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Band Structure of Magnetic Semiconductors*

Abstract: The band structure of materials in which both localized and itinerant outer electrons are simultaneously present is discussed. The Franck-Condon Principle is applied, and small and large polaron formation is taken into account. A scheme for estimating the densities-of-states of perfect crystals and doped or non-stoichiometric crystals is suggested, based on the ionic many-body states as a starting point. Screening, covalency, crystalline-field and overlap effects are quantitatively considered. In particular, the band structures of both pure and Li-doped NiO are derived and found to be in agreement with the experimental observations. It is shown that conclusions which are based on ordinary donor and acceptor techniques fail to account for the effects of doping even in a qualitatively correct manner, due to the neglect of important correlation effects.

1. Introduction

The subject of magnetic semiconductors is a relatively new one, as solid state disciplines go. This is somewhat surprising, since magnetism has been known for over 2500 years,[1] and the oldest magnet, lodestone[2] (Fe_3O_4), is indeed semiconducting. Nevertheless, even in terms of the present-day theory of solids, it is not easy to see why magnetic semiconductors exist. We are familiar with magnetic insulators, ionic materials in which all the electrons are taken to be completely localized on their respective ions. If some of the ions comprising the material contain unpaired d or f electrons, the ion has a permanent magnetic moment and the solid is magnetic. We are not usually concerned with the band structure of such a material since the energy gap is so large that no measurable electronic conduction occurs in pure samples. On the other hand, we are familiar with magnetic metals, such as most of the transition metals and rare earths, in which outer electrons that form wide bands are present. These bands are partially filled and thus lead to metallic conductivity. For such materials, band structure calculations can be performed, and the results are in good agreement with a wide range of experimental data.[3] But the concept of a magnetic semiconductor requires either a filled band of electrons possessing a nonvanishing magnetic moment or else the simultaneous existence in a crystalline solid of both localized and itinerant outer electrons. Neither of these possibilities is as intuitive as are the simple cases of magnetic insulators and magnetic metals.

It is worthwhile to pay some attention to the band structure of the more well-known metals and insulators, before attempting to analyze the semiconductors. Let us first consider a transition metal, such as Ni. Atoms of Ni contain, outside of the closed-shell argon configuration, eight 3d electrons and two 4s electrons. In the solid, the 3d and 4s electrons both overlap sufficiently to form energy bands. Since the 4s electrons are considerably farther spread out around their ion cores than are the 3d electrons, the 4s band is much wider than the 3d band. But since the 4s and 3d electrons have almost the same energies on a Ni atom,[4] these bands overlap in the solid. The combined 3d and 4s bands contain 12 states per atom, and since only ten 3d and 4s electrons are present on each Ni atom, Ni must be a metal. The band structure of metallic Ni has been calculated from first principles,[5] and is in agreement with a large collection of experimental data. Although some problems still remain, most of us feel that the main features of the magnetic metals are understood in principle.

But what about an insulator, such as NiF_2? If we insist on maintaining a band approach, it at first seems difficult to account for the absence of partially filled bands. We can consider the crystal to be made up of Ni^{2+} ions and F^- ions. The F^- ions have the closed-shell Ne configuration, but a Ni^{2+} ion has eight electrons outside of the closed-shell argon configuration. Why should we not be left with a 2/3 filled 3d-4s band, and have metallic conductivity? The explanation of this invokes two separate effects, neither of which is especially obvious. Firstly, the energy levels of the 3d and 4s electrons of Ni^{2+} are not approximately the same, as they are in Ni. In Ni^{2+}, the 4s electrons have much higher energy than the 3d elec-

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trons.[4] This means that in solid Ni^{2+} compounds, the 4s band is considerably above the 3d band. But this is still insufficient to explain the insulating nature of NiF_2, since the 3d band should remain partially (4/5) filled.

