Variation of the Jahn-Teller distortion with pressure in perovskite layers $A_2CuCl_4$. Local and crystal compressibility.

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Summary

This work investigates how pressure modifies the Jahn-Teller (JT) distortion associated with the axially elongated CuCl$_6$ octahedra in the $A_2CuCl_4$ perovskite layer ($A = Rb$, CH$_3$NH$_3$, C$_2$H$_5$NH$_3$, C$_3$H$_7$NH$_3$). The aim is to elucidate whether pressure favours disappearance of the JT distortion in the antiferrodistortive (AFD) structure exhibited by Cu$^{2+}$ within the layers or whether it induces tilts of the CuCl$_6$ octahedra preserving the molecular distortion associated with the JT effect. We have carried out X-ray absorption (XAS) and X-ray diffraction (XRD) experiments under pressure along the series of compounds whose interlayer distances at ambient pressure vary from 7.75 to 12.33 Å. The use of both XAS and XRD techniques allows us to deal with a complete local- and crystal-structural characterization in Rb$_2$CuCl$_4$ as a function of pressure in the 0 - 16 GPa range. The results indicate that pressure reduces the axial and equatorial Cu-Cl distances, $R_{ax}$ and $R_{eq}$, as well as the intra- and interlayer Cu-Cu distances, $d_1$ and $d_2$. Interestingly, the variation of $R_{ax}$ is an order of magnitude bigger than the corresponding $R_{eq}$, thus leading to a reduction of the JT distortion. However, in no way a suppression of the JT effect can be achieved below 10 GPa. Pressure-induced tilting precludes such process that we estimate to occur at 41 GPa.

Introduction

Perovskite layers $A_2CuCl_4$ ($A = Rb$, C$_n$H$_{2n+1}$NH$_3$) involve an ample variety of interesting physical phenomena related to the Jahn-Teller (JT) Cu$^{2+}$ ions (3d$^9$ configuration), and their coupling within the layer (Reinen 1991; Hitchman 1994; Valiente, 1999; Aguado, 2004). The axially elongated CuCl$_6$ octahedra display an intralayer antiferrodistortive (AFD) structure that is characterised by the alternation of $d_{x^2-y^2}$ and $d_{y^2-z^2}$ orbitals in the plane favouring ferromagnetic interaction between Cu ions (Fig.1). At variance with isomorphous AMnF$_4$ whose JT MnF$_6^{3-}$ units exhibit a significant tilting within the layer (Mn-F-Mn < 162º), the Cu-Cl-Cu angle in halide perovskites is close to 180º (nearly ideal perovskite) making it responsible for the intralayer ferromagnetic exchange interaction between nearest Cu$^{2+}$ ions (Khomskii, 1973). By contrast, the interlayer exchange interaction is about three or four orders of magnitude weaker, and can be ferromagnetic or antiferromagnetic depending on the relative Cu-Cu interlayer distance and the tilting of CuCl$_6$ octahedra (Aguado, 2004). Interestingly, the interplay between JT distortion and tilting phenomena on the properties of layer perovskites motivated research to establish structural correlations. An intense activity has been focussed on both Cu$^{2+}$- and Mn$^{3+}$-related compounds to find out structural requirements to get either insulating ferromagnets (Aguado, 2005, and references given therein) or pressure-induced disappearance of the AFD structure (Moritomo, 1994; Narita, 1996; Manaka, 2001, 2002). In perovskite halides, no indication of bulk ferromagnetism beyond (CH$_3$NH$_3$)$_2$CuCl$_4$ and K$_2$CuF$_4$ has been found. Furthermore no clear evidence of
pressure-induced JT suppression has been reported for these compounds. The application of either chemical or hydrostatic pressure changes the magnetic behaviour of these compounds. Whereas a change of the 3D magnetism from antiferro- to ferromagnetism is attained on passing from \(n=2\) or 3 to \(n=1\) in \((\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4\) (increase of chemical pressure), hydrostatic pressure induces a switch from ferromagnetism to antiferromagnetism in \((\text{CH}_3\text{NH}_3)_2\text{CuCl}_4\) (Manaka, 2001) and \(\text{K}_2\text{CuF}_4\) (Ishizuka, 1996, 1998; Mitrofanov, 1997; Manaka, 1997). However \(\text{Rb}_2\text{CuCl}_4\) is antiferromagnetic \((T_N=13.8\text{ K})\) although it presents the shortest interlayer distance in the \(\text{A}_2\text{CuCl}_4\) series. This compound is interesting since it additionally provides an in-layer Cu-Cl-Cu angle of 180º at ambient conditions (ideal perovskite).

