$L_{2,3}$ x-ray absorption spectroscopy and multiplet calculations for KMF_3 and K_2NaMF_6 (M=Ni, Cu)

C. De Nadaï,* A. Demourgues, and J. Grannec
ICMCB, UPR 9048, 87 Avenue du Dr A. Schweitzer, 33608 Pessac Cedex, France

F. M. F. de Groot
Department of Inorganic Chemistry and Catalysis, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

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The electronic structures of nickel and copper have been studied for KMF_3 and K_2NaMF_6 compounds by x-ray absorption spectroscopy at the Ni and Cu $L_{2,3}$ edges in order to characterize the M-F chemical bond. The spectral features have been interpreted based on the mixing of two ground-state configurations $|3d^n\rangle + |3d^{n+1}\rangle\underline{L}$. Multiplet calculations were used to simulate each spectrum in order to quantify the charge transfer from fluorine to the transition metal yielding a 40% ground-state contribution of the $3d^8$ configuration for K_2NaCuF_6 and 65% of the $3d^7$ configuration for K_2NaNiF_6.

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I. INTRODUCTION

The iono-covalent character of the chemical bond is often decisive in determining the electronic properties of a solid. Coulomb interaction energies, polarization effects, the stabilization of energy levels due to the crystal field, and orbital overlap determining the electron/hole (de)localization are physical parameters that contribute to the bond characteristics.

Numerous studies concerning the electronic structure and bonding of high oxidation states in nickel and copper oxides have already been reported by means of x-ray absorption spectroscopy (XAS).[1–8] Considering its high electronegativity, fluorine generates bonds with a rather ionic character. In addition, because of a marked oxidizing power, fluorine allows the stabilization of high oxidation states notably in presence of transition metals. Thus, fluoride compounds appear as a reference for the chemical bond study.

The characterization of the electronic states of nickel and copper fluorides has been investigated by XAS, which is selective in both the probed element and its symmetry. We report here the continuation of a previous XAS study[9] on a series of Ni and Cu fluorides, extended by multiplet calculations. The evolution of the chemical bond has been analyzed as a function of the charge of the transition cation: fluorides where the cation adopts a usual oxidation state (Ni^{2+}, Cu^{2+}) have been chosen as references in order to interpret the observed evolutions when the cation is stabilized in a higher oxidation state (Ni^{3+}, Cu^{3+}).

Multiplet calculations allowed the quantification of the charge transfer occurring in the M-F bond when the metal adopts a high oxidation state and to specify the degree of covalence obtained in fluorides in comparison with oxides. With this aim, the multiplet approach has been used to take into account the screening of ligand electrons towards the perturbation as seen by the $3d$ electrons of the metal. It considers systematically two configurations in the final state: $|f_1\rangle = \alpha_f|\underline{c}3d^n e_k\rangle + \beta_f|\underline{c}3d^{n+1}\underline{L}e_k\rangle$ and $|f_2\rangle = -\beta_f|\underline{c}3d^n e_k\rangle + \alpha_f|\underline{c}3d^{n+1}\underline{L}e_k\rangle$ with $\alpha_f^2+\beta_f^2=1$, and a linear combination in the ground state, $\alpha_0|3d^n\rangle + \beta_0|3d^{n+1}\underline{L}\rangle$ with $\alpha_0^2+\beta_0^2=1$, where $\underline{L}$, e_k, and $\underline{c}$ represent the ligand hole, the ejected photoelectron, and the core hole, respectively. The charge-transfer multiplet model has been explained in detail in previous studies.[10–13] In this work we have chosen to limit the number of configurations to two, $\alpha|3d^n\rangle + \beta|3d^{n+1}\underline{L}\rangle$, because this limits the number of semiempirical parameters while the spectral shapes obtained are in good agreement with the experimental spectra. It has been recently reported that for trivalent and tetravalent metal ions, it is not accurate anymore to limit the calculation to two configurations.[14] In order to discuss this point in the particular case of Ni^{3+}, a comparison between a two-configuration calculation and a three-configuration calculation: $\alpha_0|3d^n\rangle + \beta_0|3d^{n+1}\underline{L}\rangle + \gamma_0|3d^{n+2}\underline{LL}'\rangle$ in which the value of Hubbard U_{dd} will play a role, is reported in Sec. III B. In the other cases, two configurations already generate a complete basis.

