

Evidence for anomalous relaxation of the $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ center in NH_4Cl below T_c

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The temperature dependence of the (a) $e_u(\pi + \sigma, \text{Cl}) \rightarrow a_{1g}^*$ ($\sim 3z^2 - r^2$) charge-transfer transition, ν_{CT} ; (b) $e_g^* \rightarrow a_{1g}^*$ crystal-field transition, ν_{CF} ; (c) Cu-NH_3 and $\text{Cu-Cl } A_{1g}$ stretching mode frequencies (termed as ν_1 and ν_2 , respectively) corresponding to the $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ center in NH_4Cl have been measured in the 100–300-K range. Below T_c , ν_{CF} and especially ν_{CT} undergo a red shift ascribed to the increase of the $\text{Cu}^{2+}\text{-Cl}^-$ equatorial distance, R_{eq} , of the center although the lattice parameter a decreases. This anomalous relaxation is strongly supported by Raman data, giving variations $\Delta\nu_1 = 7 \pm 1 \text{ cm}^{-1}$ and $\Delta\nu_2 = -11 \pm 3 \text{ cm}^{-1}$ in the 243–213-K range. Based on these data, the variations undergone by R_{eq} and the axial $\text{Cu}^{2+}\text{-NH}_3$ distance R_{ax} in such a temperature range are estimated to be $\Delta R_{\text{eq}} \approx +2.0 \pm 0.6 \text{ pm}$, $\Delta R_{\text{ax}} \approx -0.40 \pm 0.05 \text{ pm}$. The present results emphasize the usefulness of standard spectroscopic tools for detecting this unusual local relaxation which lies beyond the resolution limit of the extended x-ray-absorption fine-structure technique. To our knowledge this is the first time that evidence of such a phenomenon is reported.

I. INTRODUCTION

Significant efforts are currently devoted to the investigation of transition-metal impurities in insulators. The interest of such a research mainly comes from the properties very often displayed by doped materials but absent in pure compounds. Microscopically the properties of a transition-metal impurity, M , in an insulator can be understood to a large extent only on the basis of the MX_n complex formed with the nearest anions or ligands. In spite of this relatively simple theoretical framework a good insight into the microscopic origin of the properties due to the impurity requires knowledge of the true metal-ligand distance R and its true variations upon applied hydrostatic pressures, phase transitions in the host material, temperature changes, etc. This task is, however, much more difficult to accomplish than for a pure crystal where the standard x-ray technique can provide us with the required information on interatomic distances and their variations. Owing to this trouble, it has been very often assumed that R is the same as R_0 , corresponding to the perfect lattice or as in under hydrostatic or chemical pressure, R follows the variations of R_0 .

Although the advent of extended x-ray-absorption fine structure (EXAFS) has helped somewhat to improve such a situation, this technique is, however, not suitable¹ for measuring changes $\Delta R < 3 \text{ pm}$. Such changes of interatomic distances are, however, produced by hydrostatic pressures smaller than $\sim 5 \text{ GPa}$, in structural phase transitions, or by thermal expansion effects.

In recent years, it has been pointed out, however, that this drawback can be overcome by looking at the variations undergone by spectroscopical parameters of transition-metal impurities such as the isotropic

superhyperfine tensor,² the crystal-field,³ and the charge-transfer bands.⁴ Indeed such variations allow one to detect^{2,3} changes of the metal-ligand distance $\Delta R \approx 0.1 \text{ pm}$ which certainly improves the EXAFS resolution.

