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# Red Shift in Optical Excitations on Layered Copper Perovskites under Pressure: Role of the Orthorhombic Instability

David Carrasco-Busturia,<sup>\*,[a]</sup> Inés Sánchez-Movellán,<sup>\*,[b]</sup> Alexander Sougaard Tygesen,<sup>[a]</sup> Arghya Bhowmik,<sup>[a]</sup> Juan María García-Lastra,<sup>[a]</sup> José Antonio Aramburu,<sup>[b]</sup> and Miguel Moreno<sup>[b]</sup>

**Abstract:** The red shift under pressure in optical transitions of layered compounds with  $\text{CuCl}_6^{4-}$  units is explored through first-principles calculations and the analysis of available experimental data. The results on  $\text{Cu}^{2+}$ -doped  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4$ , that is taken as a guide, show the existence of a highly anisotropic response to pressure related to a structural instability, driven by a negative force constant, that leads to an orthorhombic geometry of  $\text{CuCl}_6^{4-}$  units but with a hole displaying a dominant  $3z^2-r^2$  character ( $z$  being the direction perpendicular to the layer plane). As a result of such an instability, a pressure of only 3 GPa reduces by 0.21 Å the longest  $\text{Cu}^{2+}\text{-Cl}^-$  distance, lying in the layer plane, while leaving unmodified the two other metal-ligand distances. Owing to this fact, it is shown that the lowest  $d-d$  transition

would experience a red shift of 0.34 eV while the first allowed charge transfer transition is also found to be red shifted but only by 0.11 eV that reasonably concurs with the experimental value. The parallel study on Jahn-Teller systems  $\text{CdCl}_2\text{:Cu}^{2+}$  and  $\text{NaCl}\text{:Cu}^{2+}$  involving tetragonal elongated  $\text{CuCl}_6^{4-}$  units shows that the reduction of the long axis by a pressure of 3 GPa is three times smaller than that for the layered  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  compound. Accordingly, the optical transitions of such systems, which involve a positive force constant, are much less sensitive to pressure than in layered compounds. The origin of the red shift under pressure undergone by the lowest  $d-d$  and charge transfer transitions of  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  is discussed in detail.

## Introduction

Significant efforts are currently devoted to exploring insulating layered perovskites due to their important role in the realm of light-emitting and photovoltaic devices.<sup>[1–3]</sup> In this field particular attention is paid to organic-inorganic hybrid perovskites such as those belonging to the  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$ <sup>[4–7]</sup> or  $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CuX}_4$  ( $\text{X}=\text{Cl}, \text{Br}$ )<sup>[8–10]</sup> families containing  $\text{CuX}_6^{4-}$  units, as they give rise to light absorption in the V-UV domain.

Interestingly, in layered materials with  $\text{CuCl}_6^{4-}$  units particular optical transitions can experience a red rather than a blue shift upon pressure,<sup>[11–13]</sup> an experimental fact that is in principle

surprising. Indeed, if electrons are confined in an empty cubic box of side  $L$  an applied pressure enhances the energy of optical transitions as the gap between energy levels depends on  $L^{-2}$ . Similarly, in *octahedral* complexes of 3d cations the  $t_{2g}$ – $e_g$  energy gap, usually termed 10Dq, rises when the metal-ligand distance,  $R$ , is reduced by pressure as 10Dq depends on  $R^{-n}$  with the exponent  $n$  lying typically in the 4–6 range.<sup>[14–18]</sup> Along this line, in octahedral  $\text{MX}_6^{4-}$  units ( $\text{X}=\text{Cl}, \text{Br}$ ;  $\text{M}=\text{divalent 3d cation}$ ) formed inside  $\text{LiCl}\text{:M}^{2+}$  and  $\text{LiBr}\text{:M}^{2+}$  all observed charge transfer (CT) transitions are blue-shifted on passing from  $T=300\text{ K}$  to  $T=77\text{ K}$ .<sup>[19,20]</sup> As the temperature reduction gives rise to a lessening of the metal-ligand distance,  $R$ , this fact strongly suggests that charge transfer transitions due to cations like  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  or  $\text{V}^{2+}$  in cubic  $\text{LiCl}$  and  $\text{LiBr}$  lattices move to higher energies when the metal-ligand distance is shortened.<sup>[21]</sup> This behavior is also confirmed by looking at CT transitions of compounds containing square-planar  $\text{CuCl}_4^{2-}$  complexes where all ligands are equivalent and placed at the same distance,  $R$ , from the central cation.<sup>[22–24]</sup> One example of this is the blue shift<sup>[23,24]</sup> when passing from  $(\text{N-mph})_2\text{CuCl}_4$  ( $\text{N-mph}=\text{methylphenethylammonium}$ ) ( $R=2.265\text{ Å}$ ) to  $(\text{creat})_2\text{CuCl}_4$  ( $\text{creat}=\text{creatinium}=\text{C}_4\text{H}_8\text{N}_3\text{O}^+$ ) ( $R=2.250\text{ Å}$ ). The different chemical pressure exerted by the rest of the lattice upon  $\text{CuCl}_4^{2-}$  units in each compound unit leads to a 0.015 Å shorter  $R$  in  $(\text{creat})_2\text{CuCl}_4$  than  $(\text{N-mph})_2\text{CuCl}_4$  and concomitantly to 0.1 eV blue shift in the latter with respect to the former, a fact

[a] Dr. D. Carrasco-Busturia, Dr. A. S. Tygesen, Dr. A. Bhowmik, Prof. J. M. García-Lastra  
Department of Energy Conversion and Storage  
Technical University of Denmark  
Anker Engélunds Vej, Building 301, 2800 Kgs. Lyngby (Denmark)  
E-mail: dcabu@dtu.dk

[b] I. Sánchez-Movellán, Prof. J. A. Aramburu, Prof. M. Moreno  
Departamento de Ciencias de la Tierra y Física de la Materia Condensada  
Universidad de Cantabria  
Avenida de los Castros s/n, 39005 Santander (Spain)  
E-mail: ines.sanchez@unican.es

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that is also reasonably reproduced by theoretical calculations.<sup>[25,21]</sup>

Bearing these facts in mind, the existence of a pressure-induced red shift in some optical transitions of layered compounds with  $\text{CuCl}_6^{4-}$  units could arise from the non-equivalence of six involved ligands. Indeed, in all the explored compounds the  $\text{CuCl}_6^{4-}$  complex never exhibits an octahedral symmetry.<sup>[4–7,11–13,26]</sup>

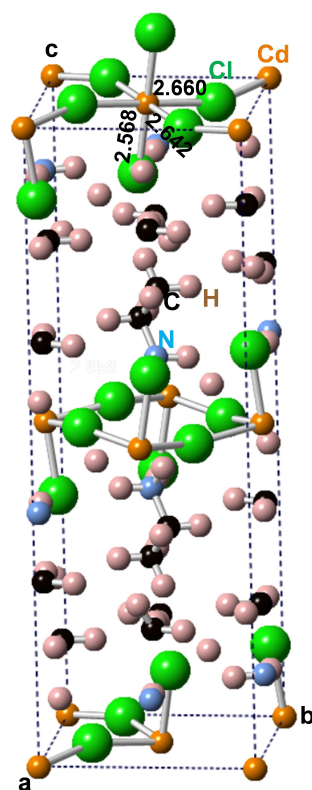
In the realm of layered materials with  $\text{CuCl}_6^{4-}$  units the lack of octahedral symmetry around  $\text{Cu}^{2+}$  has widely been ascribed to the static Jahn-Teller (JT) effect.<sup>[5,6,11–13,26]</sup> However, the JT effect requires a degenerate electronic ground state in the initial undistorted geometry,<sup>[27,28]</sup> a non-fulfilled condition when the parent lattice in which the  $\text{CuCl}_6^{4-}$  units are embedded exhibits low symmetry (e.g., tetragonal or orthorhombic), as is the case for layered materials.

The local distortion around  $\text{Cu}^{2+}$  in layered compounds such as  $\text{K}_2\text{CuF}_4$  or  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  has recently been shown to involve mechanisms clearly different from the JT effect.<sup>[7]</sup> For instance,  $\text{K}_2\text{CuF}_4$  comes from an  $I4/mmm$  tetragonal parent phase, identical to that displayed by  $\text{K}_2\text{NiF}_4$  or  $\text{K}_2\text{ZnF}_4$ , where the  $\text{CuF}_6^{4-}$  unit is tetragonally *compressed* such as it happens for  $\text{K}_2\text{ZnF}_4:\text{Cu}^{2+}$ .<sup>[29–32]</sup> It is important to note that, in the tetragonal parent phase of  $\text{K}_2\text{CuF}_4$ , the ground state of the tetragonally *compressed*  $\text{CuF}_6^{4-}$  units is not orbitally degenerated, a fact that already excludes the existence of a JT instability.<sup>[27,28,32]</sup> However, the tetragonal parent phase has a local  $b_{1g}$  mode with imaginary frequency (negative force constant  $K$ ), inducing<sup>[33]</sup> an orthorhombic *instability* in the layer planes of  $\text{K}_2\text{CuF}_4$ , also present in compounds like  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  or  $\text{Rb}_2\text{CuCl}_4$ ,<sup>[7]</sup> a singular situation not found in systems displaying a static JT effect such as  $\text{KZnF}_3:\text{Cu}^{2+}$ <sup>[34–36]</sup> or  $\text{NaCl}:\text{A}^{2+}$  ( $\text{A} = \text{Cu}, \text{Ag}, \text{Rh}$ ).<sup>[37–41]</sup> The existence of that orthorhombic symmetry around  $\text{Cu}^{2+}$  is well supported by electron paramagnetic resonance (EPR) data on  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ .<sup>[42,43]</sup> Negative  $K$  values behind structural instabilities reflect the changes on the ground state electronic density produced when interatomic distances are varied.<sup>[33,7]</sup>

The present work is devoted to exploring the existence of a red shift under pressure in some  $d-d$  or CT transitions of systems involving  $\text{CuCl}_6^{4-}$  complexes by means of first principles calculations and the analysis of available experimental data. It is particularly focused on the  $\text{Cu}^{2+}$ -doped  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4$  an orthorhombic compound<sup>[44]</sup> (Pcab space group), represented in Figure 1, which is taken as a guide for the  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4:\text{Cu}^{2+}$  family and similar layered compounds.

