
 Received: 19 November 2018, Accepted: 10 May 2019

Edited by: A. Goñi, A. Cantarero, J. S. Reparaz

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 DOI: <http://dx.doi.org/10.4279/PIP.110004>



ISSN 1852-4249

Structural correlations in Cs_2CuCl_4 : Pressure dependence of electronic structures

 E. Jara,¹ J. A. Barreda-Argüeso,¹ J. González,¹ R. Valiente,² F. Rodríguez^{1*}

We have investigated the crystal structure of Cs_2CuCl_4 in the 0-20 GPa range as a function of pressure and how pressure affects its electronic properties by means of optical absorption spectroscopy. In particular, we focused on the electronic properties in the low-pressure $Pnma$ phase, which are mainly related to the tetrahedral CuCl_4^{2-} units distorted by the Jahn-Teller effect. This study provides a complete characterization of the electronic structure of Cs_2CuCl_4 in the $Pnma$ phase as a function of the cell volume and the Cu-Cl bond length, $R_{\text{Cu-Cl}}$. Interestingly, the opposite shift of the charge-transfer band-gap and the Cu^{2+} $d-d$ crystal-field band shift with pressure are responsible for the strong piezochromism of Cs_2CuCl_4 . We have also explored the high-pressure structure of Cs_2CuCl_4 above 4.9 GPa yielding structural transformations that are probably associated with a change of coordination around Cu^{2+} . Since the high-pressure phase appears largely amorphized, any structural information from X-ray diffraction is ruled out. We use electronic probes to get structural information of the high-pressure phase.

I. Introduction

Cs_2CuCl_4 (orthorhombic $Pnma$ at ambient pressure) is a wide-band-gap Charge-Transfer (CT) semiconductor ($E_g = 2.52$ eV), which exhibits a puzzling optical behaviour under pressure, associated with the Cu^{2+} absorption and its structural changes [1]. Both $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ CT and $d-d$ absorption bands undergo unusually large pressure shifts and intensity changes showing abrupt jumps at about 5 GPa. This crystal exhibits a yellow-orange color at ambient conditions and below 5 GPa, which is mainly defined by the tail of the CT band (band gap) placed around 450 nm [2]. The isolated

CuCl_4^{2-} tetrahedra in the $Pnma$ phase show a flattened (D_{2d}) distortion by the Jahn-Teller (JT) effect, which is responsible for the low-lying CT band gap, and thus its yellow-orange color, in comparison to other transition-metal ion (M) isomorphous compounds Cs_2MCl_4 ($M = \text{Co}, \text{Zn}$) [3]. Unlike Cs_2CoCl_4 , the $d-d$ bands of Cu^{2+} ($3d^9$), which are split by the JT distortion, do not affect the color as they appear in the near-infrared range at 1110 and 1820 nm [2, 3]. Thanks to the study of electronic and crystal structures under high-pressure conditions of this relatively highly compressible material (bulk modulus: $K_0 = 15.0(2)$ GPa) [4], we are able to establish structural correlations to understand: (i) the electronic properties of Cu^{2+} in tetrahedral coordination in the less compressible oxides; and (ii) how a lattice of independent CuCl_4^{2-} units under compression evolves towards denser phases. The variation of the crystal structure of Cs_2CuCl_4 and Cs_2CoCl_4 under pressure has been previously

*E-mail: fernando.rodriguez@unican.es

¹ MALTA TEAM, DCITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain.

² Nanomaterials Group-IDIVAL, Dpto. Física Aplicada, Universidad de Cantabria, 39005 Santander, Spain.

investigated by X-ray diffraction (XRD) in the 0-5 GPa range, where both crystals are in the $Pnma$ crystallographic phase. However, Cs_2CuCl_4 undergoes a structural phase transition just above 5 GPa yielding a deep color change from orange to black. The high pressure phase could not be identified by XRD due to amorphization [4]. In general, the optical properties of Cu^{2+} chlorides like Cs_2CuCl_4 are strongly dependent on the crystal structure (polymorphism), particularly, the Cu^{2+} coordination — symmetry and crystal-field strength— and the way Cu^{2+} ions are coupled to each other, *i.e.* either as isolated units or as interconnected Cu-Cu links through Cl^- ligand sharing [5, 6]. Therefore, the knowledge of how these links and crystal-field effects express in the optical spectra are essential to extract structural information from the electronic spectra at high-pressure conditions. An important goal is to establish correlations between structure and electronic properties [3]. In this work, we investigate the relationship between dihedral Cl-Cu-Cl angle of the JT-distorted flattened tetrahedra and the Cu^{2+} d -orbital splitting experimentally observed by optical absorption and its pressure dependence. These correlations will be used to analyze how the band gap energy and $d-d$ bands vary with pressure in the Cs_2CuCl_4 $Pnma$ phase, and how they change after the structural phase transition above 5 GPa.

