

Local Structure of Cu^{2+} in the $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MCl}_4 \cdot \text{Cu}^{2+}$ ($\text{M} = \text{Cd}, \text{Mn}$) Layer Perovskites. Influence of Hydrostatic Pressure in the 0–60 kbar Range*

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This paper deals with the effects of pressure on the charge-transfer spectra of CuCl_6^{4-} complexes formed in Cu^{2+} doped $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MCl}_4$ ($\text{M} = \text{Cd}, \text{Mn}$). A pressure-induced redshift is observed for the first charge-transfer band in both crystals. While the shift is continuous for the Mn crystal at a rate of $-40 \text{ cm}^{-1}/\text{kbar}$ in the 0–60 kbar range, it experiences an abrupt jump of -1400 cm^{-1} around 26 kbar for the Cd crystal. Such a discontinuous behaviour is interpreted in terms of a structural change in the CuCl_6^{4-} coordination geometry from an axially elongated octahedron to a more compressed geometry. The present results are compared with those reported for the pure $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ crystal.

Introduction

The aim of this work is to investigate the local structure of CuCl_6^{4-} complexes formed in the $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MCl}_4$ ($\text{M} = \text{Cd}, \text{Mn}$) crystals doped with Cu^{2+} and its dependence on the hydrostatic pressure through the Charge-Transfer (CT) spectra. Attention is paid on whether the formation of *compressed*

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CuCl_6^{4-} complexes, unusual for chlorides [1, 2], is possible or not in these layer perovskites, and whether an elongated complex can be transformed into a compressed one by applying hydrostatic pressures. The selected crystals are suitable systems for such a study since they provide compressed octahedron sites for accommodating substitutional impurities. In particular, the equatorial and axial M–Cl distances of the compressed MCl_6^{4-} octahedra are $R_{\text{eq}} = 2.67 \text{ \AA}$ and $R_{\text{ax}} = 2.52 \text{ \AA}$ for $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4$ [3] while for $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4$ the distances are $R_{\text{eq}} = 2.59 \text{ \AA}$ and $R_{\text{ax}} = 2.47 \text{ \AA}$ [4]. In contrast, pure $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$ compounds display an in-plane antiferrodistortive structure of axially elongated CuCl_6^{4-} [5]. In fact, the elongated octahedron is the usual coordination structure for CuCl_6^{4-} either in pure cupric chlorides or in doped compounds. Exceptions to this behaviour are found in $(\text{enH}_2)\text{MnCl}_4:\text{Cu}^{2+}$ [6, 7] and, in general, in layer perovskites $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MnCl}_4:\text{Cu}^{2+}$ [8] where a compressed D_{4h} coordination geometry was proposed for explaining the intense CT absorption band at 21000 cm^{-1} . Nevertheless, recent investigations performed on isomorphous Cd crystals [8, 9] reveal that CuCl_6^{4-} is elongated rather than compressed, even though this is the actual symmetry of the replaced Cd^{2+} site. In order to clarify the different behaviour exhibited by the Cd and Mn crystals, we have studied the effect of the hydrostatic pressure on the CT spectra corresponding to these Cu^{2+} doped layered perovskites. Apart from the selective character of the CT bands, their high oscillator strengths ($f \sim 10^{-1} - 10^{-2}$) [8] make it suitable probes for detecting structural changes around Cu^{2+} in diluted materials ($< 1\%$) subjected to hydrostatic pressure. Interestingly, the results obtained on these diluted systems compare well with those recently obtained in the pure $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ crystal [10], in which the occurrence of a pressure-induced phase transition around 40 kbar was interpreted in terms of disappearance of the in-plane lattice distortion of CuCl_6^{4-} .

Experimental

The single crystals of $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4$ and $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4$ doped with Cu^{2+} (about 0.2 mol %) are the same ones employed in Ref. [8]. Hydrostatic pressure experiments have been performed on microcrystals of about $100 \times 100 \times 20 \mu\text{m}^3$ using a sapphire anvil cell attached to a specially designed double beam spectrometer. Details of the experimental setup are given elsewhere [11]. Paraffin oil was used as pressure transmitter and the pressure was calibrated through the shifts of the ruby R-lines. Ruby luminescence was excited by a 568 nm Coherent I-302-K Krypton laser.

