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LETTER TO THE EDITOR

The EPR of a new Cu^{2+} centre in NH_4Br (acidic)

E Di Mauro† and W Sano‡

† Departamento de Física, Universidade Estadual de Londrina, Caixa Postal 6001, 86051-970 Londrina-PR, Brazil

‡ Instituto de Física, Universidade de São Paulo, Caixa Postal 20516, 01452-990 São Paulo SP, Brazil

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Abstract. A new interstitial Cu^{2+} centre was found in NH_4Br crystals grown in acidic solution ($\text{pH} < 0.2$) that was not observed in our previously studied sample ($\text{pH} \approx 1.6$). X-band EPR at 293 K indicates that the symmetry is tetragonal and the spin-Hamiltonian parameters are $g_{\parallel} = 2.044 \pm 0.002$, $g_{\perp} = 2.188 \pm 0.002$, $A_{\parallel} = 0 \pm 5$, $A_{\perp} = 83 \pm 3$ and $A'_{\perp} = 30 \pm 1$ (A is given in units of 10^{-4} cm^{-1}). A model $\text{H}_2\text{O}-\text{Cu}^{2+}-\text{H}_2\text{O}$ was assigned after studying the appearance of three types of centre in crystals grown with pH between ~ 8 and < 0.2 . Re-examination of the previous study on NH_4Br ($\text{pH} \approx 1.6$) has indicated that the centre obtained there may be of type $\text{NH}_3-\text{Cu}^{2+}-\text{H}_2\text{O}$, which can also be ascribed to the centre in NH_4Cl known as centre III.

Cu^{2+} centres known in CsCl-type NH_4Br crystals are those obtained in crystals grown in basic and acidic solution. They have been associated with the models $\text{NH}_3-\text{Cu}^{2+}-\text{NH}_3$ and $\text{H}_2\text{O}-\text{Cu}^{2+}-\text{H}_2\text{O}$ respectively (see figure 1). These models became widely accepted after ENDOR study [1] in isomorphous NH_4Cl . In our recent works [2, 3] we reported the best known properties of these centres in NH_4Br and determined their hyperfine and superhyperfine (SHF) parameters from EPR spectra. X-band EPR equipment and crystal-growing procedures were also described there. In this work we describe a new Cu^{2+} centre found in NH_4Br using crystals grown in more acidic solution ($\text{pH} < 0.2$). We will show also that the centre studied previously by us in NH_4Br ($\text{pH} \approx 1.6$) [3] corresponds best to a model of type $\text{NH}_3-\text{Cu}^{2+}-\text{H}_2\text{O}$ and that the model ascribed there ($\text{H}_2\text{O}-\text{Cu}^{2+}-\text{H}_2\text{O}$) is most suitable for the presently described new centre.

The EPR spectrum at 293 K of the new centre is shown in figure 2. The spin Hamiltonian ascribed to this spectrum excluding the SHF interaction is

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

with $S = \frac{1}{2}$ and $I = \frac{3}{2}$. The parameters are $g_{\parallel} = 2.044 \pm 0.002$, $g_{\perp} = 2.188 \pm 0.002$, $A_{\parallel} = 0 \pm 5$ and $A_{\perp} = 83 \pm 3$ (A is given in units of 10^{-4} cm^{-1}). A_{\perp} was determined using a methodology similar to that given in [2]. The SHF interaction appears at the perpendicular side of the spectrum (figure 2) and from the line separation we obtained $A'_{\perp} = 30 \pm 1$.

The appearance of each type of Cu^{2+} centre was analysed in NH_4Br crystals grown in solutions with different pH by their characteristic EPR spectra. This new centre appears solely at extremely low pH. It should therefore correspond to an $\text{H}_2\text{O}-\text{Cu}^{2+}-\text{H}_2\text{O}$ -type centre (acidic centre). As this is the same model that we have attributed to the centre reported previously [3] we are modifying the assignment made there. Considering that the

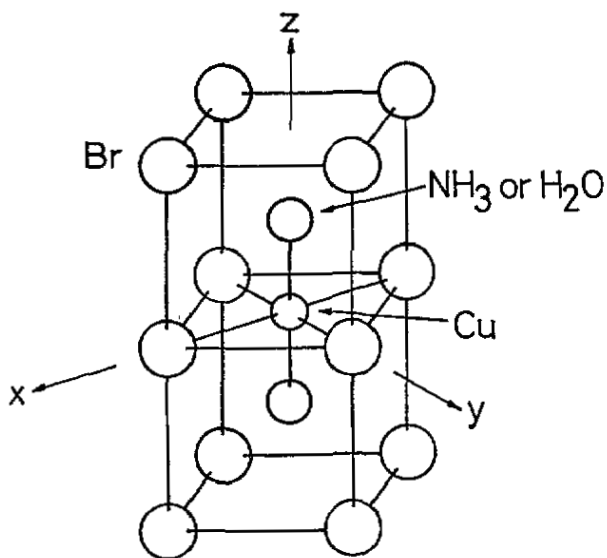


Figure 1. The Cu^{2+} centre site in NH_4Br .