The explanation of the second point has been controversial for the last 20 years, since it was first proposed by Mott.[6,7] Mott pointed out that for the case of a particularly narrow band, the reduction in energy brought about by band formation might not overcome the increase in electronic electrostatic repulsion which necessarily arises from the itinerant nature of electrons moving in Bloch states. Since the latter effect is an electronic correlation, neglected in the Hartree-Fock approximation used in all band calculations, it cannot be analyzed from the results of a band calculation. However, the appearance of very narrow, partially filled bands in any calculated band structure can alert us to a possible lack of validity of the results.

Why should the 3d band of NiF_2 be sufficiently narrow so that the 3d electrons remain localized on the Ni^{2+} ions? The answer to this seems to be primarily a combination of the decreased size of the Ni^{2+} ion relative to the Ni atom taken in conjunction with the much larger Ni-Ni nearest-neighbor separation in the compound than in the metal. However, a third condition is also necessary, that the lattice be strongly ionic, since covalency effects between the Ni^{2+} and F^- ions could effectively increase the width of the Ni^{2+} 3d band.[8]

Since NiF_2 is almost totally ionic, the result is that the 3d band is simply too narrow to support metallic conduction, and it is a more accurate starting point to assume that the 3d electrons are localized on the nickel ion cores. The eight 3d electrons on each Ni^{2+} ion then give the crystal its magnetic properties. We can estimate the energy-band structure of magnetic insulators such as NiF_2 by an extreme tight-binding approximation.[9] In this approach we begin with the ionic energy levels of Ni^{2+}, F^-, Ni^+, and F, take into account the Madelung potential, electronic screening, crystalline field, and covalency effects, and then allow the resulting levels to broaden into bands of widths consistent with the direct overlap of their respective wave functions. We can look at the creation of free carriers as the band generalization of free ion processes such as

$$Ni^{2+} + F^- \rightarrow Ni^+ + F, \qquad (1)$$

or

$$Ni^{2+} + Ni^{2+} \rightarrow Ni^+ + Ni^{3+}. \qquad (2)$$

Process (1) creates a hole in the fluorine 2p band and an electron in either the nickel $3d^9$ band or the nickel 4s band. Process (2) leaves a hole in the nickel $3d^8$ band and creates an electron in either the nickel $3d^9$ or the nickel 4s band. Even if we assume sizeable bandwidths, it turns out that the minimum energy necessary to such intrinsic electron-hole pairs is of the order of several eV. Thus even if the carriers in these bands are quite mobile in an applied electric field, we should not get a sizeable intrinsic electronic contribution to conductivity at ordinary temperatures. This type of analysis is in accord with experiment.[9]

Thus we can, in a relatively straightforward manner, obtain the band structure of magnetic insulators. There are a few additional rules we need to impose in order to use a diagrammatic representation of this type of band structure to predict the electrical and optical properties.[9,10] For example, in order to analyze photoconductivity experiments, localized states must be carefully distinguished from itinerant states. Within the set of localized states, states corresponding to excitations which leave the number of electrons on the ion core invariant must be distinguished from states of the ion core with an extra electron present, or else nonexistent transitions will appear to be possible, and the Fermi level will be set incorrectly. Nevertheless, we can claim that the main features of magnetic insulators are understood in principle.

The important question that remains is, How do we bridge the gap between magnetic metals and insulators? Can we interpolate between localized and itinerant states and between the large correlation and small correlation limits? A comforting answer to this question was given by Mott,[7] who suggested that we don't even have the problem. Mott presented several convincing reasons why the transition from localized to itinerant states in periodic crystals must be sharp. Although the existence of such a Mott transition has not been universally accepted, there is now strong theoretical[11] and experimental[12] evidence in its favor.

A quantitative model has been presented by Hubbard,[13–15] who introduced short-range electronic correlations, i.e., correlations between electrons on the same ion core only, into the ordinary band equations. Hubbard[15] found some evidence for a Mott transition, but the transition was not at all sharp. However, the neglect of interionic correlations could well have suppressed the sharpness of the transition.