Results and discussion

Fig. 1 shows the optical absorption (OA) spectra of the two title compounds at atmospheric pressure. An analysis of the corresponding spectra is given

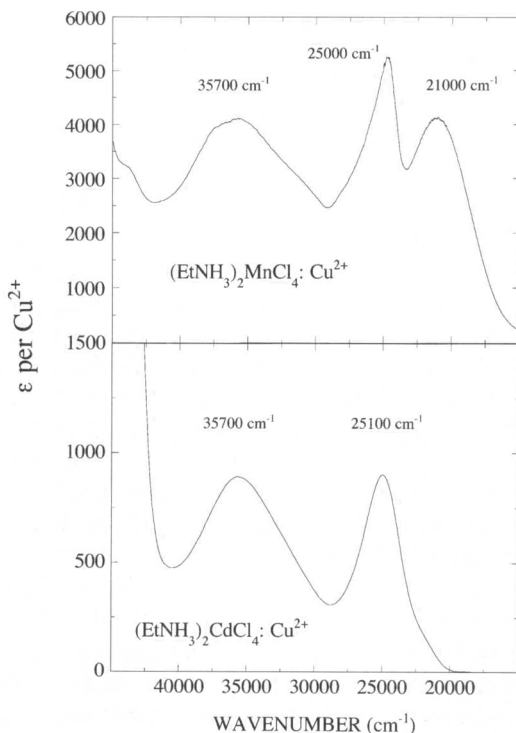


Fig. 1. Optical absorption spectra of $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4:\text{Cu}^{2+}$ and $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ at atmospheric pressure and room temperature. The spectra were obtained with polarized light propagating along the c direction (perpendicular to the layer).

in Refs. [6–9]. In both crystals, the absorption bands have been assigned to $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ CT transitions of the formed CuCl_6^{4-} complex. The spectrum of the Cd crystal is similar to those found in $\text{CdCl}_2:\text{Cu}^{2+}$, $\text{LiCl}:\text{Cu}^{2+}$, $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ where CuCl_6^{4-} complexes display an elongated octahedron structure [12–15]. In particular the two intense bands at 25100 and 35700 cm^{-1} observed in $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ are assigned within an elongated complex of D_{4h} symmetry to CT transitions from the bonding mainly $\text{Cl}^- e_u(\pi + \sigma)$ and $e_u(\sigma + \pi)$ molecular orbitals (MO) to the antibonding mainly $\text{Cu}^{2+} b_{1g}(x^2 - y^2)$ MO, respectively. In $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4:\text{Cu}^{2+}$ however the intense band at 21000 cm^{-1} is associated with a CT transition from the equatorial $\text{Cl}^- e_u(\pi + \sigma)$ MO to the $\text{Cu}^{2+} a_{1g}(3z^2 - r^2)$ MO within a compressed CuCl_6^{4-} complex with the short axial bond perpendicular to the layer [6–8]. Nevertheless, this model is unable to explain the presence of the narrower band at 25000 cm^{-1} . Recent investigations carried out on the mixed $(\text{CH}_3\text{NH}_3)_2\text{Mn}_x\text{Cd}_{1-x}\text{Cl}_4:\text{Cu}^{2+}$ crys-

