

PARAMAGNETIC RESONANCE STUDIES OF Cu^{2+} DOPED IN NH_4Br

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ABSTRACT

Electron Paramagnetic Resonance studies of Cu^{2+} doped in NH_4Br single crystals have been carried out for the first time. The room temperature data reveal that Cu^{2+} ions go predominantly to interstitial sites having square planar co-ordination of four Br^- ions. For this type of complexes the bromine: superhyperfine structure: is observed on the normal hyperfine structure lines of copper. Existence of other weak spectra indicates that a relatively few Cu^{++} ions go substitutionally to $(\text{NH}_4)^+$ ions, and are probably associated with a first or a second nearest neighbour cation vacancy, among the two, the latter being more predominant. However, the low temperature studies corresponding to the tetragonal phase of NH_4Br indicate that a number of Cu^{2+} ions at interstitial sites get readjusted to the lattice sites after phase transformation. The spectra in both the phases are analysed by the usual spin Hamiltonian method.

INTRODUCTION

THE ammonium halides offer the possibility of an interesting extension of the paramagnetic resonance studies of doped alkali halides. When divalent impurity cations are placed substitutionally for monovalent ions of the host lattice, the unbalance of the excess charge that results must be compensated. Watkins¹ and recently Shrivastava and Venkateswarlu² discussed some models of charge compensation in alkali halide crystals the principal ones being divalent anion impurities and cation vacancies. In ammonium halide single crystals relatively few paramagnetic resonance studies have been reported,³⁻⁶ those studied being mainly in NH_4Cl single crystal. The reported spectra could be interpreted by considering the formation of complexes in which the magnetic ions are associated with cation vacancies or by considering the formation of hydrated double salts. Except for the EPR studies of radiation induced defects^{7, 8} no spin resonance studies have been reported

in NH_4Br single crystal. Paramagnetic resonance studies of Cu^{2+} doped in NH_4Br single crystal reported here have been carried out for the first time in the body centred cubic and the tetragonal phases of NH_4Br and the results obtained are discussed here.

EXPERIMENTAL

Cu^{2+} doped NH_4Br single crystals are grown from saturated solution of Ammonium Bromide mixed with CuBr_2 . Small quantities of urea are added to stimulate the cubic growth of the crystal.⁹ Spectra are recorded on a Varian X-band spectrometer V-4502 with 100 Kc./sec. field modulation. Diphenyl picryl hydrazil for which $g = 2.0036$ is used as a field marker. Spectra are recorded at different temperatures by using a Varian V-4540 model variable temperature accessory.

THEORY

The free Cu^{2+} ion has an electronic configuration $3d^9$ and a ground state ${}^2D_{5/2}$, when subjected to a cubic crystalline field, the five-fold orbital level of Cu^{2+} ion is split into a lower doublet (2E) and an upper triplet (2T). Orbital degeneracy in the lower state is further lifted by the presence of either a tetragonal or an orthorhombic component in the crystalline field. The magnetic properties of the lowest orbital singlet are modified slightly by an admixture of the excited states through spin-orbit interaction. This type of admixture results in an anisotropic g -value for the EPR spectrum. The nuclear spin of copper* is $3/2$ and the hyperfine interaction gives a four-line hyperfine structure. The paramagnetic resonance spectrum of Cu^{2+} subjected to a tetragonal crystalline field can be described by the spin-Hamiltonian,³

$$\mathcal{H} = g_{11}\beta H_z S_z + g_{\perp}\beta (H_x S_x + H_y S_y) + A I_z S_z + B (I_x S_x + I_y S_y) + Q' [I_z^2 - \frac{1}{3} I(I+1)]. \quad (1)$$

First two terms represent the coupling of the electronic spin moment to the external magnetic field, third and fourth terms represent the magnetic interaction between the electron spin moment and nuclear magnetic moment. The last term represents the interaction between the nuclear electric quadrupole moment and the electric field gradient set up by the anisotropic distribution of electronic charge about the nucleus. The Hamiltonian¹ may be

* Copper has two isotopes Cu^{63} and Cu^{65} but the effects of the two different isotopes could not be separately distinguished in the present experiments. This is because the two magnetic moments are not much different from one another.