We have not yet considered interactions between the electrons and the ions. In ionic materials, it is clear that this coupling must be strong, since the electrons attract positive ions electrostatically but repel negative ions. Since longitudinal optical lattice vibrations induce alternating regions of excess positive and negative charge density in an ionic crystal, the coupling between electrons and LO phonons is particularly large. Such interactions are unimportant in both magnetic metals and magnetic insulators, since the metals are not ionic and the insulators have essentially no free electrons. On the other hand, electron-phonon interactions are particularly important in magnetic semiconductors.

In cases where the electron-phonon coupling is large, it is more accurate to use a basis of eigenstates of a part of the Hamiltonian which includes the electron-phonon interaction term.[16] These states can be looked at as those of a quasiparticle called a polaron, essentially an electron moving with an associated lattice deformation. Two limits of polaron theory have been considered quantitatively. In large-polaron theory,[17] the extent of the associated lattice deformation is sufficiently large that the lattice can be treated as an elastic continuum. Calculations within this model show that the polaronic band structure of a material resembles the electronic band structure in the absence of lattice interactions, except that the effective mass increases and the energy levels of the states decrease somewhat. On the other hand, in the limit of small-polaron theory,[18] in which the electronic bandwidth is small compared to the electron-phonon interaction energies, major modifications of the electronic band structure result. Above a critical temperature, small polarons can participate in electrical conduction only with the assistance of phonons, a process known as thermally activated hopping. This conduction process differs from ordinary semiconduction in that the mobility must be an exponentially increasing function of temperature.

One further point must be borne in mind. Formation of a small polaron requires a lattice deformation around a free electron or hole. The Franck-Condon principle suggests that the lattice cannot respond to excitations at optical frequencies. Thus, if the small-polaron binding energy is significant, the energies necessary to excite certain electronic transitions optically must exceed the thermal excitation energies. Thus the optical energy-band structure can differ considerably from the electrical energy-band structure for narrow band ionic materials.

In this paper, the optical and electrical densities-of-states of magnetic semiconductors are discussed. In section 2, pure stoichiometric single crystals are considered. In section 3, the major effects that doping or nonstoichiometry can have on this class of materials are quantitatively estimated. The conclusions are summarized in section 4.

2. Band structure of perfect crystals

In principle, we can envision three classes of magnetic semiconductors. A particularly simple type is just a semiconducting variation of a magnetic metal. It is well known that a ferromagnetic[19] or antiferromagnetic[20] alignment of spins induces an extra splitting of all the energy bands, due to the removal of the spin degeneracy. It has also been suggested recently that a localized magnetic moment, without any long-range order, can bring about the same splitting.[21] It is certainly a possibility that such a splitting could introduce a real energy gap into the density-of-states, thus producing an ordinary semiconductor. Spin-polarized band calculations have indeed predicted that the materials MnO[22] and NiO[23] are examples of this class of magnetic semiconductors. There is some evidence that NiS is a member of the class.[24] However, these conclusions are, at best, controversial.[25,26] Any materials that are magnetic semiconductors of this type can be completely understood in terms of elementary band theory, and should be as similar to magnetic metals as, say, Ge is similar to Zn.

A second type of magnetic semiconductor is very similar to a magnetic insulator. The magnetic electrons can be treated as completely localized on their ion cores. When made non-stoichiometric or doped with specific impurities, such a material can be left with excess localized electrons or holes. These excess carriers can be expected to form small polarons and hop through the lattice with phonon assistance.[27] If the thermally activated small polarons are reasonably mobile, the hopping contribution to conductivity will be sufficiently large to classify the material as a semiconductor rather than an insulator. There is some evidence that $LaCoO_3$ [28] and Pr_2O_3,[29] among others, are magnetic semiconductors of this type. Once again, this class can be understood in principle, using a consistent, localized-electron approach.

