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LETTER TO THE EDITOR

Hyperfine interaction of the $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ centre: dependence on metal–ligand distance

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Abstract. EPR measurements on $\text{NH}_4\text{Cl}_{1-x}\text{Br}_x$ and CsCl crystals containing the $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ centre together with MS-X α calculations as a function of the $\text{Cu}^{2+}\text{-N}(R_{\text{ax}})$ and $\text{Cu}^{2+}\text{-Cl}(R_{\text{eq}})$ distances have been carried out. The calculations indicate that the isotropic contribution to the hyperfine tensor, A_{is} , reflecting the probability of finding the a_{1g}^* ($\sim 3z^2 - r^2$) unpaired electron on the 4s orbital of Cu^{2+} , is very sensitive to R_{ax} and R_{eq} changes. The change experienced by the experimental hyperfine value A_{\parallel} on passing from NH_4Cl to $\text{NH}_4\text{Cl}_{0.92}\text{Br}_{0.08}$ supports this conclusion and leads to $(\partial A_{\text{is}}/\partial R_{\text{ax}}) = -2(\partial A_{\text{is}}/\partial R_{\text{eq}}) \cong -30 \text{ G pm}^{-1}$.

These figures support the attribution of the significant increase, $\delta_{\text{T}}(A_{\parallel}) = 60 \text{ G}$, experienced by A_{\parallel} of $\text{NH}_4\text{Cl}:\text{Cu}^{2+}(\text{II})$ below the phase transition at $T_c = 242.5 \text{ K}$ principally to an anomalous relaxation of the $\text{Cu}^{2+}(\text{II})$ centre involving a decrement of R_{ax} but an increase of R_{eq} in accord to the conclusion from previous optical and Raman studies. This work stresses the possibility of detecting from $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ δR_{ax} changes of the order 10^{-5} \AA through ENDOR measurements of the hyperfine tensor. To our knowledge this is the highest sensitivity reached so far for measuring variations of metal–ligand distances through spin-Hamiltonian parameters.

$\text{NH}_4\text{Cl}:\text{Cu}^{2+}(\text{II})$ is an attractive system for the following reasons:

(i) The structure of the $\text{Cu}^{2+}(\text{II})$ centre in NH_4Cl is firmly established through ENDOR measurements [1]. Such a centre can be well described as a $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ complex with D_{4h} geometry where Cu^{2+} is interstitially placed in the middle of a (100) face made of Cl^- ions while NH_3 molecules occupy NH_4^+ vacancies [1, 2].

(ii) This tetragonal Cu^{2+} complex is one of the rare examples in which the unpaired electron is placed in the antibonding a_{1g}^* ($\sim 3z^2 - r^2$) orbital and not in b_{1g}^* ($\sim x^2 - y^2$) [1, 2]. As a main consequence of this, the 3d–4s hybridization is allowed in the normalized $|a_{1g}^*\rangle$ wavefunction, which can simply be written as

$$|a_{1g}^*\rangle = \alpha_d |d(3z^2 - r^2)\rangle + \alpha_{4s} |4s\rangle - \beta_L |\chi_L\rangle \quad (1)$$

where $|\chi_L\rangle$ briefly denotes a suitable LCAO made of valence $n_L p$ and $n_L s$ ligand orbitals.

(iii) The NH_4Cl lattice experiences a $\beta \rightarrow \delta$ phase transition involving the ‘ferromagnetic’ order of NH_4^+ tetrahedra at $p = 1 \text{ atm}$ and $T_c = 242.5 \text{ K}$ [3]. Accompanying this ordering there are also significant displacive effects below T_c , so the lattice parameter a undergoes a decrease of 3.5 pm in the 243–100 K range [4, 5].

(iv) Some EPR and optical parameters of the Cu^{2+} (II) centre in NH_4Cl experience relevant changes below T_c . As regards the hyperfine tensor, \mathbf{A} , $A_{\parallel} = 191.3$ G has been measured at 293 K while $A_{\parallel} = 252.7$ G at $T = 100$ K is taken from the data reported by Hagen and Trappeniers [6]. On the other hand, the wavenumber, ν_{CT} , of the $e_u(\pi + \sigma, \text{eq}) \rightarrow a_{1g}^*$ charge transfer transition decreases by 700 cm^{-1} in the 243–100 K range [7].

