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PRESSURE-INDUCED CLOSURE OF THE JAHN-TELLER DISTORTION IN $Rb_2CuCl_4(H_2O)_2$

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This work investigates the pressure-induced variation of the local structure around Cu^{2+} as well as the crystal structure in $Rb_2CuCl_4(H_2O)_2$ through XAS and XRD techniques. The application of pressure induces a structural change in the Jahn-Teller (JT) $CuCl_4(H_2O)_2^{2-}$ complex from axially elongated to compressed. This change leads to the closing of the 2D JT distortion related to the four in-plane Cl^- ligands, which are responsible for the antiferrodistortive structure displayed by the crystal. It is shown that the presence of water ligands enhances a JT release. Their associated axial ligand-field favours the occurrence of such a local structural transition below the metallization pressure. The results are compared with recent pressure experiments on A_2CuCl_4 systems.

Keywords: Cu^{2+}; $CuCl_4(H_2O)_2$; Jahn-Teller effect; XRD and XAS under pressure; Layer perovskite

INTRODUCTION

The presence of Cu^{2+} ($3d^9$) or Mn^{3+} ($3d^4$) ions either as constituent or impurity in insulating materials gives rise to a great variety of coordination geometries. This is a direct consequence of the Jahn-Teller (JT) effect related to the e_g hole or electron ground state [1–6]. The occurrence of an elongated geometry around Cu^{2+} or Mn^{3+} can be explained on the basis of electron phonon coupling between octahedral E_g electronic states and e_g vibrations: $e \otimes E$ JT model. In hexacoordinated systems CuX_6^{4-} ($X = H_2O$, NH_3, O, F, Cl, Br), the observed coordination geometries mostly correspond to low-symmetry elongated octahedra [1–3]. Both the JT distortion and the packing of Cu^{2+} complexes strongly influence the optical and magnetic properties of these materials, hence the establishment of structural correlations is crucial for a microscopic characterization [1, 2]. Interestingly, the $e \otimes E$ model predicts that a change of the coordination geometry from elongated to compressed passing through different orthorhombic intermediates, or even JT suppressed can be attained by applying axial stress or hydrostatic pressure. Although there has been an increasing interest to release the JT distortion by applying high pressure, only few experiments were able to show a complete reduction of the JT effect [7–10]. Moreover no clear evidence of this phenomenon was reported so far using local probes [10]. In fact pressure-induced phase transitions observed in A_2CuCl_4

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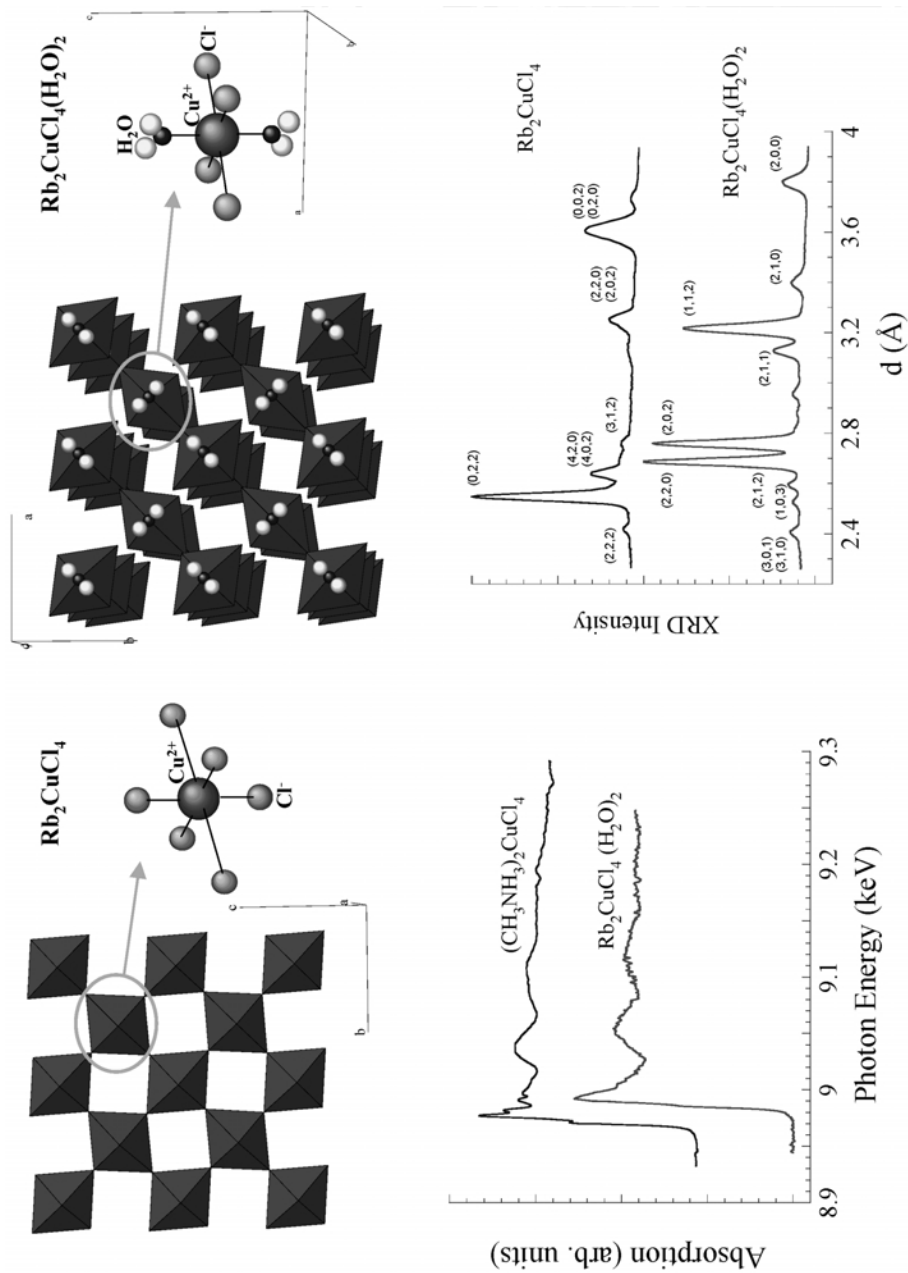FIGURE 1 (Top) Crystal structure of Rb_2CuCl_4 (*Cmca*) and $Rb_2CuCl_4(H_2O)_2$ (*P4$_2$/mnm*). Only the Cu complexes displaying an antiferrodistortive structure are depicted. (Bottom) Corresponding XAS and XRD results obtained for $CuCl_6^{4-}$ and $CuCl_4(H_2O)_2^{2-}$ at ambient conditions.