For the sake of clarity, an additional investigation is also carried out on  $\text{CdCl}_2:\text{Cu}^{2+}$  and  $\text{NaCl}:\text{Cu}^{2+}$ , which also involve  $\text{CuCl}_6^{4-}$  units but subject to a static JT effect.<sup>[37,45]</sup> Owing to this fact, in these JT compounds, the local symmetry around  $\text{Cu}^{2+}$  is tetragonal and not orthorhombic as encountered in layered systems with  $\text{CuCl}_6^{4-}$  complexes.

In the first step, the present study explores the equilibrium geometry of  $\text{CuCl}_6^{4-}$  units placed in different lattices. The second step deals with the structural changes induced by pressure, showing that in the range 0–3 GPa, only the longest axis,  $R_L$ , is reduced. Interestingly, this reduction is three times



**Figure 1.** Crystal structure of the layered  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4$  compound involving  $\text{CdCl}_6^{4-}$  complexes with a local orthorhombic symmetry. The three Cd-Cl distances (in Å) are also shown. Note that the smallest Cd-Cl distance corresponds to ligands placed in a direction perpendicular to the layer plane.

higher for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  than for JT systems as a result of the orthorhombic instability (see first and second subsections of Results and Discussion).

Once this key matter is clarified, we focus on the pressure shift experienced by the four  $d-d$  excitations (third subsection of Results and Discussion). It is shown that with an applied pressure up to 3 GPa the lowest  $d-d$  transition always experiences a red shift although it is much more pressure sensitive for layered compounds with  $\text{CuCl}_6^{4-}$  units than for  $\text{CdCl}_2:\text{Cu}^{2+}$ . Although the  $d-d$  transitions of a complex embedded in a lattice are influenced by the electrostatic field due to the rest of lattice ions,<sup>[46]</sup> this contribution plays a minor role in the case of organic-inorganic hybrid perovskites. Indeed, according to previous results<sup>[7]</sup> such a contribution would induce shifts around 0.1 eV on  $d-d$  transitions and thus pressure shifts essentially reflect structural changes in the  $\text{CuCl}_6^{4-}$  complex.

The last part of the present investigation (fourth subsection of Results and Discussion) deals with the pressure dependence of the charge-transfer transition measured<sup>[11]</sup> in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ . Although the calculations are consistent with a small red shift under pressure ( $dE_{\text{CT}}/dP = -0.038$  eV/GPa) it is also shown that they imply a tiny sensitivity of  $E_{\text{CT}}$  to variations of the long axis,  $R_L$ , when compared to the value  $dE_{\text{CT}}/dR = -9.5$  eV/Å found for compounds with square-planar  $\text{CuCl}_4^{2-}$  complexes.<sup>[25]</sup> The origin of this big difference is analyzed in some detail.

This work is organized as follows. The tools employed for carrying out the calculations are exposed in Computational Tools section while main results on equilibrium geometries and optical transitions under pressure are discussed in Results and Discussion section. Some final remarks are provided in the last section.

## Computational Tools

First-principles DFT calculations have been carried out in order to analyze the influence of pressure on the structure and d-d and charge transfer optical transitions of the layered compound  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  and compare these results with those obtained for the JT systems  $\text{NaCl:Cu}^{2+}$  and  $\text{CdCl}_2\text{:Cu}^{2+}$ . Structural relaxations of periodic structures have been carried by means of periodic CRYSTAL17<sup>[47,48]</sup> and VASP<sup>[49,50]</sup> codes, while d-d transitions of  $\text{CuCl}_6^{4-}$  units were calculated using the Amsterdam Density Functional (ADF)<sup>[51]</sup> molecular code.

On one hand, geometry optimizations at ambient pressure and under 3 GPa of pure and  $\text{Cu}^{2+}$ -doped NaCl and  $\text{CdCl}_2$  systems were carried out by means of CRYSTAL17, where the Bloch functions of the periodic systems are expanded as linear combinations of atom centred Gaussian functions.<sup>[52–54]</sup> The use of localized basis sets together with the full exploitation of symmetry in this code make it especially efficient for the calculation of the large supercells considered in these two inorganic systems, a primitive  $3\times 3\times 3$  supercell with 128 ions for  $\text{NaCl:Cu}^{2+}$  and a conventional  $3\times 3\times 1$  supercell with 81 ions for  $\text{CdCl}_2\text{:Cu}^{2+}$ . The one-parameter B1WC and PW1PW hybrid exchange-correlation functionals (involving, respectively, 16% and 20% of Hartree-Fock exchange) have been used because they have provided reliable results for geometry and properties of insulating compounds containing transition metal ions.<sup>[55]</sup> In both systems, we have optimized the geometry of the pure compound at ambient pressure, obtaining lattice parameters and metal-ligand distances that matches the experimental ones within 1% of error. Then, a supercell is built up and one of the cations is replaced by  $\text{Cu}^{2+}$ . Finally, the atomic positions are reoptimized in order to reproduce the distortion, keeping fixed the lattice parameters. The procedure is the same for calculations under 3 GPa of pressure.

Concerning organic-inorganic hybrid perovskites (where weak long-range van der Waals interactions are important), our previous experience<sup>[7]</sup> with CRYSTAL17 indicates that the errors in the full optimized geometries (both, lattice parameters and atomic positions) are much greater (around 6% but can be up to 10%), even using empirical van der Waals corrections, that in the case of inorganic materials. For this reason, many works show limited geometry optimizations of the atomic positions fixing the lattice parameters at the experimental values (if they are known), where the errors are minimized.<sup>[7]</sup> However, this procedure is not possible for the present study of the optical transitions at different pressures of pure and  $\text{Cu}^{2+}$ -doped  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4$ , where the experimental geometries under pressure are unknown. Owing this relevant fact, geometry optimizations of these systems at different pressures were

carried out by means of VASP,<sup>[49,50]</sup> where the Bloch functions of the periodic systems expand into plane waves,<sup>[56]</sup> more appropriate than using localized bases in the case of organic-inorganic hybrid systems. A geometry optimization of the lattice parameters and atomic positions is performed at zero pressure with the HSE01 functional.<sup>[57]</sup> The atomic positions are relaxed until the forces per atom converge to less than  $0.02\text{ eV}\text{\AA}^{-1}$  using the conjugate gradient algorithm.<sup>[58]</sup> The Brillouin zone is sampled using a  $3\times 3\times 1$  Monkhorst-Pack k-point mesh.<sup>[59]</sup> The valence electrons are described by a plane-wave basis set with a 520 eV energy cutoff. Twelve, seven, five, four and one valence electrons are included, respectively, for Cd, Cl, N, C and H. For Cu substitution, 12 valence electrons were used. The core electrons are described by the projector augmented wave method,<sup>[56]</sup> combined with pseudopotentials.<sup>[60]</sup> The damped velocity friction electronic minimization algorithm is employed where the break condition for the electronic self-consistent loop is set to  $10^{-5}\text{ eV}$ . The atomic positions and lattice parameters of the zero-pressure optimized structure are then relaxed at external pressures of 1, 2 and 3 GPa by relaxing both the atomic positions and lattice parameters accordingly. The structures of  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  at different pressures are generated by substitution of only one Cd ion by one Cu ion in the lattice cell (Figure 1) followed by an atomic relaxation only (i.e., keeping the lattice vectors frozen at the values obtained for the pristine lattice). Accordingly, the smallest distance between two close  $\text{Cu}^{2+}$  ions in the supercell where calculations are carried out amounts to 7.4 Å.

Regarding the optical transitions, we used two approaches. For the ligand to metal charge transfer transitions, where the electron-hole interaction is weak, we have used a simple frequency-dependent dielectric matrix approximation method, as implemented in VASP by Gajdoš et al.<sup>[61]</sup> The details of both the structural and optical simulations in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  are discussed below. Instead, the d-d transitions show large electron-hole interactions; thus, calculating them accurately with a periodic code requires expensive techniques such as the BSE approximation,<sup>[62]</sup> something that is intractable in the case of the large supercells considered in this work. Hence, we calculated the d-d transitions using the SCF technique with a  $\text{CuCl}_6^{4-}$  cluster model, employing the ADF molecular code that uses Slater-type orbitals (STOs) as basis set functions.<sup>[63]</sup> Hybrid B3LYP functional, which includes 25% of HF exchange, together with high quality triple- $\zeta$  polarized basis set have been used in all calculations, where core electrons were kept frozen. These calculations were carried out in isolated complexes because, in contrast to systems like ruby<sup>[64,46]</sup> or the Egyptian-blue pigment<sup>[65]</sup> where the effect of the internal electric field due to the rest of lattice ions is relevant, it only induces minor variations of around 0.1 eV in these organic-inorganic compounds. On the other hand, in NaCl and  $\text{CdCl}_2$  the electrostatic potential of the rest of lattice ions is fairly flat and therefore it has not significant effects on the results. With these calculations we have studied the variation of the HOMO wavefunction related to the structural changes when going from ambient pressure to 3 GPa. In addition, we have explored the variation of the optical spectra with pressure for these systems, paying

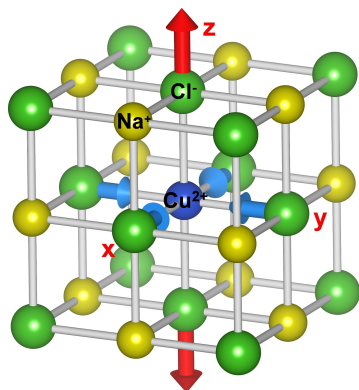
special attention to the red shift that the first d-d transition undergoes.

## Results and Discussion

### Equilibrium geometry for Jahn-Teller systems with $\text{CuCl}_6^{4-}$ units under pressure

EPR measurements carried out at 77 K on the cubic NaCl compound doped with  $\text{Cu}^{2+}$  shows the formation of tetragonal  $\text{CuCl}_6^{4-}$  complexes, whose main axis is one of the three  $C_4$  axis of the host lattice<sup>[37]</sup> (Figure 2). Accordingly, three different centers, though physically equivalent, are observed simultaneously for a general orientation of the applied magnetic field. This behavior is just the fingerprint of a static JT effect<sup>[27,28,66]</sup> also found for other impurities ( $\text{Ag}^{2+}$ ,  $\text{Rh}^{2+}$ ) in NaCl<sup>[38–41]</sup> or in  $\text{Cu}^{2+}$ -doped cubic perovskites<sup>[34,35,67]</sup> like  $\text{KZnF}_3$ . A similar situation holds<sup>[45]</sup> for  $\text{CdCl}_2\cdot\text{Cu}^{2+}$  where a trigonal host lattice still keeps a degenerate electronic ground state that makes possible the development of a static JT effect.<sup>[28,68]</sup>

The experimental g-tensor at 77 K for NaCl: $\text{Cu}^{2+}$  ( $g_{\parallel}=2.373$ ,  $g_{\perp}=2.070$ )<sup>[37]</sup> clearly proves that the ligand octahedron is *elongated* and thus the unpaired electron is placed in a  $|x^2-y^2\rangle$  molecular orbital of the  $\text{CuCl}_6^{4-}$  unit, transforming like  $x^2-y^2$ , for the center whose main axis is parallel to Z (Figure 2).<sup>[17,27,66]</sup> Above 100 K the EPR spectrum is isotropic with  $g=(2g_{\perp}+g_{\parallel})/3$  as a result of incoherent hopping among the three equivalent distortions.<sup>[37]</sup> An elongated geometry is also encountered for



**Figure 2.** Structure of NaCl: $\text{Cu}^{2+}$  displaying the local tetragonal JT distortion in a  $\text{CuCl}_6^{4-}$  complex of the lattice. The deformation corresponds to an elongated octahedron with z as main axis.