The present work is devoted to the study of the true variations experienced by the $\text{Cu}^{2+}\text{-NH}_3$ and $\text{Cu}^{2+}\text{-Cl}^-$ distances (termed as R_{ax} and R_{eq} respectively) of the $\text{Cu}^{2+}(\text{II})$ center in NH_4Cl just below the $\beta \rightarrow \delta$ transition⁵ at $T_c = 242.5 \text{ K}$. The structure of this center which corresponds to the $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ complex is depicted in Fig. 1 and was clearly established after the studies by Hagen and Trappeniers⁶ and the electron nuclear double resonance (ENDOR) measurements by Boettcher and Spaeth.⁷ These authors^{6,7} also demonstrated that, in the $\text{Cu}^{2+}(\text{II})$ center, the unpaired electron lies in the antibonding a_{1g}^* ($\sim 3z^2 - r^2$) orbital which is very unusual for D_{4h} Cu^{2+} complexes. Subsequent studies⁸ detected the $\text{NH}_3\text{-Cu}^{2+}$ stretching vibration in both Raman and crystal-field spectra of the $\text{Cu}^{2+}(\text{II})$ center and assigned the crystal-field^{8,9} and charge-transfer¹⁰ bands observed experimentally.

Below T_c , NH_4Cl displays a “ferromagnetic” ordering of the NH_4^+ tetrahedra (phase δ) and the space group becomes T_d^1 instead of O_h^1 characteristic of the disordered CsCl -type phase (phase β) which exists in the 242.5 K–458-K temperature range.⁵ The appearance of this “ferromagnetic” ordering induces significant displacive effects on the lattice.^{11–15} So, upon cooling, the lattice parameter a experiences a jump of -0.4 pm at T_c revealing a slight first-order character of the phase transition. Also, the linear thermal expansion coefficient α lies^{12,15} between 20×10^{-5} and $6 \times 10^{-5} \text{ K}^{-1}$ in the 240–210-K range, while $\alpha < 5 \times 10^{-5} \text{ K}^{-1}$ for alkali halides.¹⁶ The existence of these displacive effects accompanying the or-

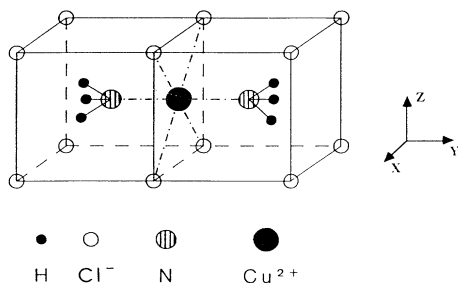


FIG. 1. Structure of the Cu²⁺(II) center in NH₄Cl.

dering has shown to be the main mechanism by which a localized CuX₄(NH₃)₂²⁻ center (X=Cl, Br) experiences the phase transition.^{17,10}

Through the present work we want to demonstrate that the metal-ligand distances of Cu²⁺(II) center in NH₄Cl do not follow at all the variations of the host lattice parameter *a* below *T_c*. More precisely, it will be shown that in the 243–200-K temperature range, where the lattice parameter decreases, the axial Cu²⁺-NH₃ distance *R_{ax}* also decreases but the equatorial Cu²⁺-Cl⁻ distance *R_{eq}* increases. Furthermore, the results shown here indicate that the variation undergone by *R_{eq}* in such a temperature range is higher than that experienced by *R_{ax}*.

In order to support this unexpected conclusion we have explored the evolution of *four distinct* spectroscopic parameters. First we have followed the variations of the *e_g*^{*} → *a_{1g}*^{*} crystal-field peak (termed as *ν_{CF}*) and of the first allowed charge-transfer transition peak assigned as *e_g*(*π* + *σ*; Cl) → *a_{1g}*^{*} and briefly denoted as *ν_{CT}*. Both transitions were identified previously.^{8,10} Moreover, a special effort has been devoted here to detect and identify the Cu-NH₃ and, especially, the Cu-Cl *A_{1g}* stretching frequencies of the Cu²⁺(II) center by means of Raman spectroscopy as well as to determine their temperature dependence.

In fact, such Cu²⁺-NH₃ and Cu²⁺-Cl⁻ frequencies (henceforth denoted as *ν₁* and *ν₂*) of the localized CuCl₄(NH₃)₂²⁻ center will be mainly dependent upon *R_{ax}* and *R_{eq}*, respectively. Thus, their changes in the 213–243-K range can provide us with a good insight into the true variations undergone by both *R_{ax}* and *R_{eq}* in a temperature domain where displacive effects in the NH₄Cl host lattice are important.

