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Compounds Containing Tetragonal Cu^{2+} Complexes: Is the $d_{x^2-y^2}-d_{3z^2-r^2}$ Gap a Direct Reflection of the Distortion?

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ABSTRACT: It is widely assumed that the gap, Δ, between $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals in fluorides and oxides containing tetragonal Cu^{2+} or Ag^{2+} complexes directly reflects the tetragonal distortion in the MX_6 complex ($M = d^9$ ion; $X = F^-$, O^{2-}). This assumption on that relevant quantity is shown to be not correct through the study of pure K_2CuF_4-, $KCuF_3$-, and Cu^{2+}-doped $KZnF_3$ and K_2ZnF_4 model compounds. Indeed, ab initio calculations prove that Δ in these insulating materials also depends on the internal electric field created by the rest of lattice ions on active electrons confined in a given CuF_6^{4-} complex. This internal field, especially important for layered compounds, is shown to explain all puzzling experimental facts on the d−d transitions of the studied systems and is of interest in the search of new Cu^{2+} and Ag^{2+} superconducting materials where a strong correlation between Δ and the transition temperature, T_c, has been conjectured.

SECTION: Molecular Structure, Quantum Chemistry, and General Theory
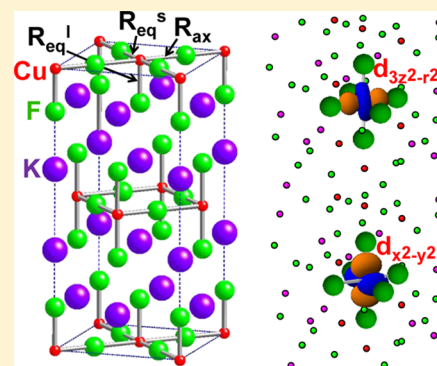
Insulating layered compounds containing $3d^9$ Cu^{2+} ions have been widely investigated because of their unique structural, optical, electrical, and magnetic properties.[1−9] In particular, since the discovery of the high-T_c superconducting cuprates by Bednorz and Müller,[1] there has been considerable progress, as well as controversy, about the physics and chemistry of not only superconducting copper oxides[2−10] but also copper oxy-fluorides.[11,12] Moreover, considerable interest has recently been shown in the solid-state chemistry of fluorides that contain the $4d^9$ Ag^{2+} ions, including prediction of super-conducting phases, charge-transfer character, and two-dimensional ferromagnetism.[13,14] A landmark question to understand these materials is how their physical properties follow from their electronic structure and to what extent simplified descriptions in the form of model Hamiltonians describe their basic physical properties in the normal state. In this sense, it has long been argued that, besides the canonical $3d_{x^2-y^2}$ copper orbital, the $3d_{3z^2-r^2}$ one plays an important role in the onset for the existence of superconductivity or orbital order,[6−10] and therefore, different authors have suggested that the transition temperature, T_c, is directly related to the magnitude of the $d_{x^2-y^2}-d_{3z^2-r^2}$ splitting, Δ.[6−9] Optical absorption measurements and resonant inelastic X-ray scattering (RIXS) spectra carried out on some copper oxides and fluorides[5,15−19] have provided detailed insight into the d−d transitions and the actual value of Δ of these materials. Although first-principles calculations have reproduced the experimental Δ value for some of these materials,[9,20] the microscopic origin of this relevant quantity is not well understood yet. In fact, it is widely assumed that, in copper complexes, the value of this gap, Δ, directly reflects the tetragonal distortion around Cu^{2+} induced by a vibronic mechanism like the Jahn−Teller effect.[21−23] This Letter is aimed at demonstrating that this idea is in general not correct. To achieve this goal, we have explored using ab initio calculations for the origin of the $d_{x^2-y^2}-d_{3z^2-r^2}$ gap in four different insulating compounds containing tetragonal (or nearly tetragonal) CuF_6^{4-} complexes and where the d−d transitions have accurately been measured.[15−19]

K_2CuF_4 and $KCuF_3$ are considered as prototype materials for a cooperative Jahn−Teller effect, orbital ordering, and low-dimensional magnetism. $KCuF_3$ (tetragonal $I4/mcm$ structure,[24] Figure 1) stands in line with $LaMnO_3$, the parent compound of the colossal magnetoresistance manganites, as models for orbitally ordered compounds and is one of the rare examples of the ideal one-dimensional (1-D) antiferromagnetic Heisenberg chain. Regarding K_2CuF_4, with orthorhombic $Bbcm$ structure[25] (Figure 1), it is a charge-transfer insulator with 2-D ferromagnetism.[25] In both cases, the cooperative distortion is characterized by an antiferrodistortive ordering of the orthorhombic CuF_6^{4-} complexes in the (001) plane. We will compare these two pure compounds with the CuF_6^{4-} complexes formed in Cu^{2+}-doped K_2ZnF_4 and $KZnF_3$ insulating
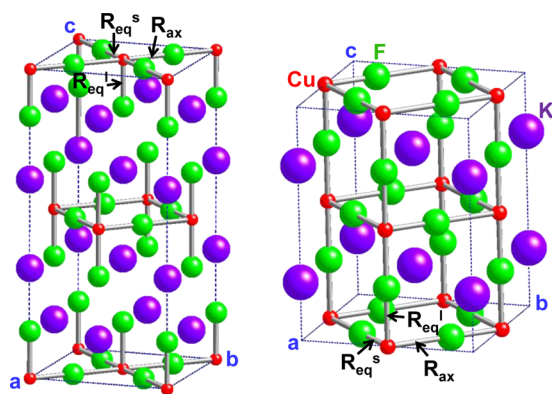
Figure 1. Picture of the unit cells of orthorhombic K_2CuF_4 (left) and tetragonal $KCuF_3$ (right) pure compounds, showing the equatorial and axial Cu−F bonds.