**Table 1.** Values of equilibrium axial,  $R_{\text{ax}}$ , and equatorial,  $R_{\text{eq}}$ ,  $\text{Cu}^{2+}\text{-Cl}^-$  distances calculated, at zero pressure, for  $\text{Cu}^{2+}$  impurities in  $\text{CdCl}_2$  and NaCl where a static Jahn-Teller effect takes place.  $R_0$  is the cation-anion distance for the host lattice while the average  $\text{Cu}^{2+}\text{-Cl}^-$  distance is given by  $R_{\text{av}}=(R_{\text{ax}}+2R_{\text{eq}})/3$ .  $\Delta R_{\text{L5}}$  just means the difference between the longest and smallest  $\text{Cu}^{2+}\text{-Cl}^-$  distance. All distances are given in Å units.

System	$R_0$	$R_{\text{ax}}$	$R_{\text{eq}}$	$R_{\text{av}}$	$\Delta R_{\text{L5}}$
NaCl: $\text{Cu}^{2+}$	2.82	2.720	2.382	2.494	0.338
$\text{CdCl}_2\cdot\text{Cu}^{2+}$	2.65	2.668	2.327	2.440	0.341

**Table 2.** Calculated variations of axial,  $\delta R_{\text{ax}}$ , and equatorial,  $\delta R_{\text{eq}}$ ,  $\text{Cu}^{2+}\text{-Cl}^-$  distances due to an applied pressure of 3 GPa in both  $\text{CdCl}_2\cdot\text{Cu}^{2+}$  and NaCl: $\text{Cu}^{2+}$  systems. The corresponding changes undergone by  $R_{\text{av}}$  and  $\delta(\Delta R_{\text{L5}})$  are also shown. All distances are given in Å units.

System	$\delta R_{\text{ax}}$	$\delta R_{\text{eq}}$	$\delta R_{\text{av}}$	$\delta(\Delta R_{\text{L5}})$
NaCl: $\text{Cu}^{2+}$	-0.084	-0.005	-0.031	-0.079
$\text{CdCl}_2\cdot\text{Cu}^{2+}$	-0.068	-0.005	-0.026	-0.063

$\text{CdCl}_2\cdot\text{Cu}^{2+}$ <sup>[45]</sup> and a good number of JT systems<sup>[66]</sup> with the known exception of  $\text{CaO:Ni}^{2+}$  which is compressed.<sup>[69,70]</sup>

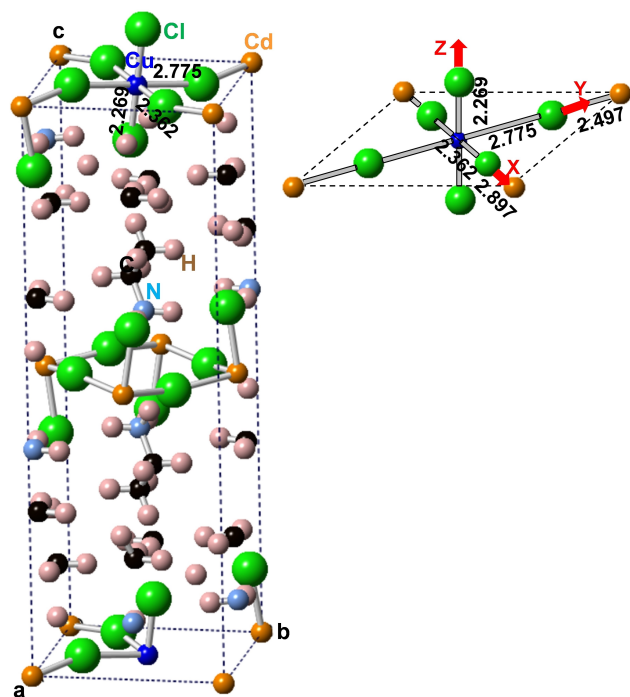
The calculated equilibrium axial,  $R_{\text{ax}}$ , and equatorial,  $R_{\text{eq}}$ , metal-ligand distances at zero pressure for both NaCl: $\text{Cu}^{2+}$  and  $\text{CdCl}_2\cdot\text{Cu}^{2+}$  are given in Table 1. Both sets are rather close although the average distance,  $R_{\text{av}}$ , is smaller for  $\text{Cu}^{2+}$  in  $\text{CdCl}_2$  than in NaCl a fact consistent with the cation-anion distance,  $R_0$ , of the host lattices (Table 1). In both cases the calculated  $R_{\text{av}}$  value is well below  $R_0$  in accord with the smaller ionic radius<sup>[71]</sup> of  $\text{Cu}^{2+}$  compared to that for  $\text{Na}^+$  or  $\text{Cd}^{2+}$ .

Interestingly, when a hydrostatic pressure up to 3 GPa is applied, the short  $\text{Cu}^{2+}\text{-Cl}^-$  distance,  $R_{\text{eq}}$ , is reduced by only 0.005 Å while  $R_{\text{ax}}$  decreases by an order of magnitude higher (Table 2). This fact just reflects that the force constant,  $2K_{\text{ax}}$ , for moving the *two distant* axial ligands is smaller than that for the four equatorial ones,  $4K_{\text{eq}}$ . Supporting this view, we have calculated for NaCl: $\text{Cu}^{2+}$  the values  $K_{\text{ax}}=2.85\text{ eV/Å}^2$  and  $K_{\text{eq}}=6.8\text{ eV/Å}^2$ . This result just reflects that due to the anharmonicity present in any molecular vibration, the force constant of a bond tends to decrease when its length increases. As  $R_{\text{av}}$  is clearly smaller than  $R_0$  for both JT systems (Table 1), then the *local* bulk modulus,  $B_L$ , can be very different from that for the pure host lattice. Indeed, from data given in Tables 1 and 2, we derive  $B_L=97\text{ GPa}$  for NaCl: $\text{Cu}^{2+}$  and  $B_L=117\text{ GPa}$  for  $\text{CdCl}_2\cdot\text{Cu}^{2+}$ . These values can be compared with the experimental ones,  $B=24\text{ GPa}$  and  $B=42\text{ GPa}$  measured for pure NaCl and  $\text{CdCl}_2$ , respectively.

### Equilibrium geometry for $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\cdot\text{Cu}^{2+}$ under pressure

Such as it is shown in Figures 1 and 3, the equilibrium geometry of  $\text{CuCl}_6^{4-}$  units in layered lattices is not tetragonal but orthorhombic with the longest axis being located in the layer plane. This general pattern is found in pure compounds of the  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$  family<sup>[4–7,26,72]</sup> and also in doped systems like  $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4\cdot\text{Cu}^{2+}$  where EPR data and first principles calculations are consistent with that view.<sup>[42,43,7]</sup>

As some optical data on  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\cdot\text{Cu}^{2+}$  under pressure have been reported<sup>[11]</sup> we have paid attention to explore in a first step the local equilibrium geometry of  $\text{CuCl}_6^{4-}$  units in that system. Results varying the applied pressure in the range 0–3 GPa are collected on Table 3. At zero pressure such results show that  $\text{CuCl}_6^{4-}$  units actually display a local orthorhombic symmetry with the longest axis lying in the layer plane and thus it can be along either the X or the Y direction.



**Figure 3.** Left: unit cell of  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4$  with a  $\text{Cu}^{2+}$  impurity replacing  $\text{Cd}^{2+}$ . Metal-ligand distances (in Å) corresponding to the  $\text{CuCl}_6^{4-}$  unit are shown. Right: the  $\text{CuCl}_6$  complex with local axes  $x$ ,  $y$  and  $z$  in red and showing the nearest  $\text{Cd}^{2+}$  ions. The Cu-Cl and Cl-Cd distances are given in Å.

**Table 3.** Lattice parameters and  $\text{Cu}^{2+}\text{-Cl}^-$  distances (all in Å units) calculated for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  as a function of the applied pressure  $P$  (in GPa units) in the 0–3 GPa range. For comparison, the distance between a long  $\text{Cl}^-$  ligand placed at the  $Y$  axis and a nearest  $\text{Cd}^{2+}$  ion is also given. The value of the volume cell,  $V$  (in Å<sup>3</sup> units) for each pressure is also reported.

$P$	$a$	$b$	$c$	$V$	$R_x$	$R_y$	$R_z$	Cl(Y)-Cd
0	7.277	7.408	11.201	603.9	2.362	2.775	2.269	2.497
1	7.201	7.330	10.870	573.7	2.367	2.699	2.267	2.496
2	7.063	7.233	10.756	549.5	2.359	2.613	2.269	2.495
3	6.980	7.179	10.640	533.2	2.353	2.564	2.264	2.494

Only for describing the equilibrium geometry we assign the  $Y$  direction as being the longest axis

Interestingly, the difference between the longest and smallest  $\text{Cu}^{2+}\text{-Cl}^-$  distance,  $\Delta R_{\text{LS}}$ , found for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  is equal to 0.51 Å and thus already 50% higher than that derived for the JT systems  $\text{NaCl}\text{:Cu}^{2+}$  or  $\text{CdCl}_2\text{:Cu}^{2+}$  (Table 1).

For the sake of clarity, the local equilibrium geometry at zero pressure of some layered systems with  $\text{CuCl}_6^{4-}$  units are gathered in Table 4. It can be noticed that  $\Delta R_{\text{LS}}$  increases significantly on passing from doped to pure compounds where  $\Delta R_{\text{LS}}$  and  $R_y$  can reach a value up to 0.80 Å and 3.10 Å, respectively. This relevant behavior has been shown to reflect a cooperative mechanism between adjacent complexes sharing a common ligand that only takes place in pure layered compounds.<sup>[7]</sup> Due to this reason the value of  $\Delta R_{\text{LS}}$  in these systems can be more than twice higher than 0.34 Å found for the JT systems (Tables 1 and 4).

