



CORRELATION EFFECTS, CHARGE-TRANSFER ENERGIES AND COVALENCY IN
NICKEL COMPOUNDS AS DETERMINED BY X-RAY ABSORPTION SPECTROSCOPY

G. van der Laan, J. Zaanen and G.A. Sawatzky

Institute for Physical Chemistry, Materials Science Center
University of Groningen, Nijenborgh 16, 9747 AG GRONINGEN, The Netherlands

R. Karnatak and J.-M. Esteve

Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE)
Universite Paris-Sud, Batiment 209c, 91405 Orsay CEDEX, France

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High resolution $L_{2,3}$ near edge absorption spectra of Ni compounds are compared to an impurity model calculation including the d-d correlation effects. Covalent mixing in the final state gives a change in the observed structure which can be used as an analytical tool to study the ground state properties. From the analysis we obtain the d-d Coulomb interactions, the charge transfer energy and the covalency in the ground state.

Recent developments in the theory and understanding of core and valence electron spectroscopies in highly correlated materials provide the basis for obtaining surprisingly detailed information concerning the ground state electronic structure of solids.^{1,2} Most of the effort however has been concentrated on rare earth systems and on core and valence photoelectron spectroscopies.³ Recently we have shown⁴ that x-ray absorption spectroscopy (XAS) has several advantages over other core spectroscopies for two reasons. 1) A suitable core state can be selected such that the electron is excited into a screening orbital in which case the perturbation on the ground state electrons is that of a screened core hole as opposed to XPS in which the perturbation is that of the unscreened core hole. 2) The dipole selection rules allow only a relatively small number of final state multiplets to be accessible as opposed to XPS in which generally the whole manifold of multiplets is accessible resulting in rather broad structureless lines. The relative intensities of the multiplets reached are then a signature for the local symmetry of the atom in the ground state of the solid.

In this Communication we present new high resolution XAS data for divalent Ni compounds. Using an impurity like many body theory¹ we show that the spectra can be understood in detail including the observed multiplet and satellite structure. Simulation of the spectra provides information concerning the charge transfer energies, d-d Coulomb interaction and the degree of covalency in the ground state.

Ni $L_{2,3}$ x-ray absorption spectra were obtained using the synchrotron radiation emitted by the Anneau de Collisions d'Orsay (ACO), and a double crystal (beryl) monochromator resulting in an energy resolution of 0.3 eV.⁵ The spectra were recorded by the electron yield method. Samples of NiF_2 , NiO , $NiCl_2$, $NiBr_2$ and NiI_2 in

powder form and sublimed on Al in high vacuum were studied.

The $L_{2,3}$ spectra obtained are shown in Fig. 1 exhibiting a much higher resolution than those reported earlier.⁶ Qualitatively the spectra show two narrow peaks close to the $2p_{3/2}$ and $2p_{1/2}$ threshold due to multiplet structure. This is followed by a broad satellite structure clearly visible in the L_3 region and a step like continuum contribution between the L_2 and L_3 edges. The step like contribution is due to transitions to a $4s$ like band which is outside the scope of the present study.⁷ The near threshold multiplet structure for the most ionic compounds has the shape and the relative intensities corresponding to transitions from a $3d$ like $^3A_{2g}$ (e_g) ground state to $2p3d$ like final states⁸ as discussed by Yamaguchi et al.⁸ Of most interest here are the decrease in the multiplet splitting and changes in the broad satellite structure with decreasing electronegativity of the anion. We now proceed to show that this is a result of configuration interaction and can be used to obtain parameters for determining the covalent mixing in the ground state.

To explain the spectra we use an impurity model to calculate the valence band structure and band gaps in the presence of strong correlations. The basic assumption is that the translational symmetry of the transition metal ions can be neglected because the dispersal width of the d bands is only about 0.5 eV.⁹ In this case the Ni ions can be treated as impurities hybridizing with an anion p valence band. For the anion p band we take into account the translational symmetry since its band width is known to be about 3-4 eV.