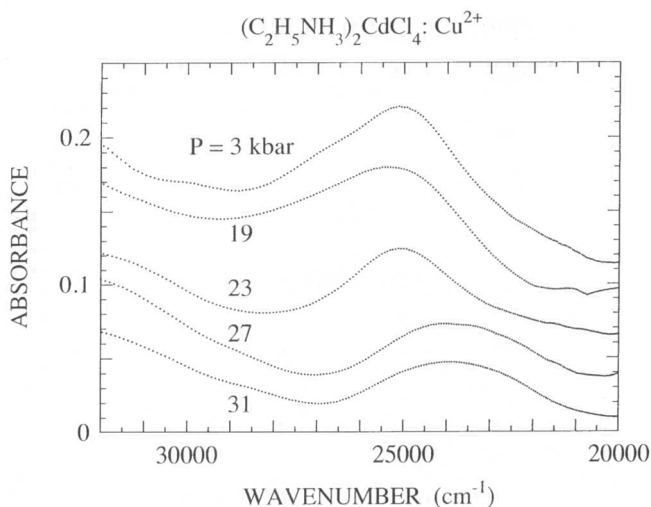


Fig. 2. Influence of the hydrostatic pressure upon the first $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ charge transfer band in $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4 \cdot \text{Cu}^{2+}$.

tal series point out the relevance of the Mn^{2+} not only for explaining the enhancement of absorption intensity on passing from $x = 0$ to $x = 1$ as well as its thermal dependence, but also for explaining the presence of the 25000 cm^{-1} band although in such a case an additional D_{2h} orthorhombic distortion for the CuCl_6^{4-} was assumed [9].

The effect of the hydrostatic pressure on the OA spectra of $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MCl}_4 \cdot \text{Cu}^{2+}$ ($M = \text{Cd}, \text{Mn}$) is illustrated in Figs. 2 and 3. The corresponding variations of the peak energy with pressure are plotted in Figs. 4 and 5. Note that in both crystals the CT bands shift to lower energies upon increasing pressure, although the variation, $E(P)$ is rather different in each case. While a continuous redshift is observed for the 25000 and 21000 cm^{-1} bands at shift rates, $\Delta E/\Delta P$, of -6.1 and $-40 \text{ cm}^{-1}/\text{kbar}$, respectively, for the $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4 \cdot \text{Cu}^{2+}$, this variation for the $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4 \cdot \text{Cu}^{2+}$ crystal undergoes an abrupt shift of -1400 cm^{-1} around 26 kbar . From atmospheric pressure to 25 kbar , the CT band experiences a small redshift of about -100 cm^{-1} . The steep variation exhibited by the first CT band at 26 kbar is noteworthy. This reflects structural changes of the CuCl_6^{4-} complexes which are probably associated with a shortening of the in-plane axial bond (and likely a lengthening of the in-plane short bonds) leading to a more compressed geometry where the shortest Cu–Cl bonds are perpendicular to the layer. The comparison of the present results with those obtained by Moritomo *et al.* in $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ using OA and Raman spectroscopy supports this view [10]. These authors report the existence of a pressure-induced structural phase transition around