lattices under the $Zn^{2+} \rightarrow Cu^{2+}$ substitution.[16,17] Although $KZnF_3$ is a cubic perovskite ($Pm3m$ group[23]) and K_2ZnF_4 a tetragonal layered perovskite ($I4/mmm$ group,[26] Figure 2) the
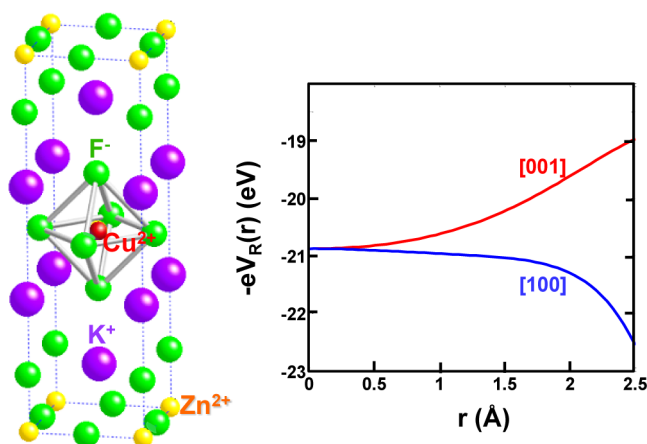

Figure 2. (Left) Picture of the CuF_6^{4-} complex in the unit cell of the tetragonal K_2ZnF_4 compound. (Right) Potential energy $(-e)V_R(\mathbf{r})$ experienced by an electron confined in the CuF_6^{4-} complex due to the electrostatic potential, $V_R(\mathbf{r})$, produced by the rest of the ions of the K_2ZnF_4 lattice depicted along the [100] and [001] crystalline directions.

octahedron surrounding Zn^{2+} in the last compound is practically perfect with a Zn^{2+}−F^- distance equal to 203 pm and thus nearly identical to the value of 202 pm measured for $KZnF_3$.

The four considered systems contain CuF_6^{4-} complexes with tetragonal or near-tetragonal symmetry involving four equatorial F^- ions at a distance R_{eq} from Cu^{2+} and two axial ones, along the C_4 axis, at a distance $R_{ax} \neq R_{eq}$. If the ground state is $^2B_{1g}$, the hole is in the planar $b_{1g}*(\sim x^2-y^2)$ orbital, while if the ground state is $^2A_{1g}$, the hole is located in the $a_{1g}*(\sim 3z^2-r^2)$ orbital, directed along the C_4 axis. Although the gap Δ between $^2B_{1g}$ and $^2A_{1g}$ states has *directly* been related to the tetragonal distortion $u \equiv R_{ax} - R_{eq}$ taking place on the CuF_6^{4-} complex,[21−23] a first analysis of experimental data casts doubts on the correctness of this interpretation. In fact, it can be noticed (Table 1) that there are remarkable differences in the Δ values measured for the four considered systems. Therefore, while the gap Δ is positive for K_2CuF_4, $KCuF_3$, and $KZnF_3/Cu^{2+}$, it is however negative for K_2ZnF_4/Cu^{2+}, thus implying that the ground state for the last system is surprisingly $^2A_{1g}$ and not $^2B_{1g}$. Also, comparing K_2CuF_4 with $KCuF_3$, we observe that the first compound displays a smaller tetragonal distortion than the second one (u is *reduced* by 16%), but the experimental splitting Δ is surprisingly 8% *larger*. Moreover, the $|\Delta|$ value for K_2ZnF_4/Cu^{2+} has been measured[16] to be equal to ~0.7 eV, while it should be below 0.5 eV for $KZnF_3/Cu^{2+}$ according to experimental data.[17]

