

## Chemical bond and hybridization in nickel compounds

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By means of ultraviolet reflectance and valence band photoemission one can get a scale of ionicity for nickel halides. The fraction of ionic character of the chemical bond, from 0.72 in NiI<sub>2</sub> to 0.80 in NiCl<sub>2</sub>, evaluated with the Phillips theory has been related to the ground state *d* electron counts  $\langle n_{dn} \rangle$  calculated from Ni2*p* core photoemission. While the chemical trends of cluster model parameters are in general well reproduced, a systematic discrepancy in band gap values (2–3 eV) has been found by comparing core-level results with optical and photoconductivity data.

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Optical and photoemission spectroscopy are useful techniques for studying the chemical bond in materials. Core-level x-ray spectroscopy (*c*-XPS) has been used for instance to obtain information about the local electronic structure, such as oxidation states and effective ionic charges. In principle, valence band x-ray photoelectron spectroscopy (VB-XPS) yields more direct and detailed information about the chemical bond and electronic structure of compounds than core spectra. To this aim, an ionicity coefficient  $f_i^{\text{XPS}}$ , measured in VB-XPS spectra, has been also defined by considering the splitting of low-lying *s*-like peaks in the density of states of semiconductors.<sup>1,2</sup> Moreover, valence spectra obtained with higher resolution ultraviolet photoelectron spectroscopy (VB-UPS), have been interpreted in terms of band structures, covalency and ligand field splitting models. However, in 3*d* transition metal compounds (TMC), the interpretation of photoemission spectra is not always easy, since it is often seriously hampered by several problems. First, the spectra are in general rather broad due to a large number of closely spaced bands, each composed of cation and anion based atomic orbitals. Secondly, the large Coulomb interaction between 3*d* electrons often invalidates the band interpretation in terms of one-electron theory.<sup>3,4</sup> For these reasons, core-level spectroscopy has been preferred in many cases.<sup>5</sup> Its advantage is that the wave function of core electrons is well known and is relatively insensitive to chemical bonding. The disadvantage is that the valence electronic structure can only be obtained in an indirect manner, namely via the response of *valence electrons* to the sudden creation of a *core hole*.

In this work we have investigated the electronic structure and chemical bonding of nickel halides, classified in Zaanen-Sawatsky-Allen (ZSA) theory,<sup>6</sup> as *charge transfer* (CT) compounds. We have here focused on the electronic properties of less studied NiBr<sub>2</sub> and NiI<sub>2</sub> compounds, by measuring their reflectance, in addition to VB-XPS and VB-UPS spectra in order to give an estimate of cluster model (CM) parameters ( $\Delta$ ,  $U$ , and  $T_{\text{eff}}$ ) for these compounds. Previous CM calculations performed on NiO and NiCl<sub>2</sub> have described the nature of their band gap more similar to a *pd* charge-transfer gap than a *dd* Mott-Hubbard gap.<sup>5,7</sup> Although NiX<sub>2</sub> ( $X = \text{Cl, Br, I}$ ) compounds have been studied in the past and the overall features have been on the whole understood, there are still interesting points which require new attention. For in-

stance, we have correlated the CM parameters and the ground-state *d*-electron counts  $\langle n_d \rangle$ , obtained from Ni2*p*-XPS spectra by Zaanen, Westra, and Sawatsky (ZWS),<sup>5</sup> to Phillips ionicity coefficients ( $f_i$ ),<sup>2,8</sup> and have found that the chemical trend of these parameters is in general respected. However, by comparing quantitatively the band gap values calculated from the Ni2*p*-XPS spectra with those obtained from reflectance and photoconductivity measurements,<sup>9</sup> a systematic discrepancy has been found for these compounds. Interesting experiments on the pressure-induced metallization and closure of the charge-transfer energy gap in NiI<sub>2</sub> have been also reported.<sup>10,11</sup>