II. Experimental

Single crystals of Cs_2CuCl_4 were grown by slow evaporation at 30°C from acidic (HCl) solution containing a 2:1 stoichiometric ratio of the CsCl and $CuCl_2 \cdot H_2O$. The $Pnma$ space group was checked by XRD on powder samples using a Bruker D8 Advance diffractometer. The measured cell parameters at ambient conditions were: $a = 9.770$ Å, $b = 7.617$ Å, $c = 12.413$ Å.

A Boehler-Almax Plate diamond anvil cell (DAC) was used for the high-pressure studies. 200 μm thickness Inconel gaskets were pre-indented and suitable 200 μm diameter holes were perforated with a BETSA motorized electrical discharge machine. Given that Cs_2CuCl_4 is soluble in common pressure transmitting media like methanol-ethanol-water (16:4:1), spectroscopic paraffin oil (Merck)

was used as alternative pressure transmitting media. It must be noted, however, that according to the ruby line broadening non-hydrostatic effects were significant in the explored range, as previously reported [6].

The microcrystals used for optical absorption in the high-pressure experiments were extracted by cleavage from a Cs_2CuCl_4 single crystal. The crystal quality was checked by means of a polarizing microscope. The $d-d$ spectra were obtained using powdered Cs_2CuCl_4 filling the gasket hole of the DAC for obtaining suitable optical and infrared absorption spectra due to the high oscillator strength of these transitions. The experimental set-up for optical absorption measurements with a DAC has been described elsewhere [8–11]. The spectra were obtained by means of an Ocean Optics USB 2000 and a NIRQUEST 512 monochromators equipped with Si- and InGaAs-CCD detectors for the VIS and NIR, respectively. A Thermo Nicolet Continuum FTIR provided with a reflective-optic microscope was used in the IR range. Pressure was calibrated from the ruby R-line luminescence shift.

III. Results and discussion

i. Electronic structure, optical absorption spectra and piezochromism of Cs_2CuCl_4

The optical absorption spectrum of Cs_2CuCl_4 at ambient pressure in the $Pmna$ phase consists of two intense bands in the near infrared associated with $d-d$ electronic transitions within the $CuCl_4^{2-}$ (D_{2d}) and a ligand-to-metal CT absorption in the visible, which is responsible for the band-gap and the concomitant yellow–orange color of this crystal (Fig. 1). $d-d$ peaks can be assigned to tetrahedral crystal-field transitions of $CuCl_4^{2-}$ using both T_d and D_{2d} irreps notation [12]. Within D_{2d} , the two main absorption peaks correspond to spin-allowed $d-d$ electric-dipole transitions from the 2B_2 ground state to the 2E and 2A_1 excited states and are located at 0.55 and 1.3 eV, respectively. It must be noted that the first transition ${}^2B_2 \rightarrow {}^2E$ is associated with the splitting of the parent-tetrahedral 2T_2 state into ${}^2B_2 + {}^2E$ due to the JT distortion of D_{2d} symmetry with 2B_2 being the electronic ground state corresponding to a flattened tetrahedron (inset of Fig. 1). Thus, the presence of this transition in the optical spectra constitutes

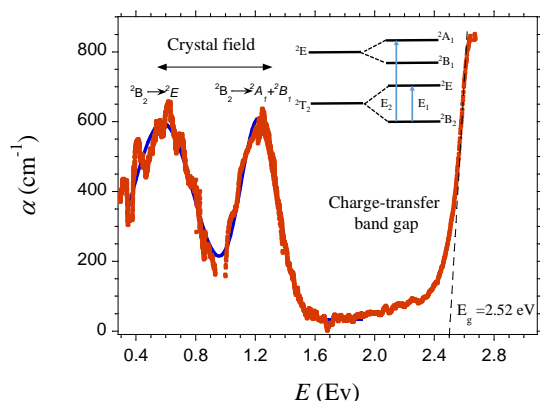


Figure 1: Optical absorption spectrum of Cs_2CuCl_4 at ambient conditions. The blue line represents the fit of the experimental points to the sum of two Gaussian profiles. The crystal-field bands correspond to crystal-field $d-d$ transitions: ${}^2B_2 \rightarrow {}^2E$ (0.55 eV) and ${}^2B_2 \rightarrow {}^2A_1$ (1.30 eV) in D_{2d} symmetry. The high-energy absorption threshold corresponds to the $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ CT band gap, which is $E_g = 2.52$ eV.

