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Bound-Polaron Hopping in NiO

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We report observation of bound-polaron hopping in pure NiO single crystals. The observed activation energy is ≈ 0.7 eV, the bandwidth $J \approx 10^{-2}$ eV, and the binding center is suggested to be the Ni^{+2} vacancy.

Conduction in NiO, and particularly in Li_2O-doped NiO, has been the subject of extensive investigation. A number of reviews[1-3] on conduction in these narrow-band oxides, including NiO in particular, have recently appeared in which the difficulties of analysis and interpretation are evident. In NiO, a major difficulty at the higher temperatures $(\Theta_D/2)$ arises in estimating the fraction of current carried by the hopping of d-state polarons: whether in fact the measured activation energies are parameters to be asso-

ciated with the hopping process or, on the other hand, with changes in the hole concentration in a wide oxygen p band. The difficulty arises in part from the lack of direct observations of free or bound polarons in the temperature region in question.

In this paper we report what we believe are observations of classic bound-polaron hopping in NiO, where the small-polaron hole (Ni^{+3}) is hopping about nickel vacancies Ni_v^{+2}. From these observations we determine the all-important
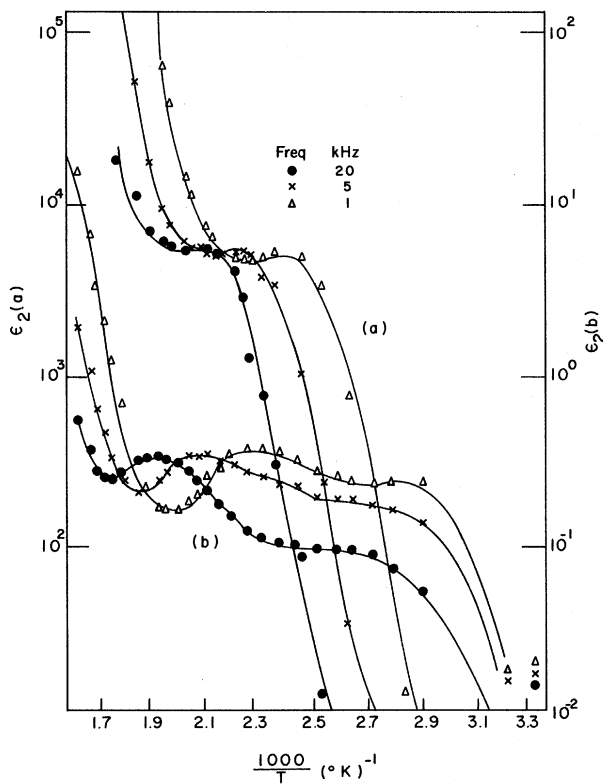
FIG. 1. Imaginary part of the dielectric constant ϵ_2 for weakly compensated (curves a) and strongly compensated (curves b) single-crystal NiO versus $1/T$. The real part ϵ_1 also exhibits Debye behavior and obeys the Kramers-Kronig relations (not shown).

bandwidth J of the small polaron in the defect.

The imaginary part of the dielectric constant for two disks of nominally pure single-crystal NiO is shown in Fig. 1.[4] The difference in magnitude is due to the different compensation in the two specimens, and this aspect is to be subsequently discussed in detail. We ascribe this dielectric behavior to a small bound polaron, Ni^{+3}, hopping in various ways around a negative binding center. Debye behavior for such systems has been suggested by Fröhlich, Machlup, and Mitra.[5] Similar bound-polaron hopping has been observed in TiO_2 single crystals for an electron hopping around Ti^{+3} interstitials and also around oxygen vacancies.[6]

The bulk origin of the relaxations was established by specifically testing for Schottky barriers and surface effects and finding such surface contributions absent. Specifically, the tests were (i) examination of the effect of an applied dc bias, (ii) examination of the effect of different electrode material, and (iii) direct measure-

ment of the potential gradient along the length of the specimen. Applied dc electric fields up to 1000 V cm^{-1} did not change either the position or the magnitude of the dielectric loss. Various electrode materials had no effect either; gold and silver electrodes, and nickel electrodes formed *in situ* by very severe reduction at low oxygen pressure, gave identical relaxation. Finally, direct measurement of the electric potential down the length of a specimen showed Schottky barriers to be absent, no detectable voltage drops across the surfaces being observed.

