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Electrical Conductivity in Narrow Energy Bands*

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The electrical conductivity for a system of electrons described by the single-band Hubbard Hamiltonian is studied. An expression for the electrical conductivity that is applicable in the narrow-band regime, i.e., the bandwidth Δ, much smaller than intra-atomic Coulomb repulsion I is derived. It is shown that the conductivity vanishes at $T=0$ to first order in Δ/I for one electron per atomic site. For the non-half-filled-band case, the degeneracy of the (atomic limit) ground-state wave function plays a crucial role in yielding a nonzero value for the conductivity. The theory is used to analyze the experimental data in Li-doped NiO. It is demonstrated how, as a consequence of this theory, the contribution to the conductivity from the narrow $3d^8$ band is suppressed in the total conductivity, contrary to an ordinary band-theory approach to the transport properties of this band.

I. INTRODUCTION

Many transition-metal and rare-earth compounds are insulating despite the fact that elementary theory predicts that they have partially filled bands.[1] It was originally suggested by Mott[2] that materials with sufficiently narrow conduction bands are insulating, independent of the fractional occupancy of these bands. The failure of the Bloch-Wilson theory of conductivity in this case must be attributed to the neglect of electronic correlations. Mott[2] showed that for narrow bands, such as the *d* and *f* bands of transition-metal and rare-earth compounds, correlations can be expected to be particularly strong. Hubbard and others have discussed a method for introducing the effects of electronic correlations into elementary band theory in a particularly simple manner, by considering correlations between electrons on the same ion cores only.[3] A model at least as sophisticated as this must be used if we want to understand quantitatively the electrical and optical properties of "Mott insulators."

In this paper we calculate the electrical conductivity of a system described by the Hubbard Hamiltonian[3] in the narrow-band regime. A formal definition of the electrical current is presented and the linear response to an external dc field is studied. It is found that the zero-temperature dc conductivity is finite to first order in the bandwidth, except for the case of exactly an integral number of electrons per site. The structure of the conductivity is analyzed in terms of the degeneracy of the ground-state wave function in the atomic limit. The resulting expression for the conductivity is then compared with that obtained using the tight-binding approximation of one-electron band theory. This comparison quantitatively makes clear how electronic correlations suppress the conduction in a material with narrow partially filled energy bands.

The expression for the conductivity is explicitly applied to analyze the experimental data on NiO, a material which optical experiments indicate has extremely narrow $3d$ bands. A long-standing puzzle about NiO has been the absence of the small-polaron hopping conduction that is expected in such a narrow-band ionic compound. We demonstrate how, as a consequence of our theory, this hopping conduction is sufficiently small that it is dominated by a bandlike contribution from the lower-lying oxygen $2p$ band.

II. FORMULATION OF THE CONDUCTIVITY PROBLEM

The model Hamiltonian for a system of electrons in a single s band in the presence of an external scalar potential is

$$H=\sum_{i,j,\sigma} t_{ij} c^\dagger_{i\sigma} c_{j\sigma}+\tfrac{1}{2} I \sum_{i,\sigma} n_{i\sigma} n_{i-\sigma}+\sum_{i,\sigma} V_i(t) n_{i\sigma} \,. \quad (1)$$

The first two terms[3] describe the competing effects of hopping between Wannier sites and intrasite Coulomb repulsion I. The operator $c^\dagger_{i\sigma}$ is the creation operator for an electron on site i and spin σ. $n_{i\sigma}$ is the corresponding number operator in that notation. The matrix element t_{ij} is related to the single-band Bloch energies $\epsilon(\vec{k})$ by

$$t_{ij}=\frac{1}{N}\sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)}\epsilon(\vec{k}) \,, \quad (2)$$

where N is the number of sites and the k summation is over the first Brillouin zone.

The last term of Eq. (1) described a weak longitudinal electric field with the potential coupled to the local density in Wannier space. The potential $V_i(t)$ is assumed to have the form

$$V_i(t)=e\vec{E}(t)\cdot\vec{R}_i \,, \quad (3)$$

where $\vec{E}(t)$ is a spatially uniform time-dependent electric field. The assumption used in obtaining Eq. (3) is that the spatial variation of the potential over the region in which a given Wannier function is localized can be ignored. This condition is fulfilled as long as the mean bandwidth is much larger than $e|E|a$, where a is the lattice spacing. This condition is consistent with our assumption of a weak external field.

Since the spatial variables that appear in Eq. (1) are the discrete Wannier-site coordinates, the notion of a spatial derivative is at best ambiguous and at worst meaningless. Consequently, one cannot define a local current operator in the straightforward way that one does in the continuum space, i.e., by taking the time derivative of the local density operator and then using the equation of motion to reexpress this quantity in terms of the spatial divergence of a second operator, which is then identified as the current operator.