It is well known that in a purely ionic configuration and in O_h symmetry the crystal field together with the d-d Coulomb interactions cause the ground state of a $3d^2$ ion to be $^3A_{2g}$ (e_g^2).¹⁰ This state can mix with states d_{k^2g}

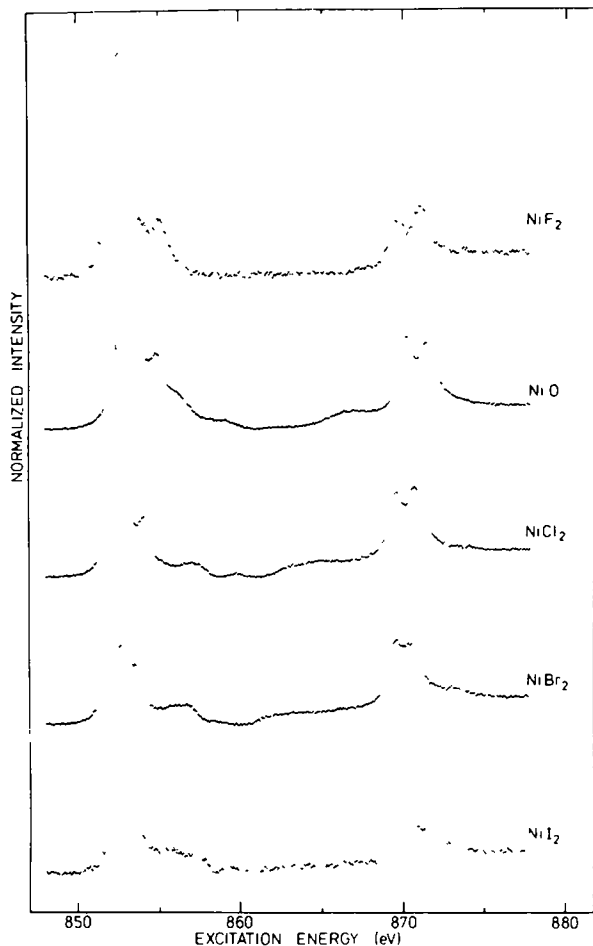


Figure 1. The L_2^3 absorption spectra of Ni compounds. The $L_3(L_2)$ edge is found at about 852 (870) eV.

of A_2 symmetry which in turn can mix with states $d_{10}^9 k k'$, where k denotes a ligand hole with wave vector k . The ground state, including the covalent mixing, is then the lowest energy two-hole state of A_2 symmetry whose energy and wave function can easily be obtained using Greens function techniques. The basic parameters involved are shown in Fig. 2a with Δ equal to the charge transfer energy, U the d-d Coulomb interaction, and W the width of the semielliptical ligand band. Not shown in Fig. 2 are the transfer integrals (T) mixing the various states. These, being one-electron matrix elements, mix only d with $d k$ and $d k$ with $d_{10}^9 k k'$ and are taken to be k independent. The final states are of the form $c d^9$ and $c d_{10}^9 k$, where c denotes a core hole. In addition to the interactions in the initial states we must take into account 1) The spin-orbit coupling of the 2p hole which splits the total spectrum into an L_2 and L_3 region, 2) The average core hole-d electron interaction (Q) which modifies the $c d^9 - c d_{10}^9 k$ splitting to $\Delta' = \Delta + U - Q$ and since Q is generally larger than U , $\Delta' < \Delta$, and 3) The higher multipole core

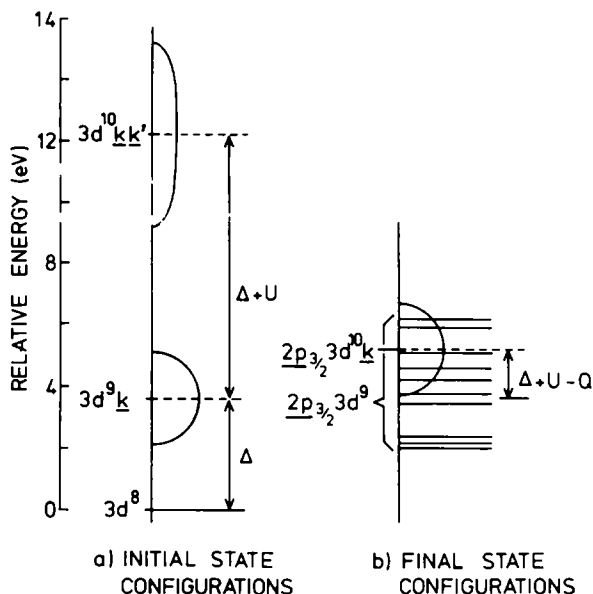


Figure 2. Schematic representation of the energy of the different configurations for the initial state (a) and final state (b) shifted by an arbitrary energy in the L_3 absorption for the case of $NiCl_2$. Configurations with a ligand hole (k) have a band width W . The $2p_{3/2} 3d^9$ configuration is multiplet split. Not drawn is the mixing between the configurations by a transfer integral T .

