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# Hole Transport in Pure NiO Crystals

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The drift mobility of excess holes has been investigated in undoped NiO crystals using a transient technique with electron-beam excitation. Specimens with low-impurity content were grown epitaxially from the gas phase. At room temperature $\mu_h$ lies between 20 and 50 $cm^2\ V^{-1}\ sec^{-1}$, and its temperature dependence shows that scattering by optical modes predominates. The results lead to a phonon energy of 0.055 eV, a polaron effective mass of $1.5m_0$, and a coupling constant of 1.6.

In spite of a great deal of work during the last two decades, the detailed nature of the electronic transport properties of NiO and of other transition metal oxides, is by no means clear. Most of the interpretable transport data on NiO have been obtained from dc conductivity and thermoelectric power measurements on Li-doped and undoped crystals[1,2] and ceramic specimens.[3] In the exhaustion range of the Li acceptors ($\simeq 1200$ K), a hole drift mobility $\mu_h$ of about 0.4 $cm^2V^{-1}sec^{-1}$ has been deduced by several authors, whereas room-temperature determinations have led to values between 0.5 and 5 $cm^2V^{-1}sec^{-1}$. The form of the temperature dependence of $\mu_h$ is not well established and depends largely on the assumptions made concerning the temperature dependence of the density of states. A detailed analysis of available transport data, and of the Hall mobility problem, has recently been carried out by Bosman and van Daal.[4] It led to the conclusion that the transport of free holes in NiO takes place in a relatively wide band and is describable on the basis of the large-polaron model. This is also in general agreement with the discussion of Adler and Feinleib.[5]

In the present state of the subject it appeared of some interest to provide independent transport results by an essentially different experimental method. Transient drift-mobility techniques are a very direct approach, which have been widely used in transport studies on molecular crystals and liquids and on amorphous solids.[6] Two previous attempts have been made to determine the drift mobility of photogenerated holes in NiO.[7,8] A value of about 0.3 $cm^2V^{-1}sec^{-1}$ was obtained at room temperature, which must be regarded as a lower limit; however, in the absence of any measurements on the temperature dependence of $\mu_h$, no further conclusions could be drawn.

The present work was stimulated by the fact that NiO crystals of considerably improved purity had become available. The crystals were produced by epitaxial deposition from the gas phase and further details are given in the paper by Lubezky and Tannhauser.[9] Analysis by emission spectroscopy showed that in the specimens used here the total metal impurities lay below 50 ppm (by weight). Neutron-activation analysis indicated a bromine content of 25 ppm or less.

In the following experiments an electron-beam technique was used[6] in which excess carriers were generated within a few $\mu$m of the specimen's top electrode by a 45-keV electron pulse of 15-nsec duration. Holes were extracted from this region by a synchronized field pulse, and their transit

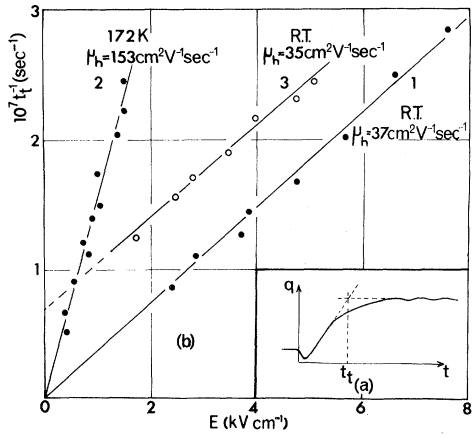


FIG. 1. (a) Integrated transit signal of holes observed in NiO, indicating how the transit time $t_t$ is defined. (b) Graph of $1/t_t$ vs $E$, the applied field. Curves 1 and 2: excitation pulse rate 2 pulses/sec; curve 3: 50 pulses/sec.

time $t_t$ across the specimen was measured on a wide-band oscilloscope after suitable preamplification. Experiments were carried out on crystal platelets between 70 and 150 $\mu$m thick, fitted with evaporated gold or aluminium electrodes.

An unusual feature, which in our experience distinguishes NiO from other crystalline materials investigated by this method, is the extremely low efficiency of hole extraction from the generation region near the top electrode. With an excitation beam of $8\times10^6$ electrons per pulse, measurements on the best specimen led to about $2\times10^6$ extracted holes at room temperature at a field of $7\times10^3$ V cm$^{-1}$. This process, therefore, requires an energy input of almost 200 keV per hole. On the other hand, the actual generation of electron-hole pairs is a surprisingly efficient process, and it is well known[10] that for nonmetallic solids the required energy amounts to about three times the energy gap (i.e., between 10 and 20 eV for NiO). The remarkable discrepancy, by four orders of magnitude, is undoubtedly associated with the generation region, because any appreciable loss of free carriers through trapping in the bulk of the specimen would make observation of the transit impossible.

There are two possible explanations: (a) Holes are generated in a comparatively wide band, but intense recombination with generated electrons takes place, most probably through recombination centers. (b) Two species of holes are generated; a comparatively large fraction in a narrow, low-mobility band having a high density of states, and an appreciably smaller fraction in a wide band leading to the observed hole transits. In either case, a buildup of positive space charge in the generation region is likely.