II. EXPERIMENT

A. Preparation of compounds

The starting materials were mixed under a dry argon atmosphere in a glove box because of oxygen and moisture sensitivity. The AMF_3 (A=Na, K, Rb and M=Ni, Cu) compounds were synthesized by solid-state reactions from stoichiometric mixtures of the binary fluorides. The reactions were carried out in sealed platinum tubes for 15 h in the temperature range 500–700 °C. All reactions were followed by temperature quenching. The A_3MF_6 and A_2NaMF_6 compounds were prepared from binary fluorides under F_2/N_2 gas mixture in the temperature range 400–500 °C for 12 h and followed by slow cooling to room temperature. Several annealings under the same conditions were necessary to obtain the appropriate phases.

The samples were characterized by their powder x-ray diffraction patterns (Philips PW 1050/70 diffractometer) us-

ing Cu $K\alpha$ radiation and a graphite monochromator. Information on the structural features can be found elsewhere.[9]

B. XAS experiments

The $L_{2,3}$ x-ray absorption near-edge structure (XANES) experiments were performed at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE) at Orsay. Spectra were obtained on beamline SA22 of Super ACO (0.8 GeV, 150 mA) using a double-crystal Be (1010) monochromator in total electron yield detection (energy resolution 0.35 eV at 900 eV). Before and during all experiments, the samples were not exposed to air in order to avoid any decomposition.

C. Charge-transfer multiplet theory

For the $3d$ transition metals, electronic repulsion (both in the $3d$ shell, and between $2p$ and $3d$ electrons) is important and has to be taken into account in the calculations. The charge-transfer multiplet calculations were based on the model developed by Theo Thole and co-workers using a package of programs including the atomic-multiplet program of Cowan,[15] the group-theory program of Butler,[16] and the charge-transfer program.[12] This model allows the determination of Coulomb interactions within the $3d$ shell and between the $2p$ and $3d$ shells, the spin-orbit coupling in both the shells and crystal field ($10Dq$ in O_h symmetry) applied on the $3d$ levels. When configuration interaction is considered, the charge-transfer energy (Δ) and the transfer integral (T) are used. The empirical relation $T(e_g) = -2T(t_{2g})$ is used for halides and oxides in octahedral symmetry.[17] The overall crystal field is described by both an ionic crystal-field term that represents the ion in an electrostatic potential and a term related to the degree of covalence. Note that the ionic crystal-field parameter ($10Dq$) obtained in this way will be lower than the total crystal field splitting since a part of the effect is included in configuration interaction.

III. RESULTS AND DISCUSSION

A. Copper fluorides

$L_{2,3}$ x-ray absorption spectra of divalent and trivalent copper fluorides are compared in Fig. 1. All spectra of divalent copper fluorides are similar showing two well-defined peaks of Lorentzian shape (labeled A) at 931.1 eV (L_3) and 951 eV (L_2) separated by the spin-orbit splitting of the $2p_{3/2}$ (L_3) and $2p_{1/2}$ (L_2) hole states. Considering that the ground state of Cu(II) is represented by a linear combination of $3d^9$ and $3d^{10}\underline{L}$ states ($\underline{L}$: ligand hole), the excited state can only be assigned to a single $2p^53d^{10}$ configuration as reported previously for divalent copper compounds such as CuO.[4,18]

Hence, the peaks labeled A (Fig. 1) that are also observed for trivalent copper fluorides are relative to a $2p^53d^{10}$ final state and indicate the presence of Cu(II) in our samples. In spite of the care to keep the samples in an inert atmosphere, a small amount of hydroxyfluorides or hydrates could be adsorbed at the surface. One should note that K-edge measurements which probe the bulk of these compounds revealed no trace of divalent copper.[9] Moreover, Cu(III) compounds are known for their instability under ultra-high vacuum.

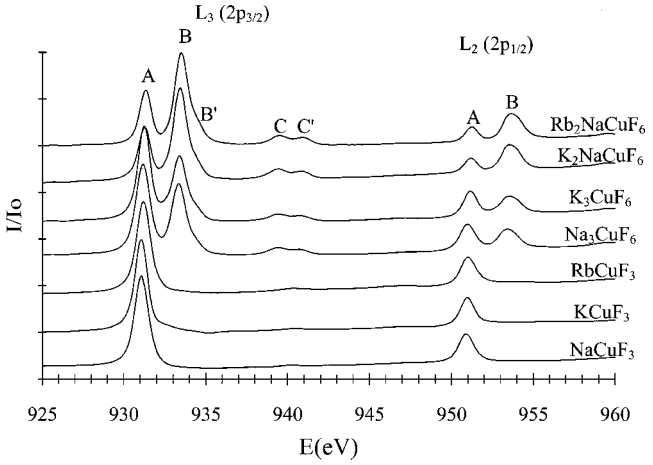

FIG. 1. XA spectra at the Cu $L_{2,3}$ edges for divalent and trivalent copper fluorides. Spectra were normalized by considering the main peak intensity as unity.