Rather than try to seek operations that are analogous to differentiation we take the following approach. The position operator in Wannier space is given by

$$\vec{R}_{\text{op}}=\sum_{i,\sigma}\vec{R}_i c^\dagger_{i\sigma} c_{i\sigma} \,. \quad (4)$$

The velocity operator can be found by using the equation of motion

$$\vec{V}_{\text{op}}=-i[\vec{R}_{\text{op}}, H] \quad (5)$$

and then evaluating the commutator. The result is simply

$$\vec{V}_{\text{op}}=-i\sum_{i,j,\sigma}(\vec{R}_i-\vec{R}_j)\, t_{ij} c^\dagger_{i\sigma} c_{j\sigma} \,. \quad (6)$$

Let us define

$$\vec{\mathcal{J}}_{ij}\equiv -i(\vec{R}_i-\vec{R}_j)t_{ij} \quad (7)$$

and use Eq. (2) to write

$$\vec{\mathcal{J}}_{ij}=\frac{1}{N}\sum_{\vec{k}}[\nabla_k\epsilon(\vec{k})]e^{i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)} \,. \quad (8)$$

The surface term has been eliminated by using the property that $\epsilon(\vec{k})$ is periodic in $\vec{k}$ space. Hence Eq. (5) can be rewritten as

$$\vec{V}_{\text{op}}=\sum_{i,j,\sigma}\vec{\mathcal{J}}_{ij} c^\dagger_{i\sigma} c_{j\sigma}=\sum_{\vec{k},\sigma}\nabla_{\vec{k}}\,\epsilon(\vec{k})\, c^\dagger_{\vec{k}} c_{\vec{k}\sigma} \,. \quad (9)$$

The latter expression is a very natural form for the velocity operator to take, since $\nabla_{\vec{k}}\epsilon(\vec{k})$ is just the group velocity of the single-particle state of energy $\epsilon(\vec{k})$.

The current operator $\vec{J}_{\text{op}}$, is just $e\vec{V}_{\text{op}}$, where e is the electric charge.

We calculate the induced current to first order in the external field. A straightforward[4] calculation of the induced current at time t yields

$$\langle J_{\text{op}}(t)\rangle_V=\langle J_{\text{op}}(t)\rangle_{V=0}$$
$$+i\int_{-\infty}^{t}\langle[e\sum_{i\sigma}\vec{R}_i\cdot\vec{E}(t')n_{i\sigma}(t'), J_{\text{op}}(t)]\rangle_{V=0}\,dt' \,.$$

Here the subscript $V=0$ denotes the expectation value in the ground state of the system in the absence of the external field. The first term in Eq. (10) is consequently zero. Thus, using Eq. (9) for $\vec{\mathrm{V}}_{\mathrm{op}}$ we find that

$$\langle J_{\mathrm{op}}(t)\rangle_V = ie^2 \sum_{i,j,l,\sigma,\sigma'} \vec{\mathcal{J}}_{ij} \int_{-\infty}^{t} \langle [n_{l\sigma'}(t'), c_{i\sigma}^\dagger c_{j\sigma}(t)]\rangle \times \vec{\mathrm{R}}_l \cdot \vec{\mathrm{E}}(t')\, dt' \,. \tag{11}$$

We define

$$J(\omega) \equiv \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle J_{\mathrm{op}}(t)\rangle_V \,, \tag{12}$$

$$\vec{\mathrm{E}}(\omega) \equiv \int_{-\infty}^{\infty} dt\, e^{i\omega t}\, \vec{\mathrm{E}}(t) \,, \tag{13}$$

$$Q_{ijl}^{\sigma\sigma'}(\omega) = \int_{-\infty}^{\infty} d(t-t')\, e^{i\omega(t-t')} \times \langle [c_{i\sigma}^\dagger(t) c_{j\sigma}(t),\, n_{l\sigma'}(t')]\rangle\, \theta(t-t') \,, \tag{14}$$

where $\theta(t-t')=1$ for $t>t'$ and vanishes otherwise. Since the expectation value on the right-hand side of Eq. (11) is a function of $t-t'$ only, we can introduce a factor of $\theta(t-t')$ in the integrand and extend the upper limit of integration to plus infinity. In terms of the Fourier transforms defined in Eqs. (12)–(14), Eq. (11) then becomes

$$J(\omega) = ie^2 \sum_{i,j,l,\sigma,\sigma'} \vec{\mathcal{J}}_{ij}\, Q_{ijl}^{\sigma\sigma'}(\omega)\, \vec{\mathrm{R}}_l \cdot \vec{\mathrm{E}}(\omega) \,. \tag{15}$$