Since the ionicity coefficient  $f_i$  plays a crucial role for the chemical considerations that follow, let us briefly recall its definition and physical meaning. The fraction of ionic character ( $f_i$ ) of the chemical bond of Ni halides is defined in the framework of the Phillips–Van Vechten (PVV) dielectric theory.<sup>2,8</sup> The PVV theory defines the average separation  $E_g$  (Phillips gap) of the valence and conduction bands as the pythagorean sum of an ionic part  $C$  and a covalent part  $E_h$

$$E_g(\text{Phillips}) = (E_h^2 + C^2)^{1/2}. \quad (1)$$

The homopolar energy gap  $E_h$  scales with the nearest neighbor distance  $d_{MX}$  as

$$E_h = a(d_{MX})^{-2.5} \quad (a \cong 40.5), \quad (2)$$

and the ionic energy  $C$  can be defined through the Phillips electronegativity by

$$C(AB) = b\{Z_A/r_A - Z_B/r_B\}e^{K_s R}, \quad (3)$$

with  $R = (r_A + r_B)/2$  and  $b \cong 1.5$ . The atomic radii  $r_A$  and  $r_B$  are defined as half of the bond length of the group IV element belonging to the same row of the periodic table as atoms  $A$  and  $B$  and  $Z_A$  and  $Z_B$  are the valence numbers of elements  $A$  and  $B$ .  $K_s$  is the Thomas-Fermi screening parameter  $K_s = (4K_f/\pi a_0)$ , where  $a_0$  is the Bohr radius and  $K_f$  is the wave number on the surface of the Fermi sphere in the free electron approximation. The fraction of ionic character of a chemical bond is defined by

$$f_i = C^2/(E_g)^2 = C^2/E_h^2 + C^2. \quad (4)$$

It should be noted that the crystal structure does not appear explicitly anywhere and therefore the model can be extended to include crystals belonging to the NaCl structure or is applicable to compounds other than  $A^N B^{8-N}$ . In TMH's the number of electrons involved in the chemical bonds is 16, eight per bond (neglecting  $3d$  electrons) and the  $E_g$  values have been calculated from Eqs. (1)–(4) with the value of the prefactor  $b$  ( $1.55 \pm 0.07$ ) adjusted to fit the experimental data and the nearest neighbor distance  $d_{MX}$ . All relevant parameters of PVV theory, such as the Phillips gap,  $E_g$ , the values of  $C$  and  $E_h$ , the experimental gap and the ionicity parameter  $f_i$  of  $NiX_2$  and other late TMC's, have been listed in Table I of the Thomas and Pollini article<sup>2</sup> to which we refer. In Fig. 2 of the same paper we have also shown the average peak energy of  $\Gamma$  excitons observed in TMH's versus the Phillips' gap  $E_g$ . The first excitonic transition, which yields the strongest structure close to the interband  $ps$  edge in UV reflectance and absorption spectra, occurs around 8.3 eV in TM chlorides, 7.4 eV in TM bromides and 6.0 eV in TM iodides. These values are mainly dependent on the nature of anions and rather independent on that of cations. On the other hand, the strongest charge transfer transitions, occurring just before the excitonic  $\Gamma$  peaks, shift according to the second ionization potential of cation and thus denote the  $3d$  final states. In order to calculate the energy gap between halogen  $p$  levels and metal  $4s$  levels, we have at first neglected the contribution of partially filled  $3d$  Ni levels in Eq. (3). The  $f_i$  values for Ni halides have been then recalculated by considering the contribution of the open  $3d$  shell with the Penn model,<sup>2</sup> obtaining the new parameters  $f_i^{DT}$ . The calculated coefficients  $f_i^{DT}$  show practically the same values of  $f_i^{XPS}$ , with the exception of  $NiCl_2$  where  $f_i^{DT} = 0.80$ .

Crystals of  $NiCl_2$  and  $NiBr_2$  have been grown from the vapor phase by the dynamical transport method. Direct chlorination and bromination of nickel powder (Merck, 99.999% pure) at 700 and 600 °C gives gold-yellow and yellow-brown crystalline flakes. Growth of black, shiny crystals of  $NiI_2$  was carried out by chemical transport from elements in a sealed ampoule with a thermal gradient of about 750 °C. Because crystals are slightly hygroscopic, samples were cleaved in a glove box filled with dry nitrogen and directly attached to the spectrometers. Nickel halides occur as strongly bonded two-dimensional  $X-M-X$  layers with a weak interlayer coupling: within the  $X-M-X$  sandwich each metal atom is surrounded by six nearest neighbor halogen atoms and the coordination of halogen ions around the Ni atom is octahedral. The crystal structure is of  $Cd(OH)_2$  type in  $NiI_2$  and  $CdCl_2$  type in  $NiCl_2$  and  $NiBr_2$ .

