The electronic structures of nickel and copper have been studied for KMF$_3$ and K$_2$NaMF$_6$ 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 $|3d^n\rangle + |3d^{n+1}L\rangle$. 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 3$d^8$ configuration for K$_2$NaCuF$_6$ and 65% of the 3$d^7$ configuration for K$_2$NaNiF$_6$.

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$_2$MF$_6$ and A$_3$NaMF$_6$ 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 Kα 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,13 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_p) = -2T(12e) 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 electro-static 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 (L1) and 951 eV (L2) separated by the spin-orbit splitting of the 2p_{3/2} (L1) and 2p_{1/2} (L2) hole states. Considering that the ground state of Cu(II) is represented by a linear combination of 3d^9 and 3d^{10}L states (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 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.

In the L_{1} 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^9L. As discussed before, we neglect the small contribution of the 3d^{10}L^2 configuration. In the excited state, the corresponding configurations are 2p^53d^9 and 2p^53d^{10}L. The energy difference between these two levels is equal to Δ + 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 shell, and the charge-transfer energy, respectively.13,19 For the ground state, the energy difference between 3d^8 and 3d^9L 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 Π^2F(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^9L and the 2p^53d^9L level is found at a lower energy than the 2p^53d^8L level in the excited state. In this way, the B peak has been predominantly assigned to a 2p^53d^{10}L excited state. Besides, the energy separation between A(2p^53d^{10}L) and B peaks is equal to 2.1 eV. This corresponds to the ionization potential of the ligand ε_0(3d^{n-3}d^{10}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^{10} excited state. The energy difference between B and C (C’) is about 6 eV (7.4 eV), in good agreement with

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.
that observed in the case of Rb$_2$KCuF$_6$ ($\sim$7 eV) and Cs$_2$KCuF$_6$ (6.5 eV).\textsuperscript{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$_2$Li$_{1/2}$Cu$_{1/2}$O$_4$: 8.4 eV (Ref. 7)].

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$_2$NaCuF$_6$, 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 $\Delta'$, 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.\textsuperscript{17} Atomic Slater integrals were used with an ionic crystal-field value of 0.5 eV. The negative value of $\Delta$ means that the ground state is comprised of 40% 3d$^8$ states and 60% 3d$^9$L states. In conclusion, the formal charge of copper (+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$_2$KCuF$_6$.\textsuperscript{7} Moreover, electronic-density calculations using the full-potential linearized augmented plane wave method (FLAPW) method have been performed for K$_2$NaCuF$_6$\textsuperscript{20,21} and K$_2$NaNiF$_6$.\textsuperscript{21} The energy separation between the 2$p$ 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 3$d$ multiplet structure on a square-planar CuO$_4^{2-}$ cluster model have established a ground state constituted of 27% 3$d^8$, 65% 3$d^9$L, and 8% 3$d^{10}$L.\textsuperscript{2,6} In the same way, 30% 3$d^8$ were obtained for La$_2$Li$_{1/2}$Cu$_{1/2}$O$_4$ oxide,\textsuperscript{7} showing a charge transfer much higher in oxides than in fluorides.

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

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

$I_{3-2}(Cu)$ represents the second or the third ionization potential, $A_1(F)$ is the electron affinity of fluorine, and $e^2/d_{M,F}$ is a repulsive energy where $d_{M,F}$ is the metal-fluorine distance. $V_M$ represents the electrostatic Madelung site potential calculated by using the Ewald method.\textsuperscript{22} The corresponding energetic parameters are given in Table I. The values obtained for KCuF$_3$ and K$_2$NaCuF$_6$ 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 2$p$ orbitals that can interact with one or more holes of the 3$d$ 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.\textsuperscript{19,23,24} In addition, the charge-transfer energy $\Delta$ calculated on the basis of an ionic model (Table I) for a Ni$^{2+}$ ion (3$d^8$) is much larger than the one obtained for a Cu$^{3+}$ ion (3$d^9$); the inversion of levels observed in the

![Image](image_url)