The function $Q_{ijl}^{\sigma\sigma'}(\omega)$ contains the information concerning the microscopic behavior of the system and is the quantity of central concern. The integral representation of the θ function,

$$\theta(t-t') = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i}\, \frac{e^{i\omega(t-t')}}{\omega - i\epsilon} \,, \tag{16}$$

allows the reexpression of Eq. (14) as

$$\begin{aligned} Q_{ijl}^{\sigma\sigma'}(\omega) &= \int_{-\infty}^{\infty} \frac{d\overline{\omega}}{i\pi}\, \frac{r_{ijl}^{\sigma\sigma'}(\overline{\omega})}{\overline{\omega} - \omega - i\epsilon} \\ &= r_{ijl}^{\sigma\sigma'}(\omega) - iP \int_{-\infty}^{\infty} \frac{d\overline{\omega}}{\pi}\, \frac{r_{ijl}^{\sigma\sigma'}(\overline{\omega})}{\overline{\omega} - \omega} \,, \end{aligned} \tag{17}$$

where

$$r_{ijl}^{\sigma\sigma'}(\omega) = \tfrac{1}{2} \int_{-\infty}^{\infty} d(t-t')\, e^{i\omega(t-t')} \times \langle [c_{i\sigma}^\dagger(t)\, c_{j\sigma}(t),\, n_{l\sigma'}(t')]\rangle . \tag{18}$$

We readily derive the sum rule

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, r_{ijl}^{\sigma\sigma'}(\omega) &= \tfrac{1}{2} \int_{-\infty}^{\infty} d(t-t')\, \delta(t-t') \times \langle [c_{i\sigma}^\dagger(t)\, c_{j\sigma}(t),\, n_{l\sigma'}(t')]\rangle \\ &= \tfrac{1}{2} \langle [c_{i\sigma}^\dagger(t)\, c_{j\sigma}(t),\, n_{l\sigma'}(t)]\rangle \\ &= \tfrac{1}{2}\, \delta_{\sigma,\sigma'} \langle c_{i\sigma}^\dagger(t)\, c_{j\sigma}(t)\rangle\, (\delta_{jl-li}) \,. \end{aligned} \tag{19}$$

The frequency-dependent conductivity $\sigma(\omega)$ is defined by[5]

$$N\vec{\mathrm{E}}(\omega) \cdot \sigma(\omega) = \vec{\mathrm{J}}(\omega) \,. \tag{20}$$

Comparing Eqs. (15) and (20), we can identify the conductivity as

$$\sigma(\omega) = ie^2 \sum_{i,j,l,\sigma,\sigma'} \vec{\mathcal{J}}_{ij}\, Q_{ijl}^{\sigma\sigma'}\, \vec{\mathrm{R}}_l \,. \tag{21}$$

Substituting Eq. (17) into Eq. (21), we find

$$\sigma(\omega) = \sigma'(\omega) - iP \int_{-\infty}^{\infty} \frac{d\overline{\omega}}{\pi}\, \frac{\sigma'(\overline{\omega})}{\overline{\omega} - \omega} \,, \tag{22}$$

where

$$\sigma'(\omega) = \frac{ie^2}{N} \sum_{i,j,l,\sigma,\sigma'} \vec{\mathcal{J}}_{ij}\, r_{ijl}^{\sigma\sigma'}(\omega)\, \vec{\mathrm{R}}_l \,. \tag{23}$$

$\sigma'(\omega)$ is called the dissipative part of the conductivity and is related to the microscopic properties of the system through Eq. (18). A useful sum rule, obtained by combining Eqs. (8), (19), and (23), is

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \sigma'(\omega) = \frac{e^2}{2N} \sum_{\vec{\mathrm{k}},\sigma} [\nabla_{\vec{\mathrm{k}}} \nabla_{\vec{\mathrm{k}}}\, \epsilon(\vec{\mathrm{k}})]\, n_{\vec{\mathrm{k}}\sigma} \,. \tag{24}$$

Here we find

$$n_{\vec{\mathrm{k}}\sigma} = \langle c_{\vec{\mathrm{k}}\sigma}^\dagger\, c_{\vec{\mathrm{k}}\sigma}\rangle \,, \tag{25}$$

with $c_{\vec{\mathrm{k}}\sigma}^\dagger$ the creation operator for an electron in Bloch state $\vec{\mathrm{k}}$ and spin σ.

