it is evident that the $2p$ and $4s$ bands are in the Bloch limit by the time the equilibrium lattice parameter of the transition-metal oxides has been reached. On the other hand, the optical results on NiO discussed in Sec. II (see Fig. 2) strongly suggest that the $3d$ band is very near the atomic limit. The Hamiltonian (3) is thus expected to be a good approximation for all the relevant bands of NiO.

1. Estimate of Optical-Absorption Spectrum of NiO

In order to accurately treat the narrow-bandwidth limit of a d band we must consider all configurations from 0 through 10 d electrons on a single ion core. We can estimate the separation in energy of the lowest multiplets of each configuration from the difference between the n th and the $(n+1)$ th ionization potential of the isolated atom. For example, the process $d^8 + d^8 \rightarrow d^7 + d^9$ in NiO can be estimated as needing an activation energy of 18.6 eV.⁷⁷ This energy is, in reality, only an upper limit, since there must be screening of the electronic interaction due to the presence of other electrons in the vicinity of the two ions which change their configurations. Part of this screening effect is due to the other d electrons and core electrons on the cations themselves, and part is due to polarization of the charge densities on the surrounding oxygen anions and covalency effects. The former is an effect which should occur in free ions, and can be estimated by noting that the Slater-Condon parameters determined from experiment are about 15% smaller than those calculated from Hartree-Fock wave functions.^{7,78} The effects of polarization and covalency can be estimated by noting that the multiplet splittings of Ni^{2+} in MgO are approximately 20% less than in the free ion.⁴⁹ We might also expect some screening from overlap between the d electrons on nearest-neighbor cations, although this should be small for reasons discussed previously. A reasonable estimate can be made from the optical data of Reinen,⁴³ who found that the Racah parameter B , which measures intra-ionic electronic repulsion, decreases about 7% from $Ni_{0.1}Mg_{0.9}O$ to pure NiO. All of these effects together result in a reduction of the intraionic Coulomb repulsion in NiO from 18.6 to approximately 12 eV. This method seems to us to be at least as

accurate a method for estimating the zeroth-order many-body effects as those used previously,^{29,44} since it is not necessary to determine the polarizabilities of the nickel and oxygen ions. These polarizabilities are not known to within an order of magnitude.⁴⁴

We are primarily interested in the separations of the ground states of different configurations of the d electrons, and for these the crystalline-field splittings must be taken into account. Therefore, we must make accurate estimates of the crystalline-field parameter Dq not only for the ordinary configuration ($3d^8$ for NiO), but also for the configurations with one excess electron ($3d^9$ for NiO) and with one deficient electron ($3d^7$ for NiO). In certain cases it is necessary to determine whether the high- or low-spin state of a particular ion is more stable in the crystal under consideration. The high- and low-spin states are identical for both the Ni^{2+} ($3d^8$) and Ni^{3+} ($3d^9$) configurations. The crystalline-field stabilizations of the ground states are $12 Dq$ for Ni^{2+} and $6 Dq$ for Ni^{3+} . An examination of the relevant experimental and theoretical crystalline-field parameters for several transition-metal monoxides indicates that Co^{3+} and Fe^{3+} are stabilized in the monoxides in low-spin states, while Ni^{3+} and Mn^{3+} are stabilized in high-spin states. The details of this argument and estimates of the parameters Dq for the various configurations are given in Appendix A. Using these results, we can conclude that the energy required in pure NiO to remove an electron from a Ni^{2+} ion and place it on a distant Ni^{2+} is approximately 13 eV. This gives the effective value of the quantity U in the Hamiltonian (3).

We can use these considerations to analyze the contributions of $d-d$ transitions to the optical spectrum of pure NiO. The low-energy (1–4 eV) absorptions are due entirely to the crystalline-field and multiplet splittings of the $3d^8$ configurations, in agreement with the experimental results.^{40, 43, 49} These transitions are, of course, between localized states, and involve no transport of charge. They should not contribute to electrical conductivity or photoconductivity.

There also should be a series of absorptions beginning at approximately 13 eV, the smallest energy necessary to create a spatially separated $d^7 + d^9$ pair, and extending to higher energies, since neither the Ni^+ ion nor the Ni^{3+} ion need be in their ground states. Thus the absorption band must be as wide as the sum of the crystalline-field and multiplet splittings of the d^7 and the d^9 configurations. If we assume the same values of Dq discussed in Appendix A to estimate the energy spread of the crystalline-field split states, we find that the spread of the d^7 state is 6 eV, while the d^9 configuration

is 1 eV wide. Thus the absorption band from these transitions should be located roughly in the 13–20-eV range. This absorption should, of course, be quite weak experimentally since it is a $d-d$ transition and the d electrons are also extremely localized. In stoichiometric material we can assume that the crystal is initially at equilibrium, so that a negligible number of Ni^{2+} ions are not in their ground states before excitation. If a significant number of Ni^{2+} are in excited states, as will happen in nonstoichiometric or intentionally doped samples, there will be a low-energy tail of up to 4 eV to the absorption band. Excitations which create spatially separated $Ni^+ - Ni^{3+}$ pairs can contribute to the conductivity or photoconductivity, but exactly how these holes and electrons conduct cannot be answered before we deal with the problem of electron-phonon interactions. We shall consider the question of conductivity in Sec. III B.

Another possible contribution to the optical absorption spectrum arises from the formation of bound $Ni^+ - Ni^{3+}$ pairs, which are called Mott excitons. For optical transitions, we can consider that such pairs attract each other with a Coulomb interaction,

$$V(R) = -e^2/\kappa_\infty R, \quad (4)$$

where R is the distance between the pair and κ_∞ is the high-frequency dielectric constant. We must use κ_∞ instead of the static dielectric constant since no ionic motion can take place in optical times. Strictly speaking, (4) is rigorous only for R large compared to an interatomic spacing, since it is based on a continuum approximation for the lattice. The maximum excitonic binding energy, however, occurs when the electron and hole are on nearest-neighbor cation sites. It is possible that the high-frequency dielectric constant has a strong k dependence which will cause deviations from (4) when R is of the order of an interatomic spacing, but this should not be a large effect in NiO and is usually ignored.¹⁵ Taking the experimental value⁵⁵ of $\kappa_\infty = 5.7$ for NiO, we find a value of 0.8 eV for the maximum excitonic binding energy. Optically, Mott excitons should contribute a sharp peak or shoulder about 0.8 eV below the 13–23-eV absorptions, and the experimentally observed shoulder at 13.0 eV⁴⁴ can be associated with these transitions. Of course, bound excitons will not give any contribution to conductivity.

These considerations should encompass all possible intraionic and interionic transitions below 20 eV between d electron states. We have not yet considered transitions involving $2p$ or $4s$ electrons. As mentioned previously, we expect that crystalline states which spread from the free ionic $2p$ and $4s$ states are in the band limit of the Hamiltonian

(3), with an effective value of U small compared to the bandwidth Δ . The $2p$ band is filled at $T=0$, the $4s$ band is empty. Excitations between the bands should represent normal, optically allowed interband transitions. It is a reasonable assumption that the augmented-plane-wave (APW) band calculations should give a good first approximation for both of these bands. The band calculations of Switendick⁷⁹ and Wilson⁸⁰ show that the $2p$ band in NiO is about 4 eV wide and the $4s$ band is about 6 eV wide. The bottom of the $4s$ band is 5.5–6 eV above the top of the $2p$ band. Thus we should expect strong optical absorption between 5.5 and 16 eV. These excitations should give intrinsic band-type conductivity and photoconductivity, as will be discussed in detail later.

Two other types of excitations exist. It is possible to optically excite a transition from a localized $3d^8$ ion to a localized $3d^7$ ion, placing an electron in the $4s$ band. The free-ion process $3d^8 \rightarrow 3d^7 4s$ takes about 7 eV.⁸¹ Assuming the $4s$ band is 6 eV wide in NiO implies that the free-ion $4s$ level spreads ± 3 eV on the average in the crystal. Thus the process should enter with a minimum energy of approximately 4 eV, which should experimentally appear as an absorption edge. The absorption may be suppressed somewhat because of the forbidden nature of $d \rightarrow s$ electric dipole transition, but covalency of the s electrons with the anion wave function overcomes the selection rule to a large extent.⁸² Since the $3d^7$ ion can be left in any of its excited states as well as the ground state, these transitions might be expected to contribute to absorption over the range 4–16 eV. They should produce n -type band conductivity and photoconductivity. It is reasonable to conclude that the onset of this process produces the 3.8-eV absorption and photoconductivity edges discussed previously.

Finally, an electron can be excited from the oxygen $2p$ band onto a localized nickel ion, producing a Ni^+ , i.e., $3d^9$ state. The process $Ni^{2+} + O^{2-} \rightarrow Ni^+ + O^-$ for free ions is highly exothermic, since Ni^{2+} has an electron affinity of 17.5 eV⁷⁷ and free O^{2-} has a negative ionization potential of 9 eV.^{29,77} Thus, were it not for the Madelung potential, this reaction would lower the total energy of the material by 26.5 eV. But the Madelung potential, 24.0 eV for NiO,^{77,83,84} stabilizes both the Ni^{2+} and the O^{2-} ions, resulting in a free-ion net stabilization of about 22 eV. Assuming the same screening and crystalline-field stabilizations discussed previously, we find a value of 16 eV for the average energy of the process. This procedure is not completely justified in this case, since the polarizabilities of the oxygen and nickel ions could differ significantly, but the final result is not very different from that (14 eV) obtained by Powell⁴⁴ in two opposite limits.