The microscopic reason for such important changes below T_c is not yet well established; it has been proposed [8, 9] that they are directly related to the ordering of NH_4^+ ions. By contrast, recent studies on the temperature dependence of ν_{CT} [7, 10, 11] have led to the conclusion that changes undergone by ν_{CT} below T_c directly reflect local changes of $\text{Cu}^{2+}-\text{Cl}^-$ and $\text{Cu}^{2+}-\text{N}$ distances, termed as R_{eq} and R_{ax} , respectively. Such variations are in turn induced by displacive effects in the host lattice, which accompany the ordering of NH_4^+ ions. Furthermore, the analysis of both optical and Raman data [7, 11] lead to the conclusion that below T_c the variations experienced by R_{ax} and R_{eq} are quite different from that of the lattice parameter a . In particular in the 243–100 K range, where the lattice parameter a decreases, R_{eq} would experience an increase although R_{ax} decreases as well. A main goal of the present work is to investigate whether the very important increase undergone by A_{\parallel} and A_{\perp} of the Cu^{2+} (II) centre in NH_4Cl and ND_4Cl below T_c can also be explained principally through such an anomalous relaxation around Cu^{2+} .

To achieve this it is necessary to investigate how the hyperfine tensor of the $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ complex depends upon both R_{ax} and R_{eq} distances. At the same time it is worth exploring the changes experienced by the hyperfine tensor of the Cu^{2+} (II) centre in the *disordered* β phase due to variations of the lattice parameter a in order to compare them to the corresponding changes in the 243–100 K range.

For carrying out this task we have performed EPR measurements on $\text{NH}_4\text{Cl}_{1-x}\text{Br}_x:\text{Cu}^{2+}$ (II) and $\text{CsCl}:\text{Cu}^{2+}$ (II) systems as well as MS-X α calculations on the $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ complex as a function of R_{ax} and R_{eq} .

The crystals employed have all been grown in our laboratory by slow evaporation, at about 30°C , of saturated solutions to which urea is added. In the case of $\text{NH}_4\text{Cl}_{1-x}\text{Br}_x$ crystals the mole fraction x is determined by measuring the lattice parameter a and using Vegard's law. For doping the crystals, besides CuCl_2 or CuBr_2 , NH_4OH was added to the mother solution in order to reach $\text{pH} \cong 8$. Centre II is formed in NH_4Cl by this procedure [1, 2]. EPR spectra were taken by means of an ESP 300 Bruker spectrometer. Details of our MS-X α calculations (made without spin polarization) can be found for instance in [12].

In figure 1 room temperature EPR spectra are portrayed, which correspond to NH_4Cl , $\text{NH}_4\text{Cl}_{0.92}\text{Br}_{0.08}$ and CsCl doped with Cu^{2+} for $H \parallel \langle 100 \rangle$ while figure 2 depicts the spectra of $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ and $\text{CsCl}:\text{Cu}^{2+}$ at 100 K. The latter spectra agree well with those previously assigned to the Cu^{2+} (II) centre in NH_4Cl and CsCl lattices [2]. At the same time the comparison between the EPR spectra at RT and at 100 K corresponding to $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ (II) and $\text{CsCl}:\text{Cu}^{2+}$ (II) reveals that important changes have taken place in the first case while the spectrum remains almost the same in the second case, in agreement with the findings of Hagen and Trappeniers [6].

As regards the $x = 0.08$ crystal, only one EPR spectrum is discovered in figure 1, which moreover looks very similar to that found for $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ at RT. This result strongly supports the belief that the main Cu^{2+} species formed in the $x = 0.08$ crystal is again the $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ centre.

