

LETTER TO THE EDITOR

A study of phase transitions in NH_4Br using charge transfer bands of Cu^{2+} centres as probes

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Abstract. Charge transfer (CT) spectra due to small amounts (~ 100 ppm) of $[\text{CuBr}_4(\text{NH}_3)_2]^{2-}$ centres in the NH_4Br lattice have been investigated in the 300–14 K temperature range. When upon cooling the $\gamma \rightarrow \delta$ phase transition occurs the assigned $e_u(\pi + \sigma; \text{Br}) \rightarrow a_{1g}^*$ and $e_u(\sigma + \pi; \text{Br}) \rightarrow a_{1g}^*$ peaks experience abrupt red shifts of 700 and 1200 cm^{-1} respectively, stressing the great sensitivity of CT peaks for detecting that transition. Those red shifts support the assertion that when the $\gamma \rightarrow \delta$ transition is produced the $\text{Cu}^{2+}\text{--Br}^-$ distance increases though the average lattice parameter of NH_4Br decreases abruptly by 2.4 pm. This is the first time that the first-order sluggish $\gamma \rightarrow \delta$ transition in NH_4Br and the hysteresis effects involved have been clearly detected using an impurity as probe. Moreover CT bands also detect the phase transition at 234 K and the possibility for the crystal to remain in a metastable tetragonal phase below 78 K.

Ammonium bromide is an attractive basic material because at $p = 1$ atm and below room temperature it exhibits two phase transitions related to the ordering of NH_4^+ tetrahedra and involving rather simple crystal structures [1–3]. In fact although such tetrahedra are disordered at room temperature (phase β) they become ‘anti-ferromagnetically ordered’ below $T = 234$ K (phase γ) and the structure changes from CsCl-type to a slightly tetragonal one. At $T = 234$ K the average lattice parameter of the tetragonal phase is 0.5 pm higher than $a = 4.049$ Å for the cubic phase [1]. Upon cooling the sample a sluggish [1, 2] transition is detected at $T = 78$ K related to the ferromagnetic ordering of NH_4^+ tetrahedra (phase δ). At such a temperature the lattice becomes again cubic and the value $a = 4.008$ Å is in this case 2.4 pm smaller than that corresponding to the average lattice parameter of phase γ [1]. This jump experienced by the lattice parameter at 78 K stresses the strong first-order character of the $\gamma \rightarrow \delta$ transition leading to marked hysteresis effects. Owing to them the $\delta \rightarrow \gamma$ transition is produced at 108 K upon warming instead of at 78 K.

The above-mentioned facts have all stimulated the study of impurities in NH_4Br . In those studies researchers have attempted to characterise the centres formed by such impurities and have also investigated the sensitivity of the centres as probes for detecting the phase transitions undergone by the host lattice.

In the case of NH_4Cl , Cu^{2+} centres in NH_4Br have received particular attention [4–9]. Efforts to detect the phase transitions of NH_4Br through them have been more concentrated on the variations of the spin-Hamiltonian parameters with temperature

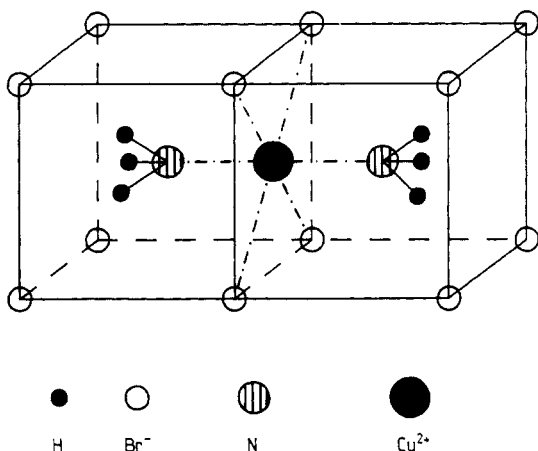


Figure 1. A model of centre II. Cu²⁺ is placed interstitially at the centre of a (100) face. The nearest neighbours are two 'axial' NH₃ molecules and four 'equatorial' Br⁻ anions.