The spreading of the oxygen $2p$ orbitals into a band 4 eV wide implies optical absorption in the range 14–18 eV. If we take into account the possibility of excitation into an excited $3d^9$ state, this absorption will extend up to approximately 19 eV. These excitations could produce p -type band conductivity, via holes in the oxygen $2p$ band, but there is no experimental information on this point. The so-called charge-transfer band⁸⁵ represents bound Mott-type excitons made up from electron-hole pairs resulting from this type of excitation. Using the same analysis previously carried out [see Eq. (4) and the subsequent discussion], but noting that the nearest-neighbor $Ni^{2+}-O^{2-}$ separation is 2.1 Å, we can estimate that this will produce an absorption peak within about 1.1 eV of the 14-eV edge. This large an energy is surprising in view of the much smaller charge-transfer energies in Ni^{2+} hydrated salts,⁸⁵ but experimentally, the peak observed at 13.8 eV could be associated with this excitonic absorption.

Together with the 0.24-eV peak probably associated with antiferromagnetism, the above excitations represent the low-energy optical absorptions of pure stoichiometric NiO. A sketch of these absorptions appears in Fig. 5.

2. Comparison with Experimental Results on NiO

Although the calculations in Sec. IIIB 1 are extremely crude, we can use them to analyze the experimental optical absorption of NiO in the 0.1–20-eV range.^{40,43,44,50} The interpretation suggested here is that the absorption peaks below 4 eV^{40,43} are purely intraionic $3d^8-3d^8$ transitions, the edge at 4 eV^{40,44,50} marks the onset of $3d^8-3d^7 4s$ transitions, the shoulder near 5.5 eV⁵⁰ represents the beginning of the strong $2p-4s$ excitations, and the

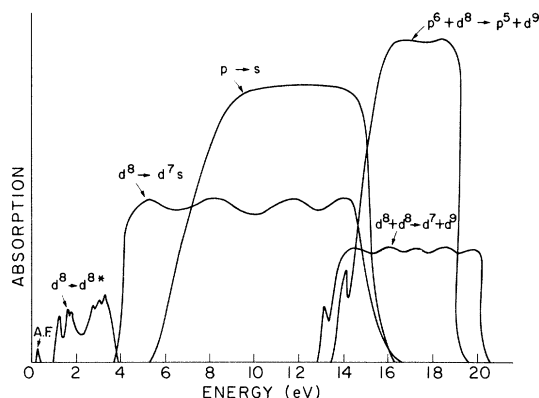


FIG. 5. Sketch of the predicted optical absorption of pure stoichiometric NiO up to 20 eV.

strong absorption above 12 eV⁴⁴ is due to the combined $2p-4s$, $2p-3d^9$, and $3d^7+3d^9$ excitations. The large absorption peak seen⁴⁴ at 17.6 eV (see Fig. 3) very likely represents the maximum contribution of the allowed $2p-3d^9$ excitations, estimated here to occur in the 14–19-eV range. The peak at 13.8 eV⁴⁴ should then be the absorption from charge-transfer excitons. The excitonic absorption, which we expect below the $3d^7+3d^9$ band, could explain the shoulder at 13.0 eV.⁴⁴ This interpretation of the optical results is consistent also with the observed photoconductivity,²⁵ since the $d-s$ transition at 4 eV is the lowest-energy intrinsic excitation to a conducting state.

B. Electrical Properties of Pure Stoichiometric Material

A major complication enters when we wish to extend the analysis of Sec. IIIA to discuss the electrical properties of narrow-band materials. The movement of electrons through the lattice generally takes place at times sufficiently long for the ions to relax around the new charge distribution, and thus we can no longer neglect ionic motion. The lowest-energy optical transitions, as discussed in Sec. IIIA, are the d^8-d^8 excitations, which do not contribute to conduction. The optical transitions with the next lowest energy are those from a d^8 ground state to a d^7 ground state plus an electron in the 4s band. The minimum energy of this process will require smaller energy because of the lattice deformation which will form around the Ni^{3+} (d^7) ion.

We have assumed that the d electrons are near the atomic limit, i. e., the overlap integral between nearest-neighboring d orbitals is negligibly small. If so, it is clear that the effects of electron-phonon coupling must be taken into account by non-adiabatic small-polaron theory.⁹ As calculated by Holstein,⁹ the polaron binding energy is

$$E_p = A^2/2M\omega_0^2, \quad (5)$$

where M is the ionic mass, ω_0 is the longitudinal optical-phonon frequency, and A is a constant giving the strength of the electron-phonon interaction. In order to obtain equivalence between this small-polaron theory and a continuum-polaron theory,⁸⁶ we must set A equal to

$$A = [(M\omega_0^2 e^2/\pi^3 a) (1/\kappa_\infty - 1/\kappa)]^{1/2}, \quad (6)$$

where a is the lattice parameter. It is possible for A to be very different from this value, due to interactions between electrons and TO, TA, and LA phonons, but this will occur only if distances of the order of a become important, and we shall show

that Eq. (6) gives excellent agreement with the experimentally observed small-polaron binding energy. For values of the constants appropriate to NiO ($\kappa \sim 12$, $\kappa_\infty \sim 5.7$, $a \sim 2 \text{ \AA}$), (5) and (6) give

$$E_p \sim 0.01 \text{ eV}.$$

These considerations indicate that small-polaron theory is applicable in these materials only to extremely localized electrons, whose bandwidths are of the order of hundredths of eV. As we have discussed previously, this is expected to be the case for the d electrons of NiO, CoO, and MnO, among others.

In the model of Holstein,⁹ small polarons conduct primarily by means of a thermally activated hopping process at high temperatures, but at low temperatures, conduction in a small-polaron band predominates, and the mobility is not thermally activated. The transition from predominantly hopping conduction to predominantly bandlike conduction can be estimated to occur at about half the Debye temperature if the overlap integral J and the coupling constant A are sufficiently large. It is difficult to make an *a priori* estimate of J for the d electrons of NiO, but for our purposes, all that is important is that it is small. The small-polaron calculations of Holstein⁹ assume much larger values of A than given by (6), and consequently, his estimate that the transition from a polaron-band regime to a polaron-hopping regime occurs in the vicinity of half the Debye temperature must be modified. Assuming an Einstein model for the longitudinal optical phonon spectrum, the transition temperature T_0 can be estimated from the solution of the transcendental equation

$$2 \operatorname{csch} \frac{\hbar\omega_0}{2kT_0} - \coth \frac{\hbar\omega_0}{2kT_0} = \frac{2J}{E_p} \ln \left[\frac{\hbar\omega_0}{J} \left(\frac{E_p}{2\pi J} \operatorname{csch} \frac{\hbar\omega_0}{2kT} \right)^{1/2} \right]. \quad (7)$$

For values of J small compared to both E_p and ω_0 , the solution of (7) is

$$T_0 \approx (J/E_p) \hbar\omega_0/k. \quad (8)$$

Thus, in the approximation of extremely narrow bands ($J \ll E_p$) the transition temperature is very small compared to the Debye temperature; i. e., the only mechanism of conduction through the $3d^8$ band at ordinary temperatures is by means of thermally activated hopping of small polarons.

Since intrinsic conduction in pure NiO comes from the excitation of the transition $3d^8-3d^7 4s$, the electron placed in the 4s band contributes to

conduction as well. Since the 4s band is expected to be in the Bloch limit of the Hamiltonian [Eq. (3)] we might anticipate that any polaron effects are adequately describable by large-polaron theory,^{87,88} as can be verified from the following considerations. The radius of the large polaron is

$$r_0 = (\hbar/2m^*\omega_0)^{1/2}, \quad (9)$$

where m^* is the band effective mass. As an estimate, we can use the calculated value $m^*/m_0 \sim 2$ obtained by Switendick⁷⁹ and Wilson⁸⁰ for the 4s band of NiO. In this case, $r_0 \sim 5$ Å. Since this is about 2.5 nearest-neighbor distances, continuum-polaron theory is a reasonable approximation. The electron-phonon coupling constant α is

$$\alpha = (e^2/2\hbar) (1/\kappa_0 - 1/\kappa_\infty) (2m^*/\hbar\omega_0)^{1/2}, \quad (10)$$

which gives $\alpha \sim 2$ for the 4s band of NiO. The polaron effective mass $m^{**} = m^* (1 + \frac{1}{2}\alpha)$ is approximately 2.7 free-electron masses for this band, and the polaron binding energy

$$E_p \approx \alpha \hbar\omega_0 \quad (11)$$

is 0.2 eV.