The defects responsible for the dielectric relaxation here are empty dipolar acceptor complexes. The evidence for this assertion is that the magnitude of the dielectric relaxations may be diminished by increasing the concentration of donors, in this case by increasing the oxygen vacancy concentration by heating the specimen in a reducing atmosphere at high temperatures. As the compensation ratio tends to unity, the concentration of empty acceptors decreases, and the magnitude of the dielectric relaxation likewise decreases. As an example of the reduction in the magnitude of the relaxation by such increased compensation, the dielectric behavior of a specimen heated in 10^{-1} Torr oxygen pressure at 900°C for 50 h (to ensure homogeneity) is compared with that of an oxidized specimen in Fig. 1. A marked decrease in the magnitude of the Debye-type relaxation has occurred with compensation. In the uncompensated specimen, we estimate N, the number of dipoles per unit volume, to be $\approx 2.0 \times 10^{21}$ cm^{-3}. This agrees very well with Mitoff's[7] data, and certainly is an acceptable small concentration in defects.

Similar relaxations and dependence on reduction are also observed in specimens cut from a nominally pure single crystal obtained from a different source.[8] Flame photometry on the Nakazumi crystals indicated the Li content to be less than 1 ppm. This similar dielectric behavior in pure specimens of different origin, and also the dependence on compensation with oxygen vacancies, strongly suggests that the acceptor center involved is the intrinsic nickel vacancy, the relaxation being due to a polaron hopping around the lattice defect.

As expected for a Debye-type dielectric relaxation, the temperature at which the maximum in ϵ_2 occurs (when $\omega\tau = 1$) increases with increasing frequency. In this way, the temperature dependence of $\tau(T_p) = 1/2\pi f$ was experimentally obtained from observations of the peak tem-
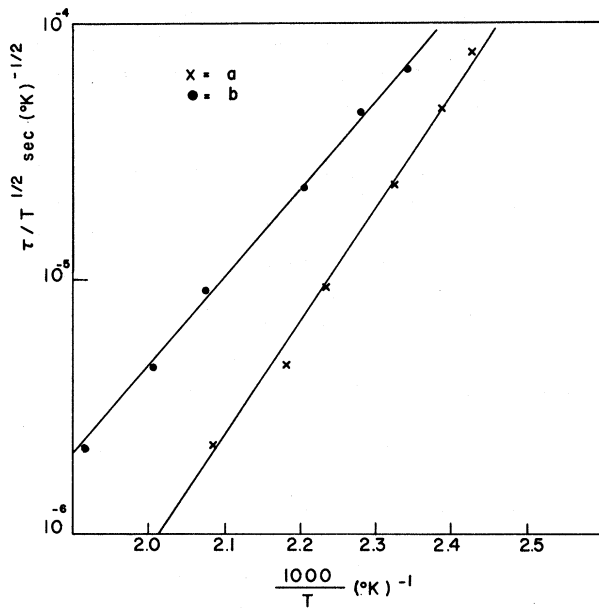
FIG. 2. $\text{Log}(\tau/T^{1/2})$ versus $1/T$ for specimens a and b. See text.

TABLE I. Activation energy Q, pre-exponential factor $\tau_0/T^{1/2}$, and bandwidth J for the relaxations.

Specimen	Q (eV)	$(\tau_0/T^{1/2})_0$ (sec $^\circ K^{-1/2}$)	J (10^{-2} eV)
a	0.89	8.3×10^{-16}	8.95
b	0.70	3.44×10^{-13}	0.42

perature T_p as a function of measuring frequency f.

An analysis of the temperature dependence of the observed relaxation times shows that the hopping is nonadiabatic. Were adiabatic hopping involved, the relaxation time τ would be of the form $\tau = \tau_0 \exp(Q/kT)$. Such plots of $\log\tau$ versus $1/T$ of the experimental data produced reasonably good straight lines, but resulted in an unreasonably small value of $\tau_0 \approx 10^{-17}$ sec. In the case of adiabatic hopping, τ_0 is expected to be $\approx 2\pi/f_0$, where f_0 is the optical phonon frequency, and such a large value of f_0 is not reasonable. Alternatively, Holstein's[9] nonadiabatic expression for τ_0,

$$\tau_0^{-1} = \pi^{1/2} J^2/2\hbar(W_H kT)^{1/2},$$

gives realistic values for the parameters. Holstein's expression implies rather plotting $\log(\tau/T^{1/2})$ versus $1/T$; and, indeed, analyzing the data in this way, good straight lines are obtained, as shown in Fig. 2, from which the activation energies and pre-exponential factors were obtained by least-mean-square analysis. The values of the various parameters of the relaxations are collected in Table I. In particular, the value of $(\tau_0/T^{1/2})_0$ is reasonable. Using the observed values of the activation energy Q for W_H, we obtain the values of J for the bandwidth relative to the transition.