The very small proportion of extracted holes proved a major complication in the experiments. The best compromise between sensitivity and bandwidth of the electronic equipment gave a detection sensitivity of $2\times10^5$ electrons/cm on the oscilloscope screen, while maintaining an over-all rise time of about 15 nsec. Altogether, 14 specimens were examined which differed widely in the number of holes that could be extracted at a given applied field $E$. In five of these the signal was large enough at sufficiently low $E$ to allow meaningful measurements of the transit time as a function of $E$ before approaching rise-time limitations. In the remaining crystals, hole signals were too small, or unobservable. No obvious correlation with impurity content was found and it appears that carrier lifetimes in this material are controlled both by impurities and by structural defects.

Figure 1(a) shows a typical integrated hole signal observed in the experiments. It is far from ideal and $t_t$ had to be defined somewhat arbitrarily as indicated on the diagram. The justification for such a procedure lies in the linearity of the $1/t_t$-vs-$E$ curves of Fig. 1(b) and in the general consistency of mobility results from different specimens. Curve 1 was obtained at room temperature, using a pulse rate of 2 pulses/sec. The deduced hole mobility is 37 cm$^2$V$^{-1}$sec$^{-1}$; room-temperature values for all five specimens ranged between 20 and 50 cm$^2$V$^{-1}$sec$^{-1}$. With decreasing $T$, the value of $\mu_h$ increases rapidly as shown by curve 2, and so does the efficiency of hole extraction. Curve 3 refers to a room-temperature experiment in which the electron beam was run at 50 pulses/sec, but only every eighth excitation pulse was accompanied by a field pulse. It can be seen from the upward shift of the line that an appreciable positive space charge has built up in the generation region producing, in this case, a field of about 2 kV cm$^{-1}$. When the applied field was reversed, some charge displacement associated with generated electrons could be observed; however, the signal showed no field dependence and appeared to be completely lifetime limited, so that the electron drift mobility could not be measured.

The temperature dependence of $\mu_h$ between 380 and 120 K was investigated in the best two specimens and is shown in Fig. 2 on a semilogarithmic plot of $\mu_h$ vs $10^3/T$. The results suggest that lattice scattering by optical modes is the predominant mechanism, but there may also be some contribution from spin-disorder scattering. The curves have been fitted to the large polaron model in the intermediate-coupling region,[11] applicable to coupling constants in the range $1<\alpha<5$. The mobility is given by

$$\mu=\frac{1}{2\alpha\omega_0}\,\frac{e}{m^*}\left(\frac{m^*}{m_p^*}\right)^3 f(\alpha)\,e^{\hbar\omega_0/kT}\,, \qquad (1)$$

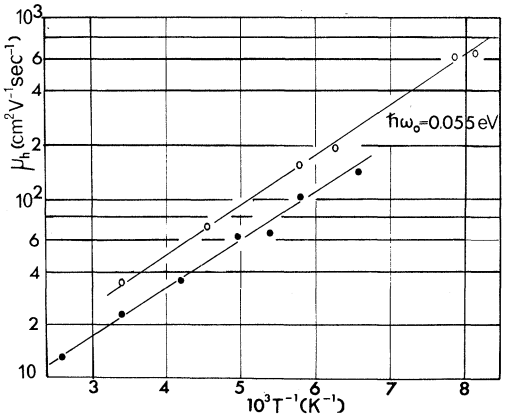


FIG. 2. Temperature dependence of the hole drift mobility for two specimens from batch 7-71.

where $f(\alpha) \simeq 1$. The polaron effective mass is

$$m_p^* = (1 + \tfrac{1}{6}\alpha)m^* \qquad (2)$$

and the coupling constant is

$$\alpha = \frac{e^2}{\sqrt{2}\hbar}\left(\frac{m_0}{\hbar\omega_0}\right)^{1/2}\left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{stat}}\right)\left(\frac{m^*}{m_0}\right)^{1/2}. \qquad (3)$$

Both sets of results in Fig. 2 lead to $\hbar\omega_0 = 0.055$ eV for the longitudinal-optical (LO) phonon energy. This should be compared with the value of 0.071 eV obtained for the zone-center LO mode by optical measurements.[12] Using the experimental $\omega_0$ and values of $\epsilon$ from Ref. 12, Eq. (3) gives $\alpha = 1.4\,(m^*/m_0)^{1/2}$. Equations (1) and (2) then lead to $m_p^* = 1.5m_0$, $m^* = 1.2m_0$, and $\alpha = 1.6$.

The results of Fig. 2 support in a very direct way the general interpretation of previous data by Bosman and van Daal.[4] However, the present results indicate appreciably weaker coupling and give a polaron effective mass of $1.5m_0$ as compared with the previous estimate of $6m_0$.

Although there is no doubt that one is observing a conventional band transport of holes, it is not clear whether this takes place in the nickel $3d$ band or in the oxygen $2p$ band. van Daal[13] estimates the width of the $3d^8$ subband to be of the order of 1 eV, so that the former possibility cannot be excluded. Adler and Feinleib,[5] on the other hand, conclude that the predominant hole conduction takes place through a broad $2p$ band and that holes in $3d$ states are strongly localized. This model would be consistent with the present drift-mobility measurements only if the narrow $3d$ band lay below the upper edge of the $2p$ band, for otherwise we would have observed either a trap-controlled transport or a hopping mobility, both with a temperature dependence opposite to that in Fig. 2.

We have attempted to explore the feasibility of the above model by some preliminary experiments on the temperature dependence of the number of extracted holes and of the positive space-charge field. Both these quantities are associated with an activated temperature dependence, but so far it has not been possible to draw any definite conclusions.

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