solved in order to obtain the magnetic field resonance values. The magnetic field values for $H//Z$ axis are given by¹⁰

$$H = H_0 - Am - \frac{B^2}{2H_0} [I(I+1) - m^2] - \frac{B^2}{2H_0} [m(2M-1)] \quad (2a)$$

The magnetic field values for $H \perp Z$ axis are given by

$$H = H_0 - Bm - \frac{A^2 + B^2}{4H_0} [I(I+1) - m^2] - \frac{AB}{2H_0} [m(2M-1)] \\ + \frac{Q'^2}{8BM(M-1)} \cdot m \cdot [2I(I+1) - m^2 - 1]. \quad (2b)$$

When subjected to an orthorhombic crystalline field the spectrum is usually described by the spin-Hamiltonian of the type

$$\mathcal{H} = \beta (g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) \\ + A_x I_x S_x + A_y I_y S_y + A_z I_z S_z \\ + Q'^2 [I_z^2 - \frac{1}{3} I(I+1)] + Q'' (I_x^2 - I_y^2) \quad (3)$$

The terms in the above expression have got their usual significance as mentioned above. The expressions for the resonant field values are obtained by solving the above Hamiltonian by Bleaney *et al.*¹¹ and these expressions are used in analysing some of the spectra in the present study.

If there is a superhyperfine (shf) magnetic interaction between the metal ion electronic cloud and the ligand nuclei, a term of the type $\sum_i \bar{S} \cdot A_i \cdot I_{(\text{ligand})i}$ is added¹² to the corresponding spin Hamiltonian. This term can be expressed in terms of an isotropic part A_s and an anisotropic part A_d as

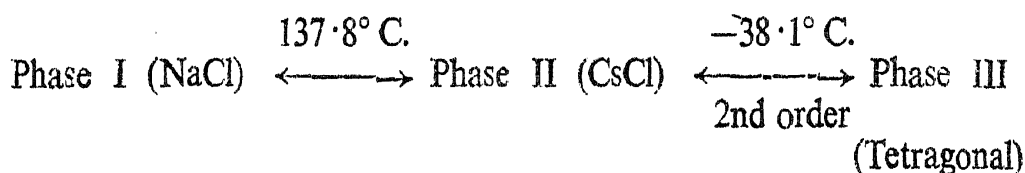
$$A_s \cdot M \sum_i m_{(L)i} + A_d M \sum_i m_{(L)i} (3 \cos^2 \theta_i - 1) \quad (4)$$

where θ_i is the angle between the direction of the magnetic field and magnetic ion-ligand distance and M and $m_{(L)i}$ are the magnetic quantum numbers of metal-ion electronic spin and i -th ligand nuclear spin respectively. The shift in the magnetic field due to the presence of superhyperfine interaction is given by¹³

$$\delta H = A_s \sum_i m_{(L)i} + A_d \sum_i m_{(L)i} (3 \cos^2 \theta_i - 1). \quad (5)$$

EXPERIMENTAL RESULTS AND DISCUSSION

Neutron Diffraction studies of Levy and Peterson¹⁴ established that ammonium bromide has three structure modifications in different temperature intervals—a high temperature phase in which the crystal structure is of the NaCl type, an intermediate temperature phase in which the crystal structure is of the CsCl type and a low temperature tetragonal phase, which is a slight distortion from the CsCl structure, due to the displacement of bromine ions by about 0.012A towards the plane of the nearby $(\text{NH}_4)^+$ ions. The transition from phase II to phase III is a 2nd order, order-disorder transition due to the reorientation of ammonium ion,



Further, Stephenson and Adams¹⁵ reported a new transition in NH_4Br at 78° K. on cooling, 108.5° K. on warming. This corresponds to conversion of ordered tetragonal to ordered cubic of CsCl type. This is further established by the pressure experiments of Stevenson.¹⁶

A. Body centred cubic phase (Phase II)

Figure 1 represents spectrum I recorded keeping the [100] axis of the crystal parallel to the direction of the magnetic field. It shows the characteristic four line hyperfine structure ($m_I: 3/2, 1/2, -1/2, -3/2$) of Cu^{2+} , while on each of the hyperfine lines a superimposed structure of 13 lines is observed. The $m_I = +3/2$ line is superimposed by some other transitions which will be discussed in the latter part of the section. A clear 13 lines shf pattern of $m_I = -3/2$ line is separately shown in Fig. 2. The angular variation of the spectrum reveals that the local symmetry about Cu^{2+} ion is tetragonal with [100] axis as the symmetry axis.