**Table 4.** Equilibrium  $\text{Cu}^{2+}\text{-Cl}^-$  distances (all in Å units) at ambient pressure determined for doped and pure layered perovskites. The difference  $\Delta R_{\text{LS}}$  between the longest and smallest  $\text{Cu}^{2+}\text{-Cl}^-$  distance together with the value of the average metal-ligand distance,  $R_{\text{av}}$ , are also reported. Distances for pure layered compounds have all been obtained experimentally by X-ray diffraction while those for  $\text{ACdCl}_4\text{:Cu}^{2+}$  ( $A = (\text{CH}_3\text{NH}_3)_2, (\text{C}_2\text{H}_5\text{NH}_3)_2$ ) have been derived through first principles calculations.

System	$R_x$	$R_y$	$R_z$	$R_{\text{av}}$	$\Delta R_{\text{LS}}$	Ref.
$(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$	2.441	2.690	2.279	2.470	0.411	[7]
$(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$	2.362	2.775	2.269	2.469	0.506	This work
$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$	2.283	2.907	2.297	2.496	0.610	[26]
$(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$	2.285	2.975	2.277	2.512	0.698	[4]
$(\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4$	2.29	3.04	2.29	2.54	0.75	[72]
EDBE $\text{CuCl}_4$	2.306	3.101	2.306	2.57	0.795	[12,13]

The results on layered systems (Table 4) show that  $R_y$  varies in the 2.70 Å–3.10 Å range,  $R_x$  in the 2.28 Å–2.44 Å range, while  $R_z$  appears in a short domain (2.27 Å–2.31 Å). These relevant facts suggest that the  $\text{Cu}^{2+}\text{-Cl}^-$  bond along the longest  $Y$  axis is much softer than those along  $Z$  or  $X$  directions. This idea is strongly underpinned looking at the influence of pressure upon the three metal-ligand distances  $R_x$ ,  $R_y$  and  $R_z$  of  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  (Table 3). Indeed, a pressure of only 3 GPa reduces the value of  $R_y$  by 0.21 Å while  $R_x$  and  $R_z$  remain constant within 0.01 Å.

Along this line, it is worth noting that in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  the  $\text{Cl}_Y^- \text{-Cd}^{2+}$  distance between a  $\text{Cl}_Y^-$  ligand in the  $Y$  axis and a neighbor  $\text{Cd}^{2+}$  (Figure 3) is essentially constant when pressure increases up to 3 GPa (Table 3). At zero pressure the  $\text{Cl}_Y^- \text{-Cd}^{2+}$  distance has a value equal to 2.497 Å clearly smaller than 2.65 Å for pure  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4$ <sup>[44]</sup> thus reflecting the expansion of the  $\text{Cu}^{2+}\text{-Cl}_Y^-$  bond and the corresponding compression of the  $\text{Cl}_Y^- \text{-Cd}^{2+}$  bond in the doped compound. When pressure increases from  $P=0$  to 3 GPa the  $\text{Cl}_Y^- \text{-Cd}^{2+}$  distance goes only from 2.497 Å to 2.494 Å (Table 3) while the  $\text{Cu}^{2+}\text{-Cl}_Y^-$  distance decreases by 0.21 Å. According to these results, a pressure of 3 GPa significantly reduces the  $\text{Cu}^{2+}\text{-Cl}_Y^-$  distance while leaving practically unmodified the distances between  $\text{Cl}_Y^-$  and the neighbor lattice ions. These facts strongly suggest that the force constant,  $K_y$ , for changing a  $\text{Cu}^{2+}\text{-Cl}_Y^-$  distance but keeping constant the distances between  $\text{Cl}_Y^-$  and the neighbor lattice ions must be particularly small. From the present calculations, we obtain a value  $K_y = 1.1 \text{ eV/Å}^2$  which is about one-third the value  $K_{\text{ax}} = 2.85 \text{ eV/Å}^2$  found for moving an axial ligand in the JT system  $\text{NaCl}\text{:Cu}^{2+}$ .

Related to this fact a hydrostatic pressure of 3 GPa leads to a much higher lessening of the longest axis in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  than in a JT system like  $\text{CdCl}_2\text{:Cu}^{2+}$ . Indeed, in this case the pressure-induced reduction  $\delta R_{\text{ax}} = -0.068 \text{ Å}$  (Table 2) is three times smaller than  $\delta R_y = -0.21 \text{ Å}$  derived for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  (Table 3). This fact already underlines that the equilibrium geometry in the latter case obeys a mechanism different from the JT effect.<sup>[7]</sup> Along this line, the results in Table 3 for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$  lead to a local bulk modulus  $B_L = 36.8 \text{ GPa}$  that is about three times smaller than  $B_L = 117 \text{ GPa}$  derived for  $\text{CdCl}_2\text{:Cu}^{2+}$ .

The local equilibrium geometry of  $\text{CuCl}_6^{4-}$  units in layered compounds has been proved to arise from *compressed* tetragonal complexes with a main axis along the Z direction, perpendicular to the layer plane.<sup>[7]</sup> In addition, they undergo an orthorhombic *instability* in the layer plane, making that the longest axis is located in that plane, a situation also found for  $\text{K}_2\text{CuF}_4$ <sup>[73,71]</sup> or in Tutton salts with  $\text{Cu}^{2+}$ .<sup>[74]</sup> Interestingly, such instability is the result of a force constant that becomes *negative*,<sup>[33,75]</sup> and thus it can give rise to bigger distortions than for JT systems which exhibit a *positive* force constant.<sup>[7,76]</sup>

In the case of  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  the mechanisms behind the equilibrium geometry are well reflected in the nature of the unpaired electron. Indeed, the HOMO wavefunction derived from the present calculations at zero pressure can shortly be written as

$$|\psi_{\text{H}}\rangle = 0.899|3z^2-r^2\rangle - 0.436|x^2-y^2\rangle \quad (1)$$

where  $|3z^2-r^2\rangle$  and  $|x^2-y^2\rangle$  are *molecular orbitals* of the  $\text{CuCl}_6^{4-}$  unit transforming like  $3z^2-r^2$  and  $x^2-y^2$ , respectively. Therefore, this wavefunction, compatible with the local orthorhombic symmetry, exhibits a dominant  $3z^2-r^2$  character (81%) consistent with an *original* geometry being tetragonally *compressed*. Such a character is also reflected in the experimental g-tensor where  $g_{\text{ZZ}}$  is in the range 2.04–2.05 for layered perovskites containing  $\text{CuCl}_6^{4-}$  complexes.<sup>[77–79]</sup> Moreover, in doped systems like  $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  or  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$   $g_{\text{ZZ}}$  is temperature independent while  $g_{\text{XX}}$  and  $g_{\text{YY}}$  change drastically with temperature as a result of incoherent hopping between the two equivalent position for the long axis in the layer plane.<sup>[42,43,7]</sup> This fact underlines again the singular character of the Z direction in layered compounds. A similar behaviour takes place in  $\text{Cu}^{2+}$ -doped Tutton salts.<sup>[74]</sup>

It is worth noting now that if we write the HOMO wavefunction derived for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  in the  $\{|3y^2-r^2\rangle, |x^2-z^2\rangle\}$  instead of the  $\{|3z^2-r^2\rangle, |x^2-y^2\rangle\}$  basis,  $|\psi_{\text{H}}\rangle$  is given by

$$|\psi_{\text{H}}\rangle = 0.997|x^2-z^2\rangle + 0.07|3y^2-r^2\rangle \quad (2)$$

thus, stressing that the *electronic density* associated with the unpaired electron essentially resides in the XZ plane perpendicular to the longest Y axis. Accordingly,  $|\psi_{\text{H}}\rangle$  looks similar to the wavefunction expected for a hypothetical static JT effect involving an *elongated* tetragonal  $\text{CuCl}_6^{4-}$  unit with Y as main axis. This similarity has given rise to misinterpretations of results due to layered compounds containing  $\text{Cu}^{2+}$  or  $\text{Ag}^{2+}$  cations widely *assumed* to arise from a JT effect.<sup>[5,6,11–13,26,80–83]</sup> Indeed, in these low symmetry systems it is not easy to understand either the existence of a JT effect or a principal axis that is not the perpendicular to the layer plane. On the other hand, a reduction of the longest axis due to pressure does not modify the character of the HOMO wavefunction in a JT system, while it changes the hybridization between  $|3z^2-r^2\rangle$  and  $|x^2-y^2\rangle$  orbitals in a layered compound. For instance, under a pressure of 3 GPa, involving a reduction  $\delta R_{\text{Y}} = -0.21 \text{ \AA}$  in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ ,  $|\psi_{\text{H}}(3 \text{ GPa})\rangle$  is found to be equal to

$$|\psi_{\text{H}}(3 \text{ GPa})\rangle = 0.934|3z^2-r^2\rangle - 0.356|x^2-y^2\rangle = 0.987|x^2-z^2\rangle + 0.160|3y^2-r^2\rangle \quad (3)$$

that entails a higher amount of the  $|3y^2-r^2\rangle$  component than at zero pressure.

In conclusion, although the longest  $\text{Cu}^{2+}-\text{Cl}^-$  distance calculated at zero pressure in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  ( $R_{\text{Y}} = 2.775 \text{ \AA}$ ) and  $\text{NaCl}:\text{Cu}^{2+}$  ( $R_{\text{ax}} = 2.720 \text{ \AA}$ ) only differ by 2% the former system is much more sensitive to pressure than the latter one thus stressing the different origin behind the equilibrium geometry.<sup>[7]</sup> The implications of this fact on the optical spectra are discussed in the next sections.