Figure 1 Left: Crystal structure of the \(\text{Rb}_2\text{CuCl}_4\)-layered perovskite at ambient conditions. Right: (top) View of the \(\text{CuCl}_6\) nearly tetragonal octahedra with the three different Cu-Cl distances. (bottom) View of the a-b plane. Note the antiferrodistortive structure displayed by the \(\text{CuCl}_6\) units.

It is worth noting that the structural variation undergone by this compound family under pressure remains still unknown in spite of the intense research carried out on the magnetic and optical properties as a function of pressure (Valiente, 1996, 1999; Aguado, 2004). This lack of information precludes any attempt to establish correlations in pressure experiments. The aim of this work is to determine the effects of pressure on the crystal and local structure around \(\text{Cu}^{2+}\). In particular, we focus on how pressure modifies the Jahn-Teller (JT) distortion associated with the axially elongated \(\text{CuCl}_6\) octahedra in \(\text{Rb}_2\text{CuCl}_4\) and compare it with previous results on \((\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4\) (Rodriguez, 2001). The aim is to elucidate whether pressure can suppress the JT distortion exhibited by \(\text{Cu}^{2+}\) and therefore the antiferrodistortive (AFD) structure of the layer or it induces tilts of the \(\text{CuCl}_6\) octahedra preserving the molecular distortion associated with the JT effect. For this purpose, we have carried out X-ray absorption (XAS) and X-ray diffraction (XRD) experiments under pressure. The use of both XAS and XRD techniques allows us to perform a complete structural study which is difficult to accomplish from only XRD due to preferential orientation and texture in the highly hygroscopic \(\text{Rb}_2\text{CuCl}_4\).
<table>
<thead>
<tr>
<th>Compound</th>
<th>Space Group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>d_{Cu-Cu} (Å)</th>
<th>d_{inter} (Å)</th>
<th>R_{ax} (Å)</th>
<th>R_{eq} (Å)</th>
<th>Q_0 (Å)</th>
<th>Q_ε (Å)</th>
<th>Reference</th>
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<tr>
<td>(CH₃NH₃)₂CuCl₄</td>
<td>P2₁/a</td>
<td>7.370</td>
<td>7.269</td>
<td>18.648</td>
<td>999.0</td>
<td>5.18</td>
<td>9.33</td>
<td>2.907</td>
<td>2.283</td>
<td>0.712</td>
<td>0.014</td>
<td>Pabst,1987</td>
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<td>(C₂H₅NH₃)₂CuCl₄</td>
<td>Pbca</td>
<td>7.47</td>
<td>7.35</td>
<td>21.18</td>
<td>1162.9</td>
<td>5.24</td>
<td>10.59</td>
<td>2.975</td>
<td>2.277</td>
<td>0.801</td>
<td>0.008</td>
<td>Steadman,1970</td>
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<tr>
<td>(C₃H₇NH₃)₂CuCl₄</td>
<td>Pbca</td>
<td>7.65</td>
<td>7.33</td>
<td>24.66</td>
<td>1382.8</td>
<td>5.30</td>
<td>12.33</td>
<td>3.040</td>
<td>2.290</td>
<td>0.866</td>
<td>-</td>
<td>Barendregt,1970</td>
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<tr>
<td>Rb₂CuCl₄</td>
<td>Cmca</td>
<td>7.187</td>
<td>7.197</td>
<td>15.534</td>
<td>803.5</td>
<td>5.09</td>
<td>7.77</td>
<td>2.716</td>
<td>2.347</td>
<td>0.426</td>
<td>0.046</td>
<td>Witteveen,1974</td>
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**Experimental Method**