Unfortunately, a third type of magnetic semiconductor can exist. It is possible for the magnetic electrons to be extremely localized and still have ordinary semiconduction occur in a given material, provided that there are wide bands, corresponding to non-magnetic electrons, in the vicinity of the Fermi energy. This class of materials is the most difficult to analyze theoretically, since localized and itinerant outer electrons are simultaneously present, and a consistent approach cannot be used. A large group of rare-earth compounds[30] appears to fall into this class, and it has been suggested[10,31] that many transition metal compounds do also. The existence of these materials forces us to bridge the gap between insulating and metallic states.

The only quantitative starting point that we have is the model of Hubbard,[13–15] who suggested the approximate Hamiltonian.

$$H = \sum_{i,j} \sum_{\sigma} T_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} . \qquad (3)$$

The first term in Eq. (3) is just the one-electron energy, and the second term adds the intraionic Coulomb repulsion U whenever a spin-up and a spin-down electron are simultaneously present on the same ion core. The Hamiltonian, (3), has the advantage of being exact in both the zero bandwidth (atomic) and the purely itinerant ($U = 0$) limits. Thus, it may be a reasonable approximation to use for the analysis of magnetic semiconductors.

Hubbard found that the problem could be handled quantitatively only for the case of a single s band, and even then only by using some ad hoc approximation procedures.[15] His final result was then quite simple.

Table 1 Conduction properties and estimated range of optical absorption energies for low-energy excitations in perfect NiO crystals. An asterisk refers to the excited crystalline-field levels.

Process	*Type of conduction*	*Range of optical absorption energies*
$3d^8 \rightarrow 3d^{8*}$	non-conducting	1–4 eV
$3d^8 + 3d^8 \rightarrow 3d^7 + 3d^9$	hopping conduction	13 eV
$3d^8 + 3d^8 \rightarrow 3d^7 + 3d^{9*}$	hopping conduction	14 eV
$3d^8 + 3d^8 \rightarrow 3d^{7*} + 3d^9$	hopping conduction	14–19 eV
$3d^8 + 3d^8 \rightarrow 3d^{7*} + 3d^{9*}$	hopping conduction	15–20 eV
$3d^8 \rightarrow 3d^7$ + (electron in 4s band)	n-type semiconduction	4–10 eV
$3d^8 \rightarrow 3d^{7*}$ + (electron in 4s band)	n-type semiconduction	5–16 eV
$3d^8$ + (electron in 2p band) $\rightarrow 3d^9$	p-type semiconduction	14–18 eV
$3d^8$ + (electron in 2p band) $\rightarrow 3d^{9*}$	p-type semiconduction	15–19 eV
(electron in 2p band) → (electron in 4s band)	n- and p-type semiconduction	5–16 eV

In the zero-bandwidth limit, the quasiparticle spectrum was just two zero-width bands, separated in energy by U. As the ratio of bandwidth to U increases, these two bands begin to spread symmetrically, then overlap, and finally merge into one. This result implies a smooth transition between localized and itinerant states.

We shall adopt this conclusion in order to analyze the band structure of magnetic semiconductors. The major implication, for our purposes, is that we can begin our analysis with the known atomic and ionic energy levels, and obtain reasonable estimates of the structure of the itinerant bands by allowing a symmetric spread around the atomic levels until the proper bandwidth is obtained. The correct bandwidths can be determined from ordinary band calculations. On the other hand, this method guarantees that the localized states are handled accurately, since only slight spreading from the atomic limit is expected. It should be remarked that this procedure gives excellent results when applied to non-magnetic insulators, such as MgO and TiO_2, even when some relatively wide ($\approx$12 eV) bands are present.[9]

