# Photoconductivity of the nickel dihalides and the nature of the energy gap

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Measurements of the photoconductivity of single crystals of the nickel dihalides  $NiX_2$  (X=Cl, Br, I) are reported. The photoconductivity energy gaps at 100 K are 4.7 eV (NiCl<sub>2</sub>), 3.5 eV (NiBr<sub>2</sub>), and 1.8 eV (NiI<sub>2</sub>). It is shown that the energy gap in these materials is due to charge-transfer transitions from the anion p band to transition-metal d states. The photoconduction is due to holes in the anion p band.

## INTRODUCTION

For the last 50 years the origin of the band gap and the characters of valence- and conduction-electron states in 3d transition-metal compounds have been a controversial topic.<sup>1-6</sup> One-electron band-structure calculations predict small energy gaps for the transition-metal oxides<sup>7,8</sup> and even metallic behavior for the nickel dihalides.<sup>9,10</sup> However, this does not agree with the observed insulating character of these compounds and the large band gaps observed optically. The origin of this discrepancy is the large interaction (exchange and correlation) between the transition-metal 3d electrons, which is not taken into account properly in the one-electron energy band theory. Mott<sup>2</sup> has shown that electron correlation introduces an energy gap in d states, and this explains at least qualitatively the insulating character of many transition-metal compounds. This Mott-Hubbard theory<sup>2,3</sup> predicts that the band gap in the transition-metal compounds is due to energy differences between states of the type  $d_i^n d_j^n$  and  $d_i^{n-1} d_j^{n+1}$ , where *i* and *j* label transition metal sites *i* and j, and n is the number of d electrons at a particular site. Thus, according to this theory, the energy gap involves d-d Coulomb and exchange interactions on the transition-metal atom, and the magnitude of the energy gap will be nearly independent of the nature of the anion.

Another possibility is that there is a large gap in the d states due to electron correlation, but that the energy gap corresponds to charge-transfer transitions from the anion p-valence band to empty metal d states  $(p-d \text{ gap}).^{4-6}$  This also leads to insulating behavior; however, in this case the energy gap will depend strongly on the electronegativity of the anion.

Recently, Zaanen *et al.*<sup>11,12</sup> presented a theory for describing the band gaps and the electronic structures of the 3*d* transition-metal compounds. The authors calculated the energy-level diagrams of the 3*d* transition-metal compounds for a cluster of a central 3*d* transition-metal ion surrounded by the nearest-neighbor anions. The parameters in the calculations are the *d*-*d* Coulomb and exchange interaction *U*, the charge-transfer energy  $\Delta$ , the width *W* of the anion valence band and the hybridization interaction (which was assumed to be independent of the wave vector *k*). The width of the *d*-band of the metal

ions, which is usually small, was not taken into account. The calculations show band gaps in these materials that are either of d-d or charge-transfer type, depending upon the relative strength of U and  $\Delta$ . The theory predicts that the band gaps in Ni $X_2$  (X = Cl,Br,I) are of the charge-transfer type.

The optical reflectivity of transition-metal halides has been studied extensively.<sup>13-18</sup> The data give experimental evidence that in the late-transition-metal halides (Co, Ni, Cu) the energy gaps are of the charge-transfer type.

There is, however, one difficulty. The optical spectra clearly show exciton peaks, but it is difficult to deduce from the spectra values of the energy gap for band-toband transitions. Moreover, cluster calculations<sup>11,12,19-21</sup> and also photoelectron spectra refer to situations where the excited electron is in the close neighborhood of the hole left behind, just as it is in the case for excitons. Therefore it is difficult to obtain from these methods reliable information about the conductivity energy gap, which is the difference between the ionization potential and the electron affinity of the solid, or the energy difference between the bottom of the conduction band (N+1)particle states) and the top of the valence band (N-1) particle states). An experimental method which comes close to determining directly the conductivity gap is a comparison of photoemission and inverse photoemission data.<sup>6,22,23</sup>

With photoconductivity measurements one determines the conductivity gap unambiguously. Exciton absorption will contribute to the photoconductivity only if the exciton energy is larger than the conductivity gap, so that the excitons can decay into free electrons and holes.

In this paper we present photoconductivity measurements of the nickel dihalides NiCl<sub>2</sub>, NiBr<sub>2</sub>, and NiI<sub>2</sub>. The results are compared with the values of the chargetransfer energy  $\Delta$ , deduced from x-ray photoemission spectroscopy measurements.<sup>24</sup> Our results are in agreement with the predictions of the theory of Zaanen *et al.* with respect to the origin of the band gaps in the investigated NiX<sub>2</sub> compounds.