Equation (24) can be trivially applied to a single band of noninteracting electrons. Since noninteracting electrons in a perfect crystal do not dissipate energy as they propagate, Eq. (24) implies that

$$\sigma'(\omega) = \pi\delta(\omega)\, \frac{e^2}{N} \sum_{\vec{\mathrm{k}},\sigma} [\nabla_{\vec{\mathrm{k}}} \nabla_{\vec{\mathrm{k}}}\, \epsilon(\vec{\mathrm{k}})]\, n_{\vec{\mathrm{k}}\sigma} \,, \tag{26}$$

where $n_{\vec{\mathrm{k}}\sigma}$ is just the ground-state momentum distribution function for Bloch electrons. Thus, in this case, Eq. (26) can be written in the more familiar form

$$\sigma'(\omega) = \pi\delta(\omega)\, n_T e^2 / m_{\mathrm{band}} \,, \tag{27}$$

where we have defined the band-mass tensor as

$$(m_{\mathrm{band}})^{-1} \equiv \sum_{\vec{\mathrm{k}},\sigma} [\nabla_{\vec{\mathrm{k}}} \nabla_{\vec{\mathrm{k}}}\, \epsilon(\vec{\mathrm{k}})]\, n_{\vec{\mathrm{k}}\sigma} \Big/ \sum_{\vec{\mathrm{k}},\sigma} n_{\vec{\mathrm{k}}\sigma} \tag{28}$$

and used the expression

$$n_T = \frac{1}{N} \sum_{\vec{k},\sigma} n_{\vec{k}\sigma} \tag{29}$$

for the density of electrons. As an illustration, in the effective-mass approximation, where $\epsilon(\vec{k}) = k^2/2m^*$, it is readily seen that

$$1/m_{\text{band}} = 1/m^* \ . \tag{30}$$

These results are quite familiar in solid-state physics. We developed this formalism to facilitate the analysis of the conductivity in the opposite limit of strong correlation.

III. STRONGLY CORRELATED ELECTRONS

From Eq. (23), we see that the conductivity has an explicit first-order dependence by virture of the appearance of the factor $\vec{g}_{ij}$. This means that we need only work out the microscopic details contained in $r_{ijl}^{\sigma\sigma'}(\omega)$ in the zero-bandwidth limit in order to obtain the conductivity to first order in the bandwidth.

In this atomic limit, we write

$$\begin{aligned} n_{l\sigma'}(t') = {} & \exp[-i(t-t')I\textstyle\sum_i n_{i\uparrow} n_{i\downarrow}]\, n_{l\sigma'}(t) \\ & \times \exp[+i(t-t')I\textstyle\sum_i n_{i\uparrow} n_{i\downarrow}] \ , \end{aligned} \tag{31}$$

which governs the time evolution of $n_{l\sigma'}$. But $[n_{i\sigma}(t), n_{l\sigma'}(t)] = 0$, so that $n_{l\sigma'}(t') = n_{l\sigma'}(t)$. Consequently, we can set the times equal in the commutator appearing in Eq. (18). This implies that the conductivity is proportional to $\delta(\omega)$ and the sum rule, Eq. (24), then guarantees that it has the form of Eq. (26). For this case, the $n_{\vec{k}\sigma}$ occurring in Eq. (26) refers to the ground state for zero bandwidth. In terms of Wannier operators,

$$n_{\vec{k}\sigma} = \textstyle\sum_j e^{i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)} \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle \ . \tag{32}$$

For a half-filled band (one electron per site), $\langle c_{i\sigma}^\dagger c_{j\sigma} \rangle$ is nonzero only for $i=j$. Thus $n_{\vec{k}\sigma}$ is independent of $\vec{k}$ and the conductivity is zero [since $\nabla_{\vec{k}} \epsilon(\vec{k})$ is periodic in $\vec{k}$ space].

For other than a half-filled band, the expectation value in Eq. (32) need not be zero for $i \neq j$ in the zero-bandwidth limit. It has been pointed out[6] that this ground state has a high multiplicity. This occurs in the zero-bandwidth limit because a given state is degenerate with all states that can be obtained from it by permutations of electrons on Wannier sites with the one constraint that the total number of doubly occupied sites remains unchanged. Thus the momentum distribution function can have a nontrivial $\vec{k}$ dependence and the conductivity need not be zero.

It is interesting to carry out the calculation of Eq. (32) in the context of the two-pole split subband approximation obtained by Hubbard[3] and subsequently treated by others.[7] In this approximation, it is found that, for finite bandwidth, $n_{\vec{k}\sigma}$ takes the form

$$n_{\vec{k}\sigma} = Z_{\vec{k}\sigma}\, \theta(\mu_\sigma - E_{\vec{k}\sigma}) \ , \tag{33}$$

where μ_σ is the chemical potential, which is determined by the condition that the total number of electrons is constant. It is assumed that the band is less than half-filled and the subbands are well split. $E_{\vec{k}\sigma}$ is the renormalized pseudoparticle energy[3,7] referring to the lower subband and $Z_{\vec{k}\sigma} \rightarrow 1 - n_{-\sigma}$, $n_{-\sigma} = \langle n_{i\,-\sigma} \rangle$, as the bandwidth approaches zero. The chemical potential and $E_{\vec{k}\sigma}$ contain the bandwidth linearly so that the θ function is independent of the bandwidth. Thus, in the zero-bandwidth limit we find

$$n_{\vec{k}\sigma} = (1 - n_{-\sigma})\, \theta(\mu_\sigma - E_{\vec{k}\sigma}) \ . \tag{34}$$