cause a further splitting within the $2p_{3/2}$ and $2p_{1/2}$ states in the presence of a d hole. The various states considered for the calculation are shown schematically in Fig. 2b. Note that since $\Delta' < \Delta$ the mixing of the $c d^9$ and $c d_{10}^9 k$ states will be larger than that for the d^9 and $d^9 k$ states in the initial states. For a purely ionic compound (i.e. Δ and $\Delta' \gg T$) the final states are $2p_{3/2} 3d^9$ which span the irreducible representations A_2 , two E_2 , two T_1 and three T_2 for the $2p_{1/2}$ parent and two A_2 , three E_1 , five T_1 and five T_2 for the $2p_{3/2}$ parent. The splittings of these states are obtained using atomic Coulomb and exchange integrals and a crystal field splitting $10 Dq = 1.5 \text{ eV}$. This calculation should correspond, after including the optical selection rules, closely to the spectrum of the highly ionic compound NiF_2 as demonstrated in Fig. 3 and agrees well with the calculation of Yamaguchi.

For the more covalent compounds both the initial and final states are no longer purely ionic and contain substantial $d_{10}^9 k$ and $c d_{10}^9 k$ character, respectively. For the final states each of the atomic $c d^9$ states couples with its own $c d_{10}^9 k$ continuum via the transfer integral T . This final state covalent mixing causes a change in the multiplet splittings and together with the initial state covalent mixing causes the spectral weight to be distributed over a band, predominantly $c d^9$, final state and a strongly distorted predominantly $c d_{10}^9 k$ continuum. To calculate these spectral shapes in addition to the calculated atomic

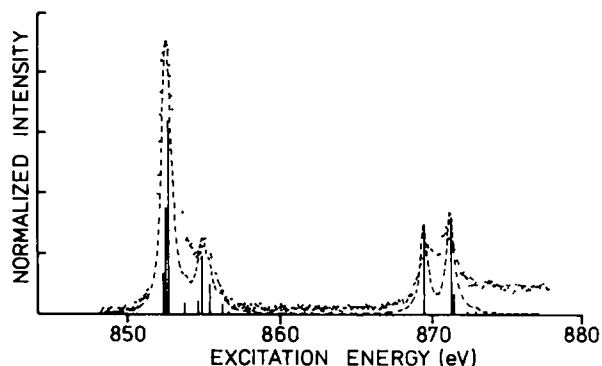


Figure 3. Calculated multiplet structure for a dipole transition $\text{Ni } 3d^8 \rightarrow 2p^5 3d^9$ ($G_1 = 5.79$, $F_2 = 7.72$, $G_3 = 3.29$ and $10Dq = 1.5$ eV), the dashed line is a convolution by a 0.6 eV FWHM Lorentzian. For comparison the experimental $L_{2,3}$ spectrum of NiF_2 is shown (dots).

interactions, four additional parameters T , Δ , Q and U . As shown in an analysis of XPS data of Cu and Ni_2 dihalides T , Q and U are nearly constant. This leaves us with only one strongly compound dependent parameter Δ . The calculated spectra for NiCl_2 and NiI_2 for the parameters listed in Table I are shown in Fig. 4. The spectra are extremely well described by the theory aside from the not included $4s$ continuum edge. We see the decrease in multiplet splitting with decreasing anion electronegativity because of covalent mixing in

	Δ (eV)	$3d^8$	$3d^9$	$3d^{10}$
NiI_2	1.5	0.47	0.44	0.09
NiBr_2	2.6	0.61	0.32	0.07
NiCl_2	3.6	0.71	0.23	0.06
NiO	4.6	0.73	0.21	0.06
NiF_2	7	- 1.0	- 0	- 0

Table I. The values for Δ and the $3d^8$, $3d^9$ and $3d^{10}$ characters in the ground state as obtained from a best fit to an impurity model. Further constant for all compounds: $Q = 7$, $U = 5$ (4,5 in NiI_2), $T = 1.5$ (1,75 in NiO), $W = 3$, $10Dq = 1.5$, $G_1 = 5.79$, $F_2 = 7.72$, $G_3 = 3.29$ eV, the effective spin-orbit splitting is 17 eV, the intrinsic line width is a 0.3 eV Lorentzian, the experimental resolution is a $\delta = 0.3$ eV Gaussian.

the final state. We also obtain the higher energy rather broad low intensity shoulder which is primarily due to accessible $c d_{10} k$ states resulting from covalent mixing in both the initial and final states. Also we note that the