### d-d transitions in JT and layered compounds with $\text{CuCl}_6^{4-}$ units: pressure effects

In the case of systems involving  $\text{CuCl}_6^{4-}$  units and displaying a static JT effect the optical spectrum has been measured<sup>[84]</sup> for  $\text{CdCl}_2:\text{Cu}^{2+}$  but not for  $\text{NaCl}:\text{Cu}^{2+}$ . The experimental values of *d-d* transition energies recorded at zero pressure for  $\text{CdCl}_2:\text{Cu}^{2+}$  are given in Table 5. As expected for an elongated  $\text{CuCl}_6^{4-}$  unit with a moderate tetragonal distortion the lowest transition corresponds to  $|3z^2-r^2\rangle \rightarrow |x^2-y^2\rangle$  reflecting the splitting,  $\Delta_{\text{e}}$ , of  $e_{\text{g}}$  orbitals in  $\text{O}_{\text{h}}$  symmetry due to the  $\text{O}_{\text{h}} \rightarrow \text{D}_{4\text{h}}$  symmetry descent. The two other transitions come from the  $t_{2\text{g}}$  orbitals in  $\text{O}_{\text{h}}$  symmetry partially split by the final tetragonal symmetry. This splitting,  $\Delta_{\text{t}} = 0.19 \text{ eV}$ , is clearly smaller than  $\Delta_{\text{e}} = 0.79 \text{ eV}$  for  $\text{CdCl}_2:\text{Cu}^{2+}$ , a fact consistent with the different kind of chemical bonding involved in  $e_{\text{g}}$  ( $\sigma$  bonding) and  $t_{2\text{g}}$  ( $\pi$  bonding) orbitals of a  $\text{CuCl}_6^{4-}$  complex.<sup>[85,21]</sup>

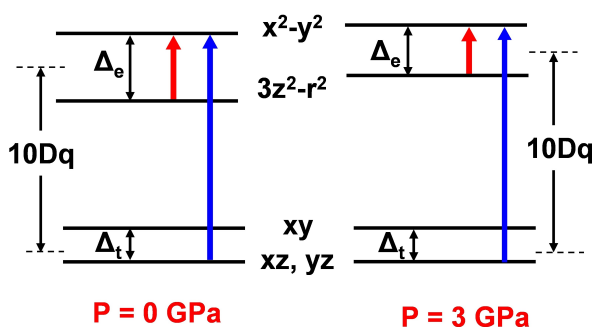
As shown in Table 5, the experimental *d-d* transitions of  $\text{CdCl}_2:\text{Cu}^{2+}$ , measured at ambient pressure, are reasonably reproduced by the present calculations using the equilibrium geometry previously derived for the  $\text{CuCl}_6^{4-}$  unit.

The changes on the calculated *d-d* transitions due to a pressure of 3 GPa are also gathered on Table 5. It can be remarked that while the two transitions coming from the splitting of  $t_{2\text{g}}$  levels are weakly blue shifted, the lowest one  $|3z^2-r^2\rangle \rightarrow |x^2-y^2\rangle$  experiences a significant red shift of 0.11 eV. This behavior under pressure is depicted on Figure 4. The shifts under pressure calculated for the other JT system,  $\text{NaCl}:\text{Cu}^{2+}$ , show a similar pattern.

The existence of a red shift in the lowest *d-d* excitation of  $\text{CdCl}_2:\text{Cu}^{2+}$  can, in principle, be surprising. Nonetheless, this fact can be understood considering that a pressure of 3 GPa reduces

**Table 5.** Experimental energies of *d-d* transitions observed for  $\text{CdCl}_2:\text{Cu}^{2+}$  at zero pressure<sup>[84]</sup> compared to those calculated at both  $P=0 \text{ GPa}$  and  $P=3 \text{ GPa}$ . All transition energies are in eV.

Transition	Experimental (P=0)	Calculated (P=0)	Calculated (P=3)
$ 3z^2-r^2\rangle \rightarrow  x^2-y^2\rangle$	0.79	0.68	0.57
$ xy\rangle \rightarrow  x^2-y^2\rangle$	1.17	1.26	1.26
$ xyz\rangle \rightarrow  x^2-y^2\rangle$	1.36	1.30	1.31



**Figure 4.** Qualitative description of pressure dependence of three  $d-d$  transitions in a tetragonal  $\text{CuCl}_6^{4-}$  unit. For the sake of clarity, the changes undergone by  $10Dq$ ,  $\Delta_e$  and  $\Delta_t$  are also shown.

the longest  $R_{ax}$  distance by 0.07 Å, while  $R_{eq}$  remains essentially unmodified, such as it is shown in Table 2. Thus, if the two negative axial ligands become closer to the electronic density it tends to enhance the energy of mainly  $d$ -orbitals. However, this energy increase will be higher for the  $|3z^2-r^2\rangle$  orbital, displaying an *axial* character, than for the HOMO  $|x^2-y^2\rangle$  whose electronic density is mainly located in the perpendicular  $XY$  plane. Therefore, this argument explains albeit qualitatively the existence of a red shift under pressure in the  $|3z^2-r^2\rangle \rightarrow |x^2-y^2\rangle$  transition.

A more quantitative view of the pattern depicted in Figure 4 can be reached writing the energy of transitions in terms of  $10Dq$ ,  $\Delta_e$  and  $\Delta_t$  quantities and using the center of the gravity theorem.<sup>[85]</sup> Accordingly, the energy of the three  $d-d$  transitions can be written as

$$\begin{aligned} E(|xy\rangle \rightarrow |x^2-y^2\rangle) &= 10Dq + \Delta_e/2 - 2(\Delta_t/3) \\ E(|xz,yz\rangle \rightarrow |x^2-y^2\rangle) &= 10Dq + \Delta_e/2 + \Delta_t/3 \\ E(|3z^2-r^2\rangle \rightarrow |x^2-y^2\rangle) &= \Delta_e \end{aligned} \quad (4)$$

Using the experimental values given in Table 5 we obtain for  $\text{CdCl}_2:\text{Cu}^{2+}$  at zero pressure  $10Dq = 0.90$  eV,  $\Delta_e = 0.79$  eV and  $\Delta_t = 0.19$  eV.

Concerning the pressure dependence of the three  $d-d$  transitions,  $10Dq$  depends on  $R_{av}$  being proportional to  $R_{av}^{-n}$  with the exponent  $n$  usually in the 4–6 range.<sup>[14–18,21]</sup> Accordingly, for a small  $R_{av}$  change,  $\delta R_{av}$ , the  $10Dq$  variation is

$$\delta 10Dq = -n(\delta R_{av}/R_{av})10Dq \quad (5)$$

The quantity  $\Delta_e$  reflects the effect of the tetragonal distortion upon the two  $e_g$  orbitals displaying  $\sigma$  bonding. For a small distortion  $\Delta_{er}$  can be written as<sup>[86,87]</sup>

$$\Delta_e = \beta(R_{ax} - R_{eq}) \quad (6)$$

where  $\beta = 2.3$  eV/Å<sup>2</sup> from experimental results at zero pressure for  $\text{CdCl}_2:\text{Cu}^{2+}$  (Table 5). This value is thus not far from  $\beta =$

2.8 eV/Å<sup>2</sup> recently derived for  $\text{CuF}_6^{4-}$  complexes.<sup>[87]</sup> Similarly, the splitting,  $\Delta_t$ , on  $t_{2g}$  levels involving  $\pi$  bonding can be written as

$$\Delta_t = \gamma(R_{ax} - R_{eq}) \quad (7)$$

with  $\gamma = 0.56$  eV/Å<sup>2</sup> for  $\text{CdCl}_2:\text{Cu}^{2+}$  at zero pressure (Tables 1 and 5).

Bearing these facts in mind a pressure of 3 GPa on  $\text{CdCl}_2:\text{Cu}^{2+}$  reduces  $R_{ax}$  by 0.068 Å, while  $R_{eq}$  is practically unmodified (Table 2). Thus, according to Eqs. (4) and (6), we expect a red shift around 0.1 eV on the lowest  $|3z^2-r^2\rangle \rightarrow |x^2-y^2\rangle$  transition, consistent with the calculated value on Table 5.

As regards the transitions coming from  $t_{2g}$  levels, the shortening of  $R_{ax}$  by pressure entails a diminution of  $R_{av}$  and consequently an increase of  $10Dq$ . Nevertheless, this increase is compensated to a good extent by the decrease of  $\Delta_e$  making that the  $|xz,yz\rangle \rightarrow |x^2-y^2\rangle$  transition is little sensitive to pressure (Table 5 and Figure 4).

It is worth noting now that  $10Dq$  and the exponent  $n$  both reflect the different chemical bonding in  $e_g$  and  $t_{2g}$  levels of  $O_h$  complexes and thus cannot properly be explained through the simple crystal field approach.<sup>[17,18,21,87]</sup> A similar situation holds for the  $\Delta_e$  splitting as discussed in a recent work.<sup>[87]</sup>

Bearing these facts in mind we have also explored the behavior of  $d-d$  transitions in layered compounds with  $\text{CuCl}_6^{4-}$  units. In such cases the local geometry of  $\text{CuCl}_6^{4-}$  complexes is no longer tetragonal but orthorhombic as discussed in the previous subsection.

The calculated energy for the four  $d-d$  transitions expected for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  at  $P=0$  and 3 GPa are both reported in Table 6. It can be remarked that the first  $|3y^2-r^2\rangle \rightarrow |x^2-z^2\rangle$  transition is clearly sensitive to pressure and experiences an important shift to the red of 0.34 eV when pressure increases from zero to 3 GPa. On the contrary, the rest of transitions, arising from  $t_{2g}$  levels in  $O_{hr}$ , move only very slightly to the blue.

It should be remarked that the variation  $dE_1/dP = -0.11$  eV/GPa shown by the first  $d-d$  transition of  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  (Table 6) is about *three times* higher than  $dE_1/dP = -0.033$  eV/GPa derived for the  $|3z^2-r^2\rangle \rightarrow |x^2-y^2\rangle$  transition of JT systems (Table 5). This important fact is connected to the quite different response to pressure of the longest distance of the  $\text{CuCl}_6^{4-}$  unit in JT and layered systems. For instance,  $dR_{ax}/dP \approx -0.023$  Å/GPa for  $\text{Cu}^{2+}$ -doped  $\text{CdCl}_2$  or  $\text{NaCl}$  (Table 2) while for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$   $dR_{av}/dP = -0.07$  Å/GPa. It should be noticed however that the sensitivity of  $E_1$  to changes of  $R_{ax}$  in JT systems ( $dE_1/dR_{ax} = 1.6$  eV/Å) is the same as that derived in

**Table 6.** Energy (in eV) of  $d-d$  transitions calculated for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  at zero pressure and  $P=3$  GPa. The energy of the lowest transition is written in *italic*. Note that as the local symmetry is orthorhombic the HOMO is described by the dominant contribution,  $|x^2-z^2\rangle$ , despite it actually involves an admixture of  $|3y^2-r^2\rangle$ .