Seeking to clear out these puzzling facts, we have first carried out ab initio periodic calculations in order to determine the equilibrium geometry of the CuF_6^{4-} complexes in the four insulating lattices. Full geometry optimizations were performed in the framework of the spin-unrestricted density functional theory (DFT) by means of the CRYSTAL09 package that employs localized Gaussian-type orbitals (GTOs) basis sets to represent the Bloch orbitals.[27] All ions have been described by means of the pob-TZVP-2012 basis sets, recently optimized by Peintinger et al.,[28] which are all-electron with triple-ζ valence with polarization quality. We have used the PW1PW hybrid exchange−correlation functional[29] (including 20% of Hartree−Fock exchange), allowing one to obtain geometries, band gaps, and optical and thermochemistry properties with great accuracy and reliability. Calculations of Cu^{2+}-doped $KZnF_3$ and K_2ZnF_4 lattices were performed using, respectively, $3 \times 3 \times 3$ (135 ions) and $3 \times 3 \times 1$ (126 ions) periodic supercells. We have previously verified that the present calculations reproduce the lattice parameters of *pure* $KZnF_3$ ($a = 403.5$ pm), K_2ZnF_4 ($a = b = 405.8$ pm and $c = 1310.9$ pm), K_2CuF_4 ($a = 1273.4$ pm and $b = c = 586.6$ pm), and $KCuF_3$ ($a = b = 585.7$ pm and $c = 784.9$ pm) with deviations smaller than 1%.

In a second step, we have calculated the energies of the d−d electronic transitions of the four systems through the cluster approach by means of the 2012.01 version of the Amsterdam density functional (ADF) code[30] using the energy difference

Table 1. Experimental Values of the $^2B_{1g}$−$^2A_{1g}$ Gap Energy, Δ, (in eV) Measured for K_2CuF_4[15] and $KCuF_3$[18] Pure Compounds As Well As for the Cu^{2+} Impurity in the Tetragonal K_2ZnF_4 Lattice[16] and in the $KZnF_3$ Cubic Perovskite[17] along with the Equilibrium Distances (in pm) for the CuF_6^{4-} Complex Calculated for the Three Systems, Given Together with the Value of the Distortion $u = R_{ax} - R_{eq}$[a]

	Δ	R_{ax}	R_{eq}^s	R_{eq}^l	u
K_2CuF_4	1.03 ± 0.01	$222.3\ (221.9 \pm 0.1)$	$190.0\ (192.7 \pm 0.1)$	$193.7\ (193.8 \pm 0.1)$	$30.4\ (28.7 \pm 0.2)$
$KCuF_3$	0.95 ± 0.02	$224.5\ (225.6 \pm 0.2)$	$188.0\ (188.5 \pm 0.2)$	$195.2\ (196.2 \pm 0.2)$	$32.9\ (33.3 \pm 0.4)$
K_2ZnF_4/Cu^{2+}	~-0.70	193.1	204.1	204.1	-11
$KZnF_3/Cu^{2+}$	<0.5	210.2	196.7	196.7	13.5

[a]For comparison, the equilibrium distances measured experimentally for the slightly orthorhombic CuF_6^{4-} complex formed in K_2CuF_4[25] and $KCuF_3$[24] are also reported in parentheses. In the later cases, for calculating u, R_{eq} is taken as the average of R_{eq}^s and R_{eq}^l.

from two fully converged total energy calculations with the adequate electronic configuration. As active electrons are *confined* in the CuF_6^{4-} unit, calculations have been performed on a simple CuF_6^{4-} complex but are subject to the electrostatic potential $V_R(\mathbf{r})$ created by the rest of the lattice ions.[31] In these calculations, we have used the popular B3LYP hybrid functional[32] in the spin-unrestricted Kohn−Sham formalism of the DFT and high-quality all-electron basis sets of triple-ζ plus polarization (TZP) type.

Calculated values of equilibrium Cu^{2+}−F^- distances, R_{eq} and R_{ax}, for the four systems are collected in Table 1. As CuF_6^{4-} complexes in K_2CuF_4 and $KCuF_3$ are slightly orthorhombic,[24,25] the calculated values of the two close equatorial distances, R_{eq}^s and R_{eq}^l, together with R_{ax}, are reported in Table 1, where they are compared to the experimental distances measured for these pure compounds. It can be noted that the difference between the calculated Cu^{2+}−F^- distances and the experimental ones is always smaller than 1.4% for both compounds. In particular, the calculations give a value of the tetragonal distortion, u, that is higher for $KCuF_3$ than that for K_2CuF_4, in agreement with experimental data.[24,25] As a salient feature, the present calculations reproduce that the CuF_6^{4-} complexes are elongated in K_2CuF_4, $KCuF_3$, and $KZnF_3/Cu^{2+}$[15,17,18,24,25] but compressed in K_2ZnF_4/Cu^{2+}, a fact that is also in agreement with experimental findings[16] and results from ab initio calculations.[31]

According to Table 1, the experimental u value for K_2CuF_4 (28.7 pm) is 16% smaller than that for $KCuF_3$ (33.3 pm). Therefore, if the observed splitting Δ depends *only* on the distortion of the fluorine octahedron, it is hard to understand why Δ for K_2CuF_4 (1.03 eV)[15] is higher than that for $KCuF_3$ (0.95 eV).[18,19] In the same vein, while the calculated value of $|u|$ is slightly higher for $KZnF_3/Cu^{2+}$ (u = 13.5 pm) than that for K_2ZnF_4/Cu^{2+} ($|u|$ = 11 pm), $|\Delta|$ = ~0.7 eV for K_2ZnF_4/Cu^{2+}[16] is much higher than that for $KZnF_3/Cu^{2+}$, where Δ < 0.5 eV.[17] Furthermore, upon going from K_2ZnF_4/Cu^{2+} to $KCuF_3$, $|u|$ grows by a factor of three, while the experimental $|\Delta|$ value increases *only* by a factor of 1.35 (Table 1).