This result means that the intrinsic transition $3d^8 \rightarrow 3d^7 4s$ requires a thermal activation energy about 0.2 eV less than the optical activation energy estimated as 4 eV in Sec. IIIA. This process contributes *p*-type conductivity from hopping of the hole in the $3d^8$ band, which forms a small polaron. However, this would be dominated by a large *n*-type conductivity resulting from the large polarons in the 4s band. The intrinsic activation energy for this process should be in the vicinity of 2 eV. Clearly, intrinsic conduction should be measurable only at extremely high temperatures. Experimentally, it may have been observed in epitaxially grown crystals of NiO, in the range 700–1200 °K, where an activation energy of 1.9 eV has been measured.²⁵ It also has been found²⁶ in the temperature range 1000–1400 °K, where effective activation energies near 1.8 eV in polycrystalline material which has been compensated by Fe, Al, or Cr impurities are observed. Presumably Fe, for example, goes in NiO as Fe^{3+} , thus compensating for *p*-type impurities, such as Li^+ ions or oxygen vacancies.

C. Optical Properties of Doped or Nonstoichiometric Material

Real samples of narrow-band materials so far prepared are not pure by ordinary semiconductor standards, and they are rarely stoichiometric. In fact, for some materials, e.g., FeO, the homo-

geneity range does not even include the stoichiometric compound.⁷⁴ This is of vital importance in any discussion of the electrical properties, but should not lead to any striking modifications of the intrinsic optical spectrum, which we described in Sec. IIIA. The main reason for this is that absorption due to impurity or vacancy concentrations of even as large as a few percent are most likely unobservable above 1 eV, since there is strong absorption already present in the range 1–20 eV in pure stoichiometric material (see Fig. 5).

The most common dopants in a divalent material such as NiO are monovalent ions, usually Li^+ , or normally trivalent ions, e.g., Cr^{3+} . Nonstoichiometry leads to the formation of vacancies rather than interstitials, and both cation and anion vacancies must be considered for each material, even if the homogeneity range includes an excess of only one type of ion. This is because defect structures with both anion and cation vacancies are common, and a partial compensation always appears to occur in any given crystal.¹

1. Li-Doped NiO

In order to understand the dominant role of impurities in the conduction process, we shall begin by analyzing the effects of introducing a monovalent impurity, such as Li^+ , into a divalent crystal. Once again, we shall use NiO as the prototype material. Since the ionic radius of Li^+ is almost identical⁸⁹ with that of Ni^{2+} , and since the NaCl structure of NiO is densely packed, we expect that the majority of the Li impurities enter the NiO lattice substitutionally for Ni^{2+} . Since the second ionization potential of Li is 40 eV larger than the third ionization potential of Ni,⁸¹ charge neutrality is achieved by forming a Ni^{3+} ion for every Li^+ ion introduced into the lattice. It is clear that the lowest energy is obtained when the Li^+ and Ni^{3+} are nearest neighbors, essentially forming an electron-hole dipole. This dipole forms a bound state whose energy may be approximated by

$$E_b \sim e^2/\kappa R, \quad (12)$$

where R is the nearest-neighbor cation separation. For NiO, this energy is 0.4 eV. A series of new optical transitions are possible in Li-doped NiO because of the presence of these bound dipoles. It is possible to free the Ni^{3+} from the Li^+ entirely by exciting an electron from a Ni^{2+} ion far from the Li center to the Ni^{3+} ion which is bound to the center. This should take about 0.4 eV. By the Franck-Condon principle, there is no energy reduction due to small-polaron formation about the free Ni^{3+} ion. A series of more weakly bound states in which the Ni^{3+} is located at farther than nearest-

neighbor cation spacings from the Li center are also possible. These could give contributions to absorption in the 0.2–0.4-eV range, although they should be quite weak being between spatially separated localized states. Clear evidence for a Li-induced absorption has been observed at 0.43 eV,²⁸ and there is no reason to doubt that this is the binding energy of the $\text{Li}^+-\text{Ni}^{3+}$ dipole.

It is also possible to optically excite an electron from the $2p$ band to the Ni^{3+} states created by the impurities, thus producing a Ni^{2+} ion and a hole in the $2p$ band. This process, in the ionic limit, is just $\text{Ni}^{3+} + \text{O}^{2-} \rightarrow \text{Ni}^{2+} + \text{O}^-$. Since the electron affinity of Ni^{3+} is 36.1 eV, the negative ionization potential of O^{2-} is 9 eV, and the Madelung potential is 24.0 eV,⁷⁷ this reaction requires about 2.9 eV for free ions. Assuming the same screening and crystalline-field stabilizations as in Sec. III A, we find a value of 2.3 eV for the average energy of the process. Taking the spreading of the $2p$ band and the binding energy of the $\text{Li}^+-\text{Ni}^{3+}$ dipoles into account, we can estimate that this process should contribute to optical absorption in the range of 0.7–4.7 eV. Because of the intrinsic crystalline-field absorption in this range, it is unlikely that this absorption can be seen. Asutin *et al.*^{45, 46} measured the absorption in Li-doped NiO, and when the absorption in pure NiO crystals was subtracted an excess background absorption remained. This background increased from 0.2 to at least 2 eV, with evidence for a peak near 1.0 eV. The subtraction procedure is quite dubious, because of the vastly different absorptions obtained in different crystals of nominally pure NiO. The peak could be due to bound excitons made up from $2p$ holes and Li^+ centers, it could be the lowest crystalline-field peak of the Ni^{3+} ions. If it is a real absorption peak it is more likely the former, since the first crystalline-field transition of a Ni^{3+} ion can be estimated⁹⁰ to be in the vicinity of 1.8 eV, owing to the large Dq value of Ni^{3+} . The extra absorptions due to Ni^{3+} should contribute a number of peaks between 1.8 and 6 eV, which will be observable only if an accurate subtraction procedure can be carried out. Austin and Mott¹⁵ attribute the 1.0-eV peak to photon-assisted hopping of bound small polarons in the $3d^8$ band, but this interpretation fails to account for the rising background.

2. Nonstoichiometric NiO

Deviations from stoichiometry play an important role in many of the physical properties of the materials under consideration, and the effects of nonstoichiometry must be determined. The homogeneity range of NiO includes excess oxygen only.⁷⁷ Thus, nonstoichiometric samples have nickel vacancies, each of which leads to the formation of two Ni^{3+} ions to obtain neutrality. The lowest-energy

state is a bound quadrupole, consisting of two Ni^{3+} ions on opposite nearest-neighbor positions of the vacancy. An estimate of the binding energy of a hole to this complex is

$$E_1 \sim 2e^2/\kappa R - e^2/\kappa(2R), \quad (13)$$

which give $E_1 \sim 0.6$ eV for NiO. The second hole is then bound to an effective doubly negative charge, and has a binding energy of

$$E_2 \sim 2e^2/\kappa R \quad (14)$$

or $E_2 \sim 0.8$ eV for NiO. At low temperatures, essentially all of the holes are bound to the vacancies. An optical absorption due to single ionization of the quadrupole should occur in the vicinity of 0.6 eV. Other low-energy excitations are due to different geometrical configurations of the two holes around the vacancy. Three excited configurations exist, requiring excitation energies of approximately 0.1, 0.3, and 0.4 eV. The excitation of one of the bound holes into the $2p$ band should require 0.2 eV more than the analogous energies calculated for the holes bound to Li^+ centers, the additional energy being due to the greater binding of the effectively doubly charged vacancy. For the reasons previously discussed, these transitions are extremely difficult to observe optically. However, they are of the utmost importance electrically, and we shall discuss them in detail in Sec. III D.

Oxygen vacancies cannot exist in NiO except to compensate for monovalent impurities or nickel vacancies.⁷⁷ As in the case of Ni vacancies, O vacancies are not of much importance in an analysis of optical properties, but they have a great deal of importance in electrical transport experiments. We shall consider them in Sec. III D.

D. Electrical Properties of Doped or Nonstoichiometric Material

In this section, we shall describe the various possible conduction processes available to the free carriers which are thermally ionized from impurity centers or vacancies. There are, in general, three aspects which complicate the description greatly compared to the problem of extrinsic conduction in the wide valence and conduction bands of more conventional semiconductors. First, we must consider how the impurity enters the lattice and determine energetically whether the impurity will create an excess or deficiency of electrons in either the oxygen $2p$ band or the $3d$ or $4s$ states of the transition-metal ions. Second, we must consider multiple processes by which the carriers may contribute to conductivity. Finally, we must estimate the mobility of the carriers in each possible conduction mechanism.

As in Sec. IIIB, we are primarily interested in the low-energy excitations to conducting states. The problem of estimating the impurity energy levels is the same as in Sec. IIIC, except that they must be modified by the effects of ionic relaxation.