We shall restrict our analysis to one material, NiO, simply because it is the only material for which sufficient experimental data exist on good single crystals for us to compare theory with reality. Although NiO is not completely ionic (the covalency parameters[32] are 4%), it is sufficiently ionic that the best starting point is a periodic arrangement of free Ni^{2+} and O^{2-} ions. The important bands of NiO are the 3d and 4s bands of the Ni^{2+} ions and the 2p band of the O^{2-} ion. Just as in the case of NiF_2, discussed in section 1, Ni^{2+} has a $3d^8$ configuration in its ground state. There is by now considerable evidence[26,27] that the 2p and 4s bands of NiO are ordinary itinerant states, so that the ratio of the bandwidth to U is quite large for these bands. On the other hand, the 3d electrons appear to be near the atomic limit.[33] The latter fact is somewhat depressing, since a localized 3d band breaks up into over 10^6 quasiparticle bands. However, the silver lining is that the energies of virtually all of these bands are known in the atomic limit,[4] and the vast majority are at sufficiently high energies to be uninteresting to all but x-ray spectroscopists.

Starting with the free-ion energy levels, and taking into account the Madelung potential, screening and covalency effects, crystalline-field splittings, and bandwidth effects, it is possible to make reasonable estimates for the energies of the important elementary excitations requiring less than 20 eV.[27] The results are shown in Table 1. We must add the spin wave and excitonic transitions to the single particle excitations of Table 1.[27] It is then found that these predictions are in excellent agreement with optical experiments in the 1–20 eV range.[33–37] The band calculation of Wilson[23] attributes the 3.8 eV edge to 2p - 3d transitions, rather than to $3d^8$ - $3d^7$ 4s transitions, as implied here. However, it is clear from Table 1 that 2p - 3d intrinsic transitions require significantly larger energy unless the Coulomb interaction U is screened to a sufficiently large extent that it would be difficult to explain the absorption below 3.8 eV.[33]

It can also be seen that Table 1 predicts that a photoconductivity edge exists at about 4 eV, and one has indeed been observed at 3.8 eV.[38] These results further imply that intrinsic conduction should appear in NiO with an activation energy of about 2 eV. The electrical activation energy should be about 0.1–0.2 eV less than half the optical edge, because of the large polaron binding energy.[27] There is some experimental indication that such conduction exists. In a relatively pure epitaxially grown crystal, an activation energy of 1.9 eV was observed between 700°K and 1200°K,[38] and in several heavily compensated samples, activation energies in the vicinity of 1.8 eV were found above 1000°K.[39]

Similar estimates of the band structure of perfect crystals of magnetic semiconductors can be made whenever the screening and covalency effects can be obtained from experiment and the bandwidths of the itinerant states have been calculated. Thus far, only NiO can be discussed with any degree of confidence, and the results appear to be in agreement with experiment.

As has been pointed out,[10] the energy-band structure of magnetic semiconductors can be represented on an effective one-electron density-of-states diagram by separating the localized from the itinerant states, and adopting a procedure in which impossible excitations can be excluded. Such a diagram is shown in Fig. 1 for the optical density-of-states of perfect NiO. Itinerant states are drawn to the left, localized states to the right. The states which are occupied at $T = 0$ are shaded. States that are shown as dashed lines are available for excitations only from occupied localized states. By bearing these rules in mind, Fig. 1 can be used to obtain the optical absorption energies given in Table 1.

We can obtain the electrical density-of-states of perfect NiO crystals from Fig. 1 by invoking the Franck–Condon principle. The energy reduction from relaxation of the lattice around the excess charge density must then be calculated. Using estimates of the small-polaron and large-polaron binding energies,[27] we find that the electrical density-of-states is easily obtained from Fig. 1 by raising the energies of the 2p states by 0.25 eV and lowering the energies of the 4s states by 0.2 eV relative to the 3d states.