A form for the conductivity that is similar to Eq. (27) can be arrived at after a few manipulations:

$$\begin{aligned} \sigma'(\omega) &= \pi\delta(\omega) \frac{e^2}{N} \sum_{\vec{k},\sigma} [\nabla_{\vec{k}} \nabla_{\vec{k}} \epsilon(\vec{k})]\, (1 - n_{-\sigma})\, \theta(\mu_\sigma - E_{\vec{k}\sigma}) \\ &= \pi\delta(\omega) e^2 \left(\frac{1}{N} \sum_{\vec{k},\sigma} (1 - n_{-\sigma})\, \theta(\mu_\sigma - E_{\vec{k}\sigma}) \right) \\ &\quad \times \left(\sum_{\vec{k},\sigma} [\nabla_{\vec{k}} \nabla_{\vec{k}} \epsilon(\vec{k})]\, (1 - n_{-\sigma})\, \theta(\mu_\sigma - E_{\vec{k}\sigma}) \Big/ \right. \\ &\quad \left. \sum_{\vec{k},\sigma} (1 - n_{-\sigma})\, \theta(\mu_\sigma - E_{\vec{k}\sigma}) \right) \ . \end{aligned} \tag{35}$$

The term in brackets can be recognized as the electron concentration n_T. Hence we can express the conductivity as

$$\sigma'(\omega) = \pi\delta(\omega) \frac{n_T e^2}{m_R} \ , \tag{36}$$

where

$$\begin{aligned} \frac{1}{m_R} = {} & \sum_{\vec{k},\sigma} [\nabla_{\vec{k}} \nabla_{\vec{k}} \epsilon(\vec{k})](1 - n_{-\sigma})\, \theta(\mu_\sigma - E_{\vec{k}\sigma}) \Big/ \\ & \sum_{\vec{k},\sigma} (1 - n_{-\sigma})\, \theta(\mu_\sigma - E_{\vec{k}\sigma}) \ . \end{aligned} \tag{37}$$

From Eq. (22), we define the dispersive part of the conductivity by

$$\sigma''(\omega) = -P \int_{-\infty}^{\infty} \frac{d\bar{\omega}}{\pi} \frac{\sigma'(\bar{\omega})}{\bar{\omega} - \omega} \ . \tag{38}$$

This implies, from Eq. (36), that

$$\sigma''(\omega)=\frac{n_T e^2}{m_R\omega} \quad . \tag{39}$$

Hence, within the approximation that we made, the narrow-band conductivity will exhibit free-acceleration behavior with a mass that is renormalized by the electron correlations.

It has been pointed out[8] that an expansion in the bandwidth does not give an adequate description of the low-frequency behavior of the Green's function and related quantities. We can expect this to be true for the conductivity as well. Equation (39) is applicable for frequencies larger than the bandwidth, or, in the presence of other scattering mechanisms, for scattering times much shorter than the hopping time.

The theory of normal Fermi liquids predicts[9] that the mass entering in Eq. (39) for the normal interacting Fermi system is the same as the noninteracting mass. That our strong correlation treatment predicts a different mass is not surprising inasmuch as we are doing our perturbation theory about the atomic limit and not about the noninteracting limit.

As a simple illustration of the behavior of the band mass and the renormalized mass m_R, we explicitly calculate them in the tight-binding approximation in one dimension.[10] Let a be the lattice spacing so that

$$\epsilon(k)=-\Delta\cos ka \;, \tag{40}$$

$$\nabla_k\nabla_k\epsilon(k)=\Delta a^2\cos ka \;. \tag{41}$$

Thus, $1/m_{\text{band}}$ is given by

$$1/m_{\text{band}}=\Delta a^2\sin\pi n/\pi n \;. \tag{42}$$

We have taken $n_\sigma=n_{-\sigma}=n$. Equation (42) yields the expected result that a completely filled band ($n=1$) is an insulator.