The basis for obtaining such information is the Gruneisen relation

$$\Delta\nu/\nu = -3\gamma(\Delta R/R), \quad (1)$$

which relates the frequency variations, $\Delta\nu$, experienced by a local vibrational mode to the variation of the corresponding metal-ligand distance, ΔR , once the value of the coefficient γ is known. This coefficient is, in general, different for each one of the vibrational modes of a given system. A similar relation to Eq. (1) holds for a pure crystal. In such a case, $3\Delta R/R$ is replaced by $\Delta V/V$,

where *V* denotes the macroscopic volume of the sample and *ν*, $\Delta\nu$, and γ , correspond to normal vibrational modes of the perfect crystal. It is necessary to remark that, for the stretching modes of molecules as well as for optical modes of crystals, γ is positive¹⁸ and so an increase of frequency would reveal that ΔR (or ΔV) decreases. Negative γ values have been, however, encountered in the case of bending modes.^{18,19} Taking as a guide the case of pure compounds involving CuCl₄²⁻ units, a value $3\gamma=6.8$ is derived for the stretching *A_{1g}* mode from the Raman data reported in Ref. 20. Thus, if Raman peaks are known with an accuracy of ± 1 cm⁻¹, ΔR changes down to about 0.1 pm can be well detected using Eq. (1).

II. EXPERIMENT

NH₄Cl and NH₄Cl:Cu²⁺(II) crystals of good optical quality have been grown as described in previous works.^{8,10} In the case of doped samples, crystals with different Cu²⁺ concentrations have been obtained. Samples with ~50 ppm of Cu²⁺ were used for detecting charge-transfer bands while samples with 1000–10 000 ppm have been used in Raman and crystal-field spectra. The presence of the Cu²⁺(II) center as the main species in our sample was ascertained by EPR measurements.

Optical data have been obtained by means of a Perkin-Elmer Lambda 9 spectrophotometer. Temperature variations were achieved by a Scientific Instruments DE-202 closed-circuit cryostat allowing temperature stabilities within 0.1 K and an accuracy of 0.5 K, with an ADP-K temperature controller. The polarized Raman spectra of pure NH₄Cl and of NH₄Cl:Cu²⁺(II) single crystals have been recorded on a DILOR Z 24 triple monochromator spectrometer, coupled with a SPECTRA-PHYSICS model 171 argon ion laser. The emission line at 454.5 nm has been used for excitation with an incident power of about 200 mW on sample.

The spectral resolution was ~4 cm⁻¹. Low-temperature measurements down to ~100 K were performed with a nitrogen cryostat C4N from DILOR, allowing temperature stabilities better than ± 0.5 K.

III. RESULTS AND DISCUSSION

First of all we show and discuss the experimental variations followed by the optical parameters *ν_{CT}* and *ν_{CF}* as a function of temperature. Figure 2 displays the variation of *ν_{CT}* together with that of the lattice parameter *a* of pure NH₄Cl. *ν_{CT}* experiences a significant *decrement* in the 243–200-K range where important changes of the lattice parameter *a* take place. Furthermore we have explored carefully the region $\Delta T=30$ K around *T_c* in order to investigate the effects of the lattice parameter jump (seen in Fig. 2) upon the optical parameters *ν_{CT}* and *ν_{CF}*. Figure 3 reveals that *ν_{CT}* undergoes a jump of -200 ± 30 cm⁻¹ at *T_c*. A similar situation was encountered in the sluggish $\gamma \rightarrow \delta$ phase transition of NH₄Br.¹⁷ This jump should then be ascribed essentially to abrupt changes undergone by *R_{eq}* and *R_{ax}* which in turn are induced by the first-order character of the $\beta \rightarrow \delta$ phase transition of the

host lattice. In the same vein the continuous decrease of ν_{CT} in the 240–200-K region can reasonably be ascribed *mainly* to variations of R_{ax} and R_{eq} driven by the significant changes undergone by the lattice parameter a in such a temperature range. To be more specific, let us recall that, in a simple thermodynamic scheme, an experimental quantity, like $(\partial\nu_{CT}/\partial T)_p$ is given by^{21,22}

$$(\partial\nu_{CT}/\partial T)_p = (\partial\nu_{CT}/\partial V)_T(\partial V/\partial T)_p + (\partial\nu_{CT}/\partial T)_V. \quad (2)$$