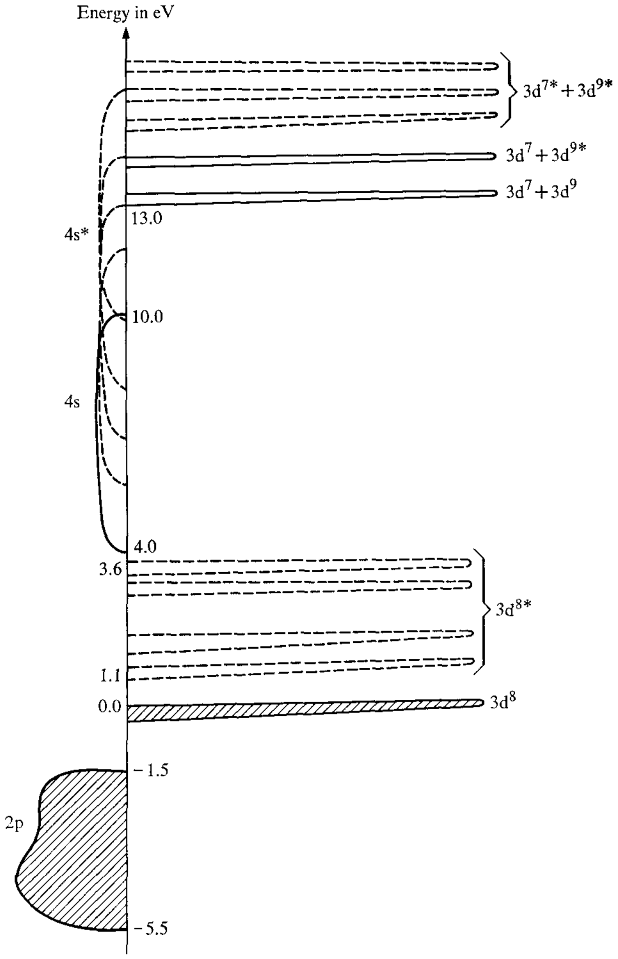

Figure 1 Optical density-of-states of perfect NiO. States which are occupied at $T = 0$ are shaded.

3. Band structure of doped or non-stoichiometric material

The electrical density-of-states of perfect crystals is of academic interest only in these materials, since the single crystals that have thus far been grown are seldom stoichiometric, have large concentrations of random impurities and are replete with defects. In wide-band semiconductors, defects, non-stoichiometry and impurities are all easily handled. Once the energies necessary to trap one or more electrons in the vicinity of each type of flaw are known, and the energies necessary to remove one or more electrons from the various impurity centers and interstitials are also known, we need only to modify the density-of-states calculated for perfect crystals by adding localized donor and acceptor levels at their proper energies. Once these levels are added and the statistics are properly taken into account, good agreement with experiment is obtained. No modifications of the valence and conduction bands are necessary. It is important to bear in mind that this is *not* the case for magnetic semiconductors and insulators.

To illustrate this point, let us consider the case of Li-doped NiO. We already have estimated the optical and electrical densities-of-states of perfect NiO, and many electrical and optical studies have been carried out on NiO doped with Li. Li enters the lattice substitutionally for Ni. Since the second ionization potential of Li is much larger than the third ionization potential of Ni[4], all Li centers are singly ionized. To preserve charge neutrality, a Ni^{3+} must be formed for each Li^+ in the crystal. In reality, some compensation appears to be always present.[40,41] This could be brought about either by the presence of trivalent cations, such as Al^{3+} or Fe^{3+}, or the self-compensation provided by formation of anion vacancies or Li interstitials. Thus, the concentration of Ni^{3+} is somewhat less than the Li^+ concentration.

The lowest energy state of the doped material is that in which all uncompensated Li^+ ions have a Ni^{3+} ion for a nearest neighbor. This comes about because a Li^+-Ni^{3+} pair on the cation sublattice forms an effective electron-hole pair, which electrostatically binds just like an exciton. The binding energy can be estimated as of the order of 0.4 eV.[42] These bound Li^+-Ni^{3+} complexes lead to new

Table 2 Conduction properties, estimated range of optical absorption energies, and estimated minimum thermal excitation energies for impurity-induced transitions in NiO which has been doped with Li. The symbol $[3d^7]$ stands for a Ni^{3+} ion bound to a Li^+ impurity center. An asterisk refers to the excited crystalline-field levels.