1. Li-Doped NiO

(a) *Thermally activated hopping conduction.* We shall consider first the introduction of Li^+ impurities into NiO. As calculated in Sec. IIIC, it takes about 0.4 eV to free a hole bound to a Li^+ center. The experimental value for the optical energy is actually 0.43 eV.²⁸ As indicated in Sec. IIIB, the hole is in the extremely localized d levels of the nickel ions and will therefore form a small polaron, resulting in a reduction in energy of the order of 0.01 eV. Thus the thermal activation energy to free a hole from the neighborhood of the Li^+ center should also be about 0.4 eV. At ordinary temperatures, the small polaron will conduct only by means of thermally activated hopping. The hopping energy is approximately half the small-polaron binding energy,^{9,15} and thus is of the order of 0.01 eV. The mobility is consequently nearly independent of temperature. The contribution of this process to the conductivity should be of the form

$$\sigma = N_{\text{Li}} e \mu_0 e^{-(0.4 \text{ eV})/kT}, \quad (15)$$

where N_{Li} is the density of uncompensated Li^+ centers and μ_0 is the hopping mobility. As the Li^+ concentration increases a drop will occur in the activation energy for conduction due to the increase in dielectric constant resulting from the presence of the charged centers.^{91,92} This effect has been estimated as producing a 30% decrease in activation energy for hopping in NiO for a Li^+ concentration of 1%.¹⁵ For Li^+ concentrations of 10% or more, a bound hole could move through the lattice without the necessity of being freed from the Li^+ centers, leading to a decrease in the hopping activation energy to the order of 0.01 eV. For reasons we shall discuss later on in this section, this has never been observed.

(b) *2p-band conduction.* Another mechanism for conduction which must be considered is via holes in the 2p band. The ionic reaction is $\text{Ni}^{3+} + \text{O}^{2-} \rightarrow \text{Ni}^{2+} + \text{O}^-$. As estimated in Sec. IIIC, the minimum optical energy necessary for this process is about 0.07 eV. Since the 2p band is expected to be an ordinary band, 4 eV wide, large-polaron theory should apply. An estimate of the 2p-band effective mass of $m^*/m_0 \sim 4$ can be made from the calculated^{79,80} 4s-band effective mass used in Sec. IIIB, if we note that the 2p band is 2/3 as wide as the 4s band. We shall subsequently show that this estimate is consistent with the experimental data.

Using this value of m^* in Eq. (9) shows that the large-polaron radius is about two lattice spacings, probably the lower limit for applicability of the theory. The coupling constant α from Eq. (10) is $\alpha \sim 3$. Thus weak-coupling theory is adequate.⁸⁶ The polaron effective mass is then $m^{**} \sim 6m_0$, and the polaron binding energy is about 0.25 eV. This gives a thermal activation energy for a hole in the 2p band in lightly doped samples of the order of 0.45 eV. It should be noted that this value depends critically on the values assumed for the Madelung potential and the ionic energies, and is not expected to be extremely accurate. But the main point we wish to make is that it is *small*. In fact, it is the same order of magnitude as the activation energy for hopping in the d band. This is true despite the fact that it takes at least 5.5 eV to excite a hole in the 2p band of intrinsic NiO. The reason for this apparent discrepancy is that the electron affinity of Ni^{3+} is 18.6 eV more than that of Ni^{2+} , so that the process $\text{Ni}^{3+} + \text{O}^{2-} \rightarrow \text{Ni}^{2+} + \text{O}^-$, which can occur in the Li-doped material, takes much less energy than the analogous process for intrinsic material, $\text{Ni}^{2+} + \text{O}^{2-} \rightarrow \text{Ni}^+ + \text{O}^-$. Even though the activation energy for holes in the 2p band may be somewhat larger than the hopping energy for holes in the $3d^8$ band, the large mobility associated with band conduction should result in a predominance of the latter mechanism at all but the lowest temperatures. Thus, hopping conduction may be completely unobservable in dc measurements. It might still be possible, however, to observe the hopping of small polarons bound to an impurity site as an additional contribution to the ac conductivity. In the remainder of this section we shall make an intensive analysis of the available experimental data, which we believe clearly points to the important role played by 2p-band conduction in NiO. We shall show that the data are consistent with the predominance of this process over the competing mechanism of small-polaron conduction by holes in the nickel $3d$ levels.

(c) *Analysis of transport data.* Excitation of a hole in the 2p band should produce a bandlike contribution to the electrical conductivity. The Li^+ level thus can be treated as an acceptor level to the 2p band. Within this basic framework we shall attempt to interpret the available experimental data. We shall assume, for the sake of simplicity in the analysis, that the activation energy for $3d^8$ holes is larger than that for 2p holes, and thus that E_F is determined purely by the 2p band and impurity states.

In order to describe the temperature dependence of the 2p-band conduction, we must consider the effects of compensation in the material. Bosman and Crevecoeur³⁶ and Austin *et al.*³⁰ have summarized the strong evidence for partial self-compensation

sation in NiO. Blakemore⁹³ has shown that in a partially compensated material, the concentration of free holes in a band at temperatures sufficiently high that $p \gg N_D$, where N_D is the donor concentration, is given by

$$p = N_v^{1/2} N_A^{1/2} e^{-E_A/2kT}, \quad (16)$$

where $N_v = \frac{1}{4} (2m^* kT / \pi \hbar^2)^{3/2}$, N_A is the Li^+ concentration, and E_A is the activation energy, estimated above as of the order of 0.4 eV. At low temperatures, when $p \ll N_D$, p is given by⁹³

$$p = N_v [(N_A - N_D) / N_D] e^{-E_A/kT}. \quad (17)$$

The large-polaron mobility in the $2p$ band will depend on the mechanism which dominates the scattering. Considering the polar nature of the material, it might be expected that optical-phonon scattering predominates. In the weak-coupling limit, the mobility resulting from scattering by a single optical phonon at temperatures small compared to the Debye temperature has been calculated by many authors^{94, 95} to be

$$\mu_s = (e/2m^* \alpha \omega_0) e^{\hbar \omega_0 / kT}. \quad (18)$$

In the same approximation, at high temperatures, the mobility becomes^{82, 92}

$$\mu_s = (4e/3m^* \alpha \omega_0) (\hbar \omega_0 / \pi kT)^{1/2}. \quad (19)$$

It has also been shown⁹⁶ that two-phonon scattering of large polarons can be important, especially at low temperatures, when the probability of phonon emission is much larger than that of phonon absorption. In such a case, it can be assumed that each absorption is followed by an emission, leading to an elastic two-phonon process called resonance scattering. At low temperatures, the mobility resulting from resonance scattering is^{98, 96}

$$\mu_r = (e/2m^* \alpha \omega_0) (m^* / m^{**})^{3/2} e^{\hbar \omega_0 / kT} \quad (20)$$

in the weak-coupling limit.

For NiO, the Debye temperature is 870 °K. Taking into account both scattering by single phonons and resonance scattering, as given by Eqs. (18) and (20), we find for the large-polaron mobility at temperatures small compared with 870 °K

$$\mu \sim (0.3 \text{ cm}^2/\text{V sec}) e^{(0.075 \text{ eV}) / kT}. \quad (21)$$

At 300 °K, this predicts a mobility of the order of 5 cm²/V sec. The mobility given by (21) decreases with increasing temperature, and should be valid

from about 200 to 600 °K. Above 600 °K, it is sufficiently near the Debye temperature so that expressions (18) and (20) are no longer appropriate, while at very low temperatures another form of scattering, either by impurities or by acoustic phonons, can be expected to predominate.

To summarize the predictions then, we expect that in Li-doped NiO, between 200 and 1000 °K, the dc conductivity will be p type and dominated by free holes in the $2p$ band. The carrier concentration should be thermally activated, with an activation energy of approximately 0.4 eV at low temperatures and 0.2 eV at high temperatures, the transition point depending on the extent of the compensation. Between 200 and 600 °K the mobility should decrease with temperature, with a negative activation energy of about 0.07 eV. The mobility should be about 5 cm²/V sec at 300 °K, and the effective mass of the holes should be of the order of six free-electron masses. Above 1000 °K or so, depending on the doping concentration, an exhaustion region may appear. In highly compensated samples, intrinsic n -type conduction, with an activation energy of about 1.9 eV, should be observable at very high temperatures. At very low temperatures, impurity conduction by hopping of electrons within the Li^+ acceptor levels should predominate.

(d) *Comparison with experiment.* We shall now summarize the experimental data on Li-doped NiO to see how well the above predictions are borne out. Since each sample of NiO is very different from any other, it is vital to consider only data where electrical conductivity, Hall constant, and thermoelectric power were all measured on the same material. The experiments on samples in which the amount of Li introduced into the material is known are the most useful to investigate. Fortunately, there are at least three sets of experiments in the literature which meet these requirements, those by Austin *et al.*,³⁰ by Bosman and Crevecoeur,³⁶ and by Ksendzoy *et al.*²⁸