[5–7]. The reported data demonstrate the existence of the $\beta \rightarrow \gamma$ phase transition. However, no strong evidence of the $\gamma \rightarrow \delta$ phase transition and the involved hysteresis phenomena in NH₄Br has been achieved using the spin-Hamiltonian parameters of Cu²⁺ centres as probes. Better results seem to be obtained, however, in ND₄Br [5]. The optical properties of Cu²⁺ centres in NH₄Br have received less attention and only [9] deals with the sensitivity of crystal-field bands of centre II (depicted in figure 1) for detecting the $\gamma \rightarrow \delta$ phase transition. Up to date, however, no work on charge transfer bands of Cu²⁺ centres has been published in spite of the fact that such bands can be detected for low Cu²⁺ concentration (down to about 5 ppm).

The data reported in [9] suggest that the $e_g^* \rightarrow a_{1g}^*$ crystal-field peak of such a centre experiences a small red shift (less than about 200 cm⁻¹) when the $\gamma \rightarrow \delta$ transition is finally reached. Takagi and co-workers [9], who do not investigate hysteresis effects, state that it is necessary to change the temperature from 9 up to 90 K several times in order to force the material to perform the sluggish $\gamma \rightarrow \delta$ transition. To our knowledge the evidence of such a transition and the involved hysteresis effects using spectroscopic measurements has only been achieved so far through the variations of the emission intensity due to the self-trapped exciton [10].

Very recently the usefulness of CT bands of centre II for detecting the phase transition at $T = 243$ K of NH₄Cl involving a ferromagnetic ordering of NH₄⁺ tetrahedra has been demonstrated [11]. In particular the peak position of such bands reflects the phase transition much better than that for crystal-field bands.

Owing to this fact we explore through the present work the sensitivity of CT bands of centre II in NH₄Br as a probe for detecting the $\beta \rightarrow \gamma$ and especially the $\gamma \rightarrow \delta$ phase transition. Furthermore a particular effort is devoted to obtain information about local geometrical changes induced on the centre by the phase transition.

NH₄Br crystals of good optical quality have been grown by slow evaporation at 30 °C of saturated solutions to which urea was added to avoid dendritic growth. Typically 100 g NH₄Br and 100 g urea were dissolved in 90 cm³ distilled water. Crystals are obtained after about ten days. The CsCl-type structure of NH₄Br crystals at room temperature was checked by x-ray diffraction. In order to form centre II, Br₂Cu and NH₄OH were added to the solution. The pH of the mother solution was equal to 8.

The copper concentration of our samples was analysed by atomic absorption spectrophotometry. The data reported in this paper correspond to a sample containing about 100 ppm Cu^{2+} . All the samples investigated gave the same results.

The presence of centre II in our samples was checked by EPR measurements [5, 7, 8]. Moreover the crystal-field spectrum of more doped samples performed at 14 K reveals the presence of progressions involving the $\text{NH}_3\text{-Cu}$ stretching frequency as for $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ [12]. Details of this work confirming the structure of centre II in $\text{NH}_4\text{Br}:\text{Cu}^{2+}$ will be published in the near future.

Optical absorption spectra were recorded by means of a Perkin-Elmer Lambda 9 spectrophotometer using a NH_4Br sample of the same thickness as the reference.

Temperatures down to 14 K were achieved through an Air Products CSA-202 E closed-circuit cryostat.

In figure 2 can be seen the CT spectrum of centre II in $\text{NH}_4\text{Br}:\text{Cu}^{2+}$ at room temperature. One peak at $28\,700\text{ cm}^{-1}$ and a shoulder at about $26\,100\text{ cm}^{-1}$ are noticed. At 234 K however, two peaks (lying at $26\,300$ and $29\,100\text{ cm}^{-1}$) are already observed in the spectrum. The first of those peaks lies about 8000 cm^{-1} below that corresponding to the same centre in $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ [13]. This experimental fact together with the much smaller optical electronegativity [14] of Br^- ($\chi = 2.8$) compared to that of NH_3 ($\chi = 3.3$) stress that the observed CT peaks should be ascribed to one-electron jumps from bromine to the a_{1g}^* level ($\sim 3z^2 - r^2$) of the $[\text{CuBr}_4(\text{NH}_3)_2]^{2-}$ complex. Taking into account the