**FIG. 2.** Comparison between (a) experimental and (b) calculated spectra at the Cu $L_{2,3}$ edges of K$_2$NaCuF$_6$ using a charge-transfer multiplet calculations model.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Ionization energy (eV)</th>
<th>Electrostatic Madelung site potential (V)</th>
<th>$e\Delta V_M$ (eV)</th>
<th>$d_{M,F}$ (Å)</th>
<th>Charge-transfer energy $\Delta_{ion}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNiF$_3$</td>
<td>18.19</td>
<td>22.19</td>
<td>33.77</td>
<td>2.006</td>
<td>4.98</td>
</tr>
<tr>
<td>KCuF$_3$</td>
<td>20.32</td>
<td>22.14</td>
<td>33.74</td>
<td>2.035</td>
<td>2.95</td>
</tr>
<tr>
<td>K$_2$NaNiF$_6$</td>
<td>35.21</td>
<td>30.90</td>
<td>43.02</td>
<td>1.890</td>
<td>-3.20</td>
</tr>
<tr>
<td>K$_2$NaCuF$_6$</td>
<td>36.88</td>
<td>30.88</td>
<td>43.00</td>
<td>1.870</td>
<td>-4.97</td>
</tr>
</tbody>
</table>
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 $2p^53d^8$ dominant character whereas the satellite at higher energy would predominantly have a $2p^53d^{10}L$ character as shown in Fig. 4. No satellite is observed for Ni(I) fluorides because of the high electronegativity of fluorine, in agreement with results reported for NiF$_2$.19

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 $2p^53d^{10}L$ excited states. On the contrary, the satellite, which is composed of $2p^53d^9$ 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(I) fluorides (2.5 eV), explained by a stronger overlapping between ligand and metal orbitals in K$_2$NaCuF$_6$, 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(I) fluorides spectra are very close to those calculated with $10Dq$ fixed at 1 eV.

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.1,5 Nevertheless, some clear similarities are observed on $L_{2,3}$ edges of divalent cobalt oxides due to their common $3d^7$ configuration.25,26
The XAS spectrum of $K_2\text{NaNiF}_6$ 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: $\Delta = 0\, \text{eV}$ in the ground state before inclusion of multiplet effects, $T(E_{g}) = 2.0\, \text{eV}$, and $T(T_{2g}) = 1.0\, \text{eV}$, $U_{dd} - U_{cd} = -1\, \text{eV}$. Atomic Slater integrals have been used with an ionic crystal-field value of $0.5\, \text{eV}$. The calculated value of $\Delta$ is relative to a ground state consisting of 65% $3d^7$ states and 35% $3d^8 L$ states. $K_2\text{NaNiF}_6$ exhibits a charge transfer from fluorine to nickel lower than in $K_2\text{NaCuF}_6$. This is in agreement with the $\Delta$ values of $-3.2\, \text{eV}$ and $-4.97\, \text{eV}$ 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. 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 $3d^7\, \text{Ni}^{3+}$ systems. If the ground state is $3d^8 + 3d^9 L + 3d^{10} L'$ (Cu$^{3+}$ and Ni$^{2+}$), only two final-state configurations are possible: $3d^9$ and $3d^{10} L$. 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 ($\Delta = 0\, \text{eV}$, $U_{dd} - U_{cd} = -1\, \text{eV}$, $T(E_g) = 2.0\, \text{eV}$, $T(T_{2g}) = 1.0\, \text{eV}$, $10Dq = 0.5\, \text{eV}$). In the case of a $3d^7 + 3d^9 L + 3d^{10}L'$ three-configuration calculation, the energy of the $3d^9 L L'$ configuration is equal to $2\Delta + U_{dd}$. We have chosen two extreme possibilities for the value of $U_{dd}$, respectively, $8\, \text{eV}$ (middle spectrum) and $5\, \text{eV}$ (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 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$^{1+}$, 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(2$p$) and Ni(3$d$) 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-
erating 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 $65\% \ 3d^7 + 35\% \ 3d^8L$ for Ni$^{III}$ and $40\% \ 3d^8 + 60\% \ 3d^9L$ 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 an $M^{3+}$ 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 $3d^nL$ 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 $\text{K} \text{NiF}_3$, $\text{K} \text{CuF}_3$, $\text{K}_2 \text{NaNiF}_6$, and $\text{K}_2 \text{NaCuF}_6$ allowed the quantification of the evolution of the charge-transfer energy $\Delta$ and the delocalization degree from ligand holes towards the transition metal. The ionic character of the $M$-$F$ chemical bond decreases following the series $\text{Ni}^{II}>\text{Cu}^{II}>\text{Ni}^{III}>\text{Cu}^{III}$, 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.\textsuperscript{21}

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20 X. Rocquefelte, F. Boucher, and P. Gressier (private communication).