Austin *et al.*³⁰ prepared single crystals of NiO by the arc-transfer process. We shall consider a typical sample doped with 0.20% Li. Assuming a negligible concentration of Ni vacancies, we can then set the acceptor density as $N_A \sim 10^{20} \text{ cm}^{-3}$. Electrical-conductivity measurements showed that below 500 °K, the activation energy was $E_A \sim 0.28 \text{ eV}$. Above 500 °K, the slope of a $\ln p$ -versus- T^{-1} plot fell to $\frac{1}{2} E_A$ or 0.14 eV. This is strong evidence for partial compensation, as can be seen from the predicted relations (16) and (17). Thus, at 500 °K, $p \sim N_D$ and the donor concentration can be estimated from

$$N_D \sim N_v^{1/2} N_A^{1/2} e^{-E_A/2kT}. \quad (22)$$

With $E_A \sim 0.28 \text{ eV}$, all bound Ni^{3+} acceptors should

be ionized by 1000 °K. At this point, $\rho \approx 0.2 \Omega \text{ cm}$ and $p \sim 10^{20} \text{ cm}^{-3}$, so that the mobility is $\mu \sim 0.3 \text{ cm}^2/\text{V sec}$. Since we know p , N_A , and E_A , Eq. (16) can be solved to give $N_v \sim 2.6 \times 10^{21} \text{ cm}^{-3}$ at 1000 °K. This value corresponds to a polaron effective mass of

$$m^{**}/m_0 = \pi \hbar^2 (4N_v)^{2/3} / 2m_0 kT \sim 6.$$

This is just the value used above in the calculations of the polaron mobility. Taking into account the temperature dependence of N_v , we can use Eq. (22) to show $N_D \sim 10^{19} \text{ cm}^{-3}$. Thus the Li acceptors are approximately 10% compensated, probably by oxygen vacancies. At 300 °K, we can apply Eq. (17) to obtain $p \sim 10^{17} \text{ cm}^{-3}$. Since $p \sim 10 \Omega \text{ cm}$, the mobility is $\mu \sim 5 \text{ cm}^2/\text{V sec}$, which just as predicted by Eq. (21). The Hall mobility at 300 °K is $0.3 \text{ cm}^2/\text{V sec}$, which implies a value of r in the usual expression for the Hall constant

$$R_H = r/\rho ec \quad (23)$$

of 0.06. The constant r is a scattering function which is difficult to calculate, although it is usually of the order of unity in ordinary semiconductors. If we set $r = 0.06$, then Eq. (23) gives $\mu_H = 0.06 \mu$, and Eq. (21) then predicts a Hall mobility between 200 and 600 °K of

$$\mu_H \sim (0.018 \text{ cm}^2/\text{V sec}) e^{(0.075 \text{ eV})/kT}, \quad (24)$$

remarkably close to the observed behavior, Eq. (1). This gives us some confidence in our analysis. The thermoelectric power α is given by

$$\alpha = (k/e)(E_F/kT + a), \quad (25)$$

where a is a term due to the transport of kinetic energy. Below 500 °K, where Eq. (17) applies, α can be calculated to be

$$\alpha = (k/2e) \{ E_A/kT - \ln[(N_A - N_D)/N_v] + 2a \}. \quad (26)$$

If, as we have assumed, optical-phonon scattering predominates, then a should vary from 2.5 at low temperatures to 3.0 at high temperatures.^{95,97} At 300 °K with $a \approx 2.5$, Eq. (25) predicts $\alpha \approx 850 \mu\text{V}/^\circ\text{K}$. The temperature dependence of the thermoelectric power between 250 and 500 °K is also in agreement with Eq. (25). However, since r does not appear to be given by ordinary semiconductor theory in the valence band of NiO, it is not clear that these values of a apply.

Bosman and Crevecoeur³⁶ prepared ceramic samples of Li-doped NiO, in which the concentration of Li^+ and Ni^{3+} were determined by chemical analy-

sis. For a sample with 0.088% Li, the acceptor concentration is $N_A \sim 5 \times 10^{19} \text{ cm}^{-3}$. The chemical analysis indicated a donor concentration of $N_D \sim 2 \times 10^{18} \text{ cm}^{-3}$, or 4% compensation. The activation energy for conduction below 450 °K was $E_A \sim 0.30 \text{ eV}$, very close to that found by Austin *et al.*³⁰ In the exhaustion region, $T \sim 1000^\circ\text{K}$, $p \sim 5 \times 10^{19} \text{ cm}^{-3}$, and $\rho \sim 0.4 \Omega \text{ cm}$. Thus the mobility is $0.3 \text{ cm}^2/\text{V sec}$, also in agreement with Austin *et al.*³⁰ The thermoelectric power of these samples was measured at 1000 °K, and found to have to have $\alpha \sim 500 \mu\text{V}/^\circ\text{K}$. Assuming a value of $a = 3$ in Eq. (25), we obtain $N_v \sim 10^{21} \text{ cm}^{-3}$ or $m^{**}/m_0 \sim 5$. We can check the amount of compensation by noting that $p \sim N_D$ at 450 °K. At this temperature, $N_v \sim 3 \times 10^{20} \text{ cm}^{-3}$ and Eq. (22) gives $N_D \sim 3 \times 10^{18} \text{ cm}^{-3}$. Thus, a slightly higher (6%) compensation appears to be present than was estimated from the chemical analysis. At 300 °K, Eq. (17) shows $p \sim 4 \times 10^{16} \text{ cm}^{-3}$. This, together with the measured resistivity of $25 \Omega \text{ cm}$, gives a mobility of $\mu \sim 6 \text{ cm}^2/\text{V sec}$, in agreement with the value we estimated from Eq. (21). The temperature dependence of the thermoelectric power and resistivity from 200 to 500 °K are just what Eqs. (16), (17), (21), and (25) predict.

Ksendzov *et al.*²⁸ grew epitaxial single-crystal films of Li-doped NiO, but did not determine the Li concentration directly. Instead they estimated the amount of doping from the magnitude of the conductivity, a dangerous procedure in partially compensated material. They estimated from this method that the most investigated sample had 0.05% Li or $N_A \sim 3 \times 10^{19} \text{ cm}^{-3}$. The activation energy for conduction below 400 °K was $E_A \sim 0.34 \text{ eV}$. Above 400 °K, the slope of $\ln \rho$ versus T^{-1} decreased to $\frac{1}{2}E_A$, in accordance with Eq. (16). If we assume the exhaustion region begins in the vicinity of 1000 °K, then the resistivity of $\rho \sim 8 \Omega \text{ cm}$ implies a mobility of $\mu \sim 0.3 \text{ cm}^2/\text{V sec}$, again in agreement with the other sets of experiments.^{30,36} The measured thermoelectric power of $\alpha \sim 450 \mu\text{V}/^\circ\text{K}$, together with the assumption $a \approx 3$, leads to a polaron effective mass of $m^{**}/m_0 \sim 3$. At 400 °K, Eq. (22) gives $N_D \sim 6 \times 10^{17} \text{ cm}^{-3}$ or 2% compensation. At 300 °K, the measured resistivity of $750 \Omega \text{ cm}$ results in a mobility of $\mu \sim 2 \text{ cm}^2/\text{V sec}$. The discrepancies between the results of Ksendzov *et al.*²⁸ and the previously analysed results^{30,36} are most likely due to an actual value of N_A much smaller than they assumed. The Hall mobility measured by Ksendzov *et al.*²⁸ is given almost exactly by Eq. (1) from 180 to 400 °K, good evidence for the predominance of optical-phonon scattering which we have proposed.

From the analysis of data on Li-doped NiO, it can be concluded that all of these experiments can

be explained by a large-polaron band model in which the polaron effective mass is of the order of six free-electron masses. The activation energy E_A is a weak function of the doping concentration, decreasing from 0.34 eV for 0.05% Li to 0.28 eV for 0.20% Li. This is in agreement with the previously discussed suggestion^{91,92} that the effective dielectric constant of the lattice increases with increasing Li content. This increase should cause a decrease in the binding energy of the Ni^{3+} to the Li^+ center. The contribution of the binding energy to the activation energy for $2p$ -band conduction thus sharply decreases. However, even if it goes to zero, as it should for 10% Li concentration, some activation energy will remain. Note that this is not true for small-polaron hopping in the $3d^8$ band, since the hopping energy is so small. It is found experimentally^{20,29} that the activation energy decreases to the order of 0.16 eV for 8% Li content, but does not vanish. It can be assumed that 0.16 eV is the additional energy required to excite an electron from the $2p$ band to a free Ni^{3+} ion. Koide²⁰ has systematically studied the activation energies for conduction in NiO crystals of Li content varying from 1 to 7%. Koide calculated the slopes of a $\ln(\rho/T)$ -versus- T^{-1} plot rather than those of a curve of $\ln\rho$ versus T^{-1} , so that his activation energies are of the order of kT too large. When the latter slopes are calculated, it is found that the activation energies at temperatures below 400°K are approximately twice those above 500°K, as expected in partially compensated material. The value of E_A in Eqs. (16) and (17) drops from 0.30 eV for 1% Li to 0.16 eV for 7% Li. The breaks in the $\ln\rho$ -versus- T^{-1} curves thus are not of magnetic origin as has previously been assumed,^{29,30} but rather represent the points where $p \sim N_D$.

If the activation energy to create a free hole in the $3d^8$ band is smaller than the energy necessary to create a hole in the $2p$ band, as our rough calculations imply, the above analysis must be modified considerably, to take into account the $3d^8$ density of states. This will primarily have the effect of lowering the actual free hole concentration p and thus increasing μ . Although the larger values of μ would be consistent with conduction in a large-polaron band, this would increase the ratio of μ to μ_B , already anomalously large at 15. In addition, it might be expected that small-polaron hopping would dominate $2p$ band conduction at sufficiently low temperatures. However, there is much evidence for the predominance of impurity conduction, i. e., hopping between ionized and unionized acceptors, below 150°K.^{27,30,36} Since the material is partially compensated, ionized acceptors, or Li^+ centers without a nearest neighbor $N \text{ Ni}^{3+}$, exist down to $T=0$. Each of these provide 12 nearest

neighbor Ni^{2+} from which an electron can hop to a bound Ni^{3+} , which is an un-ionized acceptor. This hopping needs only a very small activation energy,¹⁶ and consequently dominates both $2p$ -band conduction and $3d^8$ hopping conduction below 50°K.²⁷ Thus the small-polaron hopping is essentially unobservable in dc measurements.