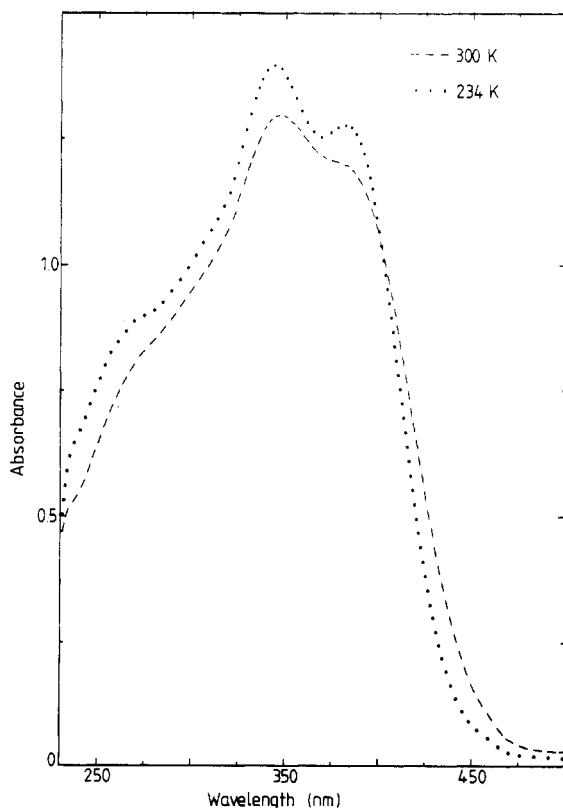


Figure 2. Charge transfer spectra of centre II in $\text{NH}_4\text{Br}:\text{Cu}^{2+}$ at room temperature and at 234 K.

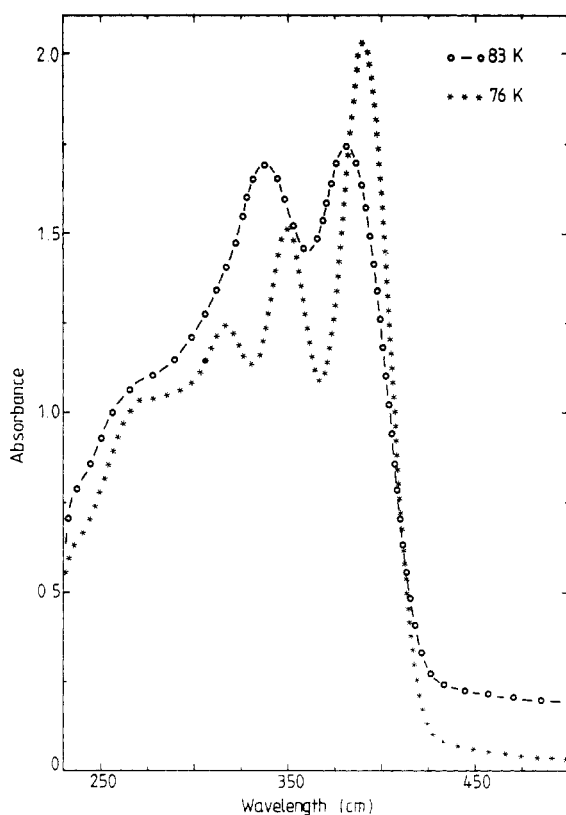


Figure 3. Charge transfer spectra of centre II in NH_4Br at 83 K and at 76 K (spectrum of series C).

selection rules for D_{4h} symmetry and the results on CT bands for centre II in $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ [13] we assign the two peaks at 26 200 and 29 000 cm^{-1} as being due to the $e_u(\pi + \sigma; \text{Br}) \rightarrow a_{1g}^*$ and $e_u(\sigma + \pi; \text{Br}) \rightarrow a_{1g}^*$ CT transitions respectively. It is worth noting here that the separation, termed $\Delta(\pi, \sigma)$, between such peaks is clearly smaller than the value $\Delta(\pi, \sigma) = 8500 \text{ cm}^{-1}$ observed in $\text{LiBr}:\text{Cu}^{2+}$ [15]. Similar features are encountered in the comparison of results in $\text{LiCl}:\text{Cu}^{2+}$ [15,16] and $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ [13] but in those cases the difference between the experimental $\Delta(\pi, \sigma)$ values is 2400 cm^{-1} .