(A: alkylammonium ion) by Raman and optical spectroscopy was initially ascribed to structural changes associated with the suppression of the JT distortion [7]. But structural studies performed by X-ray absorption (XAS) and X-ray diffraction (XRD) techniques in [C$_3$H$_7$NH$_3$]$_2$CuCl$_4$ showed that indeed such transformations are mainly related to tilts of the CuCl$_6^{4-}$ octahedral rather than to the JT suppression [10]. These pressure results reflect the tendency of the CuCl$_6^{4-}$ complex to preserve their *molecular character* associated with the JT distortion. In fact it is due to the higher compressibility of the crystal with respect to the local compressibility of CuCl$_6^{4-}$, whose molecular stiffness is enhanced by the additional binding energy of about 1 eV related to the JT distortion [3].

This work investigates the effect of pressure on the JT distortion of Cu^{2+} in the antiferro-distortive (AF) Rb$_2$CuCl$_4$(H$_2$O)$_2$ through XRD and XAS in the 0–250 kbar range. This compound is interesting since it offers the possibility of exploring structural changes related to the JT effect in isolated heteronuclear complex [CuCl$_4$(H$_2$O)$_2$]$^{2-}$ with elongated rhombic symmetry (Fig. 1). The presence of two water ligands exert an axial compression favouring release of the JT distortion at moderates pressures; *i.e.* below the metallization pressure. This aspect is important in order to establish correlations between the crystal structure and the electronic and vibrational structures from optical spectroscopy.

Our objective is to elucidate whether the application of pressure mainly induces rotation of the [CuCl$_4$(H$_2$O)$_2$]$^{2-}$ distorted octahedra or it is able to suppress the AF structure. This latter case would modify the local structure from an elongated geometry to a compressed situation with four identical Cu—Cl bonds and the short Cu—H$_2$O bond as fourfold axis. This behaviour allows us to know how the linear JT electron–phonon coupling in Cu^{2+} and high-order interaction terms depend on pressure and consequently how they affect materials properties. In particular, the proposed transformation implies a modification of the electronic ground state with the unpaired electron changing from mainly $d_{x^2-y^2}$ to $d_{3z^2-r^2}$. This latter situation is attained in [CuCl$_4$(NH$_3$)$_2$]$^{2-}$ formed in Cu^{2+}-doped NH$_4$Cl by replacing the H$_2$O axial crystal-field by NH$_3$ [11, 12].