The first term corresponds to variations of ν_{CT} due to thermal expansion effects while $(\partial\nu_{CT}/\partial T)_V$ is the so-called explicit temperature contribution which appears even if the interatomic distances are not changed upon increasing the temperature. From the present arguments we assume, however, that in the present case the term $(\partial\nu_{CT}/\partial T)_V$ plays a minor role in the 240–200-K range while the first term in Eq. (2) is mainly responsible for the observed variations of ν_{CT} .

Figure 3 shows that the change experienced by ν_{CF} in the 225–243-K region is clearly smaller than that under-

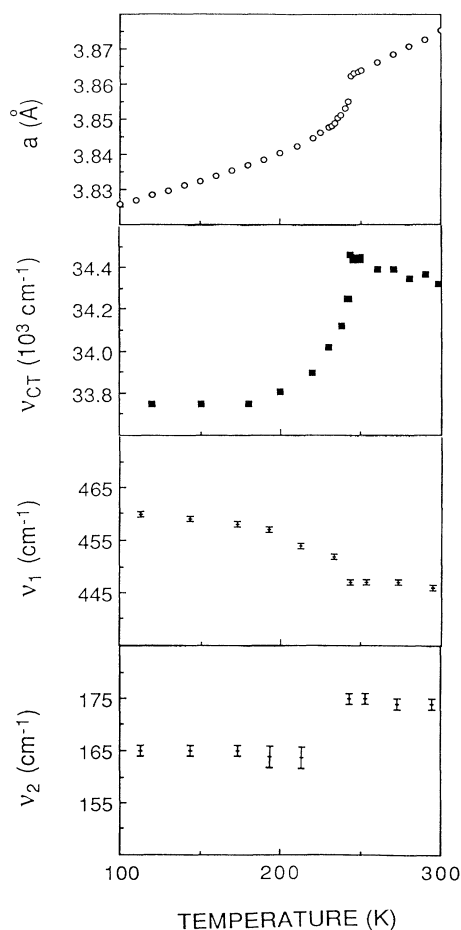


FIG. 2. Variation of the NH_4Cl lattice parameter a (Ref. 12) together with that of the three parameters ν_{CT} , ν_1 , ν_2 of the $\text{Cu}^{2+}(\text{II})$ center in the 100–300-K range.

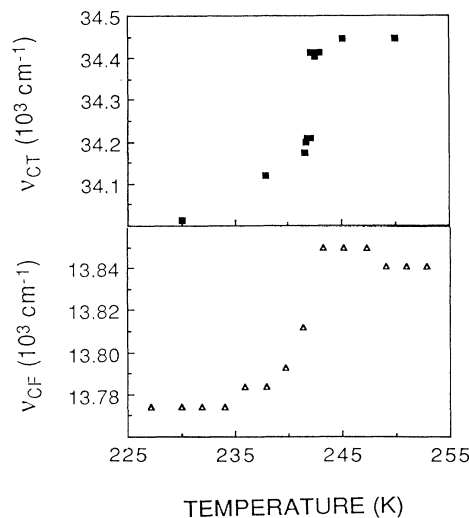


FIG. 3. Detailed variation of ν_{CT} in the 225–255-K range revealing the existence of a jump. Changes of ν_{CF} are shown for comparison.

gone by ν_{CT} . This fact can be related to the smaller sensitivity of crystal-field peaks to metal-ligand distance variations when compared to that shown by charge-transfer peaks. This behavior has been demonstrated for systems involving CuX_4^{2-} ($X = \text{Cl}, \text{Br}$) units.⁴ Figure 3 also reveals that, just below T_c , ν_{CF} experiences a red shift as well.