Single crystals of Rb₂CuCl₄ (1-0.1 mm³) were grown from dried methyl alcohol solutions. A saturated solution of RbCl in methanol was poured into CuCl₂ methanol solution, using appropriate stoichiometric amounts of RbCl and CuCl₂. After several minutes red-brownish single crystals precipitate. The orthorhombic $A_{1g}$ space group was checked by X-ray diffraction. The obtained room temperature parameters are the same given elsewhere (Witteveen, 1974): $a = 7.187(4)$ Å, $b = 7.197(4)$ Å and $c = 15.534(6)$ Å. All compounds were handled in a glove box under argon atmosphere in order to avoid hydration. In contact to air, the crystal transforms into the hydrate Rb₂CuCl₄(H₂O)₂ phase (Waizumi, 1992), which is tetragonal ($P4_2/mnm$ space group) with lattice parameters $a = b = 7.596$ Å, and $c = 8.027$ Å. Partial or total hydration can be easily identified by powder X-ray diffraction and its characteristic yellow-greenish colour.

X-ray diffraction (XRD) under pressure was performed in the ID9 white beam station at the ESRF in Grenoble. Experiments were done on a diamond anvil cell (DAC) at room temperature using helium as pressure transmitter. X-ray powder diffractograms were obtained as a function of pressure in the 0 - 15 GPa range using wavelength, $\lambda = 0.4131$ Å, which is far enough from the spectral region of the diamond absorption. The X-ray absorption (XAS) under pressure was performed at the absorption setup XAS10 of the D11 beamline at LURE (Orsay). The extended x-ray absorption fine structure (EXAFS) spectra of the investigated Rb₂CuCl₄ were measured at the Cu K-edge ($E_0 = 8.98$ keV) at room temperature using dispersive EXAFS in the 8.9-9.3 keV range. This experimental setup has been proved to be very sensitive for obtaining suitable EXAFS oscillations in a wavelength range where the diamond anvil absorption is very strong. The XRD and XAS data were analyzed by means of the FULLPROF (Rodriguez-Carvajal, 1988) and the WINXAS package programs, respectively. Pressure was applied with a membrane-type diamond anvil cell using silicon oil as pressure transmitter. The pressure was measured from the R-line shift of Ruby.

**Results and Discussion**

The structural parameters at ambient conditions for Rb₂CuCl₄ are shown in Table I together with the corresponding data of $A_2CuCl_4$ ($A = C_nH_{2n+1}NH_3; n = 1-3$). Note that the interlayer
distance \( d_{\text{inter}} = c/2 \) decreases from 12.33 Å in \((\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4\) to 7.77 Å in \(\text{Rb}_2\text{CuCl}_4\). Moreover, this layer closing up is accompanied by a reduction of volume per Cu which correlates with a reduction of the JT distortion of the \(\text{CuCl}_6\). Taking the octahedral normal coordinate, \( Q_\theta = 2/\sqrt{3} (R_{\text{ax}} - R_{\text{eq}}) \), as a measure of the JT distortion, it turns out that \( Q_\theta \) decreases from 0.87 Å for \((\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4\) to 0.43 Å for \(\text{Rb}_2\text{CuCl}_4\). However the Cu-Cl-Cu angle varies from 166.5º to 180º evolving to an ideal perovskite with the crystal-volume reduction. From these chemical pressure effects we can draw two main conclusions: i) volume reduction by cation substitution reduces the \(\text{CuCl}_6\) JT distortion. ii) The Cu-Cl-Cu bond angle tends to the ideal perovskite value. The question arising is whether hydrostatic pressure induces analogous structural effects on \(\text{Rb}_2\text{CuCl}_4\).

**Figure 2** Variation of XRD pattern of \(\text{Rb}_2\text{CuCl}_4\) as a function of pressure. The vertical bars indicate the calculated Bragg reflections of the compound in the \(\text{Pbca}\) space group at ambient pressure. The Miller indices corresponding to the most intense peaks are included.