Seeking to shed light on this matter, we have first calculated the ratio Δ/u for an *isolated* CuF_6^{4-} complex. We have found that when we move around R_{ax} = R_{eq} = 202 pm, then Δ/u = 27 meV/pm. Thus, if u = 13.5 pm for $KZnF_3/Cu^{2+}$, this implies a value of Δ = 0.36 eV, which is consistent with experimental findings.[17] By contrast, we cannot understand the experimental Δ values of K_2ZnF_4/Cu^{2+} and K_2CuF_4 (Table 1) through the calculated u values, assuming that Δ/u = 27 meV/pm.

This situation is rather baffling as in the three insulating lattices, distorted CuF_6^{4-} complexes are formed. Furthermore, active electrons are in all cases *confined* in the complex region, a key point well confirmed by calculations. It is worth noting now that complexes like CuF_6^{4-} are never isolated but embedded in insulating lattices formed by ions. Therefore, the electrons confined in such transition-metal complexes should also be subject to an internal electric field, $\mathbf{E}_R(\mathbf{r})$, created by the rest of lattice ions on the complex. This concept is closely related to the Madelung field, with the difference that here, the effect of the ions in the complex is subtracted from the sum to the whole crystal. The role of this internal field is often discarded in the traditional ligand field theory.[31]

Let us now discuss the possible influence of $\mathbf{E}_R(\mathbf{r})$ upon the optical excitations of CuF_6^{4-} in the four considered systems. To clarify this matter, we have first calculated the value of the d−d transitions for an *isolated* CuF_6^{4-} complex at the equilibrium

geometry determined for $KZnF_3/Cu^{2+}$, K_2ZnF_4/Cu^{2+}, K_2CuF_4, and $KCuF_3$ (Table 1). In a subsequent step, we have calculated the value of the same transitions considering the CuF_6^{4-} complex but subject to the influence of the corresponding internal field. Results are gathered in Tables 2−4.

Table 2. Energy Values (in eV) of the Three d−d Transitions Calculated for the CuF_6^{4-} Complex at the Equilibrium Geometry Derived for $KZnF_3/Cu^{2+a}$

transition	isolated CuF_6^{4-}	CuF_6^{4-} under $V_R(\mathbf{r})$	experimental
$B_{1g} \rightarrow A_{1g}$	0.362	0.398	<0.5
$B_{1g} \rightarrow B_{2g}$	1.042	0.968	0.942
$B_{1g} \rightarrow E_g$	1.147	1.084	1.178

[a]Results are given for the isolated CuF_6^{4-} complex and also for the complex subject to the electrostatic potential due to the rest of the lattice ions, $V_R(\mathbf{r})$. Calculated values are compared to the experimental data reported by Dubicki et al.[17]

Table 3. Energy Value (in eV) of the Three d−d Transitions Calculated for the CuF_6^{4-} Complex at the Equilibrium Geometry Derived for K_2ZnF_4/Cu^{2+a}

transitions	isolated CuF_6^{4-}	CuF_6^{4-} under V_R	experimental
$A_{1g} \rightarrow B_{1g}$	0.33	0.61	~0.70
$A_{1g} \rightarrow E_g$	1.08	1.19	~1.15
$A_{1g} \rightarrow B_{2g}$	1.17	1.35	1.33

[a]Results are given for the isolated CuF_6^{4-} complex and also for the complex subject to $V_R(\mathbf{r})$. Calculated values are compared to the experimental data reported in refs 16 and 17.

Table 4. Energy Values (in eV) of the Four d−d Transitions Calculated for the Slightly Orthorhombic CuF_6^{4-} Complexes at the Equilibrium Geometry Derived for K_2CuF_4 (first line) and $KCuF_3$ (second line, in italics)[a]

transitions	isolated CuF_6^{4-}	CuF_6^{4-} under V_R	experimental
$B_{1g} \rightarrow A_{1g}$	0.77	1.01	1.03
	0.90	*0.85*	*0.95*
$B_{1g} \rightarrow B_{2g}$	1.16	1.20	1.17
	1.20	*1.10*	*1.15*
$B_{1g} \rightarrow E_g(1)$	1.36	1.42	1.50
	1.38	*1.27*	*1.37*
$B_{1g} \rightarrow E_g(2)$	1.35	1.53	1.50
	1.46	*1.36*	*1.46*

[a]Results are given for the isolated CuF_6^{4-} complex and also for the complex subject to $V_R(\mathbf{r})$. The corresponding experimental values[15,18,19] are given for comparison. The Δ value for $KCuF_3$ has been inferred from the spectrum reported in ref 18, which coincides with the figure previously given in ref 19.