In the L_3 region, the main peak labeled B at 933.4 eV and the satellite peaks C and C' at 939.4 and 940.8 eV, respectively, have been attributed to trivalent copper by comparison with spectra reported for $NaCuO_2$.[4–6] The ground state of a nominally Cu^{3+} cation can be described as a mixing of configurations $3d^8$ and $3d^9\underline{L}$. As discussed before, we neglect the small contribution of the $3d^{10}\underline{L}^2$ configuration. In the excited state, the corresponding configurations are $2p^53d^9$ and $2p^53d^{10}\underline{L}$. The energy difference between these two last levels is equal to $\Delta + U_{dd} - U_{cd}$ where the parameters U_{cd}, U_{dd}, and Δ characterize the Coulomb interaction between the $2p$ core hole and the localized $3d$ valence electron, the Coulomb electronic repulsion between two electrons in the same $3d$ level, and the charge-transfer energy, respectively.[13,19] For the ground state, the energy difference between $3d^8$ and $3d^9\underline{L}$ configurations is equal to Δ. Due to the proximity of the $2p$ fluorine bands and the $3d$ copper bands, and the nonbonding character of the $\Pi^*\mathrm{F}(2p)$ upper band determined by band structure calculations,[20,21] Δ is expected to be negative for Cu(III). Thus, the ground state is dominated by $3d^9\underline{L}$ and the $2p^53d^{10}\underline{L}$ level is found at a lower energy than the $2p^53d^9$ level in the excited state. In this way, the B peak has been predominantly assigned to a $2p^53d^{10}\underline{L}$ excited state. Besides, the energy separation between $A(2p^53d^{10})$ and B peaks is equal to 2.1 eV. This corresponds to the ionization potential of the ligand $\varepsilon_L(3d^n\text{-}3d^n\underline{L})$ that can be found by comparing the energy position of electronic transitions determined by XAS and x-ray photoelectron spectroscopy (XPS) measurements. Finally, the shoulder identified on the right of B peak (labeled B') is due to multiplet effects; this will be discussed in the Sec. III B concerning divalent nickel fluoride. The (C,C') satellite doublet has been associated with the transitions to the $2p^53d^9$ excited state. The energy difference between B and C (C') is about 6 eV (7.4 eV), in good agreement with

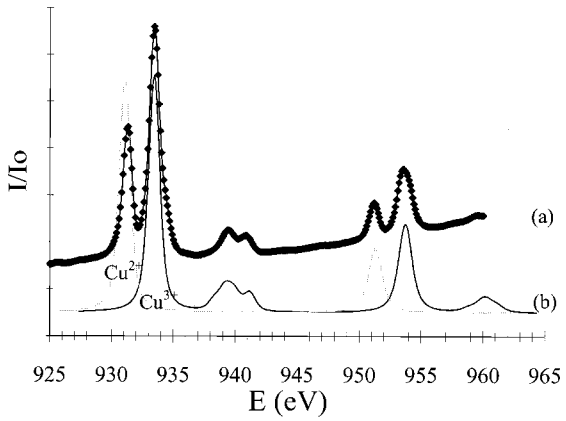

FIG. 2. Comparison between (a) experimental and (b) calculated spectra at the Cu $L_{2,3}$ edges of K_2NaCuF_6 using a charge-transfer multiplet calculations model.

that observed in the case of Rb_2KCuF_6 (~7 eV) and Cs_2KCuF_6 (6.5 eV).[4,7] It should be noted that these values are lower than those observed for trivalent copper oxides in which the degree of covalence is larger [$NaCuO_2$: 8–10 eV (Refs. 5 and 6) and $La_2Li_{1/2}Cu_{1/2}O_4$: 8.4 eV (Ref. 7)] due to the fact that the Δ value becomes more and more negative as the bond covalence increases. Moreover, the intensity of satellites in the case of fluorides is greater than that in the case of oxides.

