

DEPENDENCE OF THE $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ CHARGE TRANSFER WITH HYDROSTATIC PRESSURE IN THE PURE AND Cu-DOPED A_2MCl_4 ($\text{M} = \text{Mn}, \text{Cd}, \text{Cu}$) LAYER PEROVSKITE. STRUCTURAL CORRELATIONS

R. VALIENTE^a, F. RODRÍGUEZ^{a,*}, M.T. BARRIUSO^b,
J.A. ARAMBURU^a and M. MORENO^a

^aDCITIMAC, ^bDepartamento de Física Moderna, Facultad de Ciencias,
Universidad de Cantabria, Santander 39005, Spain

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This work investigates the dependence of the $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ Charge Transfer (CT) bands with the local structure around Cu^{2+} in the Jahn–Teller CuCl_6^{4-} complexes formed in layer chloroperovskites with the K_2NiF_4 -type structure. We present experimental results on the variation of the first CT band of CuCl_6^{4-} with hydrostatic pressure in the 0–80 kbar range. The study has been carried out in CuCl_6^{4-} formed either as impurity in Cu^{2+} -doped crystals or in pure A_2CuCl_4 compounds in order to establish structural correlations. A noteworthy feature is the redshift undergone by the first CT band at about $26\,000\text{ cm}^{-1}$, upon pressure in all the investigated systems. This redshift is interpreted in terms of anisotropic distortions of the octahedral elongated CuCl_6^{4-} complex. MS-X α and Extended Hückel calculations of the electronic structure around the D_{4h} equilibrium geometry allow us to establish correlations between the energy shift and the structural distortions of the complex.

Keywords: Jahn–Teller; CuCl_6^{4-} ; Impurity; Charge transfer; Hydrostatic pressure

1 INTRODUCTION

The optical properties of CuCl_6^{4-} strongly depend on the degree of the Jahn–Teller (JT) distortion displayed by the complex due to the $3d^9$

* Corresponding author.

configuration of Cu^{2+} [1]. The knowledge of how the Charge Transfer (CT) and Crystal Field (CF) spectra depend on the complex structure is worthwhile to understand the variations of colour or dichroism associated with these complexes upon structural changes induced by pressure or temperature.

The aim of this work is to correlate the CT states with the CuCl_6^{4-} structure, i.e. metal–ligand distances and complex symmetry. For this purpose we investigate the variation of the CT spectra of Cu^{2+} -doped A_2MCl_4 ($\text{M} = \text{Mn}, \text{Cd}$) and the pure A_2CuCl_4 with the hydrostatic pressure. Attention is paid for explaining the origin of the observed pressure-induced CT redshift. In fact, this is an unusual phenomenon and contrasts with the CT blueshift experienced by octahedral transition complexes upon totally symmetric bond length reduction [2]. In this work we interpret the observed redshift in terms of different length variation of the axial and equatorial $\text{Cu}-\text{Cl}$ bonds of the complex. The MS-X α and Self-Consistent Charge-Extended Hückel (SCCEH) calculations carried out for several CuCl_6^{4-} configurations around the equilibrium geometry support this interpretation and allow us to establish structural correlations between the CT energy and the complex structure.

2 EXPERIMENTAL

Single crystals of Cu^{2+} -doped A_2MCl_4 and A_2CuCl_4 ($\text{A} = \text{alkyl-ammonium}$; $\text{M} = \text{Cd}, \text{Mn}$) were grown from slow evaporation as indicated elsewhere [3,4]. Hydrostatic pressure experiments were performed with a Diamond Anvil Cell (High Pressure Diamond Optics, Inc). Paraffin oil was used as pressure transmitter as well as to prevent crystal hydration. We have verified that paraffin oil is able to operate as proper hydrostatic transmitter up to 80 kbar. The optical absorption spectra of the Cu^{2+} -doped single crystals were obtained with the double beam spectrometer described elsewhere [5], whereas the spectra of the pure A_2CuCl_4 crystals were taken from an implemented single-beam spectrometer adapted for measuring optical densities in the 0–5 range. This optical density range is required when dealing with CT spectra of pure A_2CuCl_4 crystals (absorption coefficient, $k \sim 5 \times 10^4 \text{ cm}^{-1}$). Electronic structure calculations were performed for

different structural configurations of CuCl_6^{4-} using SCCEH and MS-X α methods in a correlated way. This way provides a reliable procedure of estimating energy shifts [6].