The differences mentioned reflect a higher equatorial halogen– Cu^{2+} distance, R , in centre II than in $\text{LiBr}:\text{Cu}^{2+}$ or $\text{LiCl}:\text{Cu}^{2+}$, displaying an elongated octahedral geometry with $b_{1g}^*(\sim x^2 - y^2)$ instead of a_{1g}^* as ground level. Although no theoretical calculations upon CT transitions of $[\text{CuBr}_4(\text{NH}_3)_2]^{2-}$ and $[\text{CuCl}_4(\text{NH}_3)_2]^{2-}$ have been reported, recent X_α results on $[\text{CuBr}_4]^{2-}$ and $[\text{CuCl}_4]^{2-}$ [17] indicate that $\Delta(\pi, \sigma)$ decreases by about 200 cm^{-1} when R increases by 1 pm. For systems involving $[\text{CuBr}_4]^{2-}$ units R lies in the range 2.4–2.5 Å [18–20] while in $\text{CuBr}_2(\text{NH}_3)_2$ $R = 2.87 \text{ Å}$ and the Cu^{2+} –N distance has a value equal to 2.03 Å [18]. The latter value is close to that expected for the Cu^{2+} –N distance of centre II in $\text{NH}_4\text{Br}:\text{Cu}^{2+}$ if nitrogen is placed just in the middle of the cube.

On the other hand the Cu^{2+} – Br^- distance for centre II in the perfect NH_4Br lattice would be equal to 2.87 Å at room temperature.

Experimental results on systems involving $[\text{CuCl}_4]^{2-}$ and $[\text{CuBr}_4]^{2-}$ units as well as X_α calculations on both complexes reveal that the energy of CT transitions involving $e_u(\pi + \sigma)$ and $e_u(\sigma + \pi)$ one-electron levels decreases when R is increased [15–17, 21]. The reason by which the first CT transition in $\text{NH}_4\text{Br}:\text{Cu}^{2+}$ lies about 7000 cm^{-1} higher than that for $\text{LiBr}:\text{Cu}^{2+}$ relies, however, on the presence of NH_3 in the former case. These axial ligands raise the energy of the mainly 3d levels more than that of those mainly built from 4p wavefunctions of equatorial Br^- ions. In the same vein the first CT peak in $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ is placed about 6000 cm^{-1} above the corresponding peak in $\text{LiCl}:\text{Cu}^{2+}$ [13]. Preliminary X_α calculations on $[\text{CuCl}_4(\text{NH}_3)_2]^{2-}$ support the present view.

Upon cooling the sample in the range 230–83 K the two CT peaks are progressively better seen (figures 2 and 3). The energy of the second peak $e_u(\sigma + \pi; \text{Br}) \rightarrow a_{1g}^*$ increases progressively (figure 4) as well as the value of $\Delta(\pi, \sigma)$ going from $\Delta(\pi, \sigma) = 2900\text{ cm}^{-1}$ at 230 K to $\Delta(\pi, \sigma) = 3400\text{ cm}^{-1}$ at 83 K. No drastic jumps of the peak position are detected in this range as can be seen in figure 4. However, a change in the slope is noticed at $T = 234\text{ K}$ reflecting the $\beta \rightarrow \gamma$ transition of NH_4Br .

Upon cooling below 80 K two different series of spectra can be found denoted hereafter as T and C.

The spectra of series T look very similar to that at 83 K depicted in figure 3. For instance, the peak energy of the $e_u(\sigma + \pi; \text{Br}) \rightarrow a_{1g}^*$ band increases only 140 cm^{-1} on going from 83 K to 14 K (figure 5). Moreover, if at 14 K our sample exhibits a spectrum of type T no hysteresis effects are detected upon a subsequent warming up to room temperature.