We should bear in mind the possibility that bound-polaron hopping, the hopping of holes among the 12 nickel ions which are nearest neighbors to a Li^+ ion, could be observed and even dominate the ac conductivity at sufficiently high frequencies. This can arise because bound-polaron hopping increases with frequency according to Eq. (2),^{98,99} in which τ is the average time of stay of the hole on a given site. On the other hand, in the absence of inhomogeneities, large-polaron band conductivity decreases with frequency as

$$\sigma \propto 1/(1 + \omega^2 \tau^2).$$

The hopping of free small polarons should be entirely independent of frequency.^{98,100} Thus, at sufficiently high frequencies, the bound-polaron hopping conduction could eventually predominate. The ac conductivity of both pure- and doped-NiO single crystals has been measured up to microwave frequencies,^{18,19,38} and the results are consistent. The conductivity as a function of frequency shows an ω^2 dependence between 10^6 and 10^9 Hz, with a saturation occurring above 10^9 Hz. Below 10^5 Hz, the frequency dependence is that of bandlike conduction in an inhomogeneous material.¹⁰¹ Above 10^6 Hz, the results show clearly that bound-polaron hopping predominates. The dispersion curves can be fit by a single staying time, of the order of 10^{-10} sec. The temperature and frequency dependence of the conductivity is shown in Fig. 1 for a sample doped with 0.001% Li^+ . It is clear that at each frequency, the ac conductivity is the sum of two processes; bound-polaron hopping at low temperatures and bandlike conduction at high temperatures. Furthermore, the hopping conduction is independent of temperature; an upper limit for the activation energy can be set at 0.01 eV. But this is precisely in agreement with the calculations of Sec. III B, in which a hopping activation energy of the order 0.005 eV was estimated for bound small polarons. Another important result of the ac experiments is that the bound-polaron hopping remained in evidence down to at least 100°K, about $\frac{1}{5}$ the Debye temperature of NiO. This is in agreement with Eq. (8), which predicts a very low temperature for the transition from polaron band to hopping conduction when the bandwidth is extremely small.

The lack of a measurable activation energy for small-polaron hopping in NiO also finds confirma-

tion from the mechanical and dielectric relaxation experiments,^{68,69} in which an upper limit of 0.01 eV could be set on the hopping energy in lightly doped samples. These experiments were carried out down to 4 °K, and the bound-polaron hopping was still evident, giving further confirmation of an extremely narrow $3d^8$ bandwidth.

2. Nonstoichiometric NiO

We have not yet discussed conduction in undoped, but nonstoichiometric material. In this case, there must be an excess of oxygen,⁷⁷ thus producing Ni vacancies. Partial compensation can be brought about by the creation of oxygen vacancies or by the presence of trivalent impurities. The theory proceeds just as for Li-doped NiO, with the exceptions that it takes a larger energy (by about 0.2 eV) to singly ionize the vacancy than the Li^+ center, and the vacancy can be doubly ionized, whereas the Li^+ center cannot. It should be noted that partial compensation should lead to a single ionization of a sizable fraction of the vacancies, but these ionized vacancies can still act as deep acceptors since there can be a second ionization. This could explain the strange results obtained for the oxygen partial pressure dependence of the conductivity. It can be shown²² that if singly ionized nickel vacancies predominate, then $\sigma \propto [P(\text{O}_2)]^{1/4}$, where $P(\text{O}_2)$ is the partial pressure of oxygen; on the other hand, if doubly ionized vacancies predominate, $\sigma \propto [P(\text{O}_2)]^{1/6}$. However, as pointed out by Bransky and Tallan,²² if a large degree of compensation is present, the conductivity will increase proportional to $[P(\text{O}_2)]^{1/4}$, despite the predominance of doubly ionized vacancies. Thus, a simple explanation of the fact that several experimental measurements clearly show either a $P^{1/6}$ law^{21,26,102} or a $P^{1/4}$ law^{22,23,103,104} is that the latter samples are much more compensated than the former.

3. Summary

To summarize the experimental results in NiO to date, it seems clear that (a) between 200 and 1000 °K, the predominant conduction mechanism is the motion of holes in a band with an effective mass of about six free-electron masses; (b) the carrier concentration in samples lightly doped with Li is thermally activated, with an acceptor ionization energy of 0.3–0.4 eV; (c) the Li acceptors are always partially self-compensated by donors; (d) the scattering, at least between 300 and 600 °K, is dominated by free-hole optical-phonon scattering, which leads to an exponentially decreasing mobility, with a negative activation energy of 0.075 eV; (e) the room-temperature mobility is about 5 $\text{cm}^2/\text{V sec}$; (f) the Hall mobility between 300 and 600 °K is proportional to the drift mobility, with a value of the

scattering constant r of approximately 0.06; (g) impurity conduction, resulting from the hopping of holes bound to the partially compensated Li^+ centers, dominates the dc conductivity at very low temperatures; (h) intrinsic conduction is observable above 1000 °K in the more highly compensated samples; (i) the hopping of bound small polarons around the Ni^{2+} sites which are nearest neighbors to a Li^+ center dominates the ac conductivity for frequencies above 10^5 Hz and temperatures below 300 °K; and (j) the bound-polaron hopping energy is less than 0.01 eV.

As a final comment, we should note that in a partially compensated material, a large concentration of ionized donors and acceptors exists, even at $T = 0$. These act as traps for any free carriers which are excited, for example, by optical excitation. This is the likely explanation of the fact that direct measurements of the drift mobility,³⁷ using time-of-flight measurements of photoexcited carriers,¹⁰⁵ resulted in a room-temperature value of $\mu_D \sim 0.3 \text{ cm}^2/\text{V sec}$, an order of magnitude lower than the conductivity mobility estimated above. Once these free carriers are trapped by ionized donors or acceptors, they are in nonequilibrium positions; i. e., electrons are trapped above the Fermi energy, holes are below E_F . However, in order to reach equilibrium, they need phonon assistance to escape from their localized states. At low temperatures, the paucity of phonons can preserve the nonequilibrium situation for long times. This has been observed in photoconductivity experiments on MnO.⁷⁰ A study of the photocurrent decay kinetics showed a fast component of the relaxation, less than 10^{-5} sec, corresponding to the cutoff time of the illumination pulse. At 300 °K, slower decay times, from the order of 10^{-3} sec to several seconds, were observed. At 77 °K, the slow component of the decay time reached tens of minutes. This is graphic evidence for the existence of charged traps in these materials.¹⁰⁶

In Appendix B, we give a fairly extensive review of the experimental data on MnO and CoO, which exhibit physical properties similar to those of NiO. Although these data are sparser for MnO and CoO than for NiO, and there are important differences among the three materials, the experiments are nevertheless consistent with the model we have proposed.

IV. REPRESENTATION OF BAND STRUCTURE ON SINGLE-PARTICLE DIAGRAM

We have previously suggested a method for representing the effective one-electron density of states of a material in which some of the outer electrons are localized.^{14,17} It is clear from the considerations of Sec. III that the localized outer electrons

cannot merely be treated as core electrons since they contribute to both optical excitations and small-polaron conduction. However, since correlations are of vital importance, a one-electron representation will not be valid. We therefore suggested a *split* density-of-states plot, with the bandlike states drawn to the left and the localized states drawn to the right. States on the left can be treated as ordinary one-electron states, and any free carriers on the left contribute to conductivity in the normal manner. On the other hand, states on the right are quasiparticle states and contribute to conduction only by means of thermally activated hopping. These states can be handled in a one-electron-like manner only if special additional rules are introduced. However, this should be no more mysterious or cumbersome than the representation of donor, acceptor, or exciton states in more normal semiconductors.

One of the difficulties with treating simultaneously both localized and itinerant states of a polar material is the fact that, if we assume the Franck-Condon principle is valid, we must draw different energy diagrams for electrical properties than for optical properties. (This is not necessary when large-polaron theory is applicable.) However, this is not too serious when we realize that the maximum difference in energies is of the order of 0.2 eV. Another difficulty is setting the reference energies on two sides of the diagram. Since the right-hand side represents quasiparticle states, it is necessary to set the energy of one of the states on the right relative to that of one of the states on the left. The most convenient choice is to pick out the most important transition between a localized and an itinerant state and set the energy of this transition correctly. This is just what is done in handling multiple donor and acceptor states in conventional wide-band semiconductors. However, as we have seen in the discussion of Sec. III, this choice depends on whether we are interested in optical or electrical properties, in the sense that the properties of the *pure* material dominates the optical spectrum, but the energy-level structure of *impure or nonstoichiometric* material is most important in analyzing electrical behavior.