3 RESULTS AND DISCUSSION

Figure 1 shows the CT spectra of the Cu^{2+} -doped A_2CdCl_4 and A_2MnCl_4 , as well as the pure A_2CuCl_4 crystals. The spectra consist basically of two $e_u \rightarrow b_{1g}$ bands with associated transition oscillator strengths of 0.01–0.1 [3], placed around 25 000 and 36 000 cm^{-1} . These spectra have been explained on the basis of elongated CuCl_6^{4-} complexes of nearly D_{4h} symmetry having the tetragonal axis on the perovskite layer (*c*-plane), such as it has been demonstrated from polarized optical absorption [3,4] and EPR [7]. The CT redshift observed on passing from Cu to Cd and Mn (Fig. 1) were already related to structural distortions of the Cu complex taking into account that the

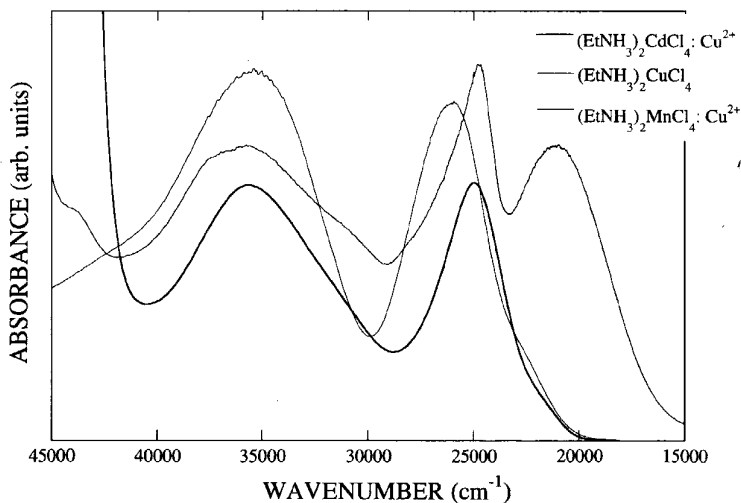


FIGURE 1 Polarized optical absorption spectra of the Cu^{2+} -doped $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{-CdCl}_4$ and $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{-MnCl}_4$ perovskite layers as well as of the pure $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{-CuCl}_4$ at room temperature. The spectra were taken with *E* parallel to the *a* and *b* basal directions.

actual CuCl_6^{4-} structure in Cu^{2+} -doped A_2MCl_4 , though similar to the elongated one displayed in the antiferrodistortive A_2CuCl_4 crystal, must be somewhat distorted toward the compressed situation of the MCl_6^{4-} site by chemical pressure effects [8]. This effect is noteworthy since it can lead to interesting chromic effects such as piezochromism if such structural changes are induced by pressure. The foresight of this model has been supported by hydrostatic pressure experiments performed on the Cu^{2+} -doped A_2MCl_4 [8] (Fig. 2). The observed redshifts were interpreted according to the model in terms of structural changes around the copper, in such a way that the effect of pressure is mainly to reduce the in-plane axial distance and probably to increase the equatorial Cu-Cl distance, this latter being responsible for the observed redshifts [9].