EXPERIMENTAL

Single crystals of [CH$_3$NH$_3$]$_2$CuCl$_4$, Rb$_2$CuCl$_4$ and Rb$_2$CuCl$_4$(H$_2$O)$_2$ were grown by slow evaporation from alcoholic solutions following the procedure given elsewhere [2].

XAS experiments under pressure were performed at the absorption setup XAS10 of the D11 beamline at LURE (Orsay). The EXAFS spectra of the investigated Rb$_2$CuCl$_4$(H$_2$O)$_2$ were measured at the Cu K-edge ($E_0 = 8.99$ 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. XRD experiments under pressure were done in the energy dispersion setup WDIS of the DW11A beamline at LURE. The XRD and XAS data were analysed by means of the FULLPROF [13] and the WINSAX package programs, respectively.

In both experiments the pressure was applied with a membrane-type diamond anvil cell employing silicon oil as pressure transmitter. The pressure was measured from the R-line shift of Ruby.

RESULTS AND DISCUSSION

Figure 1 shows the crystal structure of the Rb$_2$CuCl$_4$ and the corresponding hydrate Rb$_2$CuCl$_4$(H$_2$O)$_2$. Note the different coordination geometry of Cu^{2+} in each structure as
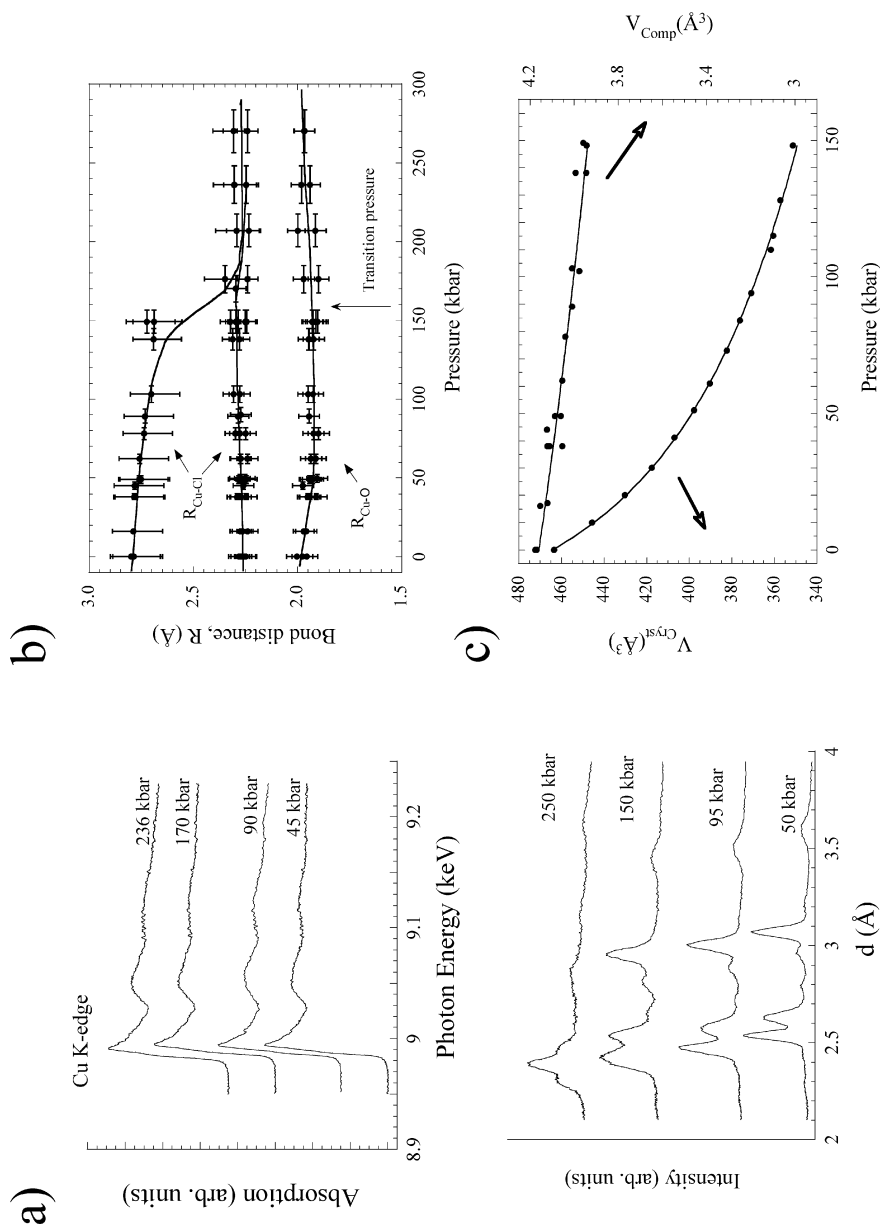
FIGURE 2 (a) Variation of XAS and XRD for $Rb_2CuCl_4(H_2O)_2$ as a function of pressure. (b) Corresponding distance variation of Cu−Cl (R_1 and R_2) and Cu−H$_2$O (R_3) derived from XAS with pressure. (c) Complex volume ($V_{Comp} = \frac{1}{3}R_1 \cdot R_2 \cdot R_3$) and crystal cell volume ($V = a^2 c$) variation as a function of pressure. The solid lines correspond to the least-square fits to the Murnaghan equation-of-state using $B_{loc} = 2300$ (300) kbar, and $B'_{loc} = 6$ for the complex, and $B_0 = 205$ (8) kbar and $B' = 5.8$ (0.2) for the crystal.

