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## The role of Jahn–Teller distortion in insulator to semiconductor phase transition in organic–inorganic hybrid compound (*p*-chloroanilinium)<sub>2</sub>CuCl<sub>4</sub> at high pressure

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(*p*-Chloroanilinium)<sub>2</sub>CuCl<sub>4</sub>(C<sub>2</sub>H<sub>14</sub>Cl<sub>6</sub>CuN<sub>2</sub>) is from an important family of organic–inorganic layered hybrid compounds which can be a possible candidate for multiferroicity. *In situ* high pressure FTIR, Raman and resistivity measurements on this compound indicate the weakening of Jahn–Teller distortion and the consequent removal of puckering of the CuCl<sub>6</sub><sup>4−</sup> octahedra within the layer. These effects trigger insulator to semiconductor phase transition along with a change in the sample colour from yellow to dark red. This article explains the crucial role of the anisotropic volume reduction of the CuCl<sub>6</sub><sup>4−</sup> octahedron (caused due to the quenching of Jahn–Teller distortion) in the observed insulator to semiconductor phase transition.

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### Introduction

Organic–inorganic hybrid perovskite compounds (OIHCs) have drawn considerable attention of researchers owing to their potential candidacy for multifunctional materials.<sup>1–4</sup> OIHCs of type A<sub>2</sub>MX<sub>4</sub> (A: alkyl or aromatic ammonium cation, M: transition metal, X: halogen) crystallize in a layered perovskite structure consisting of nearly isolated layers of corner-shared MX<sub>6</sub> octahedra sandwiched by ‘A’ cations. The NH<sub>3</sub> group of the alkyl ammonium cations occupies the cavities between the octahedra to form N–H⋯X hydrogen bonds with the octahedra. The type of organic ligand and its approach towards the metal ion are responsible for the strength of Jahn–Teller distortion (JTD) and hence the splitting of d levels. This coordination geometry around Cu<sup>2+</sup> in the CuCl<sub>6</sub><sup>4−</sup> complexes is the main reason for colour of these compounds. The effect of JTD on organic–inorganic compounds has been found to be a linear function of the length of the organic cation.<sup>5</sup> The strength of the crystal field splitting can also be tuned by applying pressure or varying temperature to explore piezochromic or thermo-chromic properties. In addition, high pressure can lift the inversion symmetry and/or change hydrogen bonding interactions in these compounds.

As a result, these compounds can show ferroelectricity in combination with ferro/antiferro magnetism making them multiferroic materials. With this aim in mind, we performed *in situ* high pressure measurements on (*p*-chloroanilinium)<sub>2</sub>CuCl<sub>4</sub> (PClAnCuCl) and detailed results are discussed in this report.

Structure of (PClAnCuCl) is monoclinic (S.G.: *P2<sub>1</sub>/c*)<sup>6,7</sup> consisting of CuCl<sub>6</sub><sup>4−</sup> octahedra strongly deformed due to the cooperative Jahn–Teller (JT) effects called JT distortion (JTD). JTD lifts the degeneracy of the e<sub>g</sub> orbital in the t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>3</sup> electron configuration of the Cu<sup>2+</sup>(3d<sup>9</sup>) ions. The CuCl<sub>6</sub><sup>4−</sup> octahedra are arranged in an anti-ferrodistortive (AFD) arrangement in the *bc* plane. This gives rise to two types of Cu–Cl distances, shorter (*D<sub>s</sub>*) and longer (*D<sub>i</sub>*) as 2.307 Å and 2.904 Å, respectively, in addition to a slight puckering in the CuCl<sub>4</sub><sup>2−</sup> layer as shown in Fig. 1(a). (PClAnCuCl) shows (Fig. 1(b)) two distinct types of NH⋯Cl hydrogen bonding interactions one with a terminal Cl and the other one with a bridging Cl atom, as revealed from single crystal X-ray diffraction studies.<sup>6,7</sup> One of the main structural features discussed in the literature for the association of thermo/piezochromic and multiferroic properties is AFD arrangement displayed by the Jahn–Teller axially elongated CuCl<sub>6</sub><sup>4−</sup> ions. AFD favours in-plane ferromagnetic interactions between metal ions *via* Cu–Cl–Cu super exchange, making the material ferromagnetic below 9 K.<sup>7</sup> In the case of a similar layered hybrid material, (C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub>,<sup>8</sup> pressure has resulted in a decrease in the charge transfer (CT) band gap energy and a selective deactivation of the Cu–Cl stretching mode in Raman spectra at 4 GPa. The probable cause was speculated as the disappearance of AFD arrangement at 4 GPa. It was indicated<sup>8</sup> and then experimentally verified<sup>9</sup> that the

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