This redshift undergone by both ν_{CT} and ν_{CF} is indeed a feature contrary to what is expected if the $\text{Cu}^{2+}(\text{II})$ center would follow the host lattice behavior. In fact, if both R_{eq} and R_{ax} follow the behavior of the lattice parameter and decrease at T_c it is certainly hard to explain through a crystal-field type model that ν_{CF} experiences a red shift instead of a blue shift. Furthermore, in the case of compounds involving CuX_4^{2-} units ($X = \text{Cl}, \text{Br}$) the experimental²³ results as well as MS- $X\alpha$ calculations⁴ have both shown that charge-transfer transitions experience a remarkable blue shift upon contraction of the metal-ligand distance. This way values of $(d\nu_{CT}/dR_{eq}) \approx -600 \text{ cm}^{-1}/\text{pm}$ were found for both systems which is certainly higher than $(d\nu_{CF}/dR_{eq}) \approx -200 \text{ cm}^{-1}/\text{pm}$ as pointed out in Ref. 4.

The negative value of $(d\nu_{CT}/dR_{eq})$ in this case reflects, to a great extent, the increase of the energy of the mainly $3d$ levels upon decreasing R_{eq} due to the increase of ligand electrostatic repulsion. Owing to this reason $(d\nu_{CT}/dR)$ has also been found to be negative for the charge-transfer transitions of other O_h or D_{4h} transition-metal complexes.^{24,25}

By virtue of the preceding arguments, the experimental red shifts undergone by both ν_{CT} and ν_{CF} would then mean that at least one of the two metal-ligand distances, R_{ax} or R_{eq} , increases just below T_c . The peak denoted as ν_{CT} corresponds to the $e_u(\pi + \sigma, \text{Cl}) \rightarrow a_{1g}^*$ transition and thus involves an electron jump from an orbital mainly built from $\text{Cl}^- 3p$ orbitals to the antibonding a_{1g}^*

($\sim 3z^2 - r^2$). In view of this it could be thought that it is the distance R_{eq} increasing when $\beta \rightarrow \delta$ transition takes place.

Looking to support this assertion we have tried to detect *both* the Cu-NH₃ and the Cu-Cl A_{1g} stretching frequencies through Raman spectroscopy and to follow their temperature dependence. The first mode, ν_1 , was already identified in a previous work⁸ and lies above the Raman spectrum of pure NH₄Cl excluding the internal vibrations of NH₄⁺. The detection of the second A_{1g} mode is, in principle, more problematic because it could be masked by the Raman spectrum of the host lattice. At room temperature such a spectrum appears below ~ 350 cm⁻¹ and it reflects the one-phonon density of states because of the NH₄⁺ disorder.²⁶ Below T_c , in the δ phase, the TO-LO pair with T_2 symmetry becomes Raman active.

In order to overcome this situation a careful investigation by means of polarized Raman spectra has been carried out. In Fig. 4, the room-temperature Raman spectra of pure NH₄Cl and the one for NH₄Cl:Cu²⁺(II) both taken under the same geometrical and polarization conditions labeled as $y(zz)x$ are compared. Here the three x, y, z directions correspond to the three crystalline axis of NH₄Cl (Fig. 1).

In such polarization conditions only three vibrational modes of the CuCl₄(NH₃)₂²⁻ complex can be expected: the two A_{1g} modes involving mainly the stretching Cu-NH₃ and Cu-Cl vibrations and the bending B_{2g} mode. The latter mode involves only displacements of the equatorial Cl⁻ ligands and thus its frequency should be clearly smaller than ν_2 corresponding to the stretching Cu-Cl vibration.

