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LETTER TO THE EDITOR

## Hyperfine and ligand hyperfine (perpendicular) parameters of $\text{Cu}^{2+}:\text{NH}_4\text{Br}$ (basic) from EPR: a new assignment

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**Abstract.** Ammonium bromide crystals doped with  $\text{Cu}^{2+}$  and grown in basic solution ( $\text{pH} \approx 8$ ) were studied at 300 K and 77 K with X-band EPR to elucidate divergent spin-Hamiltonian parameters. Careful measurements of the perpendicular part of the spectra indicated resolved 16 lines (300 K) and 19 lines (77 K). They were interpreted combining 4 hyperfine and 13 ligand (Br) hyperfine lines. We obtained  $A_{\perp} = (33 \pm 2) \times 10^{-4} \text{ cm}^{-1}$  (300 K) and  $A_{\perp} = (67 \pm 2) \times 10^{-4} \text{ cm}^{-1}$  (77 K). These values are not so different from the known values assigned to the analogous centre in  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$ . The discrepancy reported is due to the difficulty in ascribing the Br hyperfine parameter now determined as  $A'_{\perp} = (47 \pm 3) \times 10^{-4} \text{ cm}^{-1}$  (300 and 77 K). Compared with that of Cl compounds it is about five times greater, which is of the same order as the hyperfine interaction ratio for free Br and Cl atoms.

Crystals of ammonium bromide have been the object of considerable interest when doped with  $\text{Cu}^{2+}$  ions in few molar percentages. The crystals are very amenable to study by EPR and optical absorption [1–8], generally used as probes to detect the two phase transitions below room temperature related to ordering of the  $\text{NH}_4$  groups. Its structure is CsCl-type cubic at the temperatures used in our experiment, 300 K and 77 K. At 300 K,  $\text{NH}_4$  groups are disordered and at 77 K they are ‘ferromagnetically’ ordered. Between 235 and 78 K the structure is tetragonal and the ordering is ‘antiferromagnetic’. The crystal can incorporate two different types of centres depending on whether the growing solution is acidic or basic.

Authors of more recent works [6–8] adopted the model that the basic growing centres are  $\text{Cu}^{2+}$  interstitials sited at the face centre of the four Br, and localized between two  $\text{NH}_4$  vacancies (occupied by neutral  $\text{NH}_3$  groups). It forms a  $\text{NH}_3\text{--Cu}^{2+}\text{--NH}_3$  aligned system along the [001] direction. This crystal is cubic so the presence of two other equivalent centres sited along the [100] and [010] directions is just as probable. When a magnetic field is applied parallel to one of these directions, two mutually perpendicular centres are always present. Although EPR had been conclusive in confirming this model based in ligand hyperfine splitting observed at parallel orientation [6], the perpendicular portion of the spectra has received different interpretations. Therefore our spectra were carefully measured and analysed to detect more weak lines, because at first sight it can easily ascribe only 13 lines. We obtained 16 lines at 300 K and 19 lines at 77 K. The relative intensity between the larger and smaller lines can attain around two orders of magnitude. The aim of the present work is to explain how the spin Hamiltonian parameters should be determined with these unusual numbers of resolved lines.

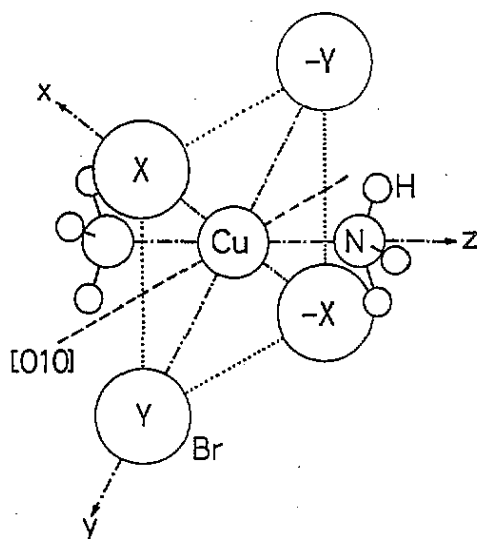


Figure 1. The  $\text{NH}_3\text{-Cu}^{2+}\text{-NH}_3$  centre site in  $\text{NH}_4\text{Br}$ , and the labelled (Br) ligands used in equation (2).