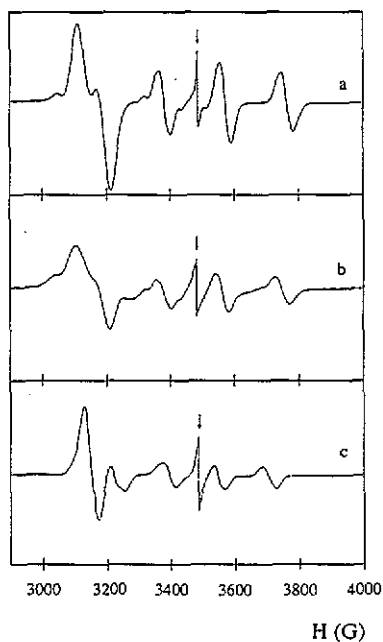


Figure 1. EPR spectra for the $\text{Cu}^{2+}(\text{II})$ centre in: (a) NH_4Cl ; (b) $\text{NH}_4\text{Cl}_{0.92}\text{Br}_{0.08}$; and (c) CsCl . $T = 293\text{ K}$ and $H \parallel \langle 100 \rangle$. Arrows indicate the DPPH signal.

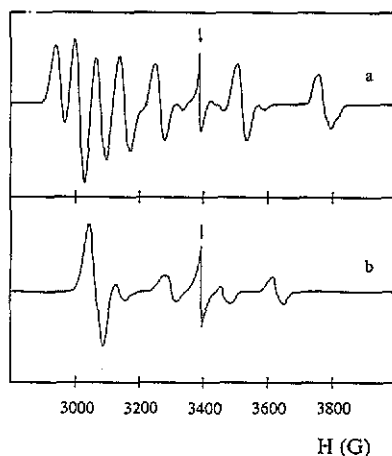


Figure 2. EPR spectra for the $\text{Cu}^{2+}(\text{II})$ centre in: (a) NH_4Cl and (b) CsCl . $T = 100\text{ K}$ and $H \parallel \langle 100 \rangle$. Arrows indicate the DPPH signal.

Table 1. Experimental values of A_{\parallel} measured at room temperature for several $\text{NH}_4\text{Cl}_{1-x}\text{Br}_x$ crystals and CsCl containing $\text{Cu}^{2+}(\text{II})$ centres. The bandwidth ΔH_{pp} ($m_l = 3/2$) of the parallel line for the highest field and lattice parameter a (in pm) are also given. A_{\parallel} and ΔH_{pp} are both referred to natural copper, and are given in G. Errors are given in parentheses.

Crystal	a	A_{\parallel}	ΔH_{pp} ($m_l = 3/2$)
NH_4Cl	387.6	191.3 (10)	40.1 (10)
$\text{NH}_4\text{Cl}_{0.92}\text{Br}_{0.08}$	389.1	185.1 (10)	46.2 (10)
$\text{NH}_4\text{Cl}_{0.84}\text{Br}_{0.16}$	390.6	182.5 (10)	50.9 (10)
$\text{NH}_4\text{Cl}_{0.82}\text{Br}_{0.33}$	393.7	177.5 (10)	60.1 (10)
CsCl	411.0	162.9 (10)	43.2 (10)
NH_4Br	405.9	187.2 (20)	70.9 (20)

Nevertheless, the spectrum corresponding to the $x = 0.08$ crystal is not identical to that for $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$. So, though it is found that g_{\parallel} and g_{\perp} are the same within the experimental uncertainty, A_{\parallel} for the former system is $6 \pm 2\text{ G}$ smaller than for the latter, as is shown in table 1. We relate this difference as being due, essentially, to the variation $\Delta a = 1.5\text{ pm}$ undergone by the lattice parameter a on passing from $x = 0$ to $x = 0.08$, so $(\Delta A_{\parallel}/\Delta a)_{\text{RT}} = -(4 \pm 1.5)\text{ G pm}^{-1}$. Using this figure, the bulk modulus $B = 185.5\text{ kbar}$ of pure NH_4Cl at RT [13] and assuming that the local compressibility around Cu^{2+} is the same as that of the host lattice, we derive $(\Delta A_{\parallel}/\partial p)_{\text{RT}} = (2.8 \pm 1)\text{ G kbar}^{-1}$ for the