In the literature only photoconductivity measurements on NiBr<sub>2</sub> have been reported thus far, by De Luca *et al.*<sup>25</sup> These authors reported weak structures in the photoconductivity spectra at 0.8 and 1.5 eV and a broad intense band at 2.0 eV at 300 K. The intensity of these bands differs strongly for different samples. The photoconductivity increases strongly with increasing energy of the incident radiation above 2.5 eV at 300 K. We observed no photoconductivity in NiBr<sub>2</sub> below 3.0 eV at temperatures below 260 K.

The absence of photoconductivity peaks in our measurements below 3.0 eV at temperatures below 260 K, together with the fact that the intensity of the photoconductivity bands below 2.5 eV differs strongly for different samples indicates that the photoconductivity of NiBr<sub>2</sub> below 2.5 eV is not an intrinsic property of NiBr<sub>2</sub>.

## EXPERIMENTAL METHODS

NiCl<sub>2</sub> and NiBr<sub>2</sub> were prepared by adding NiCO<sub>3</sub> (Johnson-Matthey Chemicals Ltd., Ultrapure) to HCl (Merck, proanalyse) and HBr (Merck, Suprapur), respectively. The product was dried under a flow of dry N<sub>2</sub> gas and sublimed in a sealed ampoule at a temperature gradient of 600–650 °C. NiI<sub>2</sub> was prepared from Ni (Koch and Light 99.9999%) and I<sub>2</sub> (Merck, doubly sublimed). In order to be able to control the iodine vapor pressure one side of the sealed ampoule was heated to 600 °C (cold-point method). A strong advantage of this method is the fact that the reaction product sublimes to the middle part of the ampoule. In this way an already sublimed reaction product is obtained at once.

The light of a 1000-W xenon arc (Oriel 6269) passed through a Jobin-Yvon H.20 uv grating monochromator. The spectral resolution used was about 0.07 eV. The direction of the incident light was parallel to the crystallographic c axis of the compounds. The sample was mounted in an Oxford MD4 flow cryostat. The temperature of the sample may be varied between 2 and 300 K.

Typical crystal dimensions were  $2 \times 2 \times 0.04$  mm.<sup>3</sup> The electrical contacts were made using either Ag paste or Ga solder. In order to prevent the illumination of the electrical contacts in the photoconductivity experiments masks were used. In this way we excluded photovoltaic contributions to the measured signal. The presence of a photovoltaic effect indicates that the electrical contacts are not Ohmic.<sup>26</sup> In general Ohmic contacts are desired in photoconductivity experiments, as potential barriers at the metal-semiconductor interface influence magnitude and temperature dependence of the photocurrents.

The investigated compounds are all hygroscopic. Therefore all crystal handling was performed in an atmosphere of dry nitrogen.

Both the dark current and the photocurrent are very small in the nickel dihalides; the observed currents were of the order of  $10^{-9}$  to  $10^{-15}$  A. This requires a sensitive detection method. We used for the measurements a Keithley 642 electrometer; all measurements were carried out with an applied voltage of 500 V.

#### EXPERIMENTAL RESULTS

Figures 1–3 show photoconductivity spectra of  $NiCl_2$  (at 137.0 K),  $NiBr_2$  (at 134.6 K), and  $NiI_2$  (at 141.0 K) with Ag as the contact material. The illuminated area of



FIG. 1. Photoconductivity spectrum of NiCl<sub>2</sub> at 137 K, using Ag as contact material. The arrow indicates the photoconductivity energy gap.

the crystal was 7.1 mm<sup>2</sup> in the case of NiCl<sub>2</sub> and 12.6 mm<sup>2</sup> in the case of NiBr<sub>2</sub> and NiI<sub>2</sub>. The thickness of the crystals was 10  $\mu$ m for NiCl<sub>2</sub>, 40  $\mu$ m for NiBr<sub>2</sub>, and 150  $\mu$ m for NiI<sub>2</sub>.

We also measured the photoconductivity spectra of  $NiBr_2$  and  $NiI_2$  using Ga as the contact material. The il-



FIG. 2. Photoconductivity spectrum of  $NiBr_2$  at 135 K, using Ag as contact material. The arrow indicates the photoconductivity energy gap.