the fingerprint of a JT distortion; in T_d the corresponding transition energy, *i.e.* 2T_2 splitting, would be zero besides splitting contributions caused by the spin-orbit interaction. As it is shown in Fig. 1, the splitting of ${}^2B_2 \rightarrow {}^2A_1 + {}^2B_1$ transitions (a single ${}^2T_2 \rightarrow {}^2E$ transition in T_d) is not observed spectroscopically as they appear as a single band in the absorption spectrum due to symmetry selection rules. Actually, in D_{2d} , there are only two allowed electric-dipole transitions from the 2B_2 ground state: ${}^2B_2 \rightarrow {}^2E$ (x, y -polarized) and ${}^2B_1 \rightarrow {}^2A_1$ (z -polarized) [7], in agreement with experimental observations.

Figure 2 shows the peak energy variations of $d-d$ transitions as a function of pressure in both $Pnma$ and high-pressure phases of Cs_2CuCl_4 . Their transition energies and corresponding pressure rates are given in Fig. 2. Interestingly, the first JT-related band associated to the ${}^2B_2 \rightarrow {}^2E$ transition shows a large redshift with pressure at a rate of -73 meV/GPa, while the second one, associated to ${}^2B_2 \rightarrow {}^2A_1$, shifts slightly towards higher energies ($+7.5$ meV/GPa). It must be noted that the transition energy variation of both bands $E(P)$ undergoes a change of slope at the structural phase transition at 4.9 GPa, thus being an adequate probe to explore phase transition phenomena.

The CT direct band gap is also very sensitive to pressure. Unlike $d-d$ bands, pressure-induced CT redshift is responsible for the strong piezochromism of Cs_2CuCl_4 , the color of which changes with pressure from yellow–orange to black, particularly at the structural transition to the high-pressure phase (Fig. 3). Cs_2CuCl_4 is a CT semiconductor with a direct gap of 2.52 eV at ambient conditions which redshifts with pressure at a rate of -20 meV/GPa. This means that significant color changes are expected at pressures well above 5 GPa as shown in Fig. 3. The direct band gap, E_g , was determined from the tail of the absorption threshold by plotting $(h\nu \times \alpha)^2$ against $h\nu$, with α being the absorption coefficient, once the absorption background was subtracted. E_g was obtained by the interception of this plot with $\alpha = 0$. As Fig. 3 shows, $E_g(P)$ experiences an abrupt jump of about 0.3 eV at the phase transition at 4.9 GPa. Above this pressure, we observe a band structure with at least two noticeable absorption peaks at 0.43 and 1.43 eV, the pressure dependence of which is shown in Fig. 2. The $Pnma$ phase is recovered in down-stroke below about 3 GPa, thus having a hysteresis of 2 GPa at room temperature. It must be also noted that the difference between the transition pressure measured in single crystal (5.4 GPa) and powder (4.9 GPa) of Cs_2CuCl_4 must be associated to a lack of hydrostaticity in powdered samples, which reduces the transition pressure. However, the phase transition can be established at 4.9 GPa in upstroke, which corresponds to initial observation of traces of the high-pressure phase within the pressure range of phase coexistence.

ii. Angular overlap model for CuCl_4^{2-}

The unusual pressure shifts of the two $d-d$ bands (Fig. 2) can be explained semi-quantitatively within the ligand-field theory through the Angular Overlap Model (AOM) [13, 15–17]. The initial flattened-tetrahedron symmetry (D_{2d}) of CuCl_4^{2-} , which splits the parent tetrahedral t_2 and e orbitals into $b_2 + e$ and $a_1 + b_1$, respectively, will change upon Cs_2CuCl_4 compression. The corresponding splitting will change depending on how the relative variations of the T_d crystal-field strength and the JT-related dihedral Cl–Cu–Cl angle evolve with pressure. According to crystal-field theory and experimental observations [1, 3], the crystal-field strength