Various estimates for the hopping energy of

free polarons in NiO have been made: 0.01 eV by Adler and Feinleib, and 0.35 eV by Austin and Mott, both of which are smaller than the value observed in these relaxations. In addition, the work of Kabashima and Kawakubo[10] (and possibly also the work of Snowden and Saltzburg[11]) suggests that the activation energy for polaron hopping around a Li^{+1} center is very small, perhaps $\approx 10^{-2}$ eV. However, direct comparison, of the behavior of the Ni_v^{+2}-Ni^{+3} center with that of the Li^{+1}-Ni^{+3} center is not realistic, since in this case considerable ionic relaxation with concomitant softening of the short-wavelength phonons is expected to lead to considerable differences between the polaron parameters. Since the polaron binding energy depends inversely on the square of the phonon frequency, a 10 to 20% softening of the mode results in a 20–45% increase in the binding energy and a similar increase in the hopping energy. In addition, the hopping of a bound polaron results in dipole reorientation. (The actual charge reorientation may be more complicated than simple dipole reorientation, but we do not wish to complicate our speculation unduly at this time.) Since there is an additional interaction between the dipole and the lattice, dipole reorientation by polaron hopping requires an additional energy, $W_{dip} = \frac{1}{2}\vec{p}\cdot\vec{R}$ in the first approximation, as may be seen by applying the argument used by Austin and Mott.[2] Here, $\vec{p}$ is the dipole moment and $\vec{R}$ is the reaction field[12] due to the polarization of the lattice by the dipole. Crudely,

$$W_{dip} \sim \frac{\epsilon-1}{2\epsilon-1}\frac{p^2}{2a^3},$$

and taking a, the cavity radius in which the dipole is supposedly located, to be twice the Ni-O distance, we find $W_{dip} \approx 0.3$ eV. Thus, we do not find the values of the activation energies for the bound-polaron hopping observed here unrealistically large in comparison to the hopping energies estimated for free polarons, and as compared to polarons hopping about the Li center. Because

of these factors, the value of J in the table is probably an overestimate by $\approx 20\%$.

It does not seem reasonable to attribute the relaxations to ionic motion or to an ionic reorientation of some ionic complex such as are observed in doped alkali halides, and in other transition-metal oxides, at relatively high temperatures. The activation energies of the relaxations here, ≈ 0.7 eV, are too low in comparison with the observed activation energies for cation diffusion in NiO (≈ 3 eV) and the implied reorientation activation energy, which, although somewhat less than this, is unlikely to be as low as that observed here for NaCl; e.g., compare the activation energy for cation diffusion, 0.70 eV, with the activation energy for reorientation of the Ca^{++}-associated vacancy complex, 0.60 eV.[13] Comparison with TiO_2 is more significant, since TiO_2 and NiO have very similar Debye temperatures.[14,15] Ionic reorientation occurs in TiO_2 with an activation energy of ≈ 1.0 eV. Secondly, the magnitudes of the relaxations here vary inversely with the intrinsic donor concentration. This immediately rules out such complexes as the oxygen-vacancy-nickel-vacancy complex (O_v-Ni_v^{+2}) being responsible, and also the oxygen-vacancy–Li-impurity complex (O_v-Li^{+1}), even if our specimens were quite impure. It is difficult to construct other ionic complexes or single defects which could give rise to the observed behavior. The observed reversible decrease of the dielectric relaxation with increasing reduction is very strong evidence that the relaxation is due to an empty dipolar (in the first approximation) acceptor state.

These experimentally determined values of J are small compared to the values of J inferred from the Néel temperature, that is, compared to $J \approx 0.35$ eV. We suggest that this small value of J indicates that the hole is hopping directly between the cations and is constrained in the (111) plane in which the spins are all parallel. The small value of J is consistent with a direct transfer integral between the cations. Although the transfer integral through the oxygen ions may be larger, the superexchange J, this latter hopping is suppressed because of the large energy of the misaligned spin which necessarily results from this hopping. (For further discussion, see the work of de Gennes.[16]) In any event, it is interesting to note that Adler and Feinleib believe that J is indeed small, and our value is in agreement with their estimate of $J < 0.01$ eV.