A relevant question is the weight of $3d^8$ configuration contained in the ground state of trivalent copper fluorides. Such an evaluation is possible by means of charge-transfer multiplet calculations. The $L_{2,3}$-edges simulation for K_2NaCuF_6, where Cu^{3+} cation is in an octahedral symmetry, is shown in Fig. 2. The Cu(II) contribution is evidenced by the superposition of the $KCuF_3$-calculated spectrum represented by the light-gray line. A good agreement between the calculated and the experimental spectra has been obtained using a charge-transfer energy $\Delta = -1.7$ eV in the ground state. The final-state charge-transfer energy Δ', equal to $\Delta + U_{dd} - U_{cd}$, has been considered using a fixed difference of $U_{cd} = U_{dd} + 1$ eV. The mixing parameters were fixed at 2.0 eV for E_g mixing and 1.0 eV for T_{2g} mixing.[17] Atomic Slater integrals were used with an ionic crystal-field value of 0.5 eV. The negative value of Δ means that the ground state is comprised of 40% $3d^8$ states and 60% $3d^9\underline{L}$ states. In conclusion, the formal charge of copper $(+\overline{3})$ in fluorides is stabilized by a charge transfer from fluorine implying that the effective ionic charge is lower than 3. The same result has been reported in the case of Cs_2KCuF_6.[7] Moreover, electronic-density calculations using the full-potential linearized augmented plane wave method (FLAPW) method have been performed for K_2NaCuF_6.[20,21] The energy separation between the $2p$ fluorine nonbonding bands and the t_{2g} and e_g copper antibonding bands has been found to be 0.25 eV and 2.25 eV, respectively, favoring an electronic transfer from fluorine to copper. However, these results must be compared with those obtained in more covalent systems such as oxides. Configuration-interaction (CI) calculations from a valence-band photoemission spectrum of $NaCuO_2$ including Cu $3d$ multiplet structure on a square-planar CuO_4^{5-} cluster model have established a ground state constituted of 27% $3d^8$, 65% $3d^9\underline{L}$, and 8% $3d^{10}\underline{L}$.[2,6] In the same way, 30% $3d^8$ were obtained for $La_2Li_{1/2}\overline{Cu}_{1/2}O_4$ oxide,[7] showing a charge transfer much higher in oxides than in fluorides.

Moreover the energy difference Δ_{ion} between a hole on a fluorine and on a copper site according to the reaction $M^{n+} + F^- \rightarrow M^{(n-1)+} + F^0$ where there is an atomic and a Madelung contribution, is given by

$$\Delta_{ion} = e[V_M(F) - V_M(Cu)] - I_{3-2}(Cu) - A_1(F) - \frac{e^2}{d_{M\text{-}F}}.$$

I_{3-2}(Cu) represents the second or the third ionization potential, A_1(F) is the electron affinity of fluorine, and $e^2/d_{M\text{-}F}$ is a repulsive energy where $d_{M\text{-}F}$ is the metal-fluorine distance. V_M represents the electrostatic Madelung site potential calculated by using the Ewald method.[22] The corresponding energetic parameters are given in Table I. The values obtained for $KCuF_3$ and K_2NaCuF_6 are equal to 2.95 and -4.97 eV, respectively. These indicate that in Cu(III) fluorides the charge transfer from fluorine to copper must exist.

B. Nickel fluorides

The XAS spectra of divalent and trivalent nickel fluorides displayed in Fig. 3 show numerous complex structures. The excited state consists of one hole in the $2p$ orbitals that can interact with one or more holes of the $3d$ orbitals resulting in extended multiplet effects. Two peaks labeled *A* and *B*, separated by 2.5 eV, are observed for Ni(II) fluorides at L_3 edge. These are characteristic of a Ni^{2+} high spin cation in an octahedral symmetry.[19,23,24] In addition, the charge-transfer energy Δ calculated on the basis of an ionic model (Table I) for a Ni^{2+} ion ($3d^8$) is much larger than the one obtained for a Cu^{3+} ion ($3d^8$); the inversion of levels observed in the

TABLE I. Energetic parameters used to calculate the energy difference between a hole on a fluorine and on a metal site.

Compounds	Ionization energy (eV)	Electrostatic Madelung site potential (V)	$e\Delta V_M$ (eV)	$d_{M\text{-}F}$ (Å)	Charge-transfer energy Δ_{ion} (eV)
$KNiF_3$	18.19	22.19	33.77	2.006	4.98
$KCuF_3$	20.32	22.14	33.74	2.035	2.95
K_2NaNiF_6	35.21	30.90	43.02	1.890	−3.20
K_2NaCuF_6	36.88	30.88	43.00	1.870	−4.97