When Cu^{2+} ion is doped in NH_4Br it can go substitutionally to a $(\text{NH}_4)^+$ site and the charge unbalance can be compensated by producing a cation vacancy. If the cation vacancy is due to the removal of a first nearest $(\text{NH}_4)^+$ ion, the Cu^{2+} ion will have a tetragonal site symmetry with [100] axis as the symmetry axis. If the cation vacancy is at a second nearest neighbour site, the site symmetry of the magnetic ion will be orthorhombic and the site symmetry axis along [110]. As the angular variation of the spectrum I shows that the local symmetry about Cu^{2+} ion is tetragonal the latter type of charge compensation is to be given up in favour of the first.

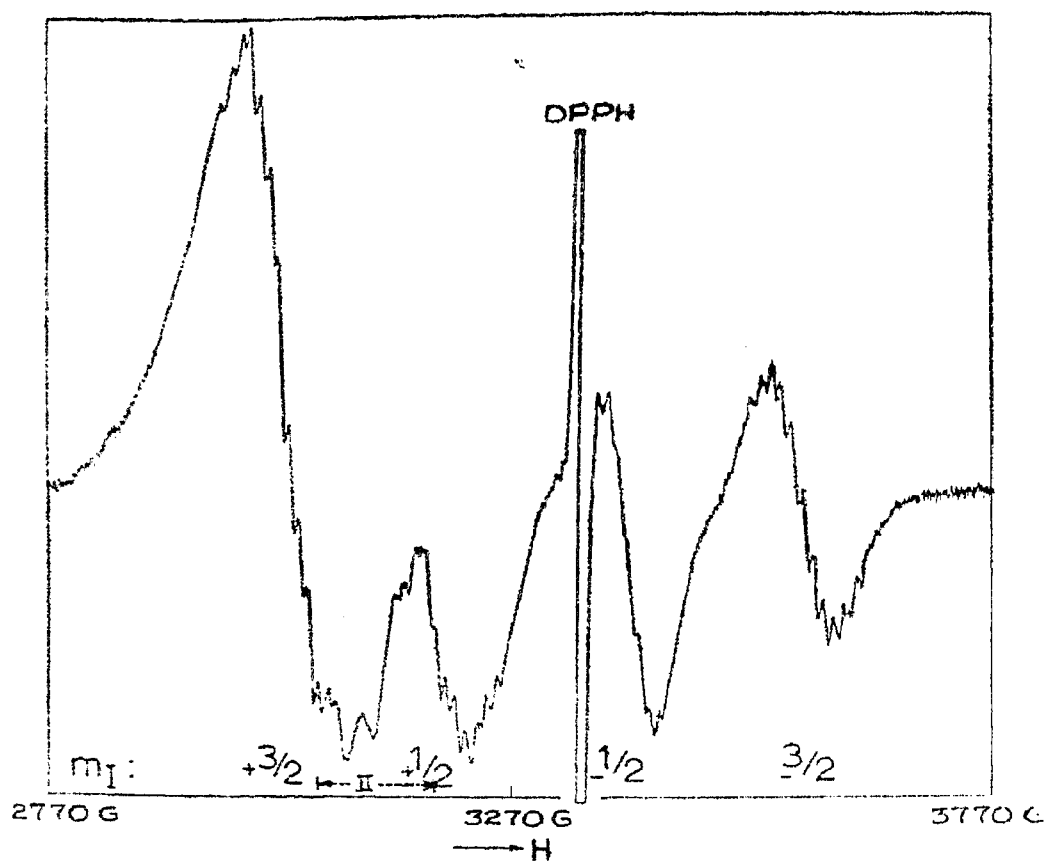


FIG. 1. EPR spectrum of Cu^{2+} in NH_4Br at room temperature with $[100]$ axis parallel to H . Lines in the region marked II are probably the 90° parts of the spectrum II_2 for this orientation.