Ultraviolet radiation from the synchrotron of the University of Paris was used as a continuum light source. The monochromator bandwidth was better than 6 Å. In the experiment we have investigated the optical reflectance of crystal planes perpendicular to the  $c$  axis. Reflectance measurements were taken at near normal incidence ( $\leq 20^\circ$ ) by means of EMI 9256S and Hamamatsu R268 photomultipliers, provided with a sodium salicylate phosphor. Photoemission measurements were performed with a XPS spectrometer ESCALAB MKII manufactured by the vacuum generators,

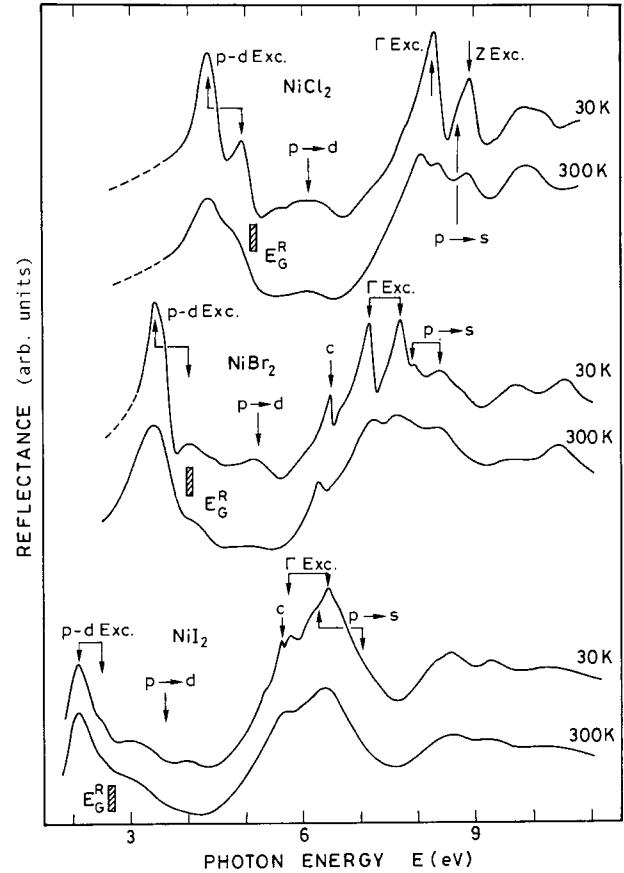


FIG. 1. Synchrotron reflectance spectra of Ni halides measured in the energy range of exciton and charge transfer transitions ( $p \rightarrow d$ ) up to the region of the fundamental absorption threshold ( $p \rightarrow s$ ). Assignments for  $\Gamma$  and Z excitons have been made by considering the band structure calculation made by Antoci and Mihich (Ref. 4). The estimated optical energy gap  $E_G^R$  indicated by vertical bars.

equipped with a monochromatized  $AlK_{\alpha 1,2}$  (1486.6 eV) radiation. VB-UPS spectra were obtained in an ultrahigh vacuum system ( $10^{-10}$  mbar) with a hemispherical energy analyzer and a He discharge lamp (21.2 eV). Photoelectrons were analyzed along the normal of the sample with an energy resolution of about 0.7 and 0.3 eV in XPS and UPS experiments, respectively. Crystalline  $NiBr_2$  and  $NiI_2$  samples were cleaved *in situ* and no significant charging effects were experienced during the photoemission measurements.