Cu^{2+} (II) ion in NH_4Cl . This figure is not far from the value $(\Delta A_{\parallel}/\partial p)_{\text{RT}} = 4.6 \text{ G kbar}^{-1}$ measured by Van der Valk by applying hydrostatic pressures [14, 15] to the Cu^{2+} (II) centre in NH_4Cl . This fact, then, supports our interpretation of the decrease experienced by A_{\parallel} , when we compare $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ (II) with $\text{NH}_4\text{Cl}_{0.92}\text{Br}_{0.08}:\text{Cu}^{2+}$ (II). It is true that in $\text{NH}_4\text{Cl}_{0.92}\text{Br}_{0.08}:\text{Cu}^{2+}$ (II) other complexes like $\text{CuCl}_{4-n}\text{Br}_n(\text{NH}_3)_2^-$ with $n \geq 1$ could be present, although no direct evidence of this is obtained from EPR spectra. It is worth noting however that *even assuming* a statistical distribution of complexes, the $\text{CuCl}_4(\text{NH}_3)_2^-$ unit would be the dominant species for $x \leq 0.20$, and for $x = 0.08$ the relative amount of $n = 0$ and $n = 1$ complexes would be about 70% and 25%, respectively.

The EPR spectra obtained for mixed crystals with $x = 0.16$, $x = 0.17$ and even for $x = 0.33$ are rather similar to those for $x = 0$ and $x = 0.08$. Again only one EPR spectrum is clearly resolved although the bandwidth of the 'parallel' lines increases with x as shown in table 1, a fact which can be related to the increase of the disorder [16]. As regards A_{\parallel} , table 1 indicates that it decreases as long as x increases, following the trend observed on passing from $x = 0$ to $x = 0.08$ where the relative amount of $\text{CuCl}_4(\text{NH}_3)_2^-$ species is certainly higher than for $x = 0.16$.

The RT value of A_{\perp} for $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ (II) cannot be measured as only a broad band having a bandwidth $\Delta H_{pp}(\perp) = 74 \pm 5 \text{ G}$ is seen in the 'perpendicular' region. This broad band masks the perpendicular hyperfine interaction as well as superhyperfine interactions with N, Cl and H nuclei. This situation is, however, improved in $\text{ND}_4\text{Cl}:\text{Cu}^{2+}$, where A_{\perp} has been determined to be equal to 29.7 G at RT [14, 2]. Assuming this same value of A_{\perp} for $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ (II) at RT, a moment analysis [17] of its bandwidth $\Delta H_{pp}(\perp) = 74 \pm 5 \text{ G}$ reveals that about 80% of the experimental value of $\Delta H_{pp}(\perp)$ is due to the hyperfine interaction. Therefore the comparison of this value with $\Delta H_{pp}(\perp) = 46 \pm 2$ determined for $\text{CsCl}:\text{Cu}^{2+}$ strongly supports that on going from $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ (II) to $\text{CsCl}:\text{Cu}^{2+}$ (II) a significant reduction of A_{\perp} has also occurred.

In order to interpret the observed variations undergone by A_{\parallel} microscopically let us recall that for the $\text{CuCl}_4(\text{NH}_3)_2^-$ complex A_{\parallel} comprises essentially the following three contributions [2, 18]

$$A_{\parallel} = -K + A_{4s} + 2A_{\text{an}} \quad (2)$$

Here the anisotropic contribution A_{an} is given by

$$A_{\text{an}} = 2\alpha_d^2 P/7$$

$$P = 2g_0 g_N \beta \beta_N \langle r^{-3} \rangle_{3d}$$

where $P = 406 \text{ G}$ can be taken for copper and α_d^2 , defined in (1), is the probability of finding the unpaired electron upon the $d(3z^2 - r^2)$ orbital. The isotropic term $-K$ depicts the core-polarization contribution arising from inner 3s, 2s and 1s shells of copper, while the isotropic A_{4s} contribution arises from the probability, α_{4s}^2 of the unpaired electron being on the 4s orbital of copper. The last contribution is symmetry forbidden for D_{4h} Cu^{2+} centres with an $\sim x^2 - y^2$ unpaired electron.