Concerning $KZnF_3/Cu^{2+}$, it can first be noticed that the calculated values of the three $B_{1g} \rightarrow A_{1g}$, $B_{1g} \rightarrow B_{2g}$, and $B_{1g} \rightarrow E_g$ transitions (Table 2) are practically unaffected by the internal field, and they are in reasonable agreement with experimental findings.[17] In particular, the gap between B_{1g} and A_{1g} states is found to be Δ = 0.398 eV, thus consistent with experimental data pointing out that Δ < 0.5 eV in this system.[17] If we write $\mathbf{E}_R(\mathbf{r})$ = $-\nabla V_R(\mathbf{r})$, it is well-known that the associated electrostatic potential, $V_R(\mathbf{r})$, is practically constant in the complex region for a cubic perovskite lattice like $KZnF_3$.[33] This explains that the d−d transitions of $KZnF_3/Cu^{2+}$ can essentially be understood, ignoring the small effects due to the internal field.

A quite different situation holds however when looking at the results obtained for K_2ZnF_4/Cu^{2+} (Table 3) and K_2CuF_4 (Table 4). Indeed, as shown in Table 3, the value of the $A_{1g} \to B_{1g}$ transition energy for K_2ZnF_4/Cu^{2+} would be equal only to 0.33 eV for the isolated CuF_6^{4-} complex, while it increases up to 0.61 eV when the addition of the internal field, $E_R(r)$, is taken into consideration. The last value $\Delta = -0.61$ eV is certainly close to the experimental figure $\Delta \approx -0.7$ eV.[16] Moreover, the calculated energy of $A_{1g} \to B_{2g}$ and $A_{1g} \to E_g$ transitions (Table 3) is again closer to experimental findings when the action of $E_R(r)$ upon electrons localized in the CuF_6^{4-} complex is incorporated. Thus, the results given in Table 3 strongly support that about half of the experimental value for the $A_{1g} \to B_{1g}$ transition energy (0.7 eV) in K_2ZnF_4/Cu^{2+} does arise from the internal field, and thus, it is not due to the small distortion characterized by $u = -11$ pm.

As shown in Table 4, a similar situation to that for K_2ZnF_4/Cu^{2+} is found for the pure compound K_2CuF_4. Indeed, the value of the $B_{1g} \to A_{1g}$ transition energy calculated for the isolated CuF_6^{4-} complex at the equilibrium geometry yields $\Delta = 0.77$ eV, which is 25% smaller than the experimental figure $\Delta = 1.03$ eV.[15] However, this discrepancy is overcome when the internal field $E_R(r)$ is also considered in the calculation. Moreover, the addition of $E_R(r)$ increases the calculated energy of $B_{1g} \to E_g(1)$ and $B_{1g} \to E_g(2)$ transitions, which are then closer to the experimental values (Table 4). It is worth noting now that for calculating the electrostatic potential due to the rest of the lattice ions, $V_R(r)$, we have used the Mulliken charges derived for copper ($Q = +1.64$ e), potassium ($Q = +0.79$ e), and fluorine ($Q = -0.79$ e). However, if we use instead the nominal charges of these ions, involving differences of around 20% with respect to the Mulliken charges, we have verified that Δ increases *only* by 4%, while the energies of the $B_{1g} \to E_g(1)$ and $B_{1g} \to E_g(2)$ transitions undergo variations of 0.6%. This result thus supports that the internal field in K_2CuF_4 cannot be overlooked to obtain a reliable understanding of experimental d−d transitions.

The results of Table 4 on $KCuF_3$ point out that the values of d−d transitions are less influenced by the internal field than those for K_2CuF_4, although $E_R(r)$ induces a slight reduction of the energy of four transitions observed for $KCuF_3$. Thus, the surprisingly higher Δ value measured for K_2CuF_4 ($\Delta = 1.03$ eV)[15] than that for $KCuF_3$ ($\Delta = 0.95$ eV),[18,19] not explained through the tetragonal distortion in the CuF_6^{4-} complex, is greatly due to the *additional* contribution to Δ of 0.25 eV arising from the internal field in the former compound (Table 4).