Figure 2 shows the evolution of the XRD pattern of \(\text{Rb}_2\text{CuCl}_4\) with pressure in the 0 – 15 GPa range. XRD patterns in the whole pressure range can be indexed like for ambient-pressure on the basis of an orthorhombic structure, although we used a general \(\text{Pbca}\) orthorhombic space group in order to allow structural distortions associated with octahedron tilts. The analysis of the XRD diagrams shows no indication of structural transitions to the monoclinic structure. The absence of splitting in \((2n \ 0 \ 0)\) and \((0 \ 2n \ 0)\) peaks supports this view. The variation of the lattice parameters and the cell volume with the corresponding Murnaghan equation of state (EOS) parameters are shown in Fig. 3. We observe an anomaly in the volume variation, \(V(P)\), at 3 GPa that associate to a pressure-induced phase transition likely related to another orthorhombic high pressure phase. Interestingly, the obtained bulk modulii, \(B_0 = 19.7 \ \text{GPa}\) and \(23.6 \ \text{GPa}\) in the low- and high-pressure phases, respectively, are bigger to that measured for \((\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4\), \(B_0 = 7.1 \ \text{GPa}\) (Rodriguez, 2001), but an order of magnitude smaller than the local bulk modulus measured for \(\text{CuCl}_6\) (\(B_{\text{loc}} = 63 \ \text{GPa}\)).
result clearly suggests that pressure induces tilting in Rb$_2$CuCl$_4$ provided that the local bulk modulus for CuCl$_6$ has a similar value. Note that the intralayer Cu-Cu distance varies from 5.08 to 4.48 Å from ambient pressure to 15 GPa (Fig. 3). This variation would lead to a reduction of the axial distance, $\Delta R_{ax} \approx -0.5$ Å provided that $\Delta R_{eq} \approx -0.1$ Å, and if the ideal perovskite structure (Cu-Cl-Cu angle = 180º) is maintained under pressure, thus yielding suppression of the JT effect. Given that the local structure of CuCl$_6$ changes slightly in this pressure range we conclude that in-layer CuCl$_6$ octahedra experience tilting phenomena under pressure. This way makes the bulk volume reduction compatible with preservation of the JT distortion.

Figure 4 shows the XAS of Rb$_2$CuCl$_4$ as a function of pressure. The analysis of the EXAFS region provides the structural parameters given in Table II. It must be noted that the EXAFS spectrum was fitted on the basis of the CuCl$_6$ unit of tetragonal (D$_{4h}$) symmetry due to the reduced number of oscillations (four) available in the diamond anvil cell. With this structural model we were able to obtain reliable Cu-Cl bondlength variations from the spectra of Fig. 4. The variation of the equatorial and axial Cu-Cl distances, $R_{eq}$ and $R_{ax}$, with pressure is shown in Fig. 5. In this figure we also compare the variations experienced by the intralayer Cu-Cu distance derived from XRD, $d_{Cu-Cu} = \frac{1}{2} (a^2 + b^2)^{1/2}$ with $d = R_{ax} + R_{eq}$ derived from EXAFS. These two distances must coincide if the Cu-Cl-Cu bond angle was 180º in the whole pressure range. Furthermore, this plot provides direct information on the tilting phenomena in Rb$_2$CuCl$_4$. In particular, we would expect a variation of the Cu-Cl-Cu towards 180º if the pressure variation $\Delta d_{Cu-Cu}$ was shorter than $\Delta (R_{ax}+R_{eq})$, while the opposite would occur if as in present case $\Delta d_{Cu-Cu} > \Delta (R_{ax}+R_{eq})$. Therefore results of Fig. 5 clearly show that pressure induces CuCl$_6$ tilting in Rb$_2$CuCl$_4$ rather than suppression of the JT effect. Actually, we do observe a progressive reduction of $R_{ax}$ and $R_{eq}$ with pressure, the axial-distance variation in the 0 -15 GPa range, $\Delta R_{ax} = -0.18$ Å, being an order of magnitude bigger that the equatorial one, $\Delta R_{eq} = -0.01$ Å. It means that apart from tilting pressure also induces a progressive reduction of the JT distortion, which is $\Delta Q_0 = Q_{0}(15) - Q_{0}(0) = 0.32 - 0.51 = -0.19$ Å from 0 to 15 GPa. The JT distortion is reduced to almost one half its ambient-pressure value at 15 GPa. Extrapolation of data indicates that the pressure required for a fully JT suppression is about 41 GPa (Fig. 5). A similar pressure was also found in (C$_3$H$_7$NH$_3$)$_2$CuCl$_4$ (Rodriguez,
However it is worth pointing out that the present results really differ from the reported values (9 GPa) derived from Raman experiments in the isomorphous (C$_2$H$_5$NH$_3$)$_2$CuCl$_4$ (Moritomo, 1994). In view of the present structural study we conclude that the use of the technique Raman for this purpose is subtle since peak disappearance may be related to tilting dynamics rather than transformations of CuCl$_6$ local structure. Experiments along this line are currently in progress.