well as the distinct character of the AF structure. In Rb$_2$CuCl$_4$(H$_2$O)$_2$, the Cu^{2+} complexes are isolated and do not share any common ligand in contrast to Rb$_2$CuCl$_4$, whose intercon-nected CuCl$_6^{4-}$ units form layers.

The XRD and XAS data of Figure 1 allow comparison between the different crystal struc-ture and local structure around Cu^{2+} in Rb$_2$CuCl$_4$ and Rb$_2$CuCl$_4$(H$_2$O)$_2$. Apart from differ-ences in XRD, which are associated with the orthorhombic *Cmca* and tetragonal *P4$_2$/mnm* structures, respectively, a salient feature is the different XANES signal observed for each complex. According to previous findings [14, 15], the disappearance of the peak around 8.991 keV reveals the change of local structure from CuCl$_6^{4-}$ to CuCl$_4$(H$_2$O)$_2^{2-}$. Also the K-edge energy, whose maximum peaks at 8.977 and 8.998 keV, respectively, reveals such dif-ference. The displacement towards high energy observed in the hydrate complex is probably due to the stronger ligand-field by the presence of water molecules.

Figure 2 shows the variation of XAS and XRD corresponding to Rb$_2$CuCl$_4$(H$_2$O)$_2$ as a function of pressure. The corresponding variations of Cu−Cl and Cu−H$_2$O bond distances derived from XAS as well as the crystal and complex volumes in Rb$_2$CuCl$_4$(H$_2$O)$_2$ as a func-tion of pressure are also included in Figure 2. Interestingly, the pressure behaviour of the complex and the crystal is rather different. This phenomenon reflects the stiffness of the Cl−Cu and H$_2$O−Cu bonds of the JT distorted complex, whose local bulk modulus is an order of magnitude greater than the crystal bulk modulus. A similar result was observed in [C$_3$H$_7$NH$_3$]$_2$CuCl$_4$ for CuCl$_6^{4-}$ [10]. However the abrupt change in the Cu−Cl distance observed in Rb$_2$CuCl$_4$(H$_2$O)$_2$ at 150 kbar is noteworthy. The short Cu−Cl distance slightly increases with pressure whereas the elongated Cu−Cl bond reduces to a common distance, $R = 2.27$ Å. This pressure-induced transformation actually corresponds to the searched clo-sure of the JT distortion, leading to a change of the Cu coordination from an elongated rhom-bic structure to a tetragonal compressed situation above 150 kbar. The associated bond lengths are 2.81 Å and 2.26 Å for Cu−Cl, and 1.97 Å for Cu−H$_2$O, in the low-pressure phase, while they are 2.27 Å and 1.96 Å for Cu−Cl and Cu−H$_2$O, respectively, in the high-pressure JT-suppressed phase. This change is also accompanied by a crystal phase-transition, which is clearly evidenced by the splitting of the (220) Bragg peak. The origin of this high-pressure phase is currently under investigation.

In conclusion, we demonstrate throughout this work that the JT distortion in Cu^{2+} can be more effectively released in axially stressed complexes. In the present case, this situation is attained through the heteronuclear complex [CuCl$_4$(H$_2$O)$_2$]$^{2-}$ whose water ligands favour the local structure transformation to occur at moderate pressures. In fact water molecules provide an axial ligand-field halfway between that attained in the homonuclear CuCl$_6^{4-}$ com-plex associated with a $x^2 - y^2$ unpaired electron and the heteronuclear tetragonal-compressed [CuCl$_4$(NH$_3$)$_2$]$^{2-}$ complex with $3z^2 - r^2$ ground state. The ammonium ligand-field prevents a 2D JT distortion associated with the Cl ligands [11, 12]. A complete account of this research will be reported in a forthcoming publication.

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