Figure 1 reports vacuum ultraviolet reflectance spectra of Ni halides, where details of exciton, charge transfer ( $p-d$ ) and interband ( $p-s$ ) transitions are shown. We see that that a main group of peaks ( $p-d$  excitons), observed in the low-energy region, is separated from interband ( $p-s$ ) transitions by charge transfer structures ( $p-d$ ), occurring around 3–4 eV in  $NiI_2$ , 4–6 eV in  $NiBr_2$  and 5–7 eV in  $NiCl_2$ , respectively. The optical gaps  $E_G^R$  of  $NiX_2$  obtained from reflectance spectra are indicated. These values are estimated by considering that  $E_G^R$  should occur at energies between those of  $p-d$  excitons and those of  $p-d$  charge transfer transitions. We have found that the values of  $E_G^R$  are in general agreement with the conduction band gaps  $E_G^{Ph}$  determined by

TABLE I. Summary of electronic and chemical parameters for nickel halides. The parameter  $f_i$  is the Phillips ionicity coefficient of the chemical bond. The energy gap ( $E_G^R$ ) is evaluated from reflection spectra and the photoconductivity gaps ( $E_G^{ph}$ ) are taken from Ref. 9 (Ronda *et al.*, 1987).  $\Delta^{VB}$  is the CT parameter  $\Delta$  estimated from reflectance and VB-XPS spectroscopy. The cluster model parameters  $\Delta^{c-XPS}$  and the ground-state counts ( $\langle n_{d8} \rangle, \langle n_{d9} \rangle$ ) are determined from  $2p$ -XPS spectra using the impurity approximation from Zaanen *et al.* (Ref. 5). All energies are in eV.

$MX_2$	$E_G^R$	$E_G^{ph}$	$\Delta^{VB}$	$\Delta^{c-XPS}$	$f_i$	$\langle n_{d8} \rangle$	$\langle n_{d9} \rangle$
NiCl <sub>2</sub>	4.6	4.7	6.0 <sup>a</sup>	3.6	0.78–0.80 <sup>b</sup>	0.71	0.23
NiBr <sub>2</sub>	3.8	3.5	5.2–5.5	2.6	0.75	0.61	0.32
NiI <sub>2</sub>	2.7	1.8	~3.5	1.5	0.72	0.47	0.44
NiO	4.0 <sup>c</sup> –4.3		7.0 <sup>a</sup>	4.6		0.73	0.21

<sup>a</sup>Values of the  $\Delta^{VB-XPS}$  parameter estimated from the photoemission valence band spectra reported by Hufner (Ref. 13).

<sup>b</sup>The coefficient  $f_i^{DT}=0.80$  has been calculated by considering the contribution of the open  $3d$  shell with the Penn model (Ref. 2).

<sup>c</sup>Optical gap due to  $p$ - $d$  transitions according Hufner-Riesterer (Ref. 14).

Ronda *et al.*<sup>9</sup> with photoconductivity measurements. However, this is true for NiCl<sub>2</sub> and NiBr<sub>2</sub>, while there is a 0.9 eV difference in the gap value of NiI<sub>2</sub> which cannot be reduced by the sight of the optical spectra. For this reason, in the case of NiI<sub>2</sub>, we have considered as a safe value of the band (conductivity) gap the value indicated by the  $E_G^{ph}$  parameter (1.8 eV). Reflectance spectra have been instrumental for evaluating the  $f_i$  parameter for Ni halides with the PVV theory. Moreover, from the combined use of reflectance, VB-XPS or VB-UPS spectroscopy, we have also given an estimate of CM parameters ( $\Delta$ ,  $U$ , and  $T_{eff}$ ), which we have compared with the ZWS results in Table I.