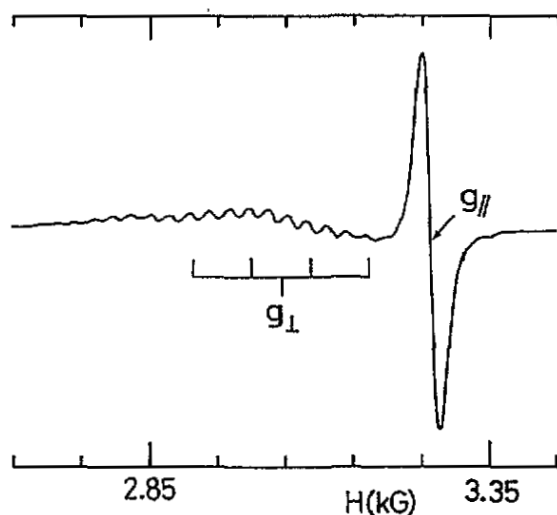


Figure 2. The EPR X-band spectrum of the Cu^{2+} centre in NH_4Br ($\text{pH} < 0.2$) obtained at 293 K with the magnetic field along one cubic axis.

solution used there [3] was less acidic we conclude that the best model for that centre is the type $\text{NH}_3\text{-Cu}^{2+}\text{-H}_2\text{O}$ (mixed centre). Our results indicated that only at high values of pH is the well known basic centre $\text{NH}_3\text{-Cu}^{2+}\text{-NH}_3$ [2] detected solely (see table 1). At the intermediate values of pH the mixed centre coexists with one of the above types, basic or acidic centre. The relative numbers of the basic (or acidic) centres and the mixed type determined by EPR intensities is directly proportional to the basic (or acidic) character of the

Table 1. The appearance of three types of Cu^{2+} centre in crystals of NH_4Br grown in solutions with different pH.

pH	Type of centre
8.0-2.5	$\text{NH}_3\text{-Cu}^{2+}\text{-NH}_3$
2.5-1.5	$\text{NH}_3\text{-Cu}^{2+}\text{-NH}_3$ and $\text{NH}_3\text{-Cu}^{2+}\text{-H}_2\text{O}$
1.5-0.2	$\text{NH}_3\text{-Cu}^{2+}\text{-H}_2\text{O}$ and $\text{H}_2\text{O-Cu}^{2+}\text{-H}_2\text{O}$
<0.2	$\text{H}_2\text{O-Cu}^{2+}\text{-H}_2\text{O}$

solution. Considering that the formation of NH_3 groups at lowest pH is improbable Cu^{2+} should be associated naturally with two H_2O in this case. At highest pH, NH_3 groups appear more easily and due to their greater ability than H_2O to bond [4] $\text{NH}_3\text{-Cu}^{2+}\text{-NH}_3$ centres should be formed. Lowering the pH reduces the number of NH_3 and H_2O bonding becomes competitive, so the mixed type of centre ($\text{NH}_3\text{-Cu}^{2+}\text{-H}_2\text{O}$) is formed at intermediate values of pH. Table 1 shows that the mixed centre appears always associated with a basic (acidic) centre if the solution is more basic (acidic), which confirms this assertion.

Classifying the centres in NH_4Cl reported in the literature in a similar form we concluded that the model of the mixed type of centre is also applicable to centre III in NH_4Cl described by Hagen and Trappeniers [5]. They had observed this centre in crystals grown in neutral solution which can be considered an intermediate value of pH in our classification. Their spectrum shows seven triplets as SHF lines in the parallel direction, which is strong evidence of the presence of one NH_3 group because N has nuclear spin $I = 1$, which agrees nicely with our model ($\text{NH}_3\text{-Cu}^{2+}\text{-H}_2\text{O}$). From this point of view a corresponding seven SHF lines were observed in our NH_4Br ($\text{pH} \simeq 1.6$) [3], although without resolved triplets, confirming the equivalency between centres.

Finally, comparing the values of the spin-Hamiltonian parameter between equivalent centres in NH_4Cl [5] and NH_4Br [2, 3], there is a nice correspondence. Therefore the features of the centres in both crystals indicate that the above models are the best assignments.

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