Transition	P=0	P=3
<i><math> 3y^2-r^2\rangle \rightarrow  x^2-z^2\rangle</math></i>	0.93	0.59
$ xz\rangle \rightarrow  x^2-z^2\rangle$	1.30	1.32
$ yz\rangle \rightarrow  x^2-z^2\rangle$	1.34	1.34
$ xy\rangle \rightarrow  x^2-z^2\rangle$	1.40	1.41



$(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  ( $dE_1/dR_V = 1.6 \text{ eV/\AA}$ ). Interestingly, such figures can be compared with  $d10Dq/dR$  for octahedral complexes of 3d ions lying typically between  $-2 \text{ eV/\AA}$  and  $-5 \text{ eV/\AA}$ .<sup>[14–18,21]</sup> In these cases, however, a reduction of the metal-ligand distance,  $R$ , implies an increase of  $10Dq$  whose actual origin has previously been discussed.<sup>[17,18,87]</sup>

The pattern found for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  under pressure is also consistent with experimental and calculated  $d-d$  transitions at zero pressure in that system, as well as in pure layered compounds<sup>[79,88]</sup> such as it is shown in Table 7. Indeed, the calculated energy of the first  $|3y^2-r^2\rangle \rightarrow |x^2-z^2\rangle$  transition grows significantly when  $R_V$  increases going from 0.93 eV for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  ( $R_V = 2.775 \text{ \AA}$ ) to 1.27 eV for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$  ( $R_V = 2.975 \text{ \AA}$ ).<sup>[88]</sup>

This general trend is followed by experimental results on  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  and  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$  (Table 7) despite the uncertainties on the values of  $d-d$  transitions in the first case due to a poor resolution of absorption spectra.<sup>[79]</sup> According to these data, it is thus quite reasonable to expect a significant red shift in the  $|3y^2-r^2\rangle \rightarrow |x^2-z^2\rangle$  transition in a layered compound containing  $\text{CuCl}_6^{4-}$  units when pressure is applied. Unfortunately, in the absorption spectra carried out under pressure in  $(\text{EDBE})[\text{CuCl}_4]$  ( $\text{EDBE} = 2,2'$ -(ethylenedioxy)bis(ethylammonium)), but only at room temperature, the four  $d-d$  transitions are not resolved<sup>[12]</sup> and only a broad band (bandwidth  $\sim 0.5 \text{ eV}$ ) is observed, whose energy maximum slightly increases at a rate of  $\sim 0.01 \text{ eV/GPa}$ . Very likely that shift corresponds to the three transitions emerging from antibonding  $t_{2g}$  orbitals in  $O_h$ .

### Charge Transfer transitions in $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ under pressure

Bearing the results of the former subsections in mind this one is addressed to gain a better insight into the red shift under pressure observed<sup>[11]</sup> for the lowest charge transfer (CT) transition in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  in the range 0–3 GPa. If  $E_{\text{CT}}$  means the energy of such a transition it is experimentally found  $dE_{\text{CT}}/dP = -0.04 \text{ eV/GPa}$ . A similar red shift is also reported for  $(\text{EDBE})[\text{CuCl}_4]$ .<sup>[12,13]</sup>

For the sake of comparison, it is worth recalling first what happens in model systems containing square-planar  $\text{CuCl}_4^{2-}$  complexes where all ligands are equivalent. In this case the first allowed CT transition comes from a  $e_u(\sigma + \pi)$  ligand orbital depicted on Figure 5 and the  $\sigma$  character in that orbital greatly

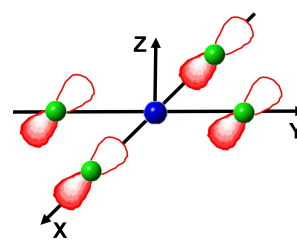


Figure 5. Graphical description of  $e_u(\sigma + \pi)$  ligand orbital, corresponding to a square planar  $\text{CuCl}_4^{2-}$  anion, responsible for the first allowed charge transfer transition.

influences the oscillator of the  $|e_u(\sigma + \pi)\rangle \rightarrow |x^2-y^2\rangle$  transition.<sup>[89]</sup> Thus, if  $E_{\text{CT}}$  just denotes the energy of such a transition, experimental<sup>[22–24]</sup> and theoretical<sup>[25]</sup> results lead to  $dE_{\text{CT}}/dR = -9.5 \text{ eV/\AA}$  implying a strong blue shift upon reduction of the metal-ligand distance,  $R$ . That shift reflects that when  $R$  decreases the energy of an electron placed in a mainly  $d$ -orbital increases due to a higher repulsion by the four ligand ions. By contrast, in that situation an electron in a ligand orbital is more attracted by the central ion with charge  $z_M e$  although partially compensated by the repulsion of three ligand ions with a charge  $-z_L e$ . According to this view the shift,  $dE_{\text{CT}}$ , undergone by a CT transition of a  $\text{CuCl}_4^{2-}$  complex due to a variation,  $dR$ , of the metal ligand distance can be estimated<sup>[17,21]</sup> through the simple expression

$$dE_{\text{CT}} = -(e^2/R^2)(2.09z_L + z_M)dR \quad (8)$$

As the total charge of a  $\text{CuCl}_4^{2-}$  unit is  $-2e$  then

$$z_M - 4z_L = -2 \quad (9)$$

Due to the covalent bonding inside the  $\text{CuCl}_4^{2-}$  unit,  $z_M < 2$ . If we take, for instance,  $z_M = 1$ ,  $z_L = 3/4$  and  $R = 2.25 \text{ \AA}$ , we obtain from Equation (8) an estimated value  $dE_{\text{CT}}/dR = -7.3 \text{ eV/\AA}$  which is thus comparable to experimental and theoretical results<sup>[22–25]</sup> on compounds involving  $\text{CuCl}_4^{2-}$  complexes.

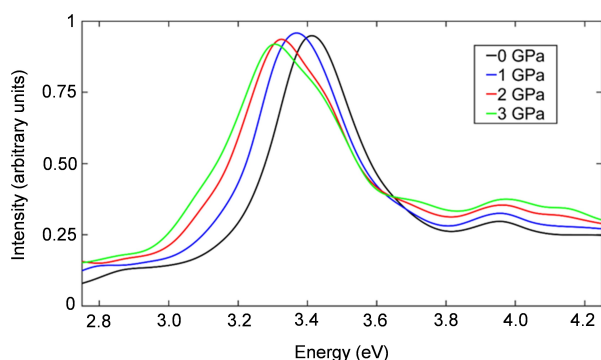
In the case of the layered system  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ , the results shown above prove that a pressure up to 3 GPa reduces  $R_V$  by  $0.21 \text{ \AA}$  while  $R_X$  and  $R_Z$  remain essentially constant. Accordingly, if  $dE_{\text{CT}}/dP = -0.04 \text{ eV/GPa}$  and  $dR_V/dP = -0.07 \text{ \AA/GPa}$ , we find  $dE_{\text{CT}}/dR_V = 0.60 \text{ eV/\AA}$ . This simple reasoning already stresses that the sensitivity of  $E_{\text{CT}}$  to variations of  $R_V$  in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  is *one order of magnitude* smaller than the absolute value of  $dE_{\text{CT}}/dR = -9.5 \text{ eV/\AA}$  found for square-planar  $\text{CuCl}_4^{2-}$  complexes.

Bearing these facts in mind, we have first calculated the pressure dependence of the charge transfer spectrum of  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  in the range 0–3 GPa. For achieving this goal, we have taken into account the variation of structural parameters with pressure reported on Table 3.

The charge transfer spectrum of  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  calculated in the range 2.8–4.2 eV for several pressures using the VASP code is displayed on Figure 6. That spectrum is dominated by a band peaked at 3.4 eV at zero pressure not far

Table 7. Energy (in eV) of  $d-d$  transitions calculated for  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  and  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$  at zero pressure. Such results are compared to experimental findings on these pure compounds<sup>[79,88]</sup> and also to those obtained for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  in this work. In all cases the value of the longest  $\text{Cu}^{2+}-\text{Cl}^-$  distance,  $R_V$ , is given. For the sake of clarity, the calculated energy of the lowest transition is written in *italic*.

Transition	$(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$	$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$		$(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$	
	$R_V = 2.775 \text{ \AA}$ Calc.	$R_V = 2.907 \text{ \AA}$ Calc.	Exp.	$R_V = 2.975 \text{ \AA}$ Calc.	Exp.
$ 3y^2-r^2\rangle \rightarrow  x^2-z^2\rangle$	<i>0.93</i>	1.15	1.34	1.27	1.38
$ xz\rangle \rightarrow  x^2-z^2\rangle$	1.30	1.39	1.51	1.43	1.54
$ yz\rangle \rightarrow  x^2-z^2\rangle$	1.34	1.47	1.51	1.50	1.65
$ xy\rangle \rightarrow  x^2-z^2\rangle$	1.40	1.45	1.65	1.50	1.65



**Figure 6.** Calculated red shift under pressure of the first charge transfer transition from  $p_x$  orbitals of Cl(X) and Cl(Z) to the mainly  $|x^2-z^2\rangle$  orbital of  $\text{Cu}^{2+}$ .

from the value  $E_{\text{CT}} = 3.12$  eV measured experimentally.<sup>[11]</sup> Moreover, Figure 6 shows that the calculated band maximum is red shifted by 0.11 eV under a 3 GPa pressure, a value close to  $\Delta E_{\text{CT}} = -0.14$  eV determined experimentally.

For the sake of completeness, we have also explored the nature of the ligand orbital, mainly responsible for the peak in Figure 6. We have verified that it is mainly built from  $p_x$  orbitals of chlorine ions Cl(X) and Cl(Z) placed at X and Z directions, lying in the plane perpendicular to the long axis Y (Figure 3). In addition, there is a small admixture of  $p_x$  orbitals of two Cl(Y) ions. Thus, that orbital resembles the shape of the  $e_u(\sigma + \pi)$  ligand orbital (Figure 5) responsible for the lowest charge transfer transition in square-planar  $\text{CuCl}_4^{2-}$  complexes.

The present results shed light on the different pressure response of the lowest charge transfer transition in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  and compounds with  $\text{CuCl}_4^{2-}$  anions. In the first case a pressure up to 3 GPa *only* moves the *longest*  $\text{Cu}^{2+}-\text{Cl}^-$  distance,  $R_y$ , while the electronic density of *both* initial and final orbitals, involved in the charge transfer transition, is essentially lying in the perpendicular plane XZ. Accordingly, it can be expected that the motion of the two farthest ligands affect in similar way to the energy of both orbitals. This situation is thus quite different from that for  $\text{CuCl}_4^{2-}$  where all ligands are equivalent and the energy of molecular orbitals  $|x^2-y^2\rangle$  and, to a minor extent,  $|e_u(\sigma + \pi)\rangle$ , is strongly influenced by the simultaneous motion of the four  $\text{Cl}^-$  ions of the complex. According to this simple reasoning, we can understand why  $dE_{\text{CT}}/dR_y = 0.60$  eV/Å derived for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  is much smaller than  $|dE_{\text{CT}}/dR| = 9.5$  eV/Å corresponding to square-planar  $\text{CuCl}_4^{2-}$  units.