In order to obtain $1/m_R$ for $\epsilon(k)$ given by Eq. (40), the corresponding $E_{k\sigma}$ must be determined. It is easily verified from the appropriate forms given in Ref. 3 or Ref. 7 that

$$E_{k\sigma}=\alpha+\beta\epsilon(k) \;, \tag{43}$$

where α and β are momentum independent and correspond to a band shift and narrowing, respectively. With $E_{k\sigma}$ of this form, $\theta(\mu_\sigma-E_{k\sigma})$ can be replaced by $\theta(k_f-|k|)$ and the momentum integration is easily performed:

$$1/m_R=\Delta a\sin k_f a/k_f \;. \tag{44}$$

From Eq. (34), we obtain

$$k_f a=\pi n/(1-n) \;. \tag{45}$$

Thus, we have

$$\frac{1}{m_R}=\frac{\Delta a^2\sin(\pi n/(1-n))}{\pi n/(1-n)} \quad . \tag{46}$$

This expression is valid for $n\leq\frac{1}{2}$ and illustrates how the conductivity vanishes as n approaches $\frac{1}{2}$ and the band becomes half-filled. Note that Eq. (46) is independent of α and β. Thus, for $\epsilon(k)$ given by Eq. (40), and to first order in Δ, the electrical conductivity is not altered by the corrections to $E_{k\sigma}$ that were introduced in Ref. 7.

In Fig. 1 we plot n/m versus n as obtained from Eqs. (42) and (46), respectively. For $n=\frac{1}{2}$, ordinary band theory predicts a maximum in this quantity, whereas the strong correlation theory predicts that this quantity is zero.

IV. APPLICATION TO EXPERIMENT

As discussed in the Introduction, many transition-metal and rare-earth compounds are believed to be Mott insulators. For these materials, electrical-conductivity experiments cannot be analyzed on the basis of one-electron-band calculations, even if the crystal symmetry and electronic structure are such that a real energy gap is obtained without the introduction of correlations. For example, although a recent spin-polarized augmented-plane-wave (APW) band calculation for NiO[11] did indeed produce a semiconductor with a 1-eV gap brought about by the cubic crystalline-field splitting, $10Dq$, there is now sufficient experimental evidence[12] that the gap in NiO is not 1 eV and is not due to crystalline-field effects. Thus an analysis of the conductivity data on the basis of the usual band expression

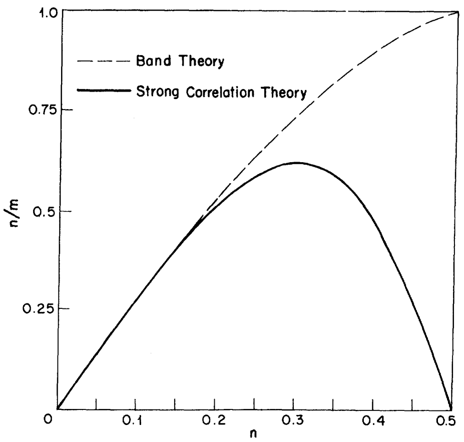

FIG. 1. n/m is plotted in units of $\Delta a^2/\pi$ for $0<n<\frac{1}{2}$. The dotted line represents the ordinary band-theory expression given by Eq. (42) and the solid line represents the strong-correlation-theory expression given by Eq. (46).

$$\sigma = \frac{1}{4}\left(\frac{2m^* kT}{\pi \hbar^2}\right)^{3/2} e\mu\, e^{-E_g/2kT} \tag{47}$$

would give incorrect estimates for the effective mass m^* and the mobility μ. Once it is known that the material is a Mott insulator, the conductivity should be analyzed only in terms of a model in which the gap is due to electronic correlations. The Hubbard model is the only quantitative model presented thus far which enables us to calculate a nonvanishing conductivity under these conditions. The expression we have derived for conductivity, Eq. (39), with effective mass given by Eq. (37), is correct to first order in Δ/I.

In this section, we explicitly apply Eq. (39) to analyze the experimental data in a known Mott insulator, for which $\Delta/I \ll 1$. The material to be discussed, NiO, was chosen because of the vast amount of experimental data now available on well-characterized samples. Consequently, many of the parameters which are necessary in order to evaluate the conductivity, Eq. (39), are known to sufficient accuracy.

The situation in NiO is much more complicated than the case of a narrow nearly half-filled s band considered in Secs. II and III. The relevant narrow band in NiO is the $3d$ band associated with the Ni^{2+} ions, and a d band is highly degenerate. Furthermore, the $2p$ band associated with the O^{2-} ions and the $4s$ band associated with the Ni^{2+} ions cannot be neglected. We shall restrict ourselves to a consideration of NiO which has been lightly doped with Li, since most of the experimental data have been compiled on such material. In this case it can be shown[12] that the Li^+ acceptor levels are approximately 0.4 eV above the ground-state $3d^8$ band, and approximately 0.45 eV above the $2p$ band. The $4s$ band is 3.4 eV above the Li^+ levels. The $2p$ and $4s$ bands are sufficiently wide compared to I that they may be treated as ordinary one-electron bands.[12] For the $3d$ band, however, Δ has been estimated as 0.3 eV,[13,14] or less,[12] and I is of the order of 13 eV.[12] Thus, the material is a Mott insulator, with $\Delta/I \ll 1$, and the first-order expression for conductivity should be quite accurate. Since only the lowest of the large number of $3d$ quasiparticle bands[15] is within 1 eV of the Fermi energy,[12] our treatment of only one band in the Hubbard model is sufficient in a discussion of the electrical conductivity. Thus, Eq. (39) can be applied to the lowest $3d^8$ band, which must be considered exactly filled when $n = \frac{1}{2}$.