Let us now discuss the VB-XPS spectrum of NiBr<sub>2</sub> shown in Fig. 2. The spectral features extending from 7.5 to 4 eV binding energy are mainly due to bromine  $4p$  states. Peak A, earlier interpreted as due to Ni  $3d^7$  states, is assigned to the  $3d^8L^{-1}$  configuration (where  $L^{-1}$  stands for ligand hole states). Since the conduction gap  $E_G^{ph}$ , which is predominantly due to  $3d^8 + 3d^8 \rightarrow 3d^8L^{-1} + 3d^9$  intracluster transitions, is 3.5 eV (the optical gap  $E_G^R \cong 3.8$  eV), we can predict that the first inverse photoemission peak  $3d^9$  will be located just above the Fermi level. By considering the ground state and final state hybridization shifts, a 5.2–5.5 eV value can be a reasonable estimate for the charge transfer parameter  $\Delta^{VB-XPS}$ . The position of the  $3d^9$  states is obtained by adding to the main photoemission peak A, the conduction gap value ( $E_G^{ph}=3.5$  eV). This means that the gap energy corresponds to a  $3d^8 + 3d^8 \rightarrow 3d^8L^{-1} + 3d^9$  transition, as implied for instance by Merlin.<sup>12</sup> However, XPS spectra measure final states, which in principle lack one electron with respect to the initial ground state, so that the system under investigation will try to *screen* the photohole, a process which originates the formation of *satellites* in photoemission spectra. In this way, the peak B can be assigned to a  $3d^7$  satellite structure in agreement with the attributions proposed in VB-XPS spectra of NiO and NiCl<sub>2</sub> compounds.<sup>13,14</sup> The approximately 8.0 eV

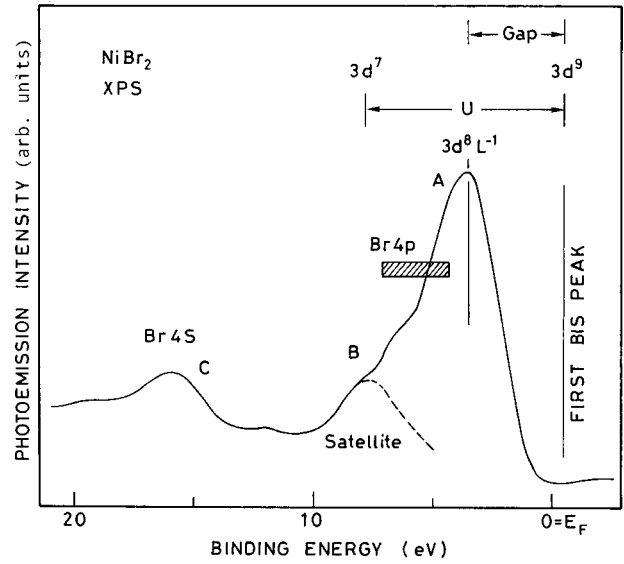


FIG. 2. VB-XPS spectrum of NiBr<sub>2</sub> compounds. The position of  $3d^9$  states is obtained by adding to the main photoemission peak the gap energy, as determined by ultraviolet reflectance spectroscopy or photoconductivity measurements by Ronda *et al.* (Ref. 9).

of the  $U$  parameter in NiBr<sub>2</sub> scales well with the values observed in NiO and in NiCl<sub>2</sub>, which are about 13 and 9.5 eV, respectively. This is an oversimplification, however, because the energy levels in NiO and NiX<sub>2</sub> are hybridized. This hybridization tends to increase the energy splittings and if one makes a proper correction for hybridization a limit of  $6.0 \text{ eV} \leq U_{eff} \leq 9.0 \text{ eV}$  is obtained.<sup>15</sup> The separation between the  $3d^7$  and  $3d^9$  configurations reflects the size of the Coulomb repulsion parameter  $U$ , which gives the correlation energy  $U$  plus a hybridization shift. Since the exact magnitude of the energy shift is not known the correlation energy in NiX<sub>2</sub> can only be given approximately. In the case of NiBr<sub>2</sub> and other halides we believe that 6–8 eV is a fair estimate for  $U$ .<sup>16</sup> For instance, according to Sawatsky and Allen,<sup>17</sup> the experimental charge transfer gap in NiO is 4.3 eV and the Ni  $dd$  Coulomb repulsion parameter  $U$  is between 7 and 8 eV, leading to a large correlation gap in the Ni $3d$  band. The relative magnitude of  $U$  and  $\Delta$  parameters and the fact that  $\Delta$  is related to the electronegativity of halide ions has made to classify nickel compounds as *charge transfer insulators*, with a conductivity band gap of  $pd$  type.<sup>6,7,13</sup>