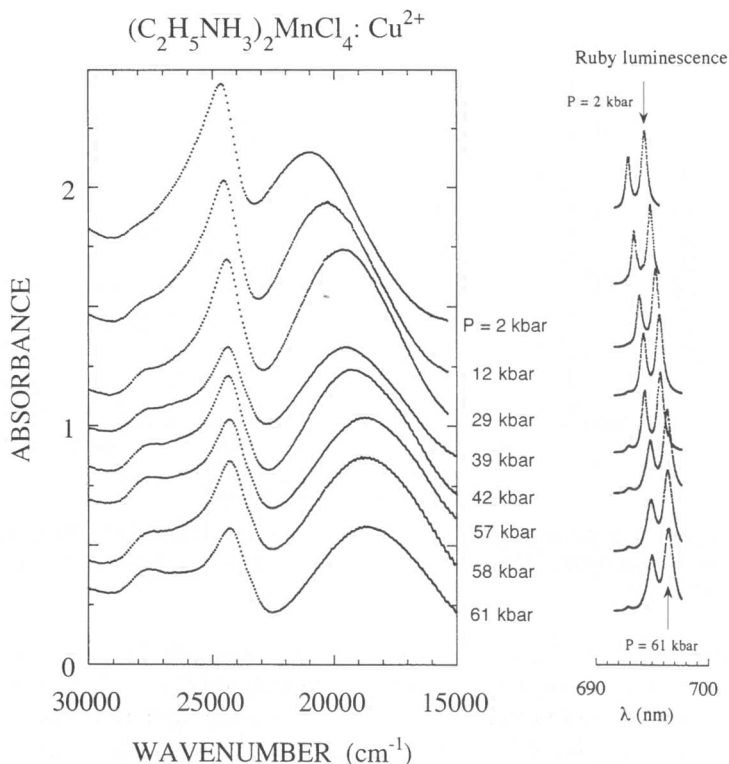


Fig. 3. Variation of the optical absorption spectra of $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4:\text{Cu}^{2+}$ with hydrostatic pressure at room temperature in the 0–61 kbar range. The corresponding variation of the Ruby luminescence used for pressure calibration, is shown on the right side.

40 kbar that involves the deactivation of the Raman peaks associated with the stretching vibrations of the in-plane axial and equatorial bonds of the elongated CuCl_6^{2-} complexes ($R_{ax} = 2.98 \text{ \AA}$ and $R_{eq} = 2.28 \text{ \AA}$) [5]. The occurrence of such a phase transition is important since it would imply the disappearance of the antiferrodistortive structure displayed by the CuCl_6^{2-} complexes and, consequently a change in the magnetic behaviour of the crystal from ferromagnetic to antiferromagnetic should be expected above 40 kbar [10]. The variation of the CT energy upon pressure reported in that work resembles those observed for the present diluted systems but in different pressure ranges. The redshift of -3200 cm^{-1} observed between 15 and 30 kbar in $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ is similar to the variation shown in Fig. 3 for $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ although a smaller shift is observed for the present case. Above 40 kbar the CT band of the pure crystal experiences a continuous redshift at a rate of $-16 \text{ cm}^{-1}/\text{kbar}$, analogous to that followed by the

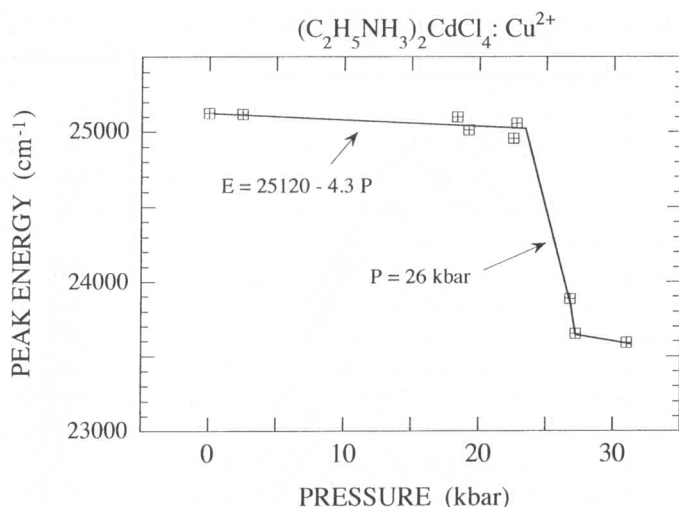


Fig. 4. Variation of the peak energy of the first CT band in $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4 : \text{Cu}^{2+}$ with the hydrostatic pressure. The straight line corresponds to the least square fit in the 0–25 kbar range.