Bearing in mind the relevance of the internal field for explaining the properties of CuF_6^{4-} complexes in insulating lattices, the shape of the electrostatic potential, $V_R(r)$, exerted on a CuF_6^{4-} complex in K_2ZnF_4, K_2CuF_4, and $KCuF_3$ lattices is depicted in Figures 2 and 3 for r running along the Cu−F directions. As shown on Figure 2, in K_2ZnF_4, the potential, which reflects the tetragonal symmetry of the K_2ZnF_4 structure, tends to increase the energy of the $a_{1g}*(\sim 3z^2-r^2)$ orbital with respect to that for $b_{1g}*(\sim x^2-y^2)$. This explains, albeit qualitatively, why the hole in K_2ZnF_4/Cu^{2+} is placed in the $a_{1g}*(\sim 3z^2-r^2)$ orbital and not in the planar $b_{1g}*(\sim x^2-y^2)$ one. In this sense, if $R_{ax} = R_{eq}$, the gap between the $^2B_{1g}$ and $^2A_{1g}$ states for K_2ZnF_4/Cu^{2+} is not equal to zero but $\Delta = -0.35$ eV as a result of the internal electric field.

The form of the electrostatic potential, $V_R(r)$, along the Cu^{2+}−F$_{ax}$, Cu^{2+}−F$_{eq}^l$, and Cu^{2+}−F$_{eq}^s$ directions (Figure 1) of
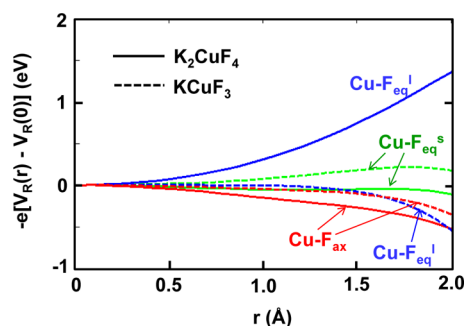

Figure 3. Electrostatic potentials, $V_R(r) - V_R(0)$, produced on a CuF_6^{4-} complex by the rest of ions of K_2CuF_4 (continuous lines) and $KCuF_3$ (dashed lines) lattices depicted along the directions from Cu to the equatorial ligands placed to short and long distances, F_{eq}^s and F_{eq}^l, respectively, and the axial ligand, F_{ax}. Note that the quantity $(-e)\{V_R(r) - V_R(0)\}$ is represented in the figure.

both K_2CuF_4 and $KCuF_3$ layered compounds is shown on Figure 3. In the case of K_2CuF_4 the quantity $(-e)\{V_R(r) - V_R(0)\}$ is attractive when r runs along the Cu^{2+}−F$_{ax}$ direction, placed in the $\{a,b\}$ plane, while it is repulsive when r is parallel to c and thus along the Cu^{2+}−F$_{eq}^l$ direction. Thus, as the mainly $d_{3z^2-r^2}$ orbital is lying along the Cu^{2+}−F$_{ax}$ direction while the unpaired electron, placed in the mainly $d_{x^2-y^2}$ orbital, is influenced by the repulsive $(-e)\{V_R(r) - V_R(0)\}$ potential energy when r is along the Cu^{2+}−F$_{eq}^l$ direction, we can understand, albeit qualitatively, that the internal field in K_2CuF_4 increases the $d_{x^2-y^2}-d_{3z^2-r^2}$ gap. A different situation holds however when looking at $V_R(r)$ for $KCuF_3$, where $(-e)\{V_R(r) - V_R(0)\}$ is essentially attractive and more flat along the three considered directions. It should be noted now that K_2CuF_4 is a *layered* compound where a $\{a,b\}$ plane containing Cu^{2+} ions is separated from another equivalent one by a layer of *monovalent* K$^+$ ions (Figure 3). By contrast, in $KCuF_3$, a ligand F_{eq}^l of a given complex is also linked to another Cu^{2+} ion along the c axis (Figure 3). This explains qualitatively the remarkable difference between $(-e)\{V_R(r) - V_R(0)\}$ for K_2CuF_4 and $KCuF_3$ when r is parallel to c, shown in Figure 3.

Obviously, the relevance of internal electric fields cannot be restricted to the studied systems as they should be present for transition-metal complexes in insulating lattices where electrons are *localized*. In this sense, such internal fields have been shown to be responsible for the different color displayed by the same CrO_6^{9-} complex in gemstones like ruby, emerald, or alexandrite[34,35] and could certainly influence other properties that strongly depend on level splitting like spin-crossover or the presence of novel phases in topological insulators.[36]

The present work thus stresses that internal fields play a key role that cannot be neglected when understanding the optical properties of model compounds like K_2CuF_4 or K_2CuF_3. Accordingly, the gap Δ in compounds containing tetragonal d^9 complexes is not a local property as it also depends on the lattice structure where the complex is embedded, a key component in orbitally ordered crystals.

The present results thus open a window for a better understanding of the $d_{x^2-y^2}-d_{3z^2-r^2}$ gap and other electronic properties in oxide and halide compounds involving Cu^{2+} and Ag^{2+} cations. As compounds like La$_2$CuO$_4$ have a layered structure, the contribution of the internal electric field to the electronic properties can be important.