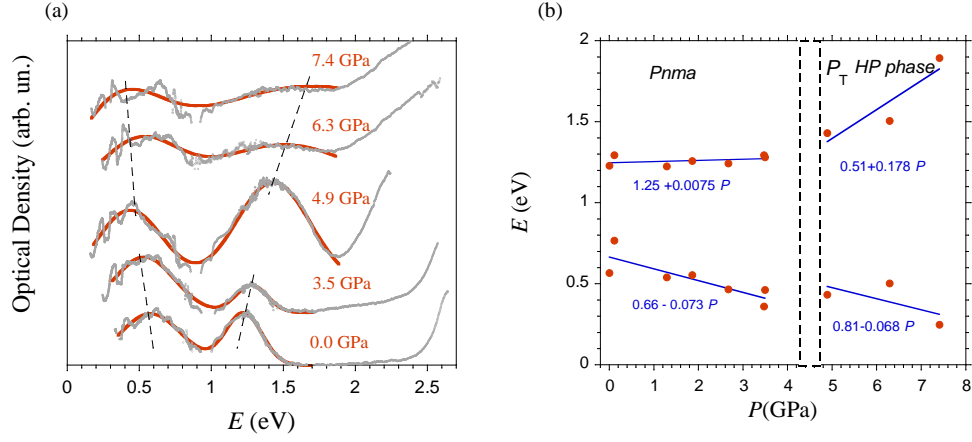


Figure 2: (a) Variation of the absorption spectrum of Cs₂CuCl₄ with pressure in the $Pnma$ and high-pressure phase ($P > 4.9$ GPa). (b) Variation of the peak energy of the main absorption bands with pressure. Pressure coefficients derived by fitting in the low-pressure $Pnma$ phase are included.

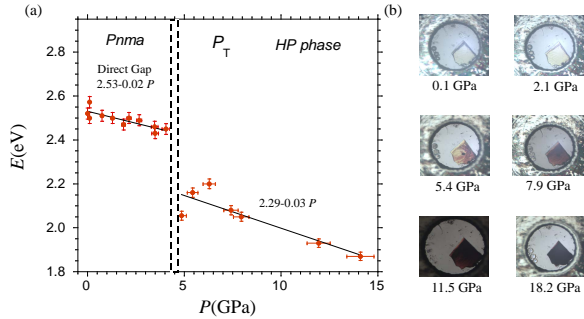


Figure 3: (a) Variation of the charge-transfer band gap with pressure in both $Pnma$ phase and high-pressure phase. The direct gap shifts toward lower energies with pressure. (b) Images of a single crystal of Cs₂CuCl₄ in a DAC at different pressures. Note how the crystal varies from yellow to dark red and eventually to black upon increasing pressure. The piezochromism is associated with the redshifted charge-transfer band gap with pressure. Single crystal dimensions (ambient pressure): $80 \times 80 \times 22 \mu\text{m}^3$.

usually increases by decreasing the Cu–Cl bond distance, R , whereas the dihedral angle tends to decrease with pressure, approaching the T_d angle (109.47°) under high compression. XRD results show that R and $\gamma_{Cl-Cu-Cl}$ change from $R = 2.230 \text{ \AA}$ and $\gamma_{Cl_3-Cu-Cl_3} = 127.4^\circ$ [17] at ambient pressure to $R = 2.199 \text{ \AA}$ and $\gamma_{Cl_3-Cu-Cl_3} = 122.3^\circ$ at 3.9 GPa [4], in agreement with expectations for a JT system. In order to apply the AOM to determine the $d-d$ transition energies of CuCl_4^{2-} as a function of structural parameters, instead of $\gamma_{Cl-Cu-Cl}$ we will use the angle $\beta = 1/2(\gamma_{Cl-Cu-Cl} - 109.47^\circ)$, which represents the deviation of the Cl–Cu–Cl angle from its T_d value. Then, $\beta = 0$ in T_d symmetry and $\beta = 35.3^\circ$ in a square-planar D_{4h} symmetry. For CuCl_4^{2-} in Cs₂CuCl₄, $\beta = 8.5 \pm 0.5^\circ$ at ambient conditions and $\beta = 6.4 \pm 0.5^\circ$ at 3.9 GPa. We will use the AOM to simulate the transition energies as a function of R and β for explaining why the first band largely shifts to lower energy whereas the second one, more sensitive to the crystal-field strength, shifts slightly to higher energies with pressure.