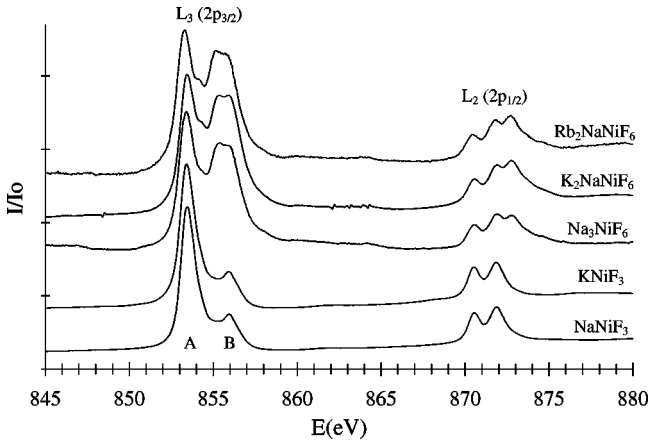

FIG. 3. XA spectra at the Ni $L_{2,3}$ edges for divalent and trivalent nickel fluorides. Spectra were normalized by considering the main peak intensity as unity.

case of copper compounds when a mixing of configurations is considered does not occur for nickel compounds. In this case, the main peak splitting into two components *A* and *B* would have a $2p^5 3d^9$ dominant character whereas the satellite at higher energy would predominantly have a $2p^5 3d^{10}\underline{L}$ character as shown in Fig. 4. No satellite is observed for Ni(II) fluorides because of the high electronegativity of fluorine, in agreement with results reported for NiF_2.[19]

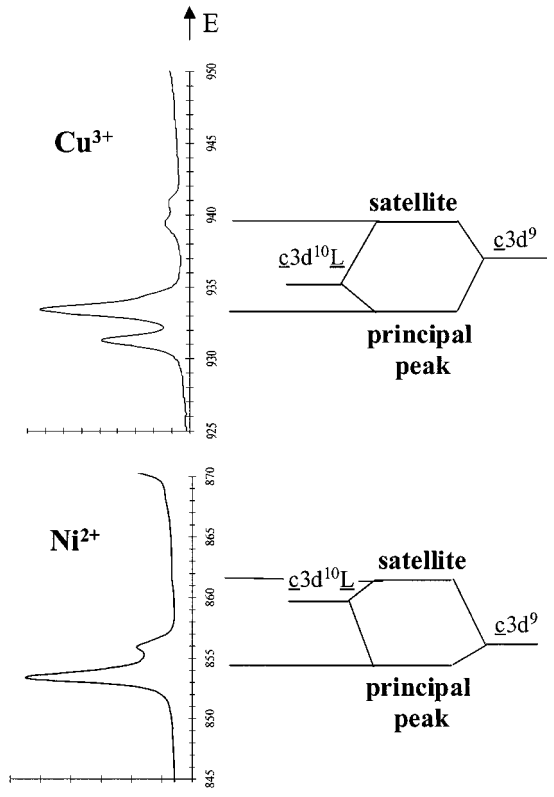

FIG. 4. Illustration of the positioning of the different peaks observed on L_3-edge XA spectra by comparison with a schematic representation of orbital diagrams for Ni^{2+} and Cu^{3+} ions in fluorides.

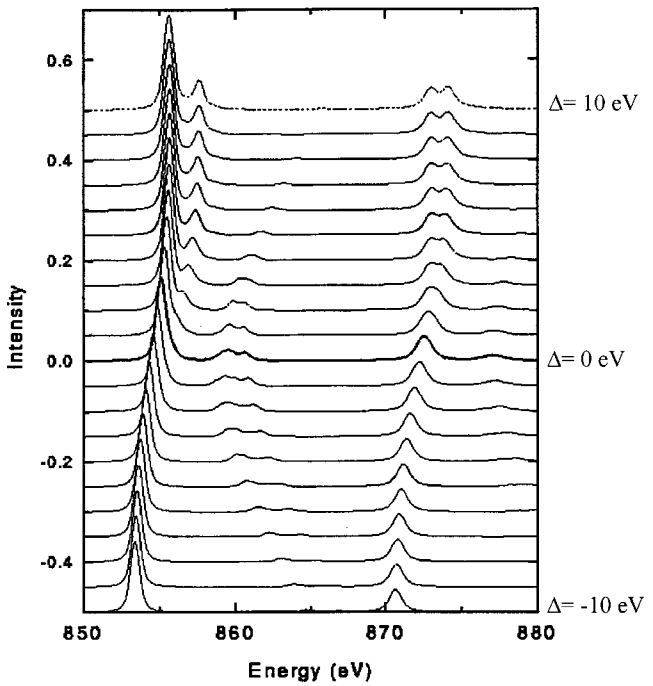

FIG. 5. Evolution of $L_{2,3}$-edges XA spectra in the case of a $3d^8$ ion in the ground state obtained using a charge-transfer multiplet calculations model as a function of charge-transfer energy Δ with $10Dq$ fixed at 1 eV.