Process	*Type of conduction*	*Range of optical absorption energies*	*Electrical excitation energy*
$[3d^7] \rightarrow [3d^{7*}]$	non-conducting	1–6 eV	—
$[3d^7] \rightarrow 3d^7$	hopping conduction	0.4 eV	0.4 eV
$[3d^7] \rightarrow 3d^{7*}$	hopping conduction	2–7 eV	2 eV
$[3d^7] \rightarrow [3d^6]$ + (4s electron)	n-type semiconduction	12–18 eV	12 eV
$[3d^7] \rightarrow [3d^{6*}]$ + (4s electron)	n-type semiconduction	14–24 eV	14 eV
$[3d^7]$ + (2p electron) $\rightarrow 3d^8$	p-type semiconduction	0.7–5 eV	0.5 eV
$[3d^7]$ + (2p electron) $\rightarrow 3d^{8*}$	p-type semiconduction	2–9 eV	2 eV

optical transitions. These include freeing of the bound hole from the Li^+ impurity center, the crystalline-field excitations of the bound Ni^{3+} ion, and excitation of a 2p electron onto a Ni^{3+} ion, leaving a Ni^{2+} ion and a hole in the 2p band. The additional optical excitations induced by Li-doping are summarized in Table 2. The energies were estimated in the same way as were those of excitations in perfect NiO crystals, as discussed in Section 2.

The optical absorption in Li-doped NiO has been measured, and there is clear evidence for a peak at 0.43 eV.[43] This absorption is most likely due to the freeing of bound holes from Li^+ centers. There is also evidence for a background absorption induced by Li doping in the range 0.2-2.0 eV.[44,45] It can be shown that a series of excitations in the 0.2-0.4 eV range, representing transitions from strongly-bound Li^+-Ni^{3+} pairs to more weakly bound pairs, in which the Ni^{3+} is farther than a nearest-neighbor distance from the Li^+ center.[27] These excitations overlap in energy with the excitonic transitions of a bound hole into the oxygen 2p band, so that the background absorption is easily explained.

The interesting features, however, do not concern the optical transitions, but rather the electronic excitations induced by Li-doping. When the small- and large-polaron binding energies are taken into account, we can obtain the minimum energies necessary to thermally excite the transitions listed in Table 2. These minimum excitation energies are given in the last column of Table 2. The transitions which free the hole from the Li^+ center lead to electrical conductivity. The minimum energy necessary to create a carrier is 0.4 eV, which frees a hole in the $3d^8$ band. This hole forms a small polaron, which can then contribute to conduction by means of thermally activated hopping. The important point is that a minimum energy of only 0.5 eV is necessary to free a hole from a Li^+ center and place it in the relatively wide 2p band. The much larger mobility that can be expected from band-like conductivity of large polarons in the 2p band, as compared to the hopping mobility, implies that 2p-band conduction should dominate 3d hopping conduction except at very low temperatures. This is a simple resolution of the problem of the band-like semiconduction that is experimentally observed in NiO,[40,41,43,46] a known Mott insulator.

The conductivity observed in Li-doped NiO is quantitatively what can be estimated from large-polaron hole conduction in the 2p band, with optical phonon scattering predominating.[27] Although small-polaron hopping in the $3d^8$ band should dominate 2p-band conduction at sufficiently low temperatures, the hopping itself is dominated by impurity conduction in the partially compensated acceptor levels below 100°K.[47] Bound small-polaron hopping among the nearest neighbors to a Li^+ center, however, dominates the ac conductivity at low temperatures and high frequencies,[48,49] and has the expected temperature dependence.[27]

An electrical density-of-states diagram for Li-doped NiO is given in Fig. 2. Once again, itinerant states are drawn to the left, localized states to the right. All states are referred to the Fermi energy, drawn here by assuming that partial compensation occurs, as appears to be the case. The density-of-states of Fig. 2 is in agreement with the vast quantity of experimental data on Li-doped and non-stoichiometric NiO.