Within the AOM, the expressions to calculate the electronic energies in a MX_4^{2-} system are given as a function of the AOM parameters e_σ, e_π, e_{sd} and e_{pd} and the X–M–X bond angle γ as shown in Eq. (1) [16].

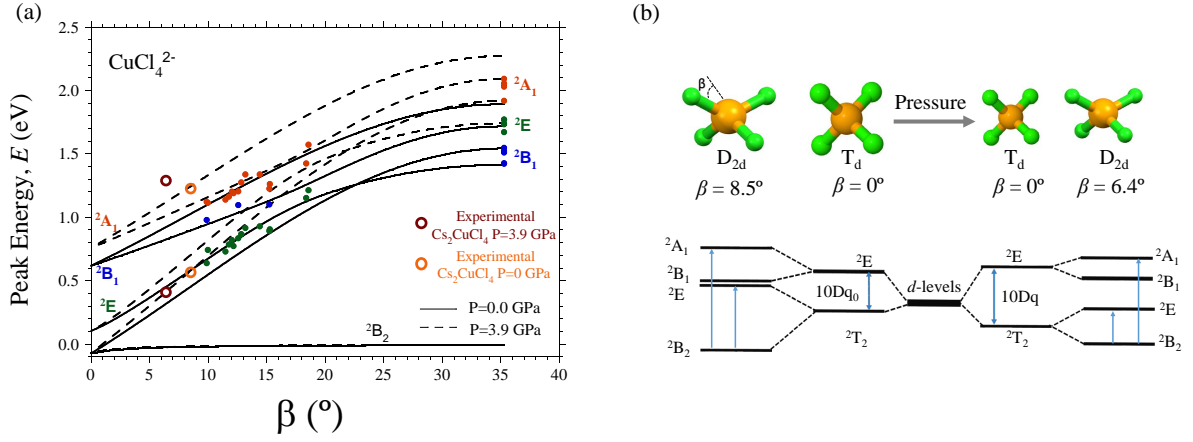


Figure 4: (a) Calculated crystal-field energies for CuCl_4^{2-} as a function of the distortion angle (β) using AOM. $\beta = 0^\circ$ corresponds to T_d (regular tetrahedron), and $\beta = 32.5^\circ$ to D_{4h} CuCl_4^{2-} (square-planar). Solid and dashed lines correspond to calculations at ambient pressure and 3.9 GPa, respectively. The spin-orbit coupling has been included in the calculations with $\lambda = -829 \text{ cm}^{-1}$ (see text for details). Filled color symbols correspond to experimental data from the compound series providing different Cl–Cu–Cl bond angles for CuCl_4^{2-} [15, 17]. Empty circles correspond to present experimental data for Cs_2CuCl_4 at ambient pressure (orange) and 3.9 GPa (dark red). Note that the trends of the variation is in agreement with structural data obtained by XRD [4]. (b) Schematic diagram of the Cu^{2+} d -orbital splitting in D_{2d} and T_d symmetry for four different configurations corresponding to ambient pressure (left) and high-pressure conditions (3.9 GPa, right). In T_d only R is changed whereas both R and β are modified in D_{2d} .

$$\begin{aligned}
 \Delta E({}^2B_2 \rightarrow {}^2E) &= 3[\sin^4(\gamma/2) - 1/2 \sin^2(\gamma)]e_\sigma \\
 &+ [\sin^2(\gamma) - 2 \cos^2(\gamma) - 2 \cos^2(\gamma/2)]e_\pi, \\
 \Delta E({}^2B_2 \rightarrow {}^2B_1) &= 3 \sin^4(\gamma/2)e_\sigma \\
 &+ [\sin^2(\gamma) - 4 \sin^2(\gamma/2)]e_\pi \\
 &- 13.3 \sin^4(\gamma/2) \cos^2(\gamma/2)e_{pd}, \\
 \Delta E({}^2B_2 \rightarrow {}^2A_1) &= 3 \sin^4(\gamma/2)e_\sigma \\
 &- 4[\cos^2(\gamma/2) - 1/2 \sin^2(\gamma/2)]^2 e_\sigma - 2 \sin^2(\gamma)e_\pi \\
 &+ 16[\cos^2(\gamma/2) - 1/2 \sin^2(\gamma/2)]^2 e_{sd} \\
 &- 13.3 \sin^4(\gamma/2) \cos^2(\gamma/2)e_{pd}.
 \end{aligned} \tag{1}$$