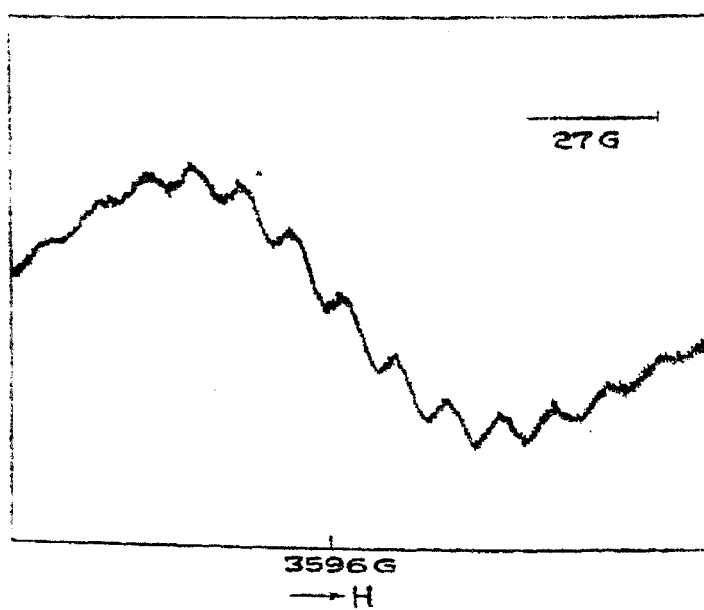


FIG. 2. Superhyperfine structure of $m_I = -3/2$ line of spectrum 1.

However, there is another possible way of incorporating Cu^{2+} ion in the lattice, still the local symmetry being tetragonal as observed. The Cu^{2+} ion can go at an interstitial site, *i.e.*, in the plane of four bromines and for the compensation of extra positive charge the two first neighbour $(\text{NH}_4)^+$ ions lying along the four-fold axis get removed, thereby giving rise to tetragonal symmetry. Existence of this type of complex (called species I for convenience) is indeed observed in the EPR studies of Mn^{2+4} and Cu^{2+5} doped NH_4Cl , wherein two water molecules are supposed to occupy the position of the two $(\text{NH}_4)^+$ ions, thereby forming stable complexes $2\text{NH}_4\text{Cl} \cdot \text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ and $2\text{NH}_4\text{Cl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ respectively. The existence of 13 line structure on each of the hyperfine lines in the present experiments indicates clearly that Cu^{2+} ion responsible for the spectrum I is not the one which goes in at a lattice site but the one which goes in interstitially at the centre of the plane face containing four equivalent† bromines. As all the bromines are equivalent the effective nuclear spin of the ligand nuclei becomes 6, which gives rise to a superhyperfine interaction resulting in the splitting of each of the Cu^{2+} hyperfine lines into 13 lines. When the Cu^{2+} ion goes in the interstitial position, as indicated above, the charge compensation is probably established by the removal of the two neighbouring $(\text{NH}_4)^+$ ions whose sites may remain vacant or may be substituted by neutral H_2O molecules. When the magnetic field is parallel to the z -axis, *i.e.*, the axis perpendicular to the plane containing four Br^- ions and along the line joining the two ammonium ion vacancies or water molecules, θ_i the angle between the direction of the magnetic field and $\text{Cu}-\text{Br}$ bond axis becomes 90° , and the shift in the field value due to shf interaction given in (5) becomes $(A_s - A_d) \cdot \sum m_{(\text{Br})_i}$. The superhyperfine structure is well resolved when the magnetic field is parallel to the z -axis [*i.e.*, (100) axis] while it gets blurred and the intensities of the corresponding lines go down as the z -axis is deviated from the direction of the magnetic field. Therefore measurements are carried out for the spectrum with H parallel to Z and the parameter $(A_s - A_d)$ could be obtained. A_s and A_d are not calculated separately. As mentioned earlier there is a clear indication from Fig. 1 that the low field component ($m_1 = 3/2$) of the hyperfine set is superimposed by some other strong line (or lines). This fact gets confirmed by Fig. 3 where the spectrum is taken with H making an angle of 9° with the [100] axis and where the superhyperfine pattern gets smeared away. The existence of the different additional

† Bromine has two isotopes Br^{79} and Br^{81} which are equally abundant. The effects of the two different isotopes could not be separately distinguished here, probably because their magnetic moments are not very much different from one another. Therefore, in this context Br^{79} and Br^{81} will be taken effectively equivalent.