The same interpretation can be suggested for the VB-UPS spectrum of NiI<sub>2</sub> in Fig. 3. The large  $B$  peak observed between 2 and 4.5 eV binding energy is mainly due to iodine  $5p$  states, while the peak A is assigned to  $3d^8L^{-1}$  final states. In NiI<sub>2</sub> the  $3d^7$  hole state could occur as a weak shoulder over the peak C at binding energy at about 6 eV. The intensity of this satellite is expected to be low at 21.22 eV, which explains why we do not observe it clearly, although the weak hump at 6 eV could be a candidate. If this is the case, since the optical gap is about 2 eV, we may estimate the order of magnitude of  $U$  around 6–7 eV, and that of the CT parameter  $\Delta^{VB}$  around 3.5 eV. In VB-UPS measurements, however, we think that the estimate of  $U$  and  $\Delta^{VB}$  parameters can only be given as an order of magnitude, ow-



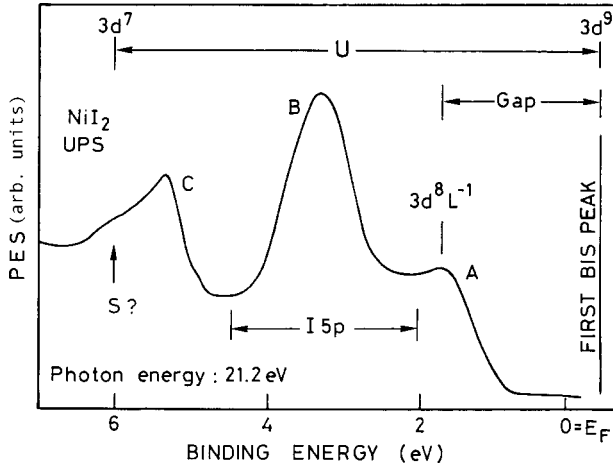


FIG. 3. VB-UPS spectrum of crystalline  $\text{NiI}_2$  measured with a He-I (21.2 eV) discharge lamp. The order of magnitude of the  $U$  parameter and conduction gap energy is shown.

ing to matrix element effects, even if the  $U$  and  $\Delta^{\text{VB}}$  values scale well with those estimated for Ni compounds. In summary, we can say that the primary consequence of the presence of electron  $dd$  correlation are the large charge transport gaps in TMC's, as suggested by Mott-Hubbard, where a strong Coulomb interaction  $U$  is a necessary, but *not* sufficient, condition to obtain a finite gap. In fact, it turns out that for *large* values of  $U$  the presence and magnitude of band gaps is basically determined by the parameter  $\Delta$ , the energy cost to transfer an electron from ligands to metal ions. Thus, it is the energy separation between the ligand  $p$  band and the metal  $3d^{n+1}$  state that governs the electronic gap in  $\text{NiX}_2$  compounds as in late TMC's. It is interesting to note that  $\text{NiI}_2$  and the other Ni halides were still referred as Mott insulators until 1990.<sup>10</sup>

Now, let us discuss the satellites occurring in valence band spectra of  $\text{NiBr}_2$  and  $\text{NiI}_2$  within the configuration interaction (CI) cluster model scheme.<sup>18–20</sup> The final state peak position for a BIS experiment in  $\text{NiBr}_2$  (and other halides) has been extrapolated by considering the ultraviolet reflectance spectra of Fig. 1, while for  $\text{NiO}$  compounds we have considered the BIS and UPS spectra reported by Hufner *et al.*<sup>14</sup> and Sawatsky and Allen.<sup>17</sup> In general, these spectra show a mixed  $3d^n L^{-1}$  density of states peak around 3–4 eV below the Fermi energy  $E_F$ , followed by the ligand  $p$ -derived density of states peaks at larger binding energies (5–7 eV). A satellite structure ( $S$ ) is observed around 8–9 eV binding energy and separated from the  $\text{Ni}3d$  main line by  $E_S \cong 5.1$  eV in  $\text{NiCl}_2$ , 4.2 eV in  $\text{NiBr}_2$ , 4 eV in  $\text{NiI}_2$ , and 7.1 eV in  $\text{NiO}$ , respectively. The main peak-satellite splitting  $E_S$  in VB-XPS spectra is given by

$$E_S = [(\Delta - U)^2 + 4(T_{\text{eff}})^2]^{1/2}, \quad (5)$$

when the Hamiltonian is restricted to  $d^n$  and  $d^{n+1}L^1$  configurations.<sup>18,19</sup>