Our crystals were grown by reacting  $\text{HBr}$  with  $(\text{NH}_4)_2\text{CO}_3$  mixed with a few mol% of  $\text{CuCO}_3$  and about 10 mol% of  $\text{CdCO}_3$  (to prevent their dendritic growth). To this solution sufficient  $\text{NH}_4\text{OH}$  to maintain a  $\text{pH} \approx 8$  was added, to achieve the desired type of centre (basic). The resultant solution was kept in a refrigerator at  $0^\circ\text{C}$ . Regular cubic monocrystals were obtained after a few days, with edges about 3 mm long and yellowish-green in colour. The structure was confirmed by x-ray, and chemical analysis detected 0.5 at.% of Cu.

EPR experiments were performed in X-band JEOL (JES-PE-3X) equipment. Measurements at 77 K were performed using a liquid nitrogen immersion Dewar.

The  $\text{Cu}^{2+}$  ion belongs to  $3d^9$  and  $^2D$  configuration. The ground state is  $^2A_{1g}$  and the orbital function is mainly  $d_{3z^2-r^2}$ . The spin Hamiltonian appropriate to tetragonal symmetry is given by

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel}I_z S_z + A_{\perp}(I_x S_x + I_y S_y) \quad (1)$$

with  $S = \frac{1}{2}$  and  $I = \frac{3}{2}$ .

Table 1. Perpendicular hyperfine and ligand-hyperfine (SHF) parameters for the  $\text{NH}_3\text{-Cu}^{2+}\text{-NH}_3$  centre in  $\text{NH}_4\text{Br}$ .

Author	$T$ (K)	$A_{\perp}$ ( $10^{-4}$ $\text{cm}^{-1}$ )	$A'_{\perp}$ ( $10^{-4}$ $\text{cm}^{-1}$ )
Larin <i>et al</i> [1]	300	$0 \pm 5$	$33.1 \pm 2$
Sastry and Venkateswarlu [2]	300	0	—
Trappeniers <i>et al</i> [5]	293	0	—
Kawamori and Rao [7]	295	$\approx 28.3$	—
	54	$\approx 39.9$	—
Sorokin and Chirkin [9]	300	$0 \pm 5$	$9 \pm 1$
( $\text{ND}_4\text{Br}$ )	77	$50 \pm 5$	$9 \pm 1$
Present work	300	$33 \pm 2$	$47 \pm 3$
	77	$67 \pm 2$	$47 \pm 3$

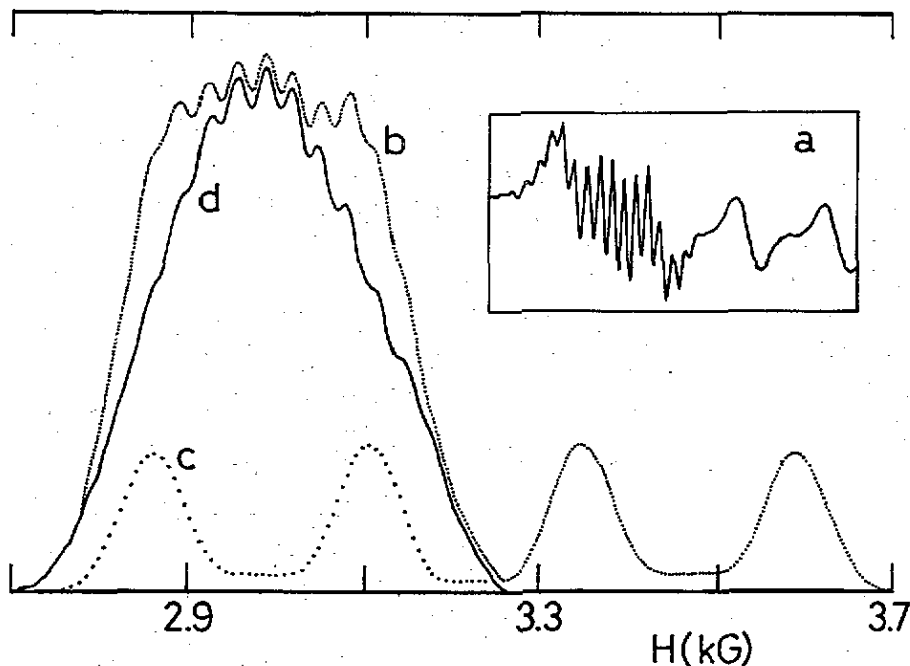


Figure 2. (a) Original X-band spectra obtained at 77 K with the magnetic field applied perpendicular to one crystal face; (b) integrated EPR spectra; (c) superposed part of the parallel spectra (reproduced from two peaks observed on the right hand side and (d) perpendicular parts of the spectra after subtraction of (c). (The scale of the magnetic field for curve (a) is not the same as for curves (b)–(d).)