These expressions are suitable to account for the transition energies in different MX_4^{2-} systems having different dihedral angles [17]. This has been especially useful for explaining the variation of transition energies obtained from absorption spectra as a function of the dihedral angle in series of Cu^{2+} chlorides, providing dihedral angles for CuCl_4^{2-} ranging between 127° and 180° or, equivalently, from $\beta = 8.5^\circ$ to $\beta = 35.3^\circ$ [13, 15–17]. The spectroscopic se-

ries of CuCl_4^{2-} can be explained using the following AOM parameters: $e_\sigma = 0.635 \text{ eV}$, $e_\pi = 0.113 \text{ eV}$, $e_{sd} = 0.114 \text{ eV}$ and $e_{pd} = -0.0025 \text{ eV}$ [13, 16, 17]. Figure 4 shows the energy of the d - d transitions of CuCl_4^{2-} as a function of β , where, additionally, we have included the spin-orbit interaction $-\lambda \vec{L} \cdot \vec{S}$ using $\lambda = 0.103 \text{ eV}$ [17]. The D_{2d} states appear additionally split as ${}^2B_2(\Gamma_7)$; ${}^2E(\Gamma_6 + \Gamma_7)$; ${}^2B_1(\Gamma_7)$; and ${}^2A_1(\Gamma_6)$ following double group irrep notation (see Fig. 4a) [7].

The pressure-induced energy shifts in Cs_2CuCl_4 have been simulated by scaling the AOM parameters to structural data at 3.9 GPa on the assumption of a power law for the volume as $(V_0/V)^{5/3}$ using the equation of state of Cs_2CuCl_4 in the $Pnma$ phase [4]. So, we obtained the following AOM parameters at 3.9 GPa: $e_\sigma = 0.78 \text{ eV}$, $e_\pi = 0.139 \text{ eV}$, $e_{sd} = 0.172 \text{ eV}$ and $e_{pd} = -0.0025 \text{ eV}$. Although this may be a rough approximation for describing the variation of AOM parameters with pressure/volume, the result of these simulations allows us to explain the band shifts with pressure (Fig.

4). Pressure-induced R (or V) reduction increases the energy separation of the parent T_d orbitals, e and t_2 , by $10Dq$, while reduction of β decreases the t_2 and e orbital splittings in D_{2d} . As illustrated in Fig. 4, both effects induce band shifts in the two $d-d$ bands similar to those observed experimentally. Therefore, these structural correlations, which are based on the energy shifts of the crystal-field bands in Cs_2CuCl_4 , indicate that the main pressure effect on the JT-flattened CuCl_4^{2-} is reducing the Cl–Cu–Cl bond angle from 8.5° at ambient pressure to 6.4° at 3.9 GPa, consistently with structural data [4]. Therefore, these results support the adequacy of the $d-d$ spectra to explore structural changes induced by pressure in transition-metal chlorides involving JT ions like Cu^{2+} .

IV. Conclusions

Electronic absorption spectra allow us to elucidate that the pressure dependence of the electronic structure of Cs_2CuCl_4 can be explained to a great extent on the basis of T_d CuCl_4^{2-} , the volume of which is roughly eight times more incompressible than Cs_2CuCl_4 bulk. The piezochromic phase transition at 4.9 GPa is mainly associated with the CT redshifts, particularly in the high-pressure phase well above 4.9 GPa. The new high-pressure phase, although it has not been identified yet, probably involves a change of coordination from CuCl_4^{2-} flattened tetrahedra to a structure consisting of ligand sharing CuCl_6^{4-} octahedra as suggested by its $d-d$ transition energies. Correlations between crystal-field bands and structure of CuCl_4^{2-} through the AOM allow us to infer structural changes undergone by CuCl_4^{2-} induced by pressure on the basis of the crystal-field energy shifts. The measured shifts are consistent with a reduction of both the bond distance and the Cl–Cu–Cl angle, *i.e.* reduction of the JT distortion, with pressure in agreement with previous XRD data.

Acknowledgements - Financial support from the Spanish Ministerio de Economía, Industria y Competitividad (Project Ref. MAT2015-69508-P) and MALTA-CONSOLIDER (Ref. MAT2015-71010REDC). EJ also thanks the Spanish Minis-

terio de Ciencia, Innovación y Universidades for a FPI research grant (Ref. No. BES-2016-077449).

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