Interestingly, while trivalent copper has the same electronic configuration as divalent nickel ($3d^8$) in the ground state, only a low multiplet effect occurs, evidenced by the small separation between *B* and *B′* structures (Fig. 1). In fact, the peaks *B* and *B′* are mainly comprised of $2p^5 3d^{10}\underline{L}$ excited states. On the contrary, the satellite, which is composed of $2p^5 3d^9$ predominant states, is highly affected by the multiplet effect since the *C* and *C′* peaks are separated by 1.8 eV. The splitting is smaller than in Ni(II) fluorides (2.5 eV), explained by a stronger overlapping between ligand and metal orbitals in K_2NaCuF_6, which decreases the multiplet effects. Such an evolution, depending on the charge-transfer energy, is clearly shown by multiplet calculations as displayed in Fig. 5. Ni(II) fluorides spectra are very close to those calculated with $0.8 < 10Dq < 1.2$ eV without any configuration mixing ($\Delta = 10$ eV) whereas the K_2NaCuF_6 spectrum resembles those for which Δ becomes negative.

XAS spectra for trivalent nickel are more complex considering the presence of two *d* holes and one *p* hole in the excited state that implies more interelectronic Coulomb interactions.[25] Moreover, Ni(III) fluorides were probably reduced at the surface because of their high hygroscopicity since the presence of divalent nickel in our compounds has been highlighted by the observation of the peak *A* (Fig. 3). Thus, the shape of the spectrum obtained results from the superposition of the two spectra related to Ni^{2+} ($3d^8$) and Ni^{3+} ($3d^7$) ions. A precise attribution of each structure is difficult in this case and few experimental results or theoretical calculations are reported in the literature.[1,8] Nevertheless, some clear similarities are observed on $L_{2,3}$ edges of divalent cobalt oxides due to their common $3d^7$ configuration.[25,26]

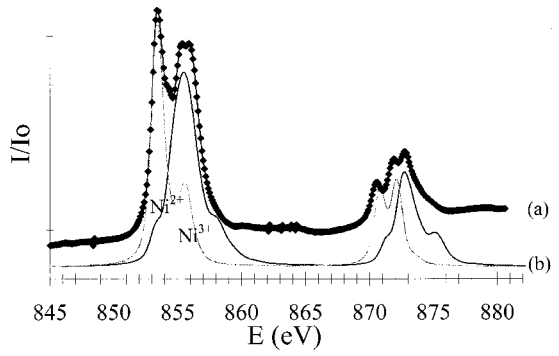

FIG. 6. Comparison between (a) experimental and (b) calculated spectra at the Ni $L_{2,3}$ edges of K_2NaNiF_6 using a charge-transfer multiplet calculations model.

The XAS spectrum of K_2NaNiF_6 has been simulated using a two-configuration calculation in the charge-transfer multiplet model and considering a Ni^{3+} cation in octahedral symmetry. It is compared with the experimental data in Fig. 6. The divalent nickel contribution is evidenced by superposition with the $KNiF_3$ calculated spectrum (in light gray). Good agreement between the calculated and the experimental spectra has been obtained using the following parameters: $\Delta=0$ eV in the ground state before inclusion of multiplet effects, $T(E_g)=2.0$ eV, and $T(T_{2g})=1.0$ eV, $U_{dd}-U_{cd}=-1$ eV. Atomic Slater integrals have been used with an ionic crystal-field value of 0.5 eV. The calculated value of Δ is relative to a ground state consisting of 65% $3d^7$ states and 35% $3d^8\underline{L}$ states. K_2NaNiF_6 exhibits a charge transfer from fluorine to nickel lower than in K_2NaCuF_6. This is in agreement with the Δ values of -3.2 eV and -4.97 eV calculated for Ni(III) and Cu(III) fluorides, respectively, on the basis of the ionic model previously described for Cu(III) fluorides.