Figure 3 shows the pressure experiments carried out on A_2CuCl_4 . The use of this crystal is advantageous since it provides an easy way to establish structural correlations. Like in doped crystals,

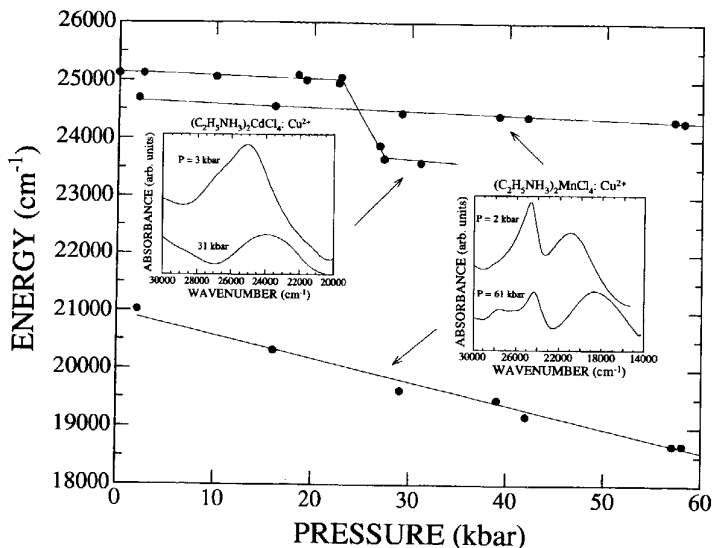


FIGURE 2 Variation of the first $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ CT band of Cu^{2+} -doped $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{-CdCl}_4$ and Cu^{2+} -doped $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4$ with pressure. The insets show the spectra of both systems for two different pressures. Note the pressure-induced redshift on the CT bands.

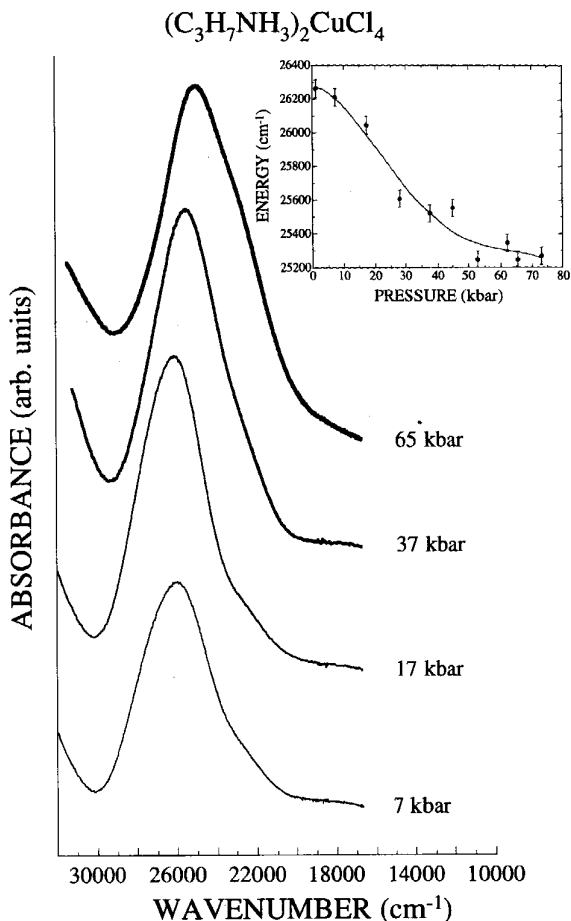


FIGURE 3 Pressure dependence of the the first $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ CT band corresponding to the pure $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4$ crystal. The inset shows the variation of the peak energy with pressure up to 73 kbar. Note the continuous redshift of -1000 cm^{-1} undergone by this band in the whole pressure range.