sets of hyperfine quartets (marked I_a and I_b) at the low field value is clear in Fig. 3. These two additional quartets are due to the two other interstitial pairs of Cu^{2+} ions with their distortion axes perpendicular to the Z-axis. In other words, the spectra marked I_a and I_b are probably the angular parts of spectrum I, and are not clearly resolved for H parallel to Z, giving the shape of a broad strong line superimposed on the low field component of spectrum I. Spectrum I is analysed using the equations (2a) and (2b) appropriate for tetragonal symmetry. For this spectrum Z-axis coincides

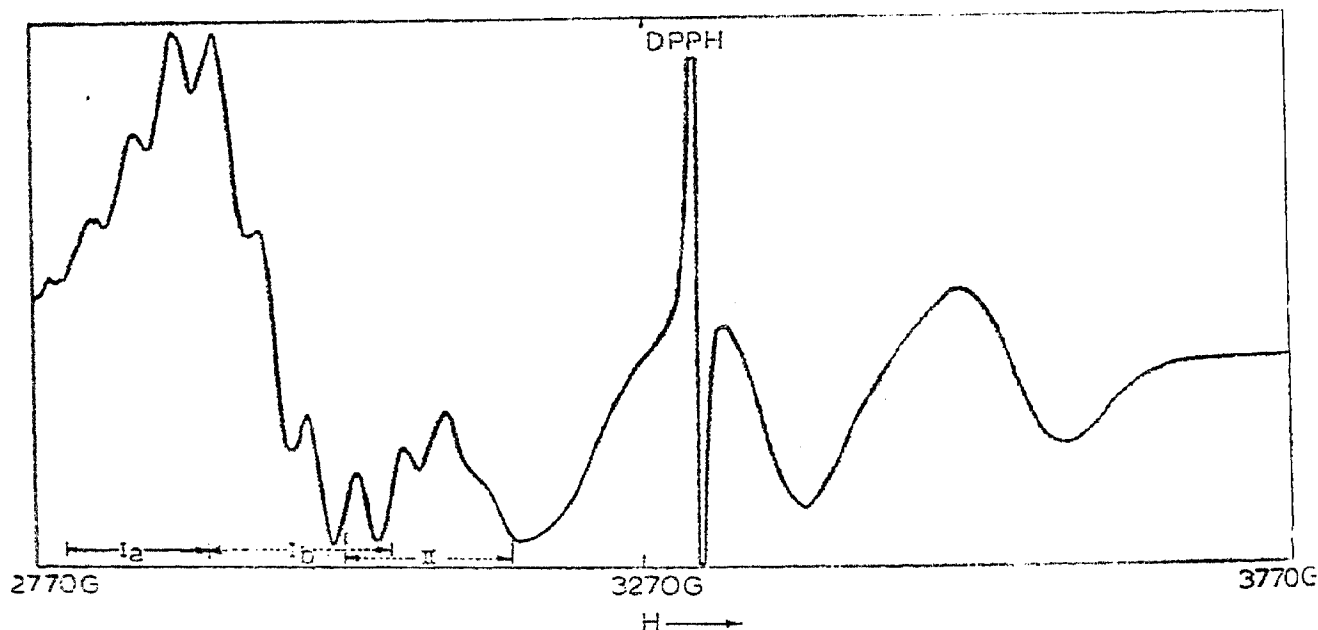


FIG. 3. EPR spectrum of Cu^{2+} in NH_4Br at room temperature with H making 9° with [100] axis. Lines in the region marked I_a and I_b are probably the 90° parts of spectrum I. Lines in the region marked II are probably 90° parts of spectrum II_2 .

with the local distortion axis (*i.e.*, [100] axis) and X and Y-axis coincides with the other two crystallographic axes [010] and [001] respectively. The intensity of the spectrum I is found to be strongly angular dependent. Fig. 4 shows the angular dependence of the intensity of $m_I = -3/2$ line and this is in agreement with the findings of Bir¹⁷ and Bir and Sochava.¹⁸

Apart from spectrum I, the presence of a very weak spectrum (spectrum II_1) is noticeable in the region 2750–2950 G when [100] axis is parallel to H, and it is shown in Fig. 5. The weak spectrum II_1 that is observed is probably because of another type of complex (species II_1). This could be due to Cu^{2+} ions which go substitutionally to $(\text{NH}_4)^+$ ions and get associated with first neighbour cation vacancies. This type of sites are relatively very few in number, as indicated by the low intensity of the spectrum. No detailed analysis of this spectrum is attempted as it is extremely weak. The