In early TMC's (Ti, V, Cr) the hybridization parameter  $T_{\text{eff}}$  may become considerably large and, in the limit  $|\Delta - U| \ll 2T_{\text{eff}}$ , the  $E_S$  values can be approximated by  $2T_{\text{eff}}$ . In many early TMC's the parameters  $\Delta$ ,  $U$ , and  $T_{\text{eff}}$  have com-

parable values and the effect of covalency becomes important in the properties of the ground state and first ionization state, suggesting that the hole introduced in the ionization state is spread over the neighboring ligand sites.<sup>19–22</sup> On the other hand, for values typical of late TMO's ( $T_{\text{eff}} \cong 2\text{--}4$  eV), satellite structures appear at 6–9 eV from the main peak and the  $E_S$  splitting will be sensitive to changes in both  $\Delta$  and  $U$  parameters. For instance, in  $\text{NiX}_2$  and  $\text{NiO}$  compounds we have estimated the effective hybridization  $T_{\text{eff}}$  between 1.6 eV ( $\text{NiI}_2$ ) and 3.5 eV ( $\text{NiO}$ ). The main  $\text{Ni}3d$  emission is in fact *screened* by a ligand electron transferred into the  $3d^8 L^{-1}$  final state configuration, while the satellite is assigned to the  $3d^7$  configuration. Trends for the  $pd\sigma$  integrals and hybridization parameters  $T_{\text{eff}}$  are primarily governed by intra-atomic distances, and these are largely determined by the ionic radii of the metal and ligand ions  $d_{MX}$ . As the distance decreases, the larger overlap of the  $3d$  orbitals with ligand  $p$  bands increases the value of  $T_{\text{eff}}$ . Values of the nearest neighbor distance<sup>2</sup>  $d_{MX}$  are 3.51 Å in  $\text{NiCl}_2$ , 3.72 Å in  $\text{NiBr}_2$ , 3.94 Å in  $\text{NiI}_2$ , giving the following values for the hybridization parameters  $T_{\text{eff}} = 2.5$  eV in  $\text{NiCl}_2$ , 2.1 eV in  $\text{NiBr}_2$ , and 1.6 eV in  $\text{NiI}_2$ . These values scale well with our estimated value of  $T_{\text{eff}} = 3.5$  eV in  $\text{NiO}$  and the 3.8 eV value reported in literature.<sup>20</sup> Late TMC's are in general classified as CT insulators ( $T_{\text{eff}} \cong T < \Delta < U$ ):  $\text{NiO}$ ,  $\text{CoO}$ , and  $\text{NiX}_2$  are typical examples. In Table I we have given a summary of electronic, chemical and CM parameters together with ground-state occupation numbers.<sup>5</sup>

The analysis of satellites observed in VB-XPS spectra can of course be replicated for  $c$ -XPS spectra, where similar trends for the parameters are in general found, although the calculated values may be in general somewhat different. The basic phenomenon measured with this technique is the response of the valence-electron system to the sudden creation of a *core-hole* (sudden approximation). If the interaction between the core-hole and the *correlated* valence electrons is sufficiently strong (high  $Q$  values), *satellites* accompanying the main line structures are observed in photoemission spectra. This opens the possibility for using  $c$ -XPS as a probe for the study of the electronic structure in these materials. A simple picture for the analysis of  $c$ -XPS spectra is offered by the Kotani-Toyozawa model,<sup>23</sup> where a CM approach with the configuration interaction (CI) is in general used. However, the analysis of photoemission spectra is difficult and requires a fair understanding of the *many-body problem* in these systems.