When NiO is doped with monovalent Li, the Li^+ enters the lattice substitutionally for Ni^{2+}. For every Li^+ in the lattice, it is expected that one Ni^{3+} is electrostatically bound to a nearest neighbor Li^+, the dipole forming an effective electron-hole pair in the normally divalent lattice. It is the binding energy of this pair which represents the Li^+ acceptor energy discussed previously. Actually, the situation is still more complicated, since some of the Li^+ ions are self-compensated by O^{2-} vacancies which form during the crystal growth.[16]

Two competing conduction processes exist in Li-doped NiO – conduction by hopping of holes in the narrow $3d^8$ band, and normal bandlike-hole conductivity in the $2p$ band. The contribution of the latter process can be estimated from the well-known one-electron relations. We must use Eq. (39) to evaluate the contribution of $3d$-band conduction.

Bosman and Crevecoeur[16] performed a number of transport experiments on a ceramic sample of NiO doped with 0.088% Li. For this doping concentration, the charged centers lead to an increase in dielectric constant,[17] which leads to a reduction of the binding energy of the Li^+-Ni^{3+} pairs to about 0.25 eV. An analysis of the experimental results[12] shows that the sample was approximately 6% compensated by oxygen vacancies, in rough agreement with a chemical analysis.[16]

The $2p$-band contribution to the conductivity, at temperatures below 450 °K, should then be[18]

$$\sigma_{2p} = 4\left(\frac{2m^{**} kT}{\pi \hbar^2}\right)^{3/2} e\mu_{2p}\, e^{-E_A/kT}, \tag{48}$$

where m^{**} is the effective mass of holes in the $2p$ band, μ_{2p} is the hole mobility, and E_A is the acceptor ionization energy, 0.3 eV for Li^+-doped NiO. Above 450 °K, this contribution should be[18]

$$\sigma_{2p} = (1.8 \times 10^{10}\ \text{cm}^{-3/2})\left(\frac{2m^{**} kT}{\pi \hbar^2}\right)^{3/4} e\mu_{2p}\, e^{-E_A/2kT}, \tag{49}$$

where we have used the fact that the Li^+ concentration is $5 \times 10^{19}\ \text{cm}^{-3}$. In a polar material such as NiO, it might be expected that optical phonon scattering predominates at low and intermediate temperatures. It can be shown[12] that, below 600 °K, single optical phonon and resonance scattering give a contribution to the mobility of

$$\mu_{2p} \sim (0.3\ \text{cm}^2/\text{V sec})\, e^{(0.075\ \text{eV})/kT}. \tag{50}$$

The measured conductivity and thermoelectric power[16] fit the predicted $2p$-band relations, Eqs. (48)–(50) from 200 to 600 °K.[12] The effective mass m^{**} can be estimated as $5m_0$, where m_0 is the free-electron mass.

The question which remains to be answered is the contribution of $3d$-band conduction. In Li-doped NiO, it appears that conduction in the $3d$ band is dominated by $2p$-band conduction at all ordinary temperatures. If the activation energy for freeing a $3d$-band hole is lower than that for a $2p$-band hole, it might be expected that the former process will dominate at sufficiently low temperatures. However, the partial self-compensation which occurs in NiO leads to the predominance of impurity conduction below 140 °K.[16, 19] Thus, it appears that $3d$-band conduction cannot be seen in dc experiments. On the other hand, conduction due to bound $3d^8$ holes hopping among the 12 equivalent nearest-neighbor Ni^{2+} sites to a Li^+ center dominates the ac conductivity above 30 MHz and below 300 °K.[20] From these data, it can be concluded that (a) conduction of holes in the $3d^8$ band occurs by means of thermally activated hopping between Ni^{2+} sites, (b) the hopping activation energy is less than 0.01 eV, and (c) the average staying time of a hole on a Ni^{2+} site is about 10^{-10} sec near 300 °K. These conclusions are consistent with dielectric loss experiments down to 4 °K[21] and predictions based on small-polaron theory.[12]