FIG. 3. Photoconductivity spectrum of NiI<sub>2</sub> at 141 K, using Ag as contact material. The arrow indicates the photoconductivity energy gap.

luminated area of the crystals was 7.1 mm<sup>2</sup> in the case of NiBr<sub>2</sub> and 12.6 mm<sup>2</sup> in the case of NiI<sub>2</sub>. The thickness of the crystals was 40  $\mu$ m for NiBr<sub>2</sub> and 120  $\mu$ m for NiI<sub>2</sub>. Due to the small size of the crystals we were not able to solder Ga contacts on NiCl<sub>2</sub> samples.

The dark current is typically 10-100 times as small as the photocurrent.

The photoconductivity spectra of NiBr<sub>2</sub> and NiI<sub>2</sub> are corrected for the emission characteristics of the light source and the transmission characteristics of the monochromator. Due to the fact that at energies above 4.5 eV the light intensity is very low, small errors in the correction procedure may cause appreciable errors in the corrected photoconductivity spectra at energies above 4.5 eV. Therefore we did not correct the photoconductivity spectra of NiCl<sub>2</sub> for the emission characteristics of the light source and the transmission characteristics of the monochromator.

Figures 4–6 show the magnitude of the photoconductivity energy gap of the compounds Ni $X_2$  as a function of the temperature, using Ga and Ag as the contact materials. The way we determined the magnitude of the photoconductivity band gap is indicated in the figures. In the temperature region 150–250 K, the magnitude of the photoconductivity energy gap of NiBr<sub>2</sub> appears to depend on the type of contact material used (Fig. 5). This effect is not understood.

Figure 7 shows the maximum photoconductivity of the compounds  $NiX_2$  as a function of the temperature using the indicated contact material. Notice the large variations in the magnitude of the photocurrent.



FIG. 4. Photoconductivity energy gap of  $NiCl_2$  vs temperature, measured with Ag as contact material.

# ORIGIN OF THE PHOTOCONDUCTIVITY IN THE NICKEL DIHALIDES

First we show that the experimental data provide strong evidence for hole conduction in the nickel dihalides. We observe that the photocurrents are much smaller for Ga contacts than for Ag contacts on  $NiBr_2$  and  $NiI_2$ . This difference indicates that the contact is influenced by the work function of the contact material, and not so much



FIG. 5. Photoconductivity energy gap of  $NiBr_2$  vs temperature, measured with Ag and Ga as contact materials.



FIG. 6. Photoconductivity energy gap of  $NiI_2$  vs temperature, measured with Ag and Ga as contact materials.

by the presence of surface states. Indeed the surface perpendicular to the c axis of layered crystals like the nickel dihalides is quite stable and inert, and surface states are not very likely.

The data show that certainly for the Ga contact there must be large potential barriers, in order to explain the



FIG. 7. Maximum photocurrent versus temperature. Curves 1 (NiCl<sub>2</sub>-Ag), 2 (NiBr<sub>2</sub>-Ag), 3 (NiBr<sub>2</sub>-Ga), 4 (NiI<sub>2</sub>-Ag), 5 (NiI<sub>2</sub>-Ga).

much smaller photocurrent for Ga contacts. This suggests perhaps Ohmic contacts with Ag, but shows that strongly non-Ohmic contacts are present for Ga. The work function of Ag is much larger than that of Ga. Also one expects that Ga, if dissolved in a thin layer in nickel dihalides, will act as a donor and form an  $n^-$ -type layer. Ag, on the other hand, will act as an acceptor and form a  $p^+$ -type layer. Consequently one expects an Ohmic contact for Ga on *n*-type material, and an Ohmic contact for Ga on *n*-type material. The much smaller photocurrents, observed with Ga contacts, show that the photoconduction in the nickel dihalides takes place by positive holes.

The reflection spectra of the compounds Ni $X_2$  have been reported by Pollini *et al.*<sup>16,17</sup> In Table I we have given the position of the observed maxima in the reflection spectra, the position of the observed maxima in the photoconductivity spectra, and the photoconductivity energy gap.

Pollini *et al.* assigned the reflection maxima given in Table I to Xp-Ni 3d exciton transitions, except for the maximum in the reflection spectrum of NiI<sub>2</sub> at 3.20 eV, which was assigned to the I5p-Ni 3d band transition. However, we think that an assignment of this transition to a I5p-Ni 3d exciton transition is more realistic. The combined effect of spin-orbit interaction in the I 5p band and a trigonal crystal field splitting leads to a threefold splitting of the I 5p band. The magnitude of the spin-orbit splitting of the I 5p states in reflection spectra of CdI<sub>2</sub> is about 1 eV.<sup>27</sup> A splitting with the same magnitude is observed in the reflection spectrum of NiI<sub>2</sub> (3.20-2.20 eV). Due to the presence of a crystal field with trigonal symmetry the I 5p state with  $j = \frac{3}{2}$  (j = 1 + s) splits into two components at 2.20 and 2.50 eV. As a result three exciton bands are observed.