Figure 4 reveals the presence of *two additional* Raman peaks at 447 and 174 cm⁻¹ in NH₄Cl:Cu²⁺(II) which are absent in the pure NH₄Cl crystal. Among them, no other

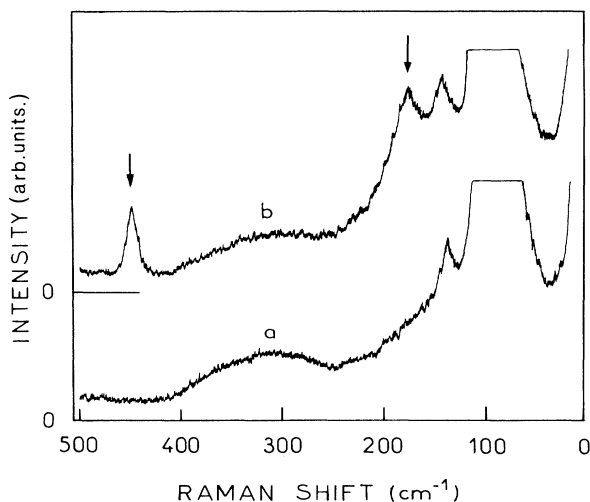


FIG. 4. Raman spectrum of NH₄Cl:Cu²⁺(II) (b) and of pure NH₄Cl (a) included for comparison purposes. Both are obtained in the same $y(zz)x$ configuration.

Raman peak due to NH₄Cl:Cu²⁺(II) has been found. The first one corresponds to the A_{1g} Cu²⁺-NH₃ stretching vibration⁸ while the second one is now assigned to the A_{1g} Cu²⁺-Cl⁻ stretching vibration founded in the comparison with the results for the square-planar CuCl₄²⁻ center. In fact, in the case of (met H)₂CuCl₄ (Ref. 20) for which $R_{\text{eq}} = 226$ pm, $\nu(A_{1g}) = 275$ cm⁻¹ while $\nu(B_{2g}) = 181$ cm⁻¹ is, as expected, clearly smaller. Although R_{eq} is not well known for NH₄Cl:Cu²⁺(II), R_{eq} values certainly higher than $R_{\text{eq}} = 226$ pm are expected for the present case in view of the presence of two NH₃ axial ligands and thus a value smaller than 275 cm⁻¹ is expected for ν_2 . This way the values $R_{\text{ax}} \approx 190$ pm and $R_{\text{eq}} \approx 245$ pm were previously⁸ estimated from the analysis of the crystal-field spectrum while $R_{\text{ax}} = 195$ pm, $R_{\text{eq}} = 276$ pm have been measured for the Cu(NH₃)₂Cl₂ compound containing CuCl₄(NH₃)₂²⁻ units.²⁷ Taking into account these arguments and that the Raman peak lying at 174 cm⁻¹ corresponds to the highest detected frequency of the Cu²⁺(II) center involving the vibration of Cl⁻ ions it appears quite consistent to assign it to the A_{1g} stretching Cu-Cl vibration.

The evolution of both ν_1 and ν_2 Raman frequencies as a function of the temperature is also shown in Fig. 2. It is necessary to remark that, in the 243–220-K range, it has not been possible to measure the ν_2 frequency because it is masked by the TO Raman peak at 170 cm⁻¹ (at 240 K) characteristic of NH₄Cl in the δ phase^{26,28} which, unfortunately, is present as a polarization leakage in the $y(zz)x$ spectrum of NH₄Cl:Cu²⁺(II). As the latter peak increases its frequency upon cooling, it has been, however, possible to measure ν_2 below 215 K. The results reported in Fig. 2 clearly reveal that, below the $\beta \rightarrow \delta$ phase transition, ν_1 increases but ν_2 decreases.

Thus, assuming that such changes *mainly* reflect the changes in R_{ax} and R_{eq} induced by the significant displacive effects appearing in NH₄Cl in the 243–200-K range, the present results certainly support the previous conclusions obtained from the variations of ν_{CT} and ν_{CF} . Therefore, R_{ax} decreases but R_{eq} increases below T_c .