Finally, it is worth noting that in K_2ZnF_4/Cu^{2+}, the tetragonal internal electric field gives rise to significant changes

in the electronic structure of the CuF_6^{4-} complex, showing that the small distortion ($u = -11$ pm) is not properly due to the Jahn−Teller effect, as has recently been demonstrated.[31] This result thus strongly supports that the distortions and Δ gaps in layered copper and silver complexes are not necessarily associated with the Jahn−Teller effect as was suggested by Pickett.[2] Obviously, this effect is much reduced in cubic lattices where the tetragonal distortion of the complex induces a weak quadrupolar field.

Further work on the influence of internal electric fields on electronic and structural properties of oxide and halide compounds involving Cu^{2+}, Ag^{2+}, and Mn^{3+} cations is now under way.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Bednorz, J. G.; Müller, K. A. Possible High T_c Superconductivity in the Ba−La−Cu−O System. *Z. Phys. B* **1986**, *64*, 189−193.

(2) Pickett, W. E. Electronic Structure of the High-Temperature Oxide Superconductors. *Rev. Mod. Phys.* **1989**, *61*, 433−512.

(3) Tretyakov, Y. D.; Goodilin, E. A. Fundamental Chemical Features of Complex Manganites and Cuprates for Advanced Functional Materials Engineering Pure. *Appl. Chem.* **2004**, *76*, 1749−1768.

(4) Keller, H.; Bussmann-Holder, A.; Müller, K. A. Jahn−Teller Physics and High-Tc Superconductivity. *Mater. Today* **2008**, *11*, 38−46.

(5) Moretti Sala, M.; Bisogni, V.; Aruta, C.; Balestrino, G.; Berger, H.; Brookes, N. B.; de Luca, G. M.; Di Castro, D.; Grioni, M.; Guarise, M.; et al. Energy and Symmetry of dd Excitations in Undoped Layered Cuprates Measured by Cu $L3$ Resonant Inelastic X-ray Scattering. *New J. Phys.* **2011**, *13*, 043026/1−043026/22.

(6) Ohta, Y.; Tohyama, T.; Maekawa, S. Apex Oxygen and Critical Temperature in Copper Oxide Superconductors: Universal Correlation with the Stability of Local Singlets. *Phys. Rev. B* **1991**, *43*, 2968−2982.

(7) Sakakibara, H.; Usui, H.; Kuroki, K.; Arita, R.; Aoki, H. Two-Orbital Model Explains the Higher Transition Temperature of the Single-Layer Hg-Cuprate Superconductor Compared to That of the La-Cuprate Superconductor. *Phys. Rev. Lett.* **2010**, *105*, 057003/1−057003/4.

(8) Sakakibara, H.; Usui, H.; Kuroki, K.; Arita, R.; Aoki, H. Origin of the Material Dependence of Tc in the Single-Layered Cuprates. *Phys. Rev. B* **2012**, *85*, 064501.

(9) Hozoi, L.; Siurakshina, L.; Fulde, P.; van den Brink, J. Ab Initio Determination of Cu 3d Orbital Energies in Layered Copper Oxides. *Nat. Sci. Rep.* **2011**, *1*, 65−69.

(10) Weber, C.; Haule, H.; Kotliar, G. Apical Oxygens and Correlation Strength in Electron- and Hole-Doped Copper Oxides. *Phys. Rev. B* **2010**, *82*, 125107/1−125107/24.

(11) Abakumov, A. M.; Rozova, M. G.; Ardashnikova, E. I.; Antipov, E. V. High-Temperature Superconductors Based on Complex Layered Copper Oxyfluorides. *Russ. Chem. Rev.* **2002**, *71*, 383−399.

(12) Tsujimoto, Y.; Yamaura, K.; Takayama-Muromachi, E. Oxyfluoride Chemistry of Layered Perovskite Compounds. *Appl. Sci.* **2012**, *2*, 206−219.

(13) Grochala, W. The Theory-Driven Quest for a Novel Family of Superconductors: Fluorides. *J. Mater. Chem.* **2009**, *19*, 6949−6968.

(14) McLain, S. E.; Dolgos, M. R.; Tennant, D. A.; Turner, J. F. C.; Barnes, T.; Proffen, T.; Sales, B. C.; Bewley, R. I. Magnetic Behaviour of Layered Ag(II) Fluorides. *Nat. Mater.* **2006**, *5*, 561−566.

(15) Riley, M. J.; Dubicki, L.; Moran, G.; Krausz, E. R.; Yamada, I. Optical Spectrum of K_2CuF_4. *Inorg. Chem.* **1990**, *29*, 1614−1626.

(16) Riley, M. J.; Dubicki, L.; Moran, G.; Krausz, E. R. Absorption and Magnetic Circular Dichroism Spectra of the Compressed Copper (II) Ion in K_2ZnF_4. *Chem. Phys.* **1990**, *14*, 363−373.

(17) Dubicki, L.; Riley, M. J.; Krausz, E. R. Electronic Structure of the Copper(II) Ion Doped in Cubic $KZnF_3$. *J. Chem. Phys.* **1994**, *101*, 1930−1939.