A comparison of Fig. 1 with Fig. 2 reveals a surprising feature. The 2p band has moved up over 1 eV relative to the $3d^8$ band in the Li-doped density-of-states. The reason for this is that the presence of Li^+ in NiO crystals produces large concentrations of Ni^{3+} ions, and it is much easier to excite a 2p electron onto a Ni^{3+} ion than onto a Ni^{2+} ion, the electron affinity Ni^{3+} being about twice that of Ni^{2+}. When localized and itinerant outer electrons are simultaneously present, effects such as these must carefully be taken into account. We would have dismissed 2p-band conduction as negligible has we just introduced the Li acceptor levels 0.4 eV above the $3d^8$ band in the density-

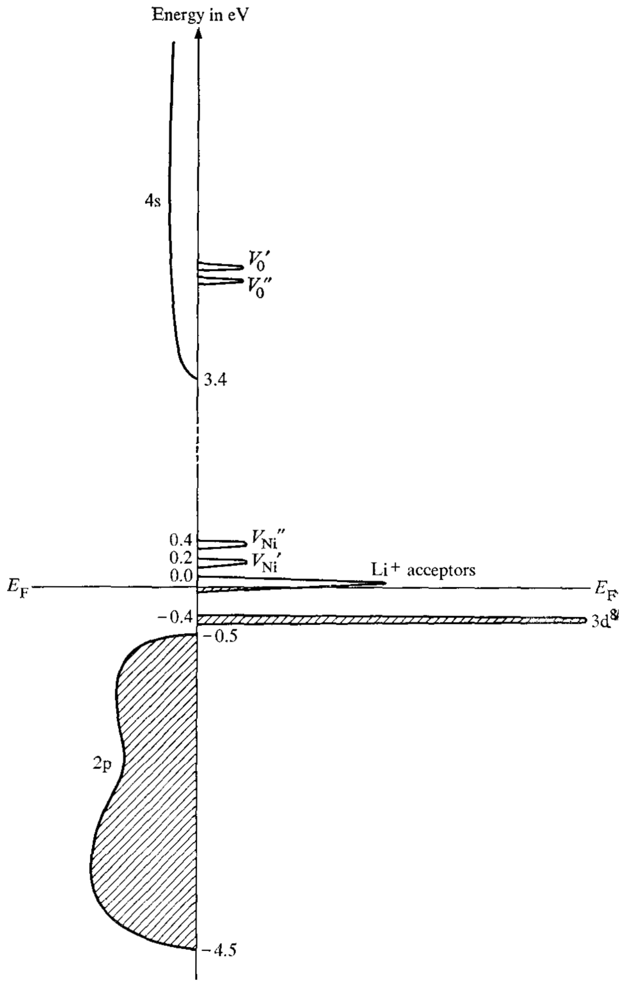

Figure 2 Electrical density-of-states of Li-doped NiO. States which are occupied at $T = 0$ are shaded. Partial self-compensation by means of oxygen vacancies is assumed. V_x' and V_x'' refer to singly and doubly ionized x vacancy levels, respectively.

of-states of perfect NiO, as given in Fig. 1. This relative variation of band energies brought about by doping or non-stoichiometry is the price we must pay for correctly dealing with the localized outer electrons of magnetic semiconductors.

4. Conclusions

When localized and itinerant outer electrons are simultaneously present in magnetic semiconductors, we cannot continue to employ one-electron methods for determining the effects of impurities or non-stoichiometry on optical absorption and electrical conductivity. A more accurate procedure is to construct the many-body energy-band structure beginning with the free-ion energies and taking into account the effects of the Madelung potential, screening, covalency, crystalline-field stabilizations, magnetic ordering, and electronic overlap. Quantitative estimates can ordinarily be calculated or obtained from experiment. Such estimates for the cases of both pure and Li-doped NiO are in agreement with the experimental data.

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