In order to better substantiate this view, it appears, however, necessary to reach *estimations* on the variations of R_{ax} and R_{eq} from the preceding results. In Table I the variations of ν_1 , ν_2 , and ν_{CT} between 213 and 243 K are given. Assuming that $(\partial\nu_{\text{CT}}/\partial R_{\text{eq}}) \approx -600$ cm⁻¹/pm as found for CuX₄²⁻ units,⁴ the variation $\Delta\nu_{\text{CT}} = 600$ cm⁻¹ measured between 243 and 213 K should correspond to $\Delta R_{\text{eq}} \approx 1$ pm provided R_{ax} remains unchanged. However, if R_{ax} decreases, then ΔR_{eq} should be higher than ~ 1 pm taking into account that a decrement of R_{ax} without modifying R_{eq} induces a blue shift of charge-transfer transitions.

Table I stresses that $\Delta\nu_2/\nu_2$ is about *four times* $\Delta\nu_1/\nu_1$. Thus, assuming that the Grüneisen coefficient γ is similar for both vibrational modes, such a result supports that $|\Delta R_{\text{eq}}|$ would be higher than $|\Delta R_{\text{ax}}|$.

To our knowledge, the Grüneisen coefficient γ is not known for the vibrational modes of the CuCl₄(NH₃)₂²⁻ center in NH₄Cl although $3\gamma = 6.8$ for the A_{1g} mode of

TABLE I. Comparison of the experimental values of ν_{CT} , ν_1 , and ν_2 (all in cm^{-1}) found at 243 and 213 K. The last row gives the corresponding relative variations.

	ν_{CT}	ν_1	ν_2
$T=243\text{ K}$	34460 ± 30	447.0 ± 0.5	175 ± 1
$T=213\text{ K}$	33860 ± 30	454.0 ± 0.5	164 ± 2
$10^2 (\Delta\nu/\nu)$	1.7 ± 0.1	1.6 ± 0.2	-6.3 ± 1.7

the CuCl_4^{2-} unit as outlined in the Introduction. For $\text{MgF}_2:\text{V}^{2+}$ a value $3\gamma=8.7$ can be derived for the A_{1g} stretching vibration of VF_6^{4-} from the theoretical results by Winter and Pitzer.²⁸ A similar value $3\gamma=6.8$ is obtained from the potential curve calculated for the isolated MnF_6^{4-} complex by Luaña *et al.*²⁵ These values are similar to $3\gamma=7.3$ corresponding to TO phonons in LiF (Ref. 18) and to the value $3\gamma=8.9$ derived for the TO phonon of NH_4Cl at 105 K. The latter figure has been obtained from the dependence $\Delta\nu_{\text{TO}}=aP$ ($a=2.1\text{ cm}^{-1}/\text{kbar}$) of the variation of the TO frequency with pressure measured experimentally by Shand, Hochheimer, and Walker²⁹ and the bulk modulus $B=257\text{ kbar}$ reported by Garland and Renard.¹¹

Thus, assuming $3\gamma=8$ for the two A_{1g} modes of the $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ center in NH_4Cl it is found from the experimental variations $\Delta\nu_1$ and $\Delta\nu_2$ (given in Table I) and Eq. (1)

$$\Delta R_{\text{eq}} = +2.0\pm 0.5\text{ pm},$$

$$\Delta R_{\text{ax}} = -0.40\pm 0.05\text{ pm}.$$

The estimation of ΔR_{eq} is thus compatible with that obtained from the analysis of ν_{CT} supporting the present view. For a more precise description of this anomalous relaxation of the $\text{NH}_4\text{Cl}:\text{Cu}^{2+}(\text{II})$ center below T_c theoretical calculations of the dependence of both ν_{CT} and ν_{CF} upon R_{eq} and R_{ax} would be helpful. Multiple-scattering $X\alpha$ results for $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ as well as the analysis of the experimental hyperfine tensor for $\text{NH}_4\text{Cl}:\text{Cu}^{2+}(\text{II})$ both support³⁰ the conclusions reached through the present work.

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¹W. F. Pong, R. A. Mayanovic, B. A. Bunker, J. K. Furdyna, and U. Debska, *Phys. Rev. B* **41**, 8440 (1990).