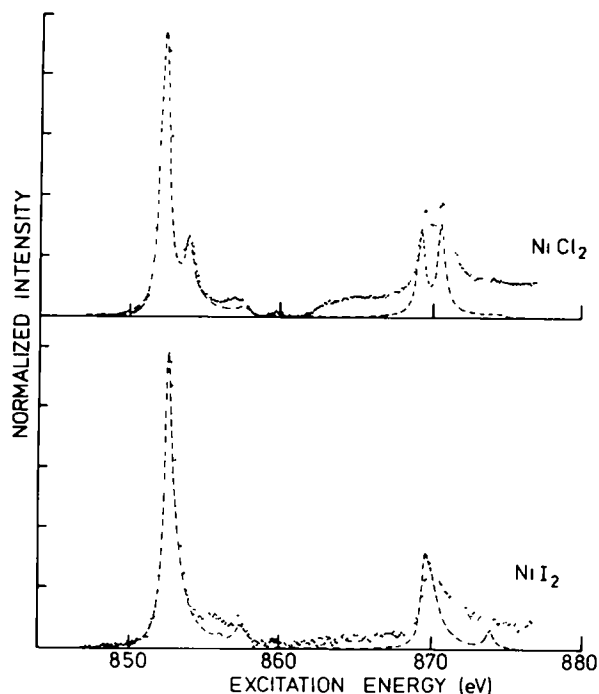


Figure 4. Impurity model calculation (dashed line) compared to the experimental $L_{2,3}$ x-ray absorption spectra of NiCl_2 and NiI_2 (dots). The values of the parameters are given in Table I and its caption.

values of Δ found follow nicely the expected electronegativity trend.

The observed changes in multiplet splitting could also be simulated by an atomic calculation with compound dependent Slater integrals. Doing this however one misses the physical reason for the compound dependence and one cannot explain the shoulder in the spectra. Also one can easily be misled to conclude that the compound dependent reduction factors are a measure of the covalency in the initial state which as we argued above is considerably less than that in the final state.

The initial state covalency is related to the amount of d_8 , $d_9 k$ and $d_{10} k k'$ character in the ground states. The values obtained from the present analysis are given in Table I and again show the expected trend based on electronegativity arguments.

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References

1. O. Gunnarsson and K. Schonhammer, Phys. Rev. B 28, 4315 (1983).
2. A. Fujimori, Phys. Rev. B 28, 4489 (1983); A. Fujimori and F. Minami, Phys. Rev. B 30, 957 (1984).
3. See e.g. J.C. Fuggle, M. Campagna, Z. Zolnieriek, R. Lasser and A. Platau, Phys. Rev. Lett. 45, 1597 (1980); E. Wuilloud, B. Delly, W.D. Schneider and Y. Baer, Phys. Rev. Lett. 53, 202 (1984); B.W. Veal and A.P. Paulikas, Phys. Rev. B 31, 5399 (1985); G. van der Laan, Solid State Commun. 42, 165 (1982).
4. B.T. Thole, R.D. Cowan, G.A. Sawatzky, J. Fink and J.C. Fuggle, Phys. Rev. B 31, 6856 (1985).
5. M. Lemonnier, O. Collet, C. Depautex, J.-M. Esteva and D. Raoux, Nucl. Instrum. Methods 152, 109 (1978).
6. C. Bonnelle and C.K. Jørgensen, J. Chimie Physique 1964, 826 (1964); C. Bonnelle, E. Belin and C. Sinimaud, Jap. J. Appl. Phys. 17, 125 (1978).
7. A detailed description of this will be given in a subsequent paper, G. van der Laan, J. Zaanen, G.A. Sawatzky, R. Karnatak and J.-M. Esteva, to be published.
8. T. Yamaguchi, S. Shibuya, S. Suga and S. Shin, J. Phys. C 15, 2641 (1982).
9. S. Antoci and L. Mihich, Phys. Rev. B 18, 5768 (1978); Phys. Rev. B 21, 3383 (1980); K. Terakura, A.R. Williams, T. Oguchi and J. Kubler, Phys. Rev. Lett. 52, 1830 (1984).
10. C.J. Ballhausen, "Introduction to ligand field theory", McGraw-Hill, New York (1962).
11. The 10 Dq value is that appropriate for the final state and includes the contribution from covalency. The ground state 10 Dq value is estimated to be about 1 eV (see Ref. 10).
12. G. van der Laan, C. Westra, C. Haas and G.A. Sawatzky, Phys. Rev. B 23, 4369 (1981).