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PHOTOCONDUCTIVITY IN DISORDERED NICKEL-OXIDE FILMS*

R. Tsu, L. Esaki, and R. Ludeke

IBM Watson Research Center, Yorktown Heights, New York 10598

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Photoconductivity measurements in the infrared and visible spectral regions have been made on disordered NiO films. The result shows a prominent peak at the energy of 0.23 eV, coinciding with the one in the infrared absorption, which is believed to be a spin-excited state due to the antiferromagnetic ordering. We propose a model to explain the observation.

We report here an experimental result of transport properties in very thin nickel-oxide films. These films, of approximately 50 Å thickness, were prepared at room temperature by vacuum evaporation of pure nickel at 10^{-6} Torr on polished sapphire substrates and subsequent oxidation in air. Then the specimens were heat treated at 10^{-2} Torr of residual air at 300°C for half an hour. Electron diffraction studies of films prepared by the same procedure show that crystallite sizes are less than 20 Å, indicating that the films are essentially in a disordered state.

Two vacuum-deposited nickel electrodes, separated by 75 μm, were used for photoconductivity as well as for electrical conductivity measurements. Although pure NiO crystals are usually good insulators, we have found that this disordered film is a semiconductor. Figure 1 shows the resistance R as well as the activation energy E_a , defined by $R = R_0 \exp(E_a/k_B T)$, as a function of reciprocal temperature. The activation energy E_a , which is about 0.5 eV at 500°K, decreases monotonically down to 0.003 eV at 20°K. This is reminiscent of the electrical conduction in $\text{Li}_x\text{Ni}_{1-x}\text{O}$ crystals.¹

We have measured the spectral response of the photoconductivity for photon energies between 0.15 and 4 eV over the temperature range from room temperature to 5°K. This is probably the first observation of infrared photoconductivity in NiO.² We have found a prominent peak at 0.23 eV on a background that increases with the photon

energy. The result at 20°K is shown in Fig. 2. The half-width of the peak seems to be independent of temperature, although it is barely observable at room temperature presumably because of decreasing carrier lifetime with increasing temperature. It is unlikely that any impurity level gives rise to such a sharp peak, particularly in a disordered system. We have also eliminated heat effects as a possible cause of this observation. We might add here that an unsuccessful attempt has been made to see this photoconductivity peak in monocrystalline NiO.

It is informative to compare our result with the absorption curve of monocrystalline NiO obtained

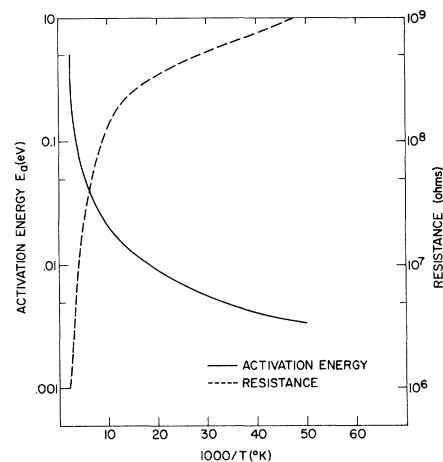


FIG. 1. Semilog plot of resistance R and activation energy E_a , defined by $R = R_0 \exp(E_a/k_B T)$, vs $1/T$.

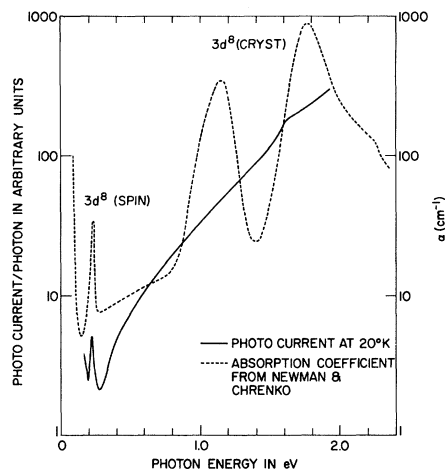


FIG. 2. Spectral response of photocurrent (full line) in comparison with absorption coefficient α (dashed line) measured by Newman and Chrenko.

by Newman and Chrenko,³ also shown in Fig. 2 as a dotted curve. Whereas the photocurrent increases with increasing absorption coefficient, it lacks the latter's structure except the peak at 0.23 eV, which we assume to be of the same origin as the 0.24-eV optical structure. We might mention here some effects of heat treatment at 300°C. Without this treatment, the film is roughly 100 times more conductive, although the prominent peak at 0.23 eV in the photoconductivity spectrum is still present.

The optical structure at 0.24 eV has been interpreted as being connected with the antiferromagnetic ordering in the crystal.³ A more detailed theory proposed its origin as due to a photon-magnon interaction.⁴ This theory was based on a model of nearest-neighbor interaction and one would thus expect optical structure even for a disordered system. For convenience, we label the ground state by the notation $3d^8$, and the excited state at 0.23 eV by $3d^8(\text{spin})$. The other excited states of the eight d electrons, denoted by $3d^8(\text{cryst})$, are brought about by the crystal field. All of these excitations do contribute to the optical absorption spectrum, as shown in Fig. 2, but not to the electrical conductivity in the ordinary situation, as pointed out by Feinleib and Adler.⁵

The semiconducting properties shown in Fig. 1 can be understood on the basis of the disordered nature of our films: Namely, the density of states $N(E)$ between the crystalline $2p$ and $4s$ bands in nonzero, representing the existence of localized states in the forbidden gap, as shown in Fig. 3. We believe that the transport properties in our films are the result of holes and/or