We find (Table I) that the first exciton reflection peaks in NiCl<sub>2</sub> and NiBr<sub>2</sub> lie below the photoconductivity gap. The optical excitation of these excitons does not lead to electrical conductivity. The exciton binding energies for these excitons are 0.4 and 0.3 eV for NiCl<sub>2</sub> and NiBr<sub>2</sub>, respectively. The higher exciton reflection peaks lie above the photoconductivity gap and correspond to pronounced maxima in the photoconductivity spectra. This must be due to a decay of these excitons into free charge carriers. For NiI<sub>2</sub> we find a photoconductivity gap of 1.8 eV, which is below the first exciton peak. This could indicate that the photoconductivity energy gap corresponds to indirect transitions, whereas the strong exciton reflection peaks are associated with direct transitions at a higher energy.

We conclude that the optical transitions which lead to the observed photoconductivity in the compounds Ni $X_2$ are ligand *p*-metal 3*d* transitions. The observed large increase of the (maximum) photoconductivity with increasing temperature could be due to an enhanced dissociation of excitons, leading to an increasing number of charge carriers. It is also possible that the increase of the photocurrent with increasing temperature is due to shallow trapping centers or a potential barrier at the contact material—Ni $X_2$  interface.

The observed photoconductivity in the compounds

|                   | Reflection maxima<br>at 30 K<br>excitons<br>(eV) | Photocond.<br>maxima<br>at 100 K<br>(eV) | Photocond.<br>energy gap<br>at 100 K<br>(eV) | Exciton<br>binding energy<br>(eV) | Δ   |
|-------------------|--|--|--|-----------------------------------|-----|
| NiCl <sub>2</sub> | 4.3,5.0  | 5.2                                      | 4.7  | 0.4                               | 3.6 |
| NiBr <sub>2</sub> | 3.2,4.0  | 3.9                                      | 3.5  | 0.3                               | 2.6 |
| NiI <sub>2</sub>  | 2.2,2.5,3.2                                      | 2.3,3.4                                  | 1.8  |                                   | 1.5 |

TABLE I. Optical data from reflection spectra (Ref. 16) and photoconductivity spectra. The data are compared with values of the charge-transfer energy  $\Delta$  (Ref. 24).

Ni $X_2$  is mainly due to hole conduction in the ligand p band. This is in agreement with the assignment of the photoconductivity energy gap to charge-transfer transitions: the holes are light, mobile particles in the broad anion valence band, the electrons are heavy particles of lower mobility as they occupy states of the narrow metal d bands.<sup>4</sup>

A consequence of the assignment of the observed maxima in the photoconductivity spectra to ligand *p*-metal 3dexcitonic transitions is that the (photoconductivity) energy gap is related to the electronegativity of the anion. This means that the magnitude of the band gap is determined mainly by the charge-transfer energy  $\Delta$  and not by the energy differences between states of the type  $d_i^n d_j^n$  and  $d_i^{n-1} d_j^{n+1}$ . In the latter case the band gap would be approximately independent of the ligand.

In Table I we have given the values of the chargetransfer energy  $\Delta$ , determined by van der Laan *et al.*<sup>24</sup> We find indeed that the magnitude of the photoconductivity energy gap and the value of  $\Delta$  for the compounds Ni $X_2$  show the same trend.

Finally, we remark that there is a considerable discrepancy between the calculated values of the energy gap  $\Delta - W/2$  (Ref. 12) and the observed conductivity gap.

This may be due to approximations in the calculations, but it can also be related to the fact that the photoelectron spectra refer to situations where the ligand hole is in the vicinity of the *d* electron,<sup>12</sup> whereas in the photoconductivity measurements the *d* electron and the ligand hole are uncorrelated.

We conclude that the holes at the top of the valence band, responsible for the photoconduction in the nickel halides Ni $X_2$  (X = Cl, Br, I), are mainly of anion p character. However, the nickel halides are strongly covalent, and there is considerable covalent mixing of anion p-hole states ( $d^8L$ , where L represents a ligand hole), and Ni 3dhole states ( $d^7$ ).

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