Table 2 contains results of MS-X α calculations for $\text{CuCl}_4(\text{NH}_3)_2^-$ carried out at several R_{ax} and R_{eq} distances. Besides offering the repartition of the unpaired electron charge for different atoms and orbitals, it provides us with the values of A_{4s} and A_{an} for each couple of R_{eq} and R_{ax} distances. Table 2 stresses that A_{4s} can be similar or higher than A_{an} although $\alpha_d^2 \approx 55\%$ is certainly much higher than $\alpha_{4s}^2 \approx 2\%$.

Table 2. Electronic charge distribution (in %) for the ground state of the $\text{CuCl}_4(\text{NH}_3)_2^{2-}$ complex calculated through the MS-X α method for several values of R_{eq} and R_{ax} (given in pm), together with the corresponding values of A_{an} and A_{4s} (given in G) defined in (2).

R_{eq}	R_{ax}	Cu		Cl		N		H	$2A_{\text{an}}$	A_{4s}
		4s	3d	3s	3p	2s	2p			
240	195	2.00	54.04	0.95	20.21	3.46	18.23	1.10	125.4	124.4
242	195	2.19	53.51	0.94	20.88	3.36	18.01	1.10	124.1	135.0
238	195	1.79	54.78	0.96	19.50	3.54	18.33	1.10	127.1	111.8
245	195	2.48	52.70	0.93	21.91	3.23	17.66	1.09	122.3	151.3
240	197	1.72	53.83	0.90	20.03	3.51	18.86	1.15	124.9	105.7
240	200	1.35	53.50	0.82	19.72	3.59	19.80	1.21	124.1	81.9

Table 3. Values of the core polarization constant K (in G) for some complexes with D_{4h} , square-planar or elongated octahedral, geometry obtained from the experimental spin-Hamiltonian parameters through the procedure of [19].

System	Complex	K
$\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$:		
Cu^{2+}	$\text{Cu}(\text{H}_2\text{O})_6^{2+}$	140.0
K_2CuF_4	CuF_6^{4-}	160.9
$\text{K}_2\text{PdCl}_4 \cdot \text{Cu}^{2+}$	CuCl_6^{2-}	137.0
$\text{CdCl}_2 \cdot \text{Cu}^{2+}$	CuCl_6^{4-}	132.5
$\text{K}_2\text{PdBr}_4 \cdot \text{Cu}^{2+}$	CuBr_6^{2-}	110.8
$\text{ZnTPP} \cdot \text{Cu}^{2+}$	CuN_4	144.3

Taking into account the values of K derived [19, 20] from careful analysis of experimental spin-Hamiltonian parameters of $D_{4h}\text{Cu}^{2+}$ complexes with a B_{1g} ground state (table 3) we can expect a K value close to 130 G for $\text{CuCl}_4(\text{NH}_3)_2^{2-}$. Therefore, assuming $A_{\text{an}} = 125$ G and $K = 130$ G, (2) implies that the value $|A_{\parallel}| = 191.3$ G, measured experimentally for $\text{NH}_4\text{Cl} \cdot \text{Cu}^{2+}(\text{II})$ at RT, corresponds to a positive sign of A_{\parallel} , thus leading to $A_{4s} \cong 200$ G, which is somewhat higher than the theoretical values gathered in table 2. Under-estimation of hyperfine constants has been encountered in several MS-X α calculations as pointed out for instance in [21].

A salient feature emerging from table 2 concerns the dependence of A_{4s} and A_{an} on metal-ligand distances. In fact, the present MS-X α results point out that A_{4s} is much more sensitive than A_{an} to changes of R_{ax} and R_{eq} . Furthermore, the results of table 2 indicate that:

- (i) $(\partial A_{4s}/\partial R_{\text{ax}})$ is negative while $(\partial A_{4s}/\partial R_{\text{eq}})$ is positive.
- (ii) $(\partial A_{4s}/\partial R_{\text{ax}}) \approx -2(\partial A_{4s}/\partial R_{\text{eq}})$.
- (iii) As regards the value of $(\partial A_{4s}/\partial R_{\text{ax}})$ itself, the present calculations lead to values around -10 G pm $^{-1}$ already stressing that A_{4s} can be very sensitive to metal-ligand distance changes.