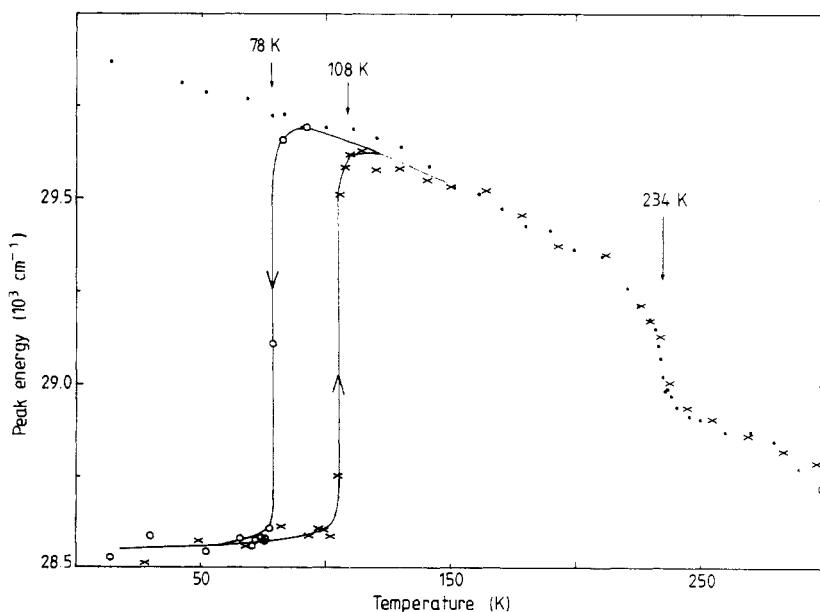


Figure 4. Experimental evolution of the energy of the assigned $e_u(\sigma + \pi; \text{Br}) \rightarrow a_{1g}^*$ peak with temperature. Full circles represent the common evolution upon cooling down to 78 K as well as that corresponding to spectra of series T in the 78–14 K range; open circles correspond to the evolution upon cooling of spectra of series C in the 78–14 K range; and crosses correspond to the evolution upon warming of a spectrum of series C from 14 K up to room temperature.

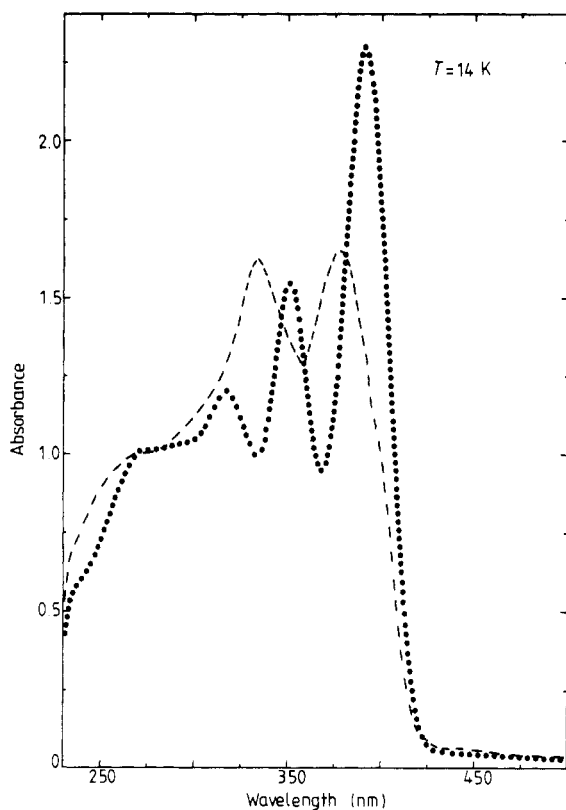


Figure 5. Comparison of spectra of series T and C at 14 K.

By contrast the spectra of series C show very dramatic changes but essentially in the 80–76 K interval (figures 3 and 4). In such a range the energy of the $e_u(\sigma + \pi; \text{Br}) \rightarrow a_{1g}^*$ transition undergoes an abrupt red shift of 1200 cm^{-1} and at the same time $\Delta(\pi, \sigma)$ decreases by 450 cm^{-1} . Moreover a new band peaked at $31\,600 \text{ cm}^{-1}$ is also observed. The remarkable differences existing between the spectra of type T and C at 14 K can be seen in figure 5.

At variance with what is observed for spectra of series T the evolution of spectra of series C on warming above 14 K (figure 4) shows significant differences with the results obtained upon cooling, which are ascribed to hysteresis effects. Upon warming, the $e_u(\sigma + \pi) \rightarrow a_{1g}^*$ transition experiences an abrupt blue shift of 1200 cm^{-1} at 108 K. Above this temperature the spectra are coincident with those observed upon cooling.