a pressure-induced redshift of the first CT band of 1000 cm^{-1} is observed in the 0–80 kbar range (inset of Fig. 3). This result is similar to that observed by Moritomo and Tokura [10] in $(\text{EtNH}_3)_2\text{CuCl}_4$ and shows the close relation between the redshift and the antiferrodistortive structure displayed by the CuCl_6^{4-} complex in A_2CuCl_4 . We have

interpreted this redshift by the different variation of R_{ax} and R_{eq} upon pressure imposed by the crystal structure of these layered systems. In particular we propose that the volume cell reduction induced by pressure, i.e. the reduction of the Cu–Cu distance, is mainly accomplished at expenses of the axial Cu–Cl length given that the associated bond is much weaker than the corresponding equatorial Cu–Cl bond, such as it is deduced from the corresponding vibrational frequencies [11]. However, topological arguments suggest that a reduction of the axial distance upon pressure can be accompanied by an increase of the equatorial distance provided that $\partial R_{ax}/\partial P$ is slightly higher than $\partial R_{Cu-Cu}/\partial P$ (note that $R_{Cu-Cu} \approx R_{ax} + R_{eq}$ in these layered structures).

Table I shows the calculated energy of the first CT transition of $CuCl_6^{4-}$ around the equilibrium geometry, $R_{ax} = 2.85 \text{ \AA}$ and $R_{eq} = 2.35 \text{ \AA}$, as well as the distance derivatives. The results indicate that a pressure-induced redshift of the CT band is possible whenever $\partial R_{ax}/\partial P < 0$ and $(\partial R_{eq}/\partial P) \geq 0.27|\partial R_{ax}/\partial P|$ keeping the D_{4h} symmetry. This conclusion is based on the high sensitivity of the CT band to changes of R_{eq} in comparison to R_{ax} . For a given variation, ΔR , the electrostatic effects of the axial ligands are weaker than those from the strongly bonded equatorial ligands, due to the different equilibrium distance. From results of Table I we can write the CT redshift

TABLE I Transition energies, E_{CT} , corresponding to the first CT $e_u \rightarrow b_{1g}$ transition of $CuCl_6^{4-}$ calculated from the SCCEH and MS- $X\alpha$ methods for several configurations. R_{eq} and R_{ax} are the equatorial and axial Cu–Cl distances, respectively. The average derivatives are given in parenthesis

Configuration $R_{eq} (\text{\AA}) - R_{ax} (\text{\AA})$	SCCEH $E_{CT} (\text{cm}^{-1})$	MS- $X\alpha$ $E_{CT} (\text{cm}^{-1})$
2.35–2.70		28 193
2.35–2.80	23 281	27 252
2.35–2.90	21 887	26 664
2.35–3.00	20 668	
2.30–2.90	24 154	
2.35–2.90	21 887	
2.40–2.90	19 804	
2.265–2.80		30 141
2.35–2.80		27 252
$\partial E_{CT}/\partial R_{ax}$ ($\text{cm}^{-1}/\text{\AA}$)	–13 100	–7 800
	(–10 450)	
$\partial E_{CT}/\partial R_{eq}$ ($\text{cm}^{-1}/\text{\AA}$)	–42 500	–34 000
	(–38 250)	

in terms of the variations ΔR_{eq} and ΔR_{ax} :

$$\begin{aligned}\Delta E_{\text{CT}} &= [(\partial E_{\text{CT}}/\partial R_{\text{eq}})_{\text{ax}}(\partial R_{\text{eq}}/\partial P) + (\partial E_{\text{CT}}/\partial R_{\text{ax}})_{\text{eq}}(\partial R_{\text{ax}}/\partial P)]\Delta P \\ &= -38250 \Delta R_{\text{eq}} - 10450 \Delta R_{\text{ax}}.\end{aligned}$$

The observed redshift, $\Delta E_{\text{CT}} = -1000 \text{ cm}^{-1}$, can be accounted for on the basis of the present model if we assume that the structural change undergone by the complex from 1 bar to 80 kbar is $\Delta R_{\text{eq}} = +0.1 \text{ \AA}$ and $\Delta R_{\text{ax}} = -0.27 \text{ \AA}$. This result confirms the strong reduction of R_{ax} in comparison to the increase of R_{eq} upon pressure, thus driving the complex to a more compressed configuration. The perovskite layers are ideal systems to achieve such an anisotropic bond-distance variation upon hydrostatic pressure.

Preliminary XANES experiments carried out on the pure A_2CuCl_4 support this interpretation.

Acknowledgments

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