Angular variation of the spectra confirmed the tetragonal symmetry, about two hours after loading the liquid nitrogen. This time is necessary to overtake the sluggish transition of the crystal ( $T_c = 78$  K). Our spin Hamiltonian parameters, for example, at 77 K are  $g_{\parallel} = 2.038 \pm 0.005$ ,  $g_{\perp} = 2.190 \pm 0.005$  and  $A_{\parallel} = (259 \pm 3) \times 10^{-4} \text{ cm}^{-1}$ , and are essentially similar to those given in the literature [7, 9]. However,  $A_{\perp}$  is an exception as shown in table 1. As the discrepancy observed is mainly due to the assignment of the perpendicular-ligand hyperfine (also known as super-hyperfine) parameter  $A'_{\perp}$ , the available values are also listed. The corresponding interaction Hamiltonian is given by

$$H_{\text{shf}} = A'_{\perp} [(S_x I'_x)_X + (S_x I'_x)_{-X} + (S_y I'_y)_Y + (S_y I'_y)_{-Y}] \quad (2)$$

where we are considering only the perpendicular part of the interaction and neglecting contributions other than those from the nearest Br ( $I' = \frac{3}{2}$ ), X,  $-X$ , Y and  $-Y$ , as represented in figure 1. With the magnetic field applied along  $[010]$ , the four Br (total spins 6) atoms contribute equally, splitting each of the four hyperfine  $\text{Cu}^{2+}$  lines into 13 lines separated by  $A'_{\perp} \cos(45^\circ)$ , and with an intensity proportional to 1, 4, 10, 20, 31, 40, 44, 40, 31, 20, 10, 4, 1, corresponding to the different ways of forming spins 6, 5, ...,  $-5$ ,  $-6$ . If  $A'_{\perp} \ll A_{\perp}$  each of the four hyperfine lines would be seen resolved into 13 lines. In the case of  $A_{\perp} = 0$  only 13 super-hyperfine lines would be apparent (some authors in table 1 assumed this condition). However, our spectra indicated more lines so that  $A'_{\perp}$  would be in the same order of  $A_{\perp}$  and consequently the exact number of them depends with the ratio  $2^{1/2} A_{\perp} / A'_{\perp}$ . We concluded that at 300 K this ratio is approximately 1 and at 77 K

is approximately 2 because we observed, respectively, 16 and 19 lines. To illustrate this we show in table 2 the structure for the last case. In figure 2 the corresponding spectra (normal and integrated) are depicted. The theoretically expected intensity is compared with our numerically integrated spectrum in table 2 and it shows that the result is in fair agreement. The  $A_{\perp}$  value (see table 1) so obtained is the same for the equivalent centre [10] in  $\text{NH}_4\text{Cl}$ . Other spin Hamiltonian parameters of equation (1) that we obtained at 77 K and 300 K also do not show significant differences if compared with those given in the same reference [10] (including  $\text{ND}_4\text{Cl}$ ).

Table 2. Structure of the perpendicular parts of the spectra: the first four lines are the intensity distributions of each ligand-hyperfine line, the fifth line is the sum (theoretical resultant intensities) and the last line is the experimental (normalized) intensities obtained from figure 2(d).

1	4	10	20	31	40	44	40	31	20	10	4	1							
		1	4	10	20	31	40	44	40	31	20	10	4	1					
				1	4	10	20	31	40	44	40	31	20	10	4	1			
						1	4	10	20	31	40	44	40	31	20	10	4	1	
1	4	11	24	42	64	86	104	116	120	116	104	86	64	42	24	11	4	1	
1	4	12	27	48	70	91	109	118	120	115	103	89	69	53	38	19	9	0	

$A'_{\perp}(\text{Br})$  is about five times greater than the magnitude attributed [10] to Cl compounds. It is so large that it even overcomes the hyperfine interaction. However, this ratio is of the same order as that verified between hyperfine structures of free Br and Cl, i.e. 4.53 [11].

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