Bearing in mind these facts the spectra of series C are to be ascribed to Cu^{2+} centres in the cubic phase of NH_4Br with ferromagnetic ordering. By contrast the spectra of type T are ascribed to Cu^{2+} centres in a metastable tetragonal phase. It is worth noting here that if upon cooling from room temperature to 14 K the spectrum is of type T it can, however, become of type C after warming and cooling several times. As we have not detected intermediate spectra between those of types T and C the coexistence of domains of both phases in the crystal below 78 K is discounted. By contrast the present results suggest that it is not always easy for the crystal to undertake the sluggish $\gamma \rightarrow \delta$ transition.

Charge-transfer bands of 3d impurities in insulators are essentially understood in

terms of the complex MX_n formed by the impurity M and the nearest anions X. Therefore changes noticed on such bands should be ascribed in principle to changes *in* the complex rather than to changes occurring beyond the MX_n unit.

Furthermore, the very different response of CT bands to the establishment of ferromagnetic or antiferromagnetic ordering supports that it is due in fact to the different displacive behaviour *accompanying* the ordering of NH_4^+ tetrahedra rather than to the ordering itself. As was pointed out before, the changes in lattice parameters of NH_4Br are much more dramatic for the $\gamma \rightarrow \delta$ transition than for the $\beta \rightarrow \gamma$ one.

Nevertheless the present results indicate that although centre II undergoes significant local structural changes upon the $\gamma \rightarrow \delta$ transition, these are of different sign to those expected for the pure NH_4Br lattice. In fact as a consequence of that transition the energies of both the $e_u(\sigma + \pi; \text{Br}) \rightarrow a_{1g}^*$ transition and the separation $\Delta(\pi, \sigma)$ experience a significant decrease (of 1200 and 450 cm^{-1} respectively—see figures 3 and 4). Both figures are consistent with an *increase* of the $\text{Cu}^{2+}\text{--Br}^-$ distance upon the $\gamma \rightarrow \delta$ transition.

It should be remarked here that for $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ the transition at $T = 243$ K involving ferromagnetic ordering of NH_4^+ tetrahedra also gives rise to red shifts in the CT transitions upon cooling [13]. Although this experimental fact also suggests an increase of the $\text{Cu}^{2+}\text{--Cl}^-$ distance upon the $\beta \rightarrow \delta$ transition preliminary Raman measurements on centre-II-doped NH_4Cl point out, however, that the $\text{Cu}^{2+}\text{--N}$ distance decreases. An account of this work will be reported in the near future.

Our data in the vicinity of $T = 234$ K (figure 4) do not show clear evidence of jumps for the $e_u(\sigma + \pi) \rightarrow a_{1g}^*$ energy. Furthermore the average lattice constant of NH_4Br undergoes a small increase of 0.5 pm in the $\beta \rightarrow \gamma$ transition at $T = 234$ K [1] while the data of figure 4 suggest that the $\text{Cu}^{2+}\text{--Br}^-$ distance decreases progressively in the range 234–80 K. These results stress again that local changes around the impurity may be quite different from those existing for the perfect lattice. In the same vein the ENDOR data of [22] on $\text{RbCdF}_3:\text{Fe}^{3+}$ indicate that Fe^{3+} exhibits an almost perfect O_h symmetry in the tetragonal phase of RbCdF_3 .

In the β phase the $e_u(\sigma + \pi) \rightarrow a_{1g}^*$ transition undergoes a progressive blue shift upon cooling. The same feature is observed below 234 K and down to 14 K when the sample remains in the tetragonal phase. This increase should be related to the usual decrease of metal–ligand distances upon cooling due to thermal contraction effects. Such behaviour has always been found for 3d cations in LiCl and LiBr lattices [15, 16] which do not exhibit phase transitions below room temperature.

The present results demonstrate the good sensitivity of CT bands of $\text{NH}_4\text{Br}:\text{Cu}^{2+}$ (centre II) as probes for detecting the phase transitions in NH_4Br below room temperature and especially the $\gamma \rightarrow \delta$ transition and the involved hysteresis effects. Also the present data illustrate that local structural changes around the impurity induced at the phase transition can differ significantly from what happens for the pure host lattice. From a spectrographic point of view the origin of the features observed above about 30 000 cm^{-1} remains to be understood—and in particular that for the band peaked at 31 600 cm^{-1} observed below 78 K for spectra of series C. In order to explain this fact as well as the apparent absence of splittings due to bromine spin–orbit coupling X_α calculations on centre II in $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ and $\text{NH}_4\text{Br}:\text{Cu}^{2+}$ are now under way.

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