With this in mind, and using the discussion in Sec. III as a guide, we present a sketch of the effective one-electron density of states of pure stoichiometric NiO in Fig. 6. Since the diagram will be most useful in optical analyses, we ignore polaronic binding energies. The top of the highest filled level sets the zero of energy. States on the left- and right-hand sides are connected by setting the energy of the lowest-energy $3d^8 \rightarrow 3d^7 + 4s$ transition. This makes all other transitions across the center line approximations. However, in this case,

the only other one of significance $2p + 3d^8 \rightarrow 3d^9$ is correct to within 0.5, as far as the minimum-energy transition is concerned.

Only one additional rule need be kept in mind to interpret Fig. 6. This is that states which are drawn with dashed lines are available only for transitions from states on the right. Bearing this in mind, the density of states as shown in Fig. 6 can be used to give the absorption spectrum, Fig. 3. This diagram is the one to use to analyze photoconductivity and photoemission spectra as well.

If we are now interested in interpreting the electrical properties of NiO, a diagram such as Fig. 7 is appropriate. Here the Fermi energy is drawn in the usual manner and taken to be the zero of energy. The energies of the $2p$ band and the $3d^8$ levels are both set relative to this energy. As noted in Sec. III, this significantly changes the apparent relative positions of these two bands, although it must be emphasized that the $3d^8$ levels cannot be treated as if they formed an ordinary one-electron band. We have assumed in Fig. 7 a Li-doped sample of NiO, with some compensation by oxygen vacancies, and also some nickel vacancies present. At very low temperatures, impurity conduction in the Li^+ band predominates. At higher temperatures, $2p$ -band hole conduction dominates thermally activated hopping of holes through the $3d^8$ band. However, hopping in the $3d^8$ band may be observed as an increase of ac conductivity with frequency. When holes in

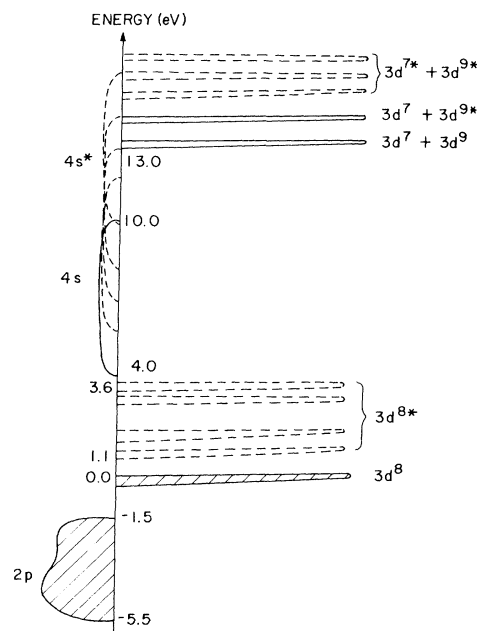
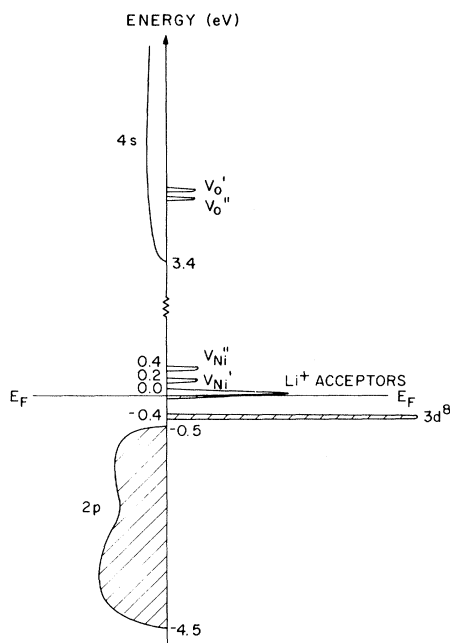


FIG. 6. Optical band structure of pure stoichiometric NiO. States which are filled at $T = 0$ are shaded.



Let us summarize the evidence in favor of the

model for NiO presented in this paper. We have suggested that (1) the $3d$ states are sufficiently localized so that the pure material is a Mott insulator and the transfer integral of a hole between a Ni^{3+} and a Ni^{2+} ion is very small; (2) holes in the $3d^8$ band contribute to conduction only by means of small-polaron hopping at all ordinary temperatures and with a very small activation energy; (3) the dominant conduction mechanism between 150 and 1000°K is by holes in the oxygen $2p$ band; and (4) the intrinsic energy gap in NiO is about 3.8 eV.

The evidence for very localized $3d$ states is (1) the insulating nature of the very similar materials MnO and CoO; (2) the excellent correlation of the optical absorption spectrum between 1 and 4 eV with that of dilute solutions of Ni^{2+} in MgO; (3) the activation energy of 0.2 eV which remains when the Li concentration exceeds 10%; (4) the fact that no Mott transition has ever been observed in NiO, despite Li concentrations of up to 40%, which creates acceptor concentrations of 10^{22} cm^{-3} and reduces the lattice parameter 2%,¹⁰⁸ or, even more striking, despite application of pressures up to 500 kbar,¹⁰⁹ which reduces the lattice parameter about 7%¹¹⁰; and (5) the long staying time of 10^{-10} sec for a hole bound to an impurity site, as estimated from the ac conductivity.

The evidence for small-polaron hopping with a low activation energy at all ordinary temperatures, as is suggested by Eqs. (5)–(8), is primarily from the ac conductivity and dielectric-loss results, which imply (1) bound holes hop among the nearest-neighbor Ni^{2+} sites to a Li^+ center with an activation energy not greater than 0.01 eV; (2) this hopping is observable down to at least 100°K , less than $\frac{1}{8}$ the Debye temperature; (3) the agreement of the dielectric-loss experiments with the ac conductivity results down to 4°K , 0.4% of the Debye temperature; and (4) the absence of any region where conductivity decreases with frequency, even at low temperatures and optical frequencies.

The evidence for the predominance of $2p$ -band conduction in the 150– 1000°K range is (1) the fact that the $2p$ band is near the Fermi energy in Li-doped or nonstoichiometric material, as calculated in Sec. IIID and borne out by the observation of 0.2-eV activation energy in samples doped with over 10% Li; (2) the bandlike nature of the conductivity in the 150– 1000°K range; (3) the relatively low effective mass of about six free-electron masses which is consistent with at least three sets of conductivity data; and (4) the calculation of a mobility as a function of temperature, Eq. (21), which is in agreement with the measured thermoelectric power and is proportional to the observed Hall mobility. We should note that the reason for the low room-temperature mobility of $5\text{ cm}^2/\text{V sec}$ in NiO is the

fact that optical-phonon scattering predominates, and that NiO has a very large Debye temperature, 870°K .

Finally, the evidence for an intrinsic gap of 3.8 eV comes from (1) the absorption edge; (2) the photoconductivity edge; (3) the very high-temperature activation energy of 1.9 eV, particularly in compensated samples; and (4) the electroreflectance data,⁵² which fixes the edge at 3.7 ± 0.1 eV.

Another suggestion we have made (see Appendix C) concerns the possible phase separation or spinodal decomposition of NiO heated in air or at a high partial pressure of oxygen at high temperatures. The consequent formation of spinodal networks of n -type Ni_3O_4 could be responsible for the Hall anomaly and the lack of consistency of the high-temperature data. In connection with this, we should note that references to thermal decomposition of NiO at 650°K appear in the literature,^{111,112} and during a recent photoabsorption study, emission of oxygen and the appearance of regions of metallic nickel were noted, beginning at 600°K .¹¹³ This suggests another explanation for high-temperature anomalies, since very small regions of metallic nickel could lead to considerable havoc in the electrical properties.

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APPENDIX A: CRYSTALLINE-FIELD STABILIZATIONS

In order to calculate the crystalline-field stabilizations of various ions in the transition-metal monoxides, it is important to determine whether the high-spin state or the low-spin state of the ions is stable in the crystal. For many ions, such as Ni^+ ($3d^9$) and Ni^{2+} ($3d^8$), these two states are identical. When the high-spin and low-spin states differ, the ground state is determined by a comparison of the pairing energy to the difference in crystalline-field stabilizations of the two states. For example, the low-spin and high-spin states of Ni^{3+} are quite different, and there is no direct experimental evidence for the occurrence of either in NiO. The high-spin state has a stabilization of $8Dq$ and the low-spin state one of $18Dq$. Thus if $10Dq$ is larger than the Hund's-rule multiplet splitting, Ni^{3+} will be in the low-spin state. The relevant multiplet splittings, or pairing energies, have been calculated in terms of the Racah parameter B and C .⁹⁰ For Ni^{3+} , it is

$4(B+C)$, which can be evaluated from the experimental values of the Slater-Condon parameters¹¹⁴ as 2.4 eV. From the estimated⁴⁴ value of Dq for Ni^{3+} , $10Dq \sim 2.3$ eV, and thus Ni^{3+} might be expected to be in a high-spin state in NiO. Although the above energy difference is small the conclusion is probably valid, since these calculations underestimate the pairing energy below the Néel temperature, where the antiferromagnetic order favors the high-spin state. On the other hand, for the case of CoO, the pairing energy for a Co^{3+} ion can be estimated as 2.8 eV, but the crystalline-field stabilization of the low-spin state is $20Dq$, or approximately 4.4 eV.^{44,115} Thus, a Co^{3+} ion in CoO should be in a low-spin state, in accordance with experiment.⁶³ A similar calculation for Mn^{3+} in MnO, using recent experimental data for the Racah parameters,¹¹⁶ gives 2.7 eV for the pairing energy and 2.6 eV for the crystalline-field stabilization of the low-spin state. In general, the crystalline-field stabilization energies are largest for the d^5 and d^6 configuration, and the pairing energies are lowest for d^6 and d^7 configuration, for equal values of Dq , B , and C . It is a reasonable conclusion that Co^{3+} and Fe^{3+} in their respective monoxides are in low-spin states, while Mn^{3+} and Ni^{3+} are in high-spin states.