The red shift of  $E_{\text{CT}}$  under pressure in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  is helped by the local orthorhombic symmetry displayed by  $\text{CuCl}_6^{4-}$  complexes. We have verified that when the long metal-ligand distance is reduced it enhances the admixture of the HOMO (mainly  $x^2-z^2$  character) with the orbital lying below (mainly  $3y^2-r^2$  character), a fact that is symmetry avoided for tetragonal  $\text{CuCl}_4^{2-}$  units. Such an admixture decreases the energy of the HOMO. In the same way upon reduction of  $R_y$  the mixing of  $p_x(\text{Cl}_y)$  orbitals into the charge transfer orbital also

increases favoring an increase of the energy and thus a decrease of  $E_{\text{CT}}$ .

The influence of the lower symmetry in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  on the shift of  $E_{\text{CT}}$  under pressure is reflected in the comparison with the calculated value of  $dE_{\text{CT}}/dP$  for the JT systems  $\text{CdCl}_2:\text{Cu}^{2+}$  or  $\text{NaCl}:\text{Cu}^{2+}$ . In these cases, we have found  $dE_{\text{CT}}/dP \approx 0.01$  eV/GPa thus implying a tiny blue shift. This figure, when compared to  $dE_{\text{CT}}/dP \approx -0.04$  eV/GPa found for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ , reflects again the different sensitivity to pressure of the longest metal-ligand distance in both cases, a matter already discussed in the second subsection.

## Final Remarks

The present results prove that the energies of the lowest  $d-d$  transition and the first allowed CT transition in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  are both red shifted under pressure,  $dE/dP$  being equal to  $-0.10$  eV/GPa and  $-0.04$  eV/GPa, respectively. As this sensitivity to pressure is three times higher than that found for JT systems, like  $\text{CdCl}_2:\text{Cu}^{2+}$  or  $\text{NaCl}:\text{Cu}^{2+}$ , involving tetragonal  $\text{CuCl}_6^{4-}$  units, this fact already emphasizes the key role played by the orthorhombic instability in layered compounds like  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  leading to a bond between  $\text{Cu}^{2+}$  and the farthest ligands extremely soft.

Structural instabilities arise from a negative vibronic contribution,  $-K_v$ , to the total force constant,  $K$ , of a given distortion mode,<sup>[33,75,76,77]</sup> written as

$$K = K_0 - K_v \quad (10)$$

Here the  $K_0$  contribution only considers the electronic density *frozen* at the equilibrium geometry. By contrast,  $K_v$  basically reflects the *change* of the ground state electronic density due to the coupling between the electronic density and the distortion vibrational mode. Thus, the  $K_v$  contribution tends to soften the force constant of a given distortion making that even  $K$  becomes negative and then the instability develops. This situation is obviously favored for weak rather than for stronger bonds.<sup>[7,74]</sup> For this reason, the orthorhombic instability takes place in layered compounds like  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4$  doped with  $\text{Cu}^{2+}$  while not in  $\text{K}_2\text{ZnF}_4:\text{Cu}^{2+}$ , involving tetragonal  $\text{CuF}_6^{4-}$  units, as fluorine gives rise to stronger bonds than chlorine.<sup>[29–32]</sup> Nevertheless, when complexes share common ligands, it is easier to reach the orthorhombic instability such as it has previously been discussed.<sup>[7]</sup> For this reason, it takes place in the pure compounds  $\text{K}_2\text{CuF}_4$ <sup>[7,73]</sup> and  $\text{Na}_2\text{CuF}_4$ <sup>[86]</sup> but not in  $\text{Cu}^{2+}$ -doped  $\text{K}_2\text{ZnF}_4$ <sup>[29–32]</sup> or  $\text{Ba}_2\text{ZnF}_6$ .<sup>[36]</sup> Supporting this idea, the orthorhombic distortion increases significantly on passing from doped systems like  $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$  to pure layered compounds like  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  as seen in Table 4.

Interestingly, a reduction of a bond length tends to increase  $K_0$ , a fact that also acts against the development of a structural instability. By this reason, the orthorhombic instability is observed in compressed rather than in elongated complexes<sup>[7,73,74]</sup> of  $d^9$  ions as ligands lying in the perpendicular plane to the main axes move *outwards* thus increasing the

value of the corresponding metal-ligand distance and weakening  $K_0$ .

It is worth noting now that structural instabilities arising from  $K < 0$  are often described in the scientific literature as a pseudo-Jahn-Teller effect.<sup>[33,75]</sup> This term is however confusing in view of the significant differences between instabilities driven by a negative force constant and the JT effect discussed in this work.

The reduction or total suppression of a distortion due to shortening bond lengths is a general behavior in the realm of structural instabilities. For instance,  $\text{Cu}^{2+}$  impurities in  $\text{BaF}_2$  and  $\text{SrF}_2$  move off-center by 1.3 Å and only 0.30 Å, respectively, while such instability is suppressed in  $\text{CaF}_2$  displaying the smallest lattice parameter.<sup>[90–92,17]</sup> In the same vein, the destruction of the ferroelectricity on passing from  $\text{BaTiO}_3$  to  $\text{CaTiO}_3$  is also related to the reduction of lattice parameter as it has previously been discussed.<sup>[93]</sup>

The present work stresses the differences between JT and non-JT systems involving  $d^n$  ( $n=4,9$ ) complexes in insulating lattices. It is worth noting now that for non-JT complexes other interesting phenomena can also be observed. In particular an applied pressure can switch the long axis of an orthorhombic complex such as it has been observed for  $\text{Na}_3\text{MnF}_6$  with a pressure of 2.8 GPa.<sup>[94]</sup> Interestingly in that case, recently analyzed, the value of  $\Delta R_{15}$  at zero pressure is equal only to 0.15 Å and thus much smaller than those gathered in Table 4.<sup>[95]</sup>

In summary, due to the orthorhombic instability, a layered compound like  $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4 \cdot \text{Cu}^{2+}$  shows a highly anisotropic response to pressure making that in the range 0–3 GPa only the longest metal-ligand distance is reduced by 0.21 Å. This contraction would give rise to a significant red shift around 0.30 eV for the lowest d-d transition. Further experimental work would be necessary to verify that behavior.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** charge-transfer transitions · hybrid organic-inorganic compounds · Jahn-Teller effect · layered perovskites · red-shift

- [1] J. P. Correa-Baena, M. Saliba, T. Buonassisi, M. Grätzel, A. Abate, W. Tress, A. Hagfeldt *Science* **2017**, *358*, 739–744.
- [2] K. Lin, J. Xing, L. N. Quan, F. P. G. de Arquer, X. Gong, J. Lu, L. Xie, W. Zhao, D. Zhang, C. Yan, W. Li, X. Liu, Y. Lu, J. Kirman, E. H. Sargent, Q. Xiong, Z. Wei, *Nature* **2018**, *562*, 245–248.
- [3] Q. A. Akkerman, L. Manna, *ACS Energy Lett.* **2020**, *5*, 604–610.
- [4] J. P. Steadman, R. D. Willett, *Inorg. Chim. Acta* **1970**, *4*, 367–371.
- [5] Y. Moritomo, Y. Tokura, *J. Chem. Phys.* **1994**, *101*, 1763–1766.
- [6] K. Ohwada, K. Ishii, T. Inami, Y. Murakami, T. Shobu, H. Ohsumi, N. Ikeda, Y. Ohishi, *Phys. Rev. B* **2005**, *72*, 014123.
- [7] J. A. Aramburu, P. García-Fernández, N. R. Mathiesen, J. M. García-Lastra, M. Moreno, *J. Phys. Chem. C* **2018**, *122*, 5071–5082.
- [8] A. R. Lim, L. K. Kwac, *Sci. Rep.* **2022**, *12*, 8769.
- [9] M. Y. Choi, S. J. Lee, H. Ju, A. R. Lim, *RSC Adv.* **2022**, *12*, 20679.
- [10] A. R. Lim, *J. Mol. Struct.* **2022**, *1252*, 132204.
- [11] R. Vallente, F. Rodríguez, J. A. Aramburu, M. Moreno, M. T. Barriuso, C. Sousa, C. De Graaf, *Int. J. Quantum Chem.* **2002**, *86*, 239–244.
- [12] A. Jaffe, Y. Lin, W. L. Mao, H. I. Karunadasa, *J. Am. Chem. Soc.* **2015**, *137*, 1673.
- [13] S. Gupta, T. Pandey, A. K. Singh *Inorg. Chem.* **2016**, *55*, 6817–6824.
- [14] H. G. Drickamer, *J. Chem. Phys.* **1967**, *47*, 1880.
- [15] S. Ducloux, Y. K. Vohra, A. L. Ruoff, *Phys. Rev. B* **1990**, *41*, 5372–5381.
- [16] J. F. Dolan, A. G. Rinzier, L. A. Kappers, R. H. Bartram, *J. Phys. Chem. Solids* **1992**, *53*, 905–912.
- [17] M. Moreno, M. T. Barriuso, J. A. Aramburu, P. García-Fernández, J. M. García-Lastra, *J. Phys. Condens. Matter* **2006**, *18*, R315–R360.
- [18] A. Trueba, P. García-Fernández, J. M. García-Lastra, J. A. Aramburu, M. T. Barriuso, M. Moreno, *J. Phys. Chem. A* **2011**, *115*, 1423–1432.
- [19] J. Simonetti, D. S. McClure, *J. Chem. Phys.* **1979**, *71*, 795–801.
- [20] S. Hirako, R. Onaka, *J. Phys. Soc. Jpn.* **1982**, *51*, 1255–1263.
- [21] M. Moreno, J. A. Aramburu, M. T. Barriuso, *Struct. Bonding* **2004**, *106*, 127–152.
- [22] S. R. Desjardins, K. W. Penfield, S. L. Cohen, R. L. Musselman, E. I. Solomon, *J. Am. Chem. Soc.* **1983**, *105*, 4590–4603.
- [23] M. A. Hitchman, P. J. Cassidy, *Inorg. Chem.* **1979**, *18*, 1745.
- [24] R. G. Mc Ronald, M. A. Hitchman, *Inorg. Chem.* **1986**, *25*, 3273.
- [25] J. A. Aramburu, M. Moreno, A. Bencini, *Chem. Phys. Lett.* **1987**, *140*, 462–467.
- [26] I. Pabst, H. Fuess, J. W. Bats, *Cryst. Struct. Commun.* **1987**, *43*, 413–416.
- [27] P. García-Fernández, A. Trueba, M. T. Barriuso, J. A. Aramburu, M. Moreno, *Prog. Theor. Chem. Phys.* **2011**, *23*, 105–142.
- [28] F. S. Ham, *Electron Paramagnetic Resonance* (Ed.: S. Geschwind), Plenum, New York, **1972**.
- [29] M. A. Hitchman, R. G. Mc Ronald, D. Reinen, *Inorg. Chem.* **1986**, *25*, 519–522.
- [30] J. M. García-Lastra, J. A. Aramburu, M. T. Barriuso, M. Moreno, *Chem. Phys. Lett.* **2004**, *385*, 286–291.
- [31] J. M. García-Lastra, J. A. Aramburu, M. T. Barriuso, M. Moreno, *Phys. Rev. Lett.* **2004**, *93*, 226402.
- [32] J. A. Aramburu, J. M. García-Lastra, P. García-Fernández, M. T. Barriuso, M. Moreno, *Inorg. Chem.* **2013**, *52*, 6923–6933.
- [33] I. B. Bersuker, V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer-Verlag, Berlin Heidelberg **1989**, Vol 49.
- [34] E. M. C. Minner, *Etude Spectroscopique des Ions Jahn-Teller Cuivre et Argent Bivalents dans des Monocristaux de Fluoroperovskites de Composition Chimique AMF<sub>3</sub>*, PhD thesis, University of Geneva, **1993**.
- [35] L. Dubicki, M. J. Riley, E. R. Krausz, *J. Chem. Phys.* **1994**, *101*, 1930–1938.
- [36] J. A. Aramburu, P. García-Fernández, J. M. García-Lastra, M. Moreno, *J. Phys. Chem. C* **2017**, *121*, 5215–5224.
- [37] R. H. Borcherts, H. Kanzaki, H. Abe, *Phys. Rev. B: Solid State* **1970**, *2*, 23–27.
- [38] J. Sierro, *J. Phys. Chem. Solids* **1967**, *28*, 417–422.
- [39] A. Trueba, J. M. García-Lastra, C. De Graaf, P. García-Fernández, J. A. Aramburu, M. T. Barriuso, M. Moreno, *Chem. Phys. Lett.* **2006**, *430*, 51–55.
- [40] H. Vercammen, D. Schoemaker, B. Briat, F. Ramaz, F. Callens, *Phys. Rev. B* **1999**, *59*, 11286–11292.
- [41] M. T. Barriuso, P. García-Fernández, J. A. Aramburu, M. Moreno, *Solid State Commun.* **2001**, *120*, 1–5.