(18) Deisenhofer, J.; Leonov, I.; Eremin, M. V.; Kant, Ch.; Ghigna, P.; Mayr, F.; Iglamov, V. V.; Anisimov, V. I.; van der Marel, D. Optical Evidence for Symmetry Changes above the Néel Temperature of $KCuF_3$. *Phys. Rev. Lett.* **2008**, *101*, 157406/1−157406/4.

(19) Reinen, D.; Krause, S. Local and Cooperative Jahn−Teller Interactions of Copper(2+) in Host Lattices with Tetragonally Compressed Octahedra. Spectroscopic and Structural Investigation of the Mixed Crystals $K(Rb)_2Zn_{1-x}Cu_xF_4$. *Inorg. Chem.* **1981**, *20*, 2750−2759.

(20) de Graaf, C.; Broer, R. Midinfrared Spectrum of Undoped Cuprates: d−d Transitions Studied by Ab Initio Methods. *Phys. Rev. B* **2000**, *62*, 702−709.

(21) Deeth, R. J.; Anastasi, A.; Diedrich, C.; Randell, K. Molecular Modelling for Transition Metal Complexes: Dealing with d-Electron Effects. *Coord. Chem. Rev.* **2009**, *253*, 795−816.

(22) Riley, M. Geometric and Electronic Information from the Spectroscopy of Six-Coordinate Copper(II) Compounds. *Top. Curr. Chem.* **2001**, *214*, 57−80.

(23) Babel, D.; Tressaud, A. In *Inorganic Solid Fluorides*; Hagenmuller, P., Ed.; Academic Press: New York, 1985; pp 77−20.

(24) Buttner, R. H.; Maslen, E. N.; Spadaccini, N. Structure, Electron Density and Thermal Motion of $KCuF_3$. *Acta Crystallogr., Sect. B* **1990**, *46*, 131−138.

(25) Liang, C. T.; Schotte, K. D. Structural Changes and Jahn−Teller-Effect of K_2CuF_4 under Pressure. *J. Phys. Jpn.* **2005**, *74*, 3221−3226.

(26) Herdtweck, E.; Babel, D. Verfeinerung der Kristallstrukturen von K_2ZnF_4 und $K_3Zn_2F_7$. *Z. Kristallogr.* **1980**, *153*, 189−199.

(27) *CRYSTAL basis sets*. http://www.crystal.unito.it/Basis_Sets/Ptable.html (2013).

(28) Peintinger, M. F.; Vilela Oliveira, D.; Bredow, T. Consistent Gaussian Basis Sets of Triple-Zeta Valence with Polarization Quality for Solid-State Calculations. *J. Comput. Chem.* **2013**, *34*, 451−459.

(29) Bredow, T.; Gerson, A. Effect of Exchange and Correlation on Bulk Properties of MgO, NiO and CoO. *Phys. Rev. B* **2000**, *61*, 5194−5201.

(30) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; van Gisbergen, S. J. A.; Snijders, J. D.; Ziegler, T. Chemistry with ADF. *J. Comput. Chem.* **2001**, *22*, 931−967.

(31) Aramburu, J. A.; García-Lastra, J. M.; García-Fernández, P.; Barriuso, M. T.; Moreno, M. Cu^{2+} in Layered Compounds: Origin of the Compressed Geometry in the Model System $K_2ZnF_4:Cu^{2+}$. *Inorg. Chem.* **2013**, *52*, 6923−6933.

(32) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(33) Trueba, A.; García-Lastra, J. M.; Garcia-Fernandez, P.; Barriuso, M. T.; Aramburu, J. A.; Moreno, M. Cr^{3+}-Doped Fluorides and Oxides: Role of Internal Fields and Limitations of the Tanabe-Sugano Approach. *J. Phys. Chem. A* **2011**, *115*, 13399−13406.

(34) Garcia-Lastra, J. M.; Aramburu, J. A.; Barriuso, M. T.; Moreno, M. Optical Properties of Cr^{3+}-Doped Oxides: Different Behavior of Two Centers in Alexandrite. *Phys. Rev. B* **2006**, *74*, 115118/1−115118/5.

(35) Aramburu, J. A.; Garcia-Fernandez, P.; Garcia-Lastra, J. M.; Barriuso, M. T.; Moreno, M. Internal Electric Fields and Color Shift in Cr^{3+}-Based Gemstones. *Phys. Rev. B* **2012**, *85*, 245118/1−245118/10.

2389

dx.doi.org/10.1021/jz401227x | *J. Phys. Chem. Lett.* 2013, 4, 2385−2390

(36) Hozoi, L.; Gretarsson, H.; Clancy, J. P.; Jeon, B.-G.; Lee, B.; Kim, K. H.; Yushankhai, V.; Fulde, P.; Kim, Y.-J.; van den Brink, J. Topological States in Pyrochlore Iridates: Long-Range Anisotropy Strongly Competing with Spin-Orbit Interaction. *arXiv:1212*, p 4009.

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dx.doi.org/10.1021/jz401227x | *J. Phys. Chem. Lett.* 2013, 4, 2385−2390