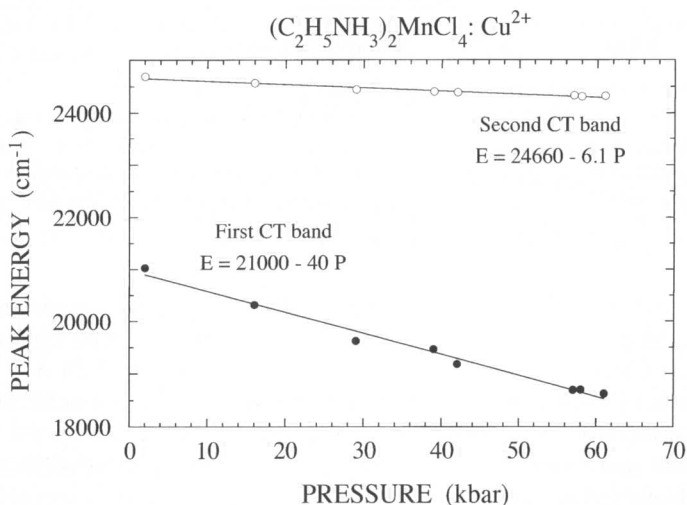


Fig. 5. Pressure dependence of CT bands at 21000 and 25000 cm^{-1} in $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4 : \text{Cu}^{2+}$. The straight lines are least square fits.

21000 cm^{-1} band in $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4 : \text{Cu}^{2+}$ (Fig. 5). Moreover the CT energy of $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ at 90 kbar, $E = 21500 \text{ cm}^{-1}$, is near the CT energy of the $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4 : \text{Cu}^{2+}$ crystal at atmospheric pressure.

These two facts suggest that the CT band observed in the high-pressure phase of the pure crystal and in the Mn crystal at atmospheric pressure is probably associated with similar CT states of compressed CuCl_6^{4-} complexes of either tetragonal (D_{4h}) or orthorhombic (D_{2h}) symmetry. Consequently, the variations experienced by the first CT band upon pressure in the three related crystals can be reasonably explained in terms of structural changes of CuCl_6^{4-} taking into account that the effect of pressure on the elongated CuCl_6^{4-} complex is mainly to reduce significantly the axial Cu–Cl distance, and only slightly (or even increase) the in-plane short Cu–Cl distance, leading to a more compressed geometry with the shortest Cu–Cl bonds perpendicular to the layer. This anisotropic compression of the CuCl_6^{4-} complex upon pressure is probably responsible for the observed CT band redshifts. A structural study of the high-pressure phase of the pure Cu crystal using diffraction techniques would be very useful to clarify the coordination geometry of CuCl_6^{4-} in this phase.

Finally, it must be noted that the narrow band appearing at 25000 cm^{-1} in the OA spectrum of $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4:\text{Cu}^{2+}$, is not observed in the high pressure phase of either $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ or $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$. This feature is consistent with the interpretation given in [9] for such a band as due to an electronic transition involving both $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ CT states of the CuCl_6^{4-} complex and the ${}^4\text{A}_1{}^4\text{E}(\text{G})$ excited state of the exchange-coupled Mn^{2+} neighbours, although in such a case, an additional orthorhombic D_{2h} distortion was assumed for CuCl_6^{4-} . The similar pressure-induced shift rates measured for this band ($\Delta E/\Delta P = -6\text{ cm}^{-1}/\text{kbar}$) and for the ${}^4\text{A}_1{}^4\text{E}(\text{G})$ peak in MnCl_2 ($\Delta E/\Delta P = -5\text{ cm}^{-1}/\text{kbar}$) [16] supports that interpretation.

From the pressure shift of the broad band at 21000 cm^{-1} , we estimate that the pressure required to shift the first CT band from $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ to $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4:\text{Cu}^{2+}$ is about 100 kbar.

Summary

Hydrostatic pressure experiments carried out in $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ show the existence of a structural change in the CuCl_6^{4-} complex from an elongated octahedron to a nearly compressed one at above 25 kbar. This change is evidenced through the abrupt shift of -1400 cm^{-1} undergone by the first CT band around that pressure. The comparison of these results with those available for $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ indicates that the high-pressure structure of the CuCl_6^{4-} in this crystal is probably similar to that attained for $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4:\text{Cu}^{2+}$ at atmospheric pressure. The present hydrostatic pressure experiments performed on these Cu^{2+} -doped layer perovskites provide direct evidence about the redshift undergone by the first CT band of CuCl_6^{4-} complexes upon pressure in *diluted systems*.

Further work in order to investigate whether the steep redshift around 26 kbar is associated with a structural phase transition of the host crystal or whether is just a pure local phenomenon, using diffraction techniques is under way.

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