APPENDIX B: EXPERIMENTAL DATA FOR MnO AND CoO

The situation in other narrow-band materials is much less clear than in NiO, primarily because many fewer experimental studies have been carried out.^{1,117} There is some evidence, however, that the ideas discussed in this section apply to other Mott insulators as well as to NiO. Even in rare-earth compounds, such as EuO ,¹¹⁸ the crystalline-field and multiplet splittings of $4f^n$ bands have now been observed in pure material. In Sec. II, we noted some differences between the results for NiO and other transition-metal oxides. For example, dielectric-loss experiments on CoO ⁶⁷ indicate an activation energy for bound-polaron hopping of 0.20 eV, much higher than the small-polaron binding energies we calculated in Sec. III B. Bosman and Crevecoeur^{63,67} suggested that this excess activation energy arises because Co^{3+} is in a low-spin state in CoO, and hopping of an electron from a high-spin $3d^7$ state ($S=\frac{3}{2}$) to a low-spin $3d^6$ state ($S=0$) requires a spin flip. The calculations in Appendix A indicate Co^{3+} is stabilized in a low-spin state in CoO, and tend to confirm this interpretation. Thus, there is no evidence that the hopping energy of small polarons in CoO is any larger than in NiO.

Furthermore, recent transport measurements⁶³ in CoO show great similarities between that material and NiO. For a ceramic sample of CoO doped

with 0.08% Li, Bosman and Crevecoeur⁶³ find that 1200°K a resistivity of $\rho \sim 0.5 \Omega \text{ cm}$ and a thermoelectric power of $\sim 500 \mu\text{V}/^\circ\text{K}$. If we assume that all acceptors are ionized, $\rho \sim 5 \times 10^{19} \text{ cm}^{-3}$, and thus $\mu \sim 0.25 \text{ cm}^2/\text{V sec}$, very nearly the same as determined for NiO above. Assuming, as in NiO, the predominance of optical-phonon scattering, we can evaluate a polaron effective mass $m^{**}/m_0 \sim 4$. For $T \sim 500^\circ\text{K}$, the activation energy was $E_A \sim 0.04$ eV, and Eq. (17) shows $N_D \sim 2 \times 10^{18} \text{ cm}^{-3}$, or a 4% compensation. At 300°K we can estimate $\mu \sim 6 \text{ cm}^2/\text{V sec}$, also very similar to the estimated value for NiO. The data clearly shows that the Hall mobility is essentially proportional to the conductivity mobility and that the thermoelectric power is proportional to the logarithm of the resistivity, very strong evidence for bandlike conduction. There is as yet insufficient data to definitely conclude whether or not this conduction is in a d band or the $2p$ band, but the dielectric-loss experiments, in particular, and the similarities with NiO indicate the probability of p -band predominance.

MnO also appears to be similar to NiO in most respects.¹ The optical absorption below 3.8 eV is characterized by peaks which correlate with the crystalline-field splittings,^{42,76,72,116} and an absorption edge appears in the vicinity of 3.8 eV.^{71,116} However, photoconductivity was not only associated with excitations across the intrinsic edge, but also with excitations corresponding to each crystalline-field peak.⁷⁰ This should not be surprising if we recall that in impure or nonstoichiometric material, the energy necessary to free a $2p$ hole is less than 1 eV; for MnO, it is of the order of 0.6 eV.⁶⁵ The crystalline-field peaks are located in the 2.0–3.5-eV range. Thus, nonradiative decay of the excited Mn^{2+} ions via inelastic phonon scattering can free $2p$ carriers. The sign of the photocurrent indeed showed that the carriers were holes.⁶⁵ Furthermore, although the photocurrent corresponding to intrinsic excitation was temperature independent from 77 to 300°K, that corresponding to the crystalline-field excitations increased with temperature. Between 200 and 300°K, the photocurrent resulting from the lowest (2.0 eV) crystalline-field excitation appeared to be thermally activated, with an activation energy of 0.07 eV, essentially the optical-phonon energy.¹¹⁹ Pekar¹²⁰ has shown that this is the expected temperature dependence for two-phonon scattering of large polarons at low temperatures.

A comprehensive study of electrical transport in single crystals of Li-doped MnO has been carried out.⁶⁵ As was found in NiO and CoO, at low temperatures the activation energy for conduction is twice that at high temperatures, strong evidence for partial compensation. However, in this case, the authors obtained still more compelling evidence.

They took a sample whose high-temperature activation energy was 0.34 eV and subjected it to intensive fast-neutron irradiation. After irradiation, the conductivity was sharply reduced, owing to induced crystalline defects. The irradiated samples were then heated to 900°K, and showed an activation energy of 0.71 eV, almost exactly twice that of the original material. Slow cooling then produced exactly the preirradiation conductivity-versus-temperature curve. Clearly, the structural defects introduced were donors, most likely oxygen vacancies, which further compensated the material. This increased the region of applicability of Eq. (17) to much higher temperatures. The annealing process, however, removed all the radiation-induced defects.

The analysis of the transport data of MnO is complicated by the fact that both the magnitude and the temperature dependence of the thermoelectric data strikingly depend on the atmosphere in which the crystal is heated. The difference in α for a sample measured in a pure argon atmosphere and one measured in argon containing 260-ppm oxygen is a factor of 3 at 400°K. Furthermore, even in pure argon, the thermoelectric power decreases considerably after a number of heating cycles. These results can be explained by assuming that oxidation leads to the introduction of *donor* centers which further compensate the material. This is quite surprising, since the most logical donor center is an oxygen vacancy. However, the possibility exists that oxidation leads to the formation of large regions of the spinel phase, Mn_3O_4 , which is *n* type.

Nevertheless, it is clearly dangerous to use the thermoelectric power measurements in any quantitative analysis of the data. The Hall-effect measurements were performed in a vacuum, and thus provide a more reliable guide to the mechanisms for transport. The activation energy of R_H between 400 and 700°K was 0.34 eV, exactly the same as that of the conductivity. The Hall mobility was thus virtually temperature independent, $\mu_H \sim 0.007 \text{ cm}^2/\text{V sec}$. The sample contained 0.027% Li^+ , which corresponds to $N_A \sim 10^{19} \text{ cm}^{-3}$. The activation energy for conduction was $E_A \sim 0.68 \text{ eV}$, and from the break in the *n*-versus- T^{-1} curve, the donor concentration can be estimated as $N_D \sim 10^{15} \text{ cm}^{-3}$. Thus the original sample was only 0.01% compensated, much less

than the NiO and CoO samples previously analyzed. Without either reliable thermoelectric data or resistivity measurements in the exhaustion region, neither an effective-mass nor a room-temperature mobility can be estimated. Let us note, however, that a μ_H/μ ratio of 0.25, that found in CoO, leads to an effective mass of seven free-electron masses and a mobility of $0.03 \text{ cm}^2/\text{V sec}$ at 700°K; on the other hand, the NiO value of $r \sim 0.06$ would indicate an effective mass equal to the free-electron mass, and a mobility of $0.1 \text{ cm}^2/\text{V sec}$ at 700°K.

APPENDIX C: FAST-NEUTRON IRRADIATION OF NiO

The irradiation results described in Appendix B are not unique to MnO. NiO has also been subjected to intensive bombardment by fast neutrons,^{121,122} with similar results. The resistivity measurements were only carried out below 300°K, where Eq. (17) is applicable even in the nonirradiated material, so that no change in activation energy was observed. However, conductivity and thermoelectric power both decreased sharply after irradiation, implying the formation of *n*-type defects, further compensating the material. Cojocaru¹²² pointed out that the results of radiation exposure could also be explained by an increase in *p*-type defects, but a sharp decrease in carrier mobility. However, this decrease must be three orders of magnitude, which seems much too large for the predicted increase of a factor of 45 in the acceptor concentration. The former explanation appears preferable, and is also consistent with the MnO results.

Analogous to the suggestion in Appendix B with respect to MnO, a possible source of radiation-induced compensation in NiO is the formation of regions of *n*-type Ni_3O_4 . The further possibility that Ni_3O_4 regions appear in oxygen-rich NiO samples, obtained, for example, by heating nearly stoichiometric NiO in air has interesting consequences. The presence of free electrons in Ni_3O_4 could conceivably be responsible for the sign reversal that occurs in the Hall constant above 600°K. The second phase may also explain the discrepancies between the results of the very high-temperature measurements^{21-23,26} and those at ordinary temperatures.

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