With the information obtained from these ac conductivity experiments, we can use Eqs. (39) and (46) to evaluate the contribution of the hopping of holes in the $3d^8$ band to the dc conductivity. In Li-doped NiO, the situation can be thought of as a slightly less than half-filled band. In this case, we may write $n = \frac{1}{2} - \delta$, where δ is the fractional free-hole concentration. Using Eq. (46), we find that to first order in δ

$$1/m_R = \Delta a^2 (4\delta) \; . \tag{51}$$

However, as we have pointed out, the holes are initially bound to the Li^+ centers. In the samples under consideration (0.088% Li), the binding energy can be estimated as 0.25 eV.[12] Recalling that the material is 6% self-compensated, we can evaluate δ below 450 °K as[18]

$$\delta = 16 e^{-(0.25\,\mathrm{eV})/kT} \; . \tag{52}$$

If impurities or phonons are present, then we must modify Eq. (39) by the substitution $\omega \to 1/\tau$, where τ is a scattering time. As we have discussed in Sec. III, the scattering time must be shorter than the hopping time in order that we may apply Eq. (39) to the conductivity. If phonons play the dominant role in determining the scattering time, then, as is shown below, the condition for applying Eq. (39) is satisfied. Noting this and substituting Eqs. (51) and (52) into Eq. (39), we can evaluate the $3d$ conductivity below 450 °K as

$$\sigma_{3d} = n_T e^2 \tau_{3d} \Delta a^2 \left[64 e^{-(0.25\,\mathrm{eV})/kT} \right] . \tag{53}$$

Here, τ_{3d} refers to the explicit scattering mechanism and the expression in brackets represents the effects of the electron correlations within our theory.

If, instead of treating the strong electron correlations as fundamental, we had applied ordinary band theory to this problem, then from Eq. (42), the bracketed term in Eq. (53) would be replaced by $2/\pi$ in the half-filled band case. At $T = 200$ °K, the ratio of these quantities is $\sim 3 \times 10^{-5}$ (at $T = 300$ °K, it is 4.6×10^{-3}). This small ratio leads to a suppressed $3d$ conductivity even if normal scattering times exist.

If we assume that small-polaron theory applies to the $3d$ band of NiO, then sufficient parameters are known to estimate τ_{3d}. It can be shown that[22]

$$\tau_{3d} = \frac{\Delta}{4\omega_0 kT} \left(\frac{\pi}{\gamma \,\mathrm{csch}(\omega_0/2kT)} \right)^{1/2} e^{-2\gamma \tanh(\omega_0/4kT)} , \tag{54}$$

where ω_0 is the longitudinal optical-phonon frequency and γ is a constant which gives the strength of the electron-phonon coupling. For NiO, $\omega_0 \sim 0.08$ eV,[23] and $\gamma \sim 0.08$,[12] and Eq. (54) gives, in the high-temperature limit

$$\tau_{3d} \sim (4 \times 10^{-19}\ \mathrm{sec}) \left(\frac{900\ {}^\circ\mathrm{K}}{T} \right)^{3/2} e^{-(0.003\,\mathrm{eV})/kT} . \tag{55}$$

We note that τ_{3d} is much less than the hopping time, 10^{-10} sec in NiO, which is consistent with our applying Eq. (39) to the conductivity.

At temperatures where Eq. (53) is applicable, Eq. (54) has a complex temperature dependence, but it is clear that the $3d$ scattering time is itself small, and will further reduce the relative contribution of hopping of $3d$ holes to the total conductivity. Thus it is not surprising that this contribution is dominated at all temperatures.

V. CONCLUSION

We have obtained an expression for the electrical conductivity in the Hubbard model that is applicable to the narrow-band regime. We have shown that the conductivity vanishes to first order in Δ/I for one electron per site, in agreement with the notion of a Mott insulator. For the non-half-filled-band case, we have demonstrated how the degeneracy of the ground-state wave function plays a crucial role in determining the behavior of the conductivity in the narrow-band regime. It has been shown that the electronic correlations suppress the conductivity from that which would have been obtained in a partially filled band.

We have applied our results to the experimental data available for NiO and have demonstrated that, as a consequence of our theory, the hopping conduction in the narrow $3d^8$ band is suppressed in the total conductivity and that the contribution from the oxygen $2p$ band dominates the conductivity. Thus, the conductivity analysis in Sec. III can be useful even in a case where hopping transport is not seen experimentally. In Mott insulators other than NiO, the $2p$ band or its analog may be sufficiently far below the Fermi energy that its contribution to conductivity can be neglected at ordinary temperatures. In such cases, hopping transport may be expected to predominate, despite a suppression analogous to the bracketed factor in Eq. (53). Unforunately, no other Mott insulator has been subjected to the vast number of experiments which have been performed on NiO, so a detailed experimental test of the relations derived here must be postponed. Nevertheless, we wish to emphasize the point that the ordinary transport expression cannot be used in an analysis of the conductivity of Mott insulators and that strong correlations must be taken into account in narrow bands, as has been done here, in order to adequately describe transport and other properties.

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