**Figure 4** Variation of XAS for Rb$_2$CuCl$_4$ as a function of pressure. The inset shows the XANES part of spectra in the same pressure range. There is no direct evidence of drastic changes in the local structure around Cu$^{2+}$ from the variation of XANES signal under pressure.

**Figure 5** (left) Pressure dependence of local Cu-Cl distances ($R_{ax}$ and $R_{eq}$) of Rb$_2$CuCl$_4$ with pressure. The inset shows the extrapolation of these distances that converge at 41 GPa what implies the disappearance of the Jahn-Teller distortion in the CuCl$_6$ octahedra. (right) Variation of Cu-Cu intralayer distance ($d_{Cu-Cu}$) derived from XRD and $R_{ax} + R_{eq}$ from XAS. Inset shows the tilting angle calculated from $\varphi = \arccos \left( \frac{d_{Cu-Cu}^2 - R_{ax}^2 - R_{eq}^2}{-2R_{ax}R_{eq}} \right)$. 
Anyhow the high-pressure range required to suppress the JT distortion, \( P = 41 \text{ GPa} \) in \( \text{Rb}_2\text{CuCl}_4 \) (Fig. 5), could be anticipated from the JT energy of \( \text{CuCl}_6 \) derived from optical absorption spectroscopy, \( E_{JT} = 0.3 \text{ eV/Cu} \) (Aguado, 2005). This JT energy and the associated distortion, \( Q_\theta = 0.51 \text{ Å} \), likely suggest that the JT-suppression pressure at which \( Q_\theta = 0 \) must be above 20 GPa, confirming the present estimates.

### Table II

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>( R_{ax} ) (Å)</th>
<th>( R_{eq} ) (Å)</th>
<th>( Q_{\theta} ) (Å)</th>
<th>( V_{oct} ) (Å³)</th>
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<tr>
<td>0.6</td>
<td>2.73</td>
<td>2.26</td>
<td>0.543</td>
<td>18.59</td>
</tr>
<tr>
<td>15.9</td>
<td>2.53</td>
<td>2.24</td>
<td>0.335</td>
<td>16.93</td>
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</table>

Table II Local Cu-Cl bond distances and structural parameters of \( \text{Rb}_2\text{CuCl}_4 \) under pressure obtained from XAS data. Note that \( V_{oct} = 4/3R_{ax}R_{eq}^2 \).

### Conclusions

From XRD and EXAFS experiments carried out in \( \text{Rb}_2\text{CuCl}_4 \) we conclude that pressure induces reduction of the Cu-Cl distances, \( R_{ax} \) and \( R_{eq} \), of the elongated octahedron as well as the intra- and interlayer Cu-Cu distances. Interestingly, the different compressibility of the bulk crystal and the \( \text{CuCl}_6 \) octahedron is associated with \( \text{CuCl}_6 \) tilts. Apart from the anisotropic variation of the crystal volume, the local \( \text{CuCl}_6 \) bulk modulus is an order of magnitude bigger than the crystal bulk modulus. This huge difference has been related to the stiffness of the Cu-Cl bonds which preserves the JT distortion of the \( \text{CuCl}_6 \) octahedra for pressures up to 20 GPa according to the JT energy \( (E_{JT} = 0.3 \text{ eV/Cu}) \). A salient conclusion is that the application of pressure to these layered perovskites in the 0 – 16 GPa range induces both octahedron tilting and reduction of the JT distortion, although in no way a suppression of the JT distortion can be achieved below 20 GPa.

### Acknowledgments

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