²M. T. Barriuso and M. Moreno, *Phys. Rev. B* **29**, 3623 (1984).

³F. Rodriguez and M. Moreno, *J. Chem. Phys.* **84**, 692 (1986).

⁴J. A. Aramburu, M. Moreno, and A. Bencini, *Chem. Phys. Lett.* **140**, 462 (1987).

⁵J. E. Callanan, R. D. Weir, and L. A. K. Staveley, *Proc. R. Soc. London, Ser. A* **372**, 489 (1980).

⁶S. H. Hagen and N. J. Trappeniers, *Physica* **47**, 165 (1970).

⁷F. Boettcher and J. M. Spaeth, *Phys. Status Solidi B* **61**, 465 (1974).

⁸F. Rodriguez, A. G. Breñosa, J. A. Aramburu, M. Moreno, and J. M. Calleja, *J. Phys. C* **20**, L641 (1987).

⁹J. L. Rao, A. Kawamori, K. Miyazaki, and K. Suzuki, *J. Phys. Soc. Jpn.* **55**, 4068 (1986).

¹⁰A. G. Breñosa, M. Moreno, and F. Rodriguez, *Solid State Commun.* **63**, 543 (1987).

¹¹C. W. Garland and R. Renard, *J. Chem. Phys.* **44**, 1130 (1966).

¹²A. A. Boiko, *Kristallografiya* **14**, 639 (1969) [*Sov. Phys. Crystallogr.* **14**, 539 (1970)].

¹³G. E. Fredericks, *Phys. Rev. B* **4**, 911 (1971).

¹⁴B. B. Weiner and C. W. Garland, *J. Chem. Phys.* **56**, 155 (1972).

¹⁵E. B. Amitin and O. A. Nabutovskaya, *Fiz. Tverd. Tela (Leningrad)* **26**, 1159 (1984) [*Sov. Phys. Solid State* **26**, 702 (1984)].

¹⁶G. K. White, *Proc. R. Soc. London, Ser. A* **286**, 204 (1965).

¹⁷A. G. Breñosa, F. Rodriguez, and M. Moreno, *J. Phys. C* **21**,

L623 (1988).

¹⁸P. Brüesch, in *Phonons: Theory and Experiments I*, edited by P. Fulde (Springer-Verlag, Berlin, 1982), pp. 174 and 198.

¹⁹Slawomir Biernacki and Matthias Scheffler, *Phys. Rev. Lett.* **63**, 290 (1989).

²⁰R. G. McDonald and M. A. Hitchman, *Inorg. Chem.* **25**, 3273 (1986).

²¹W. M. Walsh, J. Jeener, and N. Bloembergen, *Phys. Rev.* **139**, A1338 (1965).

²²F. Rodriguez, M. Moreno, J. M. Dance, and A. Tressaud, *Solid State Commun.* **69**, 67 (1989).

²³S. R. Desjardins, K. W. Penfield, S. L. Cohen, R. L. Musselman, and E. I. Solomon, *J. Am. Chem. Soc.* **105**, 4590 (1983).

²⁴M. T. Barriuso, J. A. Aramburu, and M. Moreno, *J. Chim. Phys.* **86**, 897 (1989).

²⁵V. Luaña, M. Bermejo, M. Florez, J. M. Recio, and L. Pueyo, *J. Chem. Phys.* **90**, 6409 (1989).

²⁶M. Couzi, J. B. Sokoloff, and C. H. Perry, *J. Chem. Phys.* **58**, 2965 (1973).

²⁷Von. F. Hanic and I. A. Cakajdova, *Acta Crystallogr.* **11**, 610 (1958).

²⁸N. W. Winter and R. M. Pitzer, *J. Chem. Phys.* **89**, 446 (1988).

²⁹M. L. Shand, H. D. Hochheimer, and C. T. Walker, *Solid State Commun.* **20**, 1043 (1976).

³⁰A. G. Breñosa, M. Moreno, and J. A. Aramburu, *J. Phys. Condens. Matter* (to be published).