It is argued that for trivalent and tetravalent transition metal ions, it is not accurate anymore to limit the calculation to two configurations.[14] To be sure that the two-configuration basis that we use in this paper is correct, we have compared a two-configuration calculation with two three-configuration calculations. Note that this comparison is only useful in the case of $3d^7$ Ni^{3+} systems. If the ground state is $3d^8+3d^9\underline{L}+3d^{10}\underline{LL}'$ (Cu^{3+} and Ni^{2+}), only two final-state configurations are possible: $3d^9$ and $3d^{10}\underline{L}$. This implies, as far as the spectral shape is concerned, that a two-configuration calculation does give exactly the same result as a three-configuration calculation (there being only two final state configurations). However, in the case of the Ni^{3+} system a difference will occur. To test this, three calculations are compared in Fig. 7: the bottom line is the two-configuration calculation using the parameters as given above ($\Delta=0$ eV, $U_{dd}-U_{cd}=-1$ eV, $T_{Eg}=2.0$ eV, $T_{T2g}=1.0$ eV, $10Dq=0.5$ eV). In the case of a $3d^7+3d^8\underline{L}+3d^9\underline{LL}'$ three-configuration calculation, the energy of the $3d^9\underline{LL}'$ configuration is equal to $2\Delta+U_{dd}$. We have chosen two extreme possibilities for the value of U_{dd}, respectively, 8 eV (middle spectrum) and 5 eV (top spectrum). All the other parameters have been kept constant. It can be seen in Fig. 7 that the three spectra are almost identical. The difference spectra do show some small energy shifts that can

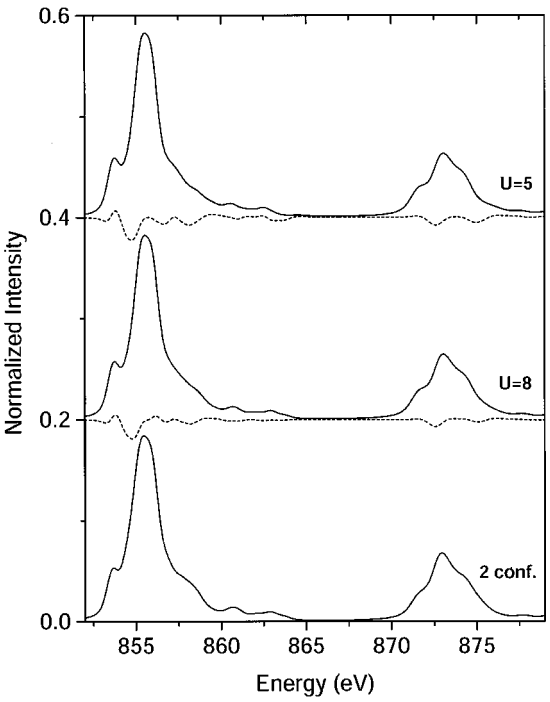

FIG. 7. Comparison between two-configuration calculation (bottom) and three-configuration calculations, respectively, with $U=8$ (middle) and $U=5$ (top). Given are the calculated spectra and the difference of the three-configuration spectra with the two-configuration spectrum.

be directly related to the small differences in ground-state configurations. The ground-state percentages go from 65% to 35% to 0% for the two configurations to, respectively, 58% to 40% to 2% for $U=8$ and 55% to 41% to 4% for $U=5$. Thus significant variations are visible in the covalency numbers while the spectral shape does hardly change. We conclude that in case of Ni^{3+}, one can just as well use two configurations, which is also favorable because in the other three cases discussed (Ni^{2+}, Cu^{3+}, and Cu^{2+}) two configurations are used. In addition, one does not have to determine the value of U_{dd} as it does not play a role in a two-configuration calculation.

In conclusion, as for trivalent copper, a strong configuration mixing between F($2p$) and Ni($3d$) occurs in Ni(III) fluorides leading to the conclusion that for higher oxidation states, even in the so-called ionic compounds such as fluorides, electronic holes are delocalized between ligand and transition metal.

IV. CONCLUSION

In order to determine the degree of electron/hole delocalization in the M-F chemical bond, XAS measurements have been investigated at Ni $L_{2,3}$ and Cu $L_{2,3}$ edges in fluorides where the high electronegativity of fluorine produces a rather ionic bond. The assignment of each structure in the experimental spectra was made based on multiplet calculations. While in Ni(II) and Cu(II) fluorides, the M^{2+}-F bond exhibits a marked ionic character, multiplets calculations consid-

ering crystal-field effects and charge-transfer phenomena have shown the occurrence of F($2p$)-M($3d$) configuration mixing when the transition metal adopts a higher oxidation state Ni^{III}, Cu^{III}. The ground state is characterized by 65% $3d^7+35\%$ $3d^8\underline{L}$ for Ni^{III} and 40% $3d^8+60\%$ $3d^9\underline{L}$ for $Cu^{(III)}$. This work demonstrates that a M^{3+} ion with an effective charge $3+$ is inappropriate in the description of fluoride compounds. Instead, $(MF_6)^{3-}$ octahedra must be considered as isolated entities with a rather strong covalent character. Nevertheless, the proportion of states relative to a strong overlapping with the ligand ($3d^n\underline{L}$) remains smaller than that obtained in the case of oxides, in good agreement with the stronger electronegativity of fluorine compared to oxygen.