For comparison let us recall that for the octahedral complex MnF_6^{4-} , $dA_s/dR = -0.6$ G pm $^{-1}$, where A_s is the isotropic superhyperfine constant [22, 23]. A much weaker dependence on R for MnF_6^{4-} is exhibited by the hyperfine constant A essentially arising

from the core polarization contribution [23–25]. In view of the preceding theoretical results, the change, ΔA_{\parallel} , experienced by A_{\parallel} on passing from NH_4Cl to other lattices (table 1) can be explained reasonably as being due mainly to changes of A_{4s} produced by variations, ΔR_{eq} and ΔR_{ax} , undergone by the equatorial and axial metal–ligand distances respectively. Experimentally this idea is supported by the decrease experienced by both A_{\parallel} and A_{\perp} on going from $\text{NH}_4\text{Cl}:\text{Cu}^{2+}(\text{II})$ to $\text{CsCl}:\text{Cu}^{2+}(\text{II})$. A similar situation arises when hydrostatic pressures are applied to $\text{ND}_4\text{Cl}:\text{Cu}^{2+}(\text{II})$ [14, 15].

The relation of ΔA_{\parallel} with ΔR_{ax} and ΔR_{eq} is given by

$$\Delta A_{\parallel} = (\partial A_{\parallel}/\partial R_{\text{ax}})\Delta R_{\text{ax}} + (\partial A_{\parallel}/\partial R_{\text{eq}})\Delta R_{\text{eq}} \quad (3)$$

and assuming, in a first approximation,

$$(\partial A_{\parallel}/\partial R_{\text{ax}}) \cong (\partial A_{4s}/\partial R_{\text{ax}}) = -2(\partial A_{4s}/\partial R_{\text{eq}}) \cong -2(\partial A_{\parallel}/\partial R_{\text{eq}}) \quad (4)$$

(3) becomes

$$\Delta A_{\parallel} \cong (\partial A_{\parallel}/\partial R_{\text{ax}})(\Delta R_{\text{ax}} - \frac{1}{2}\Delta R_{\text{eq}}). \quad (5)$$

On passing from $\text{NH}_4\text{Cl}:\text{Cu}^{2+}(\text{II})$ to $\text{NH}_4\text{Cl}_{0.92}\text{Br}_{0.08}:\text{Cu}^{2+}(\text{II})$ the variations ΔR_{eq} and ΔR_{ax} are induced by the change, Δa , undergone by the lattice parameter a . Therefore, in order to relate ΔA_{\parallel} and Δa through (3) a knowledge of how ΔR_{ax} and ΔR_{eq} depend on Δa is required. For estimating this dependence the recent results for Mn^{2+} and Ni^{2+} impurity-doped fluoroperovskites [22, 26] are a great help. In these cases the variations of impurity–ligand distances, ΔR , due to changes of the host lattice can be written as

$$\Delta R = f\Delta R_0 \quad (6a)$$

where ΔR_0 corresponds to the metal–ligand distance of the *perfect* lattice and the f factor, equal to about 0.4, reflects the tendency of the complex to keep the R value expected on the basis of ionic radii, and thus the inertia to follow changes in the host lattice.

Now assuming in the present case

$$\Delta R_{\text{ax}} = f_{\text{ax}}(\Delta a/2) \quad \Delta R_{\text{eq}} = f_{\text{eq}}(\Delta a/\sqrt{2}) \quad (6b)$$

we arrive at

$$\Delta A_{\parallel}/\Delta a = \frac{1}{2}(\partial A_{4s}/\partial R_{\text{ax}})[f_{\text{ax}} - (f_{\text{eq}}/\sqrt{2})]. \quad (7)$$

If we now make the supplementary assumption that $f_{\text{ax}} = f_{\text{eq}} = f$, the value $\Delta A_{\parallel} = -(6 \pm 2)$ G, measured on passing from $x = 0$ to $x = 0.08$, leads to

$$(\partial A_{4s}/\partial R_{\text{ax}})f \approx -(8 \pm 3)/0.3 = -(25 \pm 10) \text{ G pm}^{-1}. \quad (8)$$

As $f < 1$ this result suggests that $|\partial A_{4s}/\partial R_{\text{ax}}|$ is still higher than the value $|\partial A_{4s}/\partial R_{\text{ax}}| = 10 \text{ G pm}^{-1}$ obtained through MS- $X\alpha$ calculations. As pointed out before, MS- $X\alpha$ on Cu^{2+} complexes usually leads to underestimation of the hyperfine tensor, although they reproduce the *main trends* of the dependence of optical and EPR parameters on metal–ligand distances.