Now we would like to compare the values obtained in the *impurity approximation* with the ionicity parameters of the Phillips–Van Vechten theory. The ionicity coefficients  $f_i$  (which also scale well with the dielectric constants<sup>2</sup>) have values around 0.78, 0.75, and 0.72 for  $\text{NiCl}_2$ ,  $\text{NiBr}_2$ , and  $\text{NiI}_2$ , respectively. However, in Table I, we have a value  $f_i = 0.72$  in  $\text{NiI}_2$ , instead of about 0.50, as implied by the  $d$ -electron count number. Although we have found a general agreement for the chemical bond parameters, we have however noted a large difference for the band gap magnitude. Our results indicate that the ionicity coefficients in  $\text{NiCl}_2$  and  $\text{NiBr}_2$  compounds are in good correspondence with  $d$ -electron count numbers, and that  $\text{NiI}_2$  is the more covalent

of nickel compounds. Yet, our figures indicate a lower degree of covalency than expected from the values of the  $d$ -electron count parameters.

We have finally considered the photoconductivity data of nickel halides, which give the experimental values of the conductivity energy gap, that is, 4.7 eV (NiCl<sub>2</sub>), 3.5 eV (NiBr<sub>2</sub>), and 1.8 eV (NiI<sub>2</sub>).<sup>9</sup> These values are found in good agreement with band gaps observed in ultraviolet reflectance reported in Table I. Energy gaps have been assigned to charge-transfer transitions from anion  $p$  bands to transition-metal  $3d$  states with the electrical conduction due to holes in the anion  $p$  band. The holes are light, mobile particles in the broad anion valence band ( $W$ ) and the electrons are heavy particles of lower mobility as they occupy states of the narrow ( $w$ ) metal  $d$  bands. In this way, the gap energy is related to the electronegativity of the anions and the magnitude of the band gaps is mainly determined by the charge transfer energy  $\Delta$  and not by the energy differences between states of the type  $d_i^n d_j^n$  and  $d_i^{n-1} d_j^{n+1}$ . We know that in the ZSA model the conduction-band gap in TMC's is expected to be either of Mott-Hubbard ( $E_{\text{gap}} \propto U$ ) or charge-transfer ( $E_{\text{gap}} \propto \Delta - \frac{1}{2}W$ ) nature. However, we see in Table I that the value of the parameter  $\Delta$ , as determined from  $c$ -XPS of NiX<sub>2</sub>, presents a problem. In fact, the photoconductivity ( $E_G^{Ph}$ ) or optical ( $E_G^R$ ) energy gaps show the same trend as the energy parameter  $\Delta$  found in  $2p$ -XPS spectra, but things work less well if one considers the magnitude of the band gap, as a

considerable discrepancy is found between the calculated values of the energy gap  $\Delta - W/2$  and the observed conductivity and optical energy gaps. In fact, using the core XPS values for  $\Delta$ , one finds energy band gaps 2–3 eV smaller than experimental gaps.

In conclusion, we have shown how recent results obtained with reflectance, ultraviolet, and x-ray photoemission spectroscopy, coupled to a cluster model analysis of valence band photoemission spectra, allow to get an estimate of characteristic parameters of ZSA theory for nickel compounds. We have in particular recalculated from experiment the values of  $\Delta$ ,  $U$ , and  $T_{\text{eff}}$ , and we have found that  $U > \Delta$ , i.e., that the correlation energy is larger than both the charge transfer energy and dispersional  $3d$  bandwidth [ $w \leq 0.5$  eV (Refs. 6 and 24)]. Moreover, their effective hybridization energy  $T_{\text{eff}}$  varies from about 1.6 to 3.8 eV and is lower than the  $U$  and  $\Delta$  parameters. All parameters have shown a good agreement with literature results. We have further related the fraction of ionic character of chemical bond to covalency parameters obtained from Ni $2p$ -XPS spectra by Sawatsky and co-workers.<sup>5</sup> It turns out that the quantity which is strongly altered in going through the nephelauxetic series is the charge-transfer energy. This is also in qualitative agreement with the behavior of the optical gap in these materials. To our knowledge, no other attempt has been previously undertaken to correlate the ground-state  $d$ -electron counts with experimental parameters related to the degree of ionicity of the chemical bond.

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