Finally, the comparison of $L_{2,3}$-edges XAS spectra for the series of fluorides $KNiF_3$, $KCuF_3$, K_2NaNiF_6, and K_2NaCuF_6 allowed the quantification of the evolution of the charge-transfer energy Δ and the delocalization degree from ligand holes towards the transition metal. The ionic character of the M-F chemical bond decreases following the series $Ni^{II}>Cu^{II}>Ni^{III}>Cu^{III}$, in agreement with calculations of charge-transfer energy based on a purely ionic model.

Complementary Ni and Cu K edges analyses were performed on the same compounds with full multiple scattering and band structure calculations.[21]

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*Corresponding author. Present address: ESRF, Boîte Postale 220, F-38043 Grenoble Cedex, France. Fax: (33)-(0)4-76-88-27-43. Email address: denadai@esrf.fr

[1] M. Medarde, A. Fontaine, J. L. Garcia-Munoz, J. Rodriguez-Carvajal, M. de Santis, M. Sacchi, G. Rossi, and P. Lacorre, Phys. Rev. B **46**, 14 975 (1992).
[2] J. Garcia, J. Blasco, M. G. Proietti, and M. Benfatto, Phys. Rev. B **52**, 15 823 (1995).
[3] S. L. Stoll, R. M. Bornick, A. M. Stacy, and P. D. Vernooy, Inorg. Chem. **36**, 1838 (1997).
[4] G. Kaindl, O. Strebel, A. Kolodziejczyk, W. Schafer, R. Kiemel, S. Losch, S. Kemmler-Sack, R. Hoppe, H. P. Müller, and D. Kissel, Physica B **158**, 446 (1989).
[5] K. Okada, A. Kotani, B. T. Thole, and G. A. Sawatzky, Solid State Commun. **77**, 835 (1991).
[6] T. Mizokawa, A. Fujimori, H. Namatame, K. Akeyama, and N. Kosugi, Phys. Rev. B **49**, 7193 (1994).
[7] Z. Hu, G. Kaindl, S. A. Warda, D. Reinen, F. M. F. de Groot, and B. G. Müller, Chem. Phys. **232**, 63 (1998).
[8] Z. Hu, C. Mazumdar, G. Kaindl, F. M. F. de Groot, S. A. Warda, and D. Reinen, Chem. Phys. Lett. **297**, 321 (1998).
[9] C. De Nadaï, A. Demourgues, and J. Grannec, Nucl. Instrum. Methods Phys. Res. B **133**, 1 (1997).
[10] B. T. Thole, G. van der Laan, and P. H. Butler, Chem. Phys. Lett. **149**, 295 (1988).
[11] F. M. F. de Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky, Phys. Rev. B **41**, 928 (1990).
[12] K. Okada, A. Kotani, and B. T. Thole, J. Electron Spectrosc. Relat. Phenom. **58**, 325 (1992).
[13] F. M. F. de Groot, J. Electron Spectrosc. Relat. Phenom. **67**, 529 (1994).
[14] P. Mahadevan and D. D. Sarma, Phys. Rev. B **61**, 7402 (2000).
[15] T. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, CA, 1981).
[16] P. H. Butler, *Point Group Symmetry, Applications, Methods and Tables* (Plenum, New York, 1981).
[17] A. Kotani and K. Okada, Technical Report of ISSP A No. 2562, 1992 (unpublished).
[18] A. S. Koster, Mol. Phys. **26**, 625 (1973).
[19] G. van der Laan, J. Zaanen, G. A. Sawatzky, R. Karnatak, and J. M. Esteva, Phys. Rev. B **33**, 4253 (1986).
[20] X. Rocquefelte, F. Boucher, and P. Gressier (private communication).
[21] C. De Nadaï, Ph.D. thesis, University of Bordeaux I, France, 1998.
[22] P. P. Ewald, Ann Phys. **64**, 253 (1921).
[23] T. Yamaguchi, S. Shibuya, S. Suga, and S. Shin, J. Phys. C **15**, 2641 (1982).
[24] G. van der Laan, T. Thole, G. A. Sawatzky, and M. Verdaguer, Phys. Rev. B **37**, 6587 (1988).
[25] F. M. F. de Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky, Phys. Rev. B **42**, 5459 (1990).
[26] F. M. F. de Groot, Ph.D. thesis, University of Nijmegen, The Netherlands, 1991.