- [42] R. Valiente, L. M. Lezama, F. Rodríguez, M. Moreno, *Mater. Sci. Forum* **1997**, 239–241, 729–732.
- [43] R. Valiente, F. Rodríguez, M. Moreno, L. M. Lezama in *Vibronic Interactions: Jahn-Teller Effect in Crystals and Molecules* (Eds.: M. D. Kaplan, G. O. Zimmerman), Kluwer Academic Publishers: Norwell, MA, **2001**, pp 221–228.
- [44] G. Chapuis, *Phys. Stat. Sol. a* **1977**, 43, 203–212.
- [45] M. Hayashi, H. Nakagawa, H. Matsumoto, *Mem. Fac. Eng. Fukui Univ* **1978**, 26, 15–27.
- [46] J. A. Aramburu, P. García-Fernández, J. M. García-Lastra, M. T. Barriuso, M. Moreno, *J. Phys. Condens. Matter* **2013**, 25, 175501–17558.
- [47] CRYSTAL web site. <https://www.crystal.unito.it> (accessed in March 2022).
- [48] R. Dovesi, et al. CRYSTAL17 User's Manual (University of Torino, Torino), **2017**.
- [49] G. Kresse, J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, 49, 14251.
- [50] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, 54, 11169–11186.
- [51] G. Te Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. Van Gisbergen, J. D. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, 22, 931–967.
- [52] M. F. Peintinger, D. V. Oliveira, T. J. Bredow, *J. Comput. Chem.* **2013**, 34, 451–459.
- [53] CRYSTAL basis sets. <https://www.crystal.unito.it/basis-sets.php> (accessed in March 2022).
- [54] Y. Dou, R. G. Egdell, D. S. L. Law, N. M. Harrison, B. G. Searle, *J. Phys. Condens. Matter* **1998**, 10, 8447–8458.
- [55] T. Bredow, A. Gerson, *Phys. Rev. B* **2000**, 61, 5194–5201.
- [56] P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, 50, 17953–17979.
- [57] L. Schimka, J. Harl, G. Kresse, *J. Chem. Phys.* **2011**, 134, 024116.
- [58] W. H. Press, S. A. Teukolsky, W. T. Vetterling, B. P. Flannery, *Numerical Recipes: The Art of Scientific Computing*, Cambridge University Press, New York, **1986**.
- [59] J. D. Pack, H. J. Monkhorst, *J. Chem. Inf. Model.* **1977**, 16, 1748.
- [60] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, 59, 1758–1775.
- [61] M. Gajdoš, K. Hummer, G. Kresse, J. Furthmüller, F. Bechstedt, *Phys. Rev. B* **2006**, 73, 045112.
- [62] G. Onida, L. Reining, A. Rubio, *Rev. Mod. Phys.* **2002**, 74, 601.
- [63] SCM Team, ADF Manual: Amsterdam Modeling Suite 2022.1, **2022**.
- [64] J. M. García-Lastra, M. T. Barriuso, J. A. Aramburu, M. Moreno, *Phys. Rev. B* **2009**, 79, 241106(R).
- [65] P. García-Fernández, M. Moreno, J. A. Aramburu, *Inorg. Chem.* **2015**, 54, 192–199.
- [66] H. Bill, *The Dynamical Jahn-Teller Effect in Localized Systems* (Eds.: Y. E. Perlin, M. Wagner), Elsevier, Amsterdam, **1984**.
- [67] E. Minner, D. Lovy, H. Bill, *J. Chem. Phys.* **1993**, 99, 6378–6383.
- [68] I. Sánchez-Movellán, J. Moreno-Ceballos, P. García-Fernández, J. A. Aramburu, M. Moreno, *Chem. Eur. J.* **2021**, 27, 13582–13590.
- [69] W. Low, J. T. Suss, *Phys. Lett.* **1963**, 7, 310–312.
- [70] J. A. Aramburu, P. García-Fernández, J. M. García-Lastra, M. Moreno, *ChemPhysChem* **2016**, 17, 2146–2156.
- [71] R. D. Shannon, *Acta Crystallogr.* **1976**, A32, 751–767.
- [72] F. Barendregt, H. Schenk *Physica* **1970**, 49, 465–468.
- [73] P. García-Fernández, M. Moreno, J. A. Aramburu, *J. Phys. Chem. C* **2014**, 118, 7554–7561.
- [74] J. A. Aramburu, A. Bhowmik, J. M. García-Lastra, P. García-Fernández, M. Moreno, *J. Phys. Chem. C* **2019**, 123, 3088–3101.
- [75] I. B. Bersuker, *Chem. Rev.* **2013**, 113, 1351–1390.
- [76] P. García-Fernández, J. M. García-Lastra, A. Trueba, M. T. Barriuso, J. A. Aramburu, M. Moreno, *Phys. Rev. B* **2012**, 85, 094110.
- [77] R. J. H. Wong, R. D. Willett, J. E. Drumheller, *J. Chem. Phys.* **1981**, 74, 6018–6021.
- [78] K. E. Halvorson, B. Patyel, R. G. Willett, *J. Chem. Crystallogr.* **1995**, 25, 537–542.
- [79] C. Furlani, A. Sgamellotti, F. Magrini, D. Cordischi, *J. Mol. Spectrosc.* **1967**, 24, 270–276.
- [80] S. E. McLain, M. R. Dolgos, D. A. Tennant, J. F. C. Turner, T. Barnes, T. Proffen, B. C. Sales, R. I. Bewley, *Nat. Mater.* **2006**, 5, 561–566.
- [81] D. Reinen, *Inorg. Chem.* **2012**, 51, 4458–4472.
- [82] D. Kurzydłowski, T. Jaroń, A. Ozarowski, S. Hill, Z. Jagličić, Y. Filinchuk, Z. Mazej, W. Grochala, *Inorg. Chem.* **2016**, 55, 11479–11489.
- [83] C. Liu, G. Zhao, T. Hu, Y. Chen, S. Cao, L. Bellaiche, W. Ren, *Phys. Rev. B* **2021**, 104, L241105.
- [84] K. Kan'no, S. Mukai, Y. Nakai, *J. Phys. Soc. Jpn.* **1974**, 36, 1492–1492.
- [85] C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill Book Company Inc., New York, **1962**.
- [86] I. Sánchez-Movellán, J. A. Aramburu, M. Moreno, *Phys. Chem. Chem. Phys.* **2020**, 22, 7875–7887.
- [87] J. A. Aramburu, M. Moreno, *J. Phys. Chem. A* **2021**, 125, 2284–2293.
- [88] M. Hichman, P. Cassidy, *Inorg. Chem.* **1978**, 17, 1682–1684.
- [89] M. T. Barriuso, J. A. Aramburu, C. Daul, M. Moreno, *Int. J. Quantum Chem.* **1997**, 61, 563–570.
- [90] S. K. Hoffmann, J. Goslar, S. Lijewski, V. A. Ulanov, *J. Chem. Phys.* **2007**, 127, 124705.
- [91] P. García-Fernández, J. A. Aramburu, M. T. Barriuso, M. Moreno, *Phys. Rev. B* **2004**, 69, 174110.
- [92] V. A. Ulanov, M. Krupski, S. K. Hoffmann, M. M. Zaripov, *J. Phys. Condens. Matter* **2003**, 15, 1081.
- [93] J. M. García-Lastra, P. García-Fernández, F. Calle-Vallejo, A. Trueba, J. A. Aramburu, M. Moreno, *Inorg. Chem.* **2014**, 53, 6534–6543.
- [94] S. Carlson, Y. Xu, U. Halenius, R. Norrestam, *Inorg. Chem.* **1998**, 37, 1486–1492.
- [95] I. Sánchez-Movellán, D. Carrasco-Busturia, J. M. García-Lastra, P. García-Fernández, J. A. Aramburu, M. Moreno, *Chem. Eur. J.* **2022**, 28, e202200948.

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