The compensation in our specimens may be also inferred from the values of the dc conductiv-

ity. As expected, the more highly compensated the specimen, the lower the conductivity and the higher the activation energy. In fact, these dielectric relaxations could be observed only because the dc conductivity is so low. The specimens in this paper have the second lowest dc conductivity on record for single crystals, only those of Rosenblum and Tannhauser[17] being lower. The conductivities reported by Austin[18] et al. at 400°K, namely, $\approx 10^{-2}$ Ω^{-1} cm^{-1}, by Kabashima and Kawakubo, $\approx 10^{-1}$ Ω^{-1} cm^{-1}, etc., are sufficiently high to preclude observation of these relaxations which are presumably always present to some degree. The dc conductivity of these specimens will be the subject of another paper.

We have also not considered the fact that two or more closely spaced relaxations are involved; cf. Fig. 1(b). Presumably, there are different relaxation modes of the complex defect.

We appreciate some discussion with D. Adler and are grateful to Dr. H. Sahagian for providing us with a NiO single crystal.

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Plasmon Dispersion Curve for bcc Potassium

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The plasmon dispersion curve for bcc potassium has been calculated for propagation along the (110) direction by specifically incorporating the electronic energy band structure. Calculated results are in excellent agreement with experiment.

That bulk plasmons can be excited and detected optically appears now to be an established fact. Melnyk and Harrison[1] were the first to demonstrate that for p-polarized light incident on a thin film of a free-electron gas, the absorptance was dominated by a series of sharp peaks for frequencies $\omega \gtrsim \omega_p$, where ω_p is the plasma frequency. They concluded that this structure was due to resonances occurring when standing waves of plasmons are set up inside the thin film. This calculation involved the addition of a longitudinal field, associated with the plasmons, to the classical optical theory.

Similar observations were made independently by Jones, Kliewer, and Fuchs,[2] who, assuming specular surface scattering for the electrons, obtained the optical properties from surface impedance expressions which included nonlocal dielectric functions for the electron gas. The calculations reported in this paper were done using dielectric functions obtained from the Boltzmann equation and, for $\omega \gtrsim \omega_p$, the results were essentially equivalent to those of Ref. 1. Since the wave vector at which the resonances occur are in most cases above those for which the Boltzmann equation is valid, these calculations were repeated[3] using self-consistent-field (SCF) dielectric functions. As expected, the frequencies of the resonances changed significantly from those obtained using the Boltzmann dielectric functions. Since the physical content of the SCF dielectric functions is clearly superior to that of the Boltzmann dielectric functions for large wave vectors, calculations based upon the SCF dielectric functions should provide a better description of the actual physical situation.

The appearance of the resonant structure in the optical properties provides a means for experimentally determining the plasmon dispersion curve. The resonances occur for wave vectors $n\pi/d$, where $n = 1$, 3, 5, etc., and d is the film thickness. By measuring the resonant frequencies and associating them with the appropriate values of q, the plasmon dispersion curve is obtained. Such experiments have been reported for silver,[4] and more recently for potassium.[5] In the latter experiment, the wavelength-modulated photoelectric yield[6] displayed the plasmon characteristics predicted in Refs. 1–3 for frequencies $\omega_p \le \omega \le 1.4\omega_p$. The experiment was performed for three different films whose relative thicknesses were known, but no absolute determination of any thickness was made. The authors then fitted their data for the thickest film by the curve[5]

$$\omega^2 = \omega_p{}^2 + (\tfrac{3}{5})v_F{}^2 q^2, \tag{1}$$

with Fermi velocity v_F given by $v_F = 8.5 \times 10^7$ cm/sec, and obtained an excellent fit to their data. The results from the thinner films also fit this curve. From this they concluded that the plasmon dispersion relation for potassium is well represented by the free-electron description afforded by the Boltzmann equation. It should be noted here that Eq. (1) is the first two terms in an expansion of the plasmon dispersion curve in powers of q^2 and, as such, is valid only for small q.[7] The wave vectors involved in the experiment of Ref. 5 were in most cases beyond those for which Eq. (1) is valid. However, the fact remains that Eq. (1) did represent the data and, since this equation approximates better the plasmon dispersion relation as obtained from the Boltzmann dielectric function than that obtained from the SCF dielectric function, this would seem