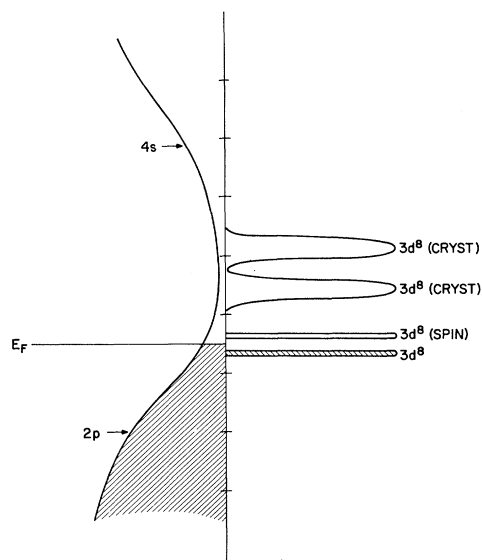


FIG. 3. Sketch of suggested density-of-states and location of Fermi energy E_F . Conducting and nonconducting states are shown to the left and the right of the vertical line, respectively.

electrons in the smeared $2p$ -band tail, resulting from thermal or optical excitation of electrons into the empty localized states in the formerly forbidden gap region.

An important question here, then, is why we see the peak in photoconductivity at 0.23 eV. If conduction by the d electrons in NiO is to be ruled out, the existence of an unknown coupling mechanism between the $3d^8(\text{spin})$ excited states and a quasicontinuum of localized states in the forbidden gap may be invoked to explain our results. Namely: Electrons excited to the $3d^8(\text{spin})$ from the $3d^8$ ground state may be transferred to the midgap states and, probably simultaneously, the hole in the $3d^8$ state transferred to the $2p$ band. Intuitively one may argue that hole conduction is the more favorable mechanism. This model would thus give rise to a peak in photoconductivity as sharp as that in the optical absorption. In this case, the Fermi level E_F should be placed at an energy between the $3d^8(\text{spin})$ and the $3d^8$ ground state, as shown in Fig. 3. This strongly suggests that the $3d^8$ ground state is near and possibly above the top of the unperturbed $2p$ band, rather than at 1.5 eV below, as suggested previously.⁵

We do not observe structure in the photoconductivity spectrum at the energies of the $3d^8(\text{cryst})$ states. We may cite several reasons for this observation: The density of states $N(E)$ of the band gap states at energies corresponding to the

$3d^8(\text{cryst})$ states is rather small, the $3d^8(\text{cryst})$ states have spread in energy as a consequence of the disorder in the film, and the background photocurrent in the quasicontinuum "band" is rapidly increasing with photon energy and may disguise the contribution from the $3d^8(\text{cryst})$ states. In addition one may also speculate on an inherent reason: The $3d^8(\text{spin})$ and $3d^8(\text{cryst})$ excited states are of entirely different origin: While the former depends on a spin-spin interaction between several Ni atoms, the latter states can be interpreted as "internal" excitations of the Ni^{++} ion and hence may be less likely to be coupled to conduction-supporting states in the NiO system.

In conclusion, we believe that in disordered NiO there exists a coupling between nonconducting states and conducting states. As a result, the spectral response of the photoconductivity shows a structure due to the nonconducting states. These measurements can be easily extended to other disordered systems in order to

obtain information on nonconducting states.

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LATTICE ANISOTROPY IN ANTIFERROMAGNETIC CHROMIUM*

M. O. Steinitz, L. H. Schwartz, and J. A. Marcus
Northwestern University, Evanston, Illinois 60201

and

E. Fawcett and W. A. Reed
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
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Thermal expansion and magnetostriction measurements on single- \vec{Q} single-crystal chromium give the lattice parameter ratios in the orthorhombic phase below the Néel temperature and through the transition to the tetragonal phase at the spin-flip temperature, $T_F = 122^\circ\text{K}$. The \vec{Q} direction is the longest axis at 300°K and becomes the shortest axis below $\sim 200^\circ\text{K}$. The anisotropic discontinuities in length at T_F result in a net volume dilatation, 1.4×10^{-6} with decreasing temperature.

Recent experimental work^{1,2} has demonstrated the expected and long-sought³⁻⁵ deviations from cubic symmetry of the lattice parameters of chromium in its antiferromagnetic state. In this paper we wish to report our measurements of these deviations over the temperature range from 115°K to the Néel temperature and show that the longest axis at 300°K becomes the shortest axis below 220°K .

At the Néel temperature, $T_N = 312^\circ\text{K}$, Cr undergoes a first-order transition⁶ from a body-centered cubic paramagnetic state to an antiferromagnetic transverse spin-density-wave state (AF_1). At the spin-flip temperature, $T_F = 122^\circ\text{K}$,

Cr undergoes a first-order transition⁷ from the transverse spin-density-wave state to one with longitudinal polarization (AF_2). The wave vector of the spin density wave is denoted by \vec{Q} and the spin polarization by \vec{s} . Both \vec{Q} and \vec{s} lie along $\langle 100 \rangle$ directions.⁴ If a crystal of Cr is cooled through T_N in the presence of a sufficiently large magnetic field along a $\langle 100 \rangle$ direction,⁸ it will have a single \vec{Q} throughout most of its volume, with \vec{Q} parallel to the cooling field, \vec{H}_C . The field may be removed below T_N without disturbing the single- \vec{Q} state. Graebner and Marcus⁹ showed that a crystal cooled through T_N in zero field consists of regions in each of which there