Bearing in mind the preceding analysis we can reasonably explain the main origin of the significant increase $\delta_{\text{T}}(A_{\parallel}) = 60 \text{ G}$ undergone by A_{\parallel} of $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ on going from RT to 100 K. This increase is comparable to $\delta_{\text{T}}(A_{\perp}) = 46 \text{ G}$ experienced by the perpendicular component and thus supports the belief that it comes mainly from variations

undergone by the isotropic contribution to A_{\parallel} (equal to $A_{4s} - K$ in (2)) as was suggested by Hagen and Trappeniers [6]. From the present results it is therefore consistent to attribute $\delta_T(A_{\parallel})$ mainly to the change $\delta_T(A_{4s})$ experienced by A_{4s} .

From a qualitative point of view this relevant increase is quite consistent with the anomalous relaxation proposed in [7, 10, 11] and (5). In fact, if on passing from RT to 100 K $\Delta R_{ax} < 0$ but $\Delta R_{eq} > 0$ it favours higher ΔA_{\parallel} values than when both ΔR_{ax} and ΔR_{eq} have the same sign. The latter situation occurs on applying hydrostatic pressures or on placing the $\text{CuCl}_4(\text{NH}_3)_2^-$ complex in another host lattice with a different a parameter. Quantitatively, data taken from recent Raman and optical measurements give $\Delta R_{ax} \approx -0.5$ pm and $\Delta R_{eq} \approx 2$ pm [11] on passing from RT to 100 K for the $\text{Cu}^{2+}(\text{II})$ centre in NH_4Cl . Now assuming $(\partial A_{4s}/\partial R_{ax}) = -30$ G pm $^{-1}$ from (8), we obtain $\delta_T(A_{4s}) = -45$ G and thus this figure can explain the main changes experienced by A_{\parallel} and A_{\perp} of $\text{NH}_4\text{Cl}:\text{Cu}^{2+}(\text{II})$ below T_c .

Although further work is required to obtain more precise values of quantities like $(\partial A_{\parallel}/\partial R_{ax})$, $(\partial A_{\parallel}/\partial R_{eq})$, etc the interpretation of $\delta_T(A_{\parallel})$ in $\text{NH}_4\text{Cl}:\text{Cu}^{2+}(\text{II})$ given here appears as consistent. Besides this conclusion, the present work stresses the outstanding sensitivity of the hyperfine tensor of the $\text{CuCl}_4(\text{NH}_3)_2^-$ complex to changes of metal-ligand distance. In this way, if the hyperfine tensor is measured through ENDOR and the uncertainty reached is $\pm 10^{-2}$ G, variations δR_{ax} down to $\sim 10^{-3}$ pm can be detected if $\delta R_{eq} = 0$.

As this high sensitivity of the hyperfine tensor has been shown to be related to the admixture of the 4s orbital of copper into the wavefunction of the unpaired electron, effects of this kind can be expected for d^9 systems with orthorhombic symmetry as well as for d^7 ions (like Rh^{2+} and Pd^{3+}) in an elongated octahedral geometry and thus with the unpaired electron being placed again in a_{1g}^* .

Of course the conclusions reached through this work point out that A_{\parallel} can be a very sensitive parameter for studying $\text{Cu}^{2+}(\text{II})$ centres in mixed $\text{NH}_4\text{Cl}_{1-x}\text{Br}_x$ crystals in tetragonal and cubic phases. We hope to report an account of this work together with further insight into the origin of the strong dependence of A_{4s} upon R_{ax} for $\text{CuCl}_4(\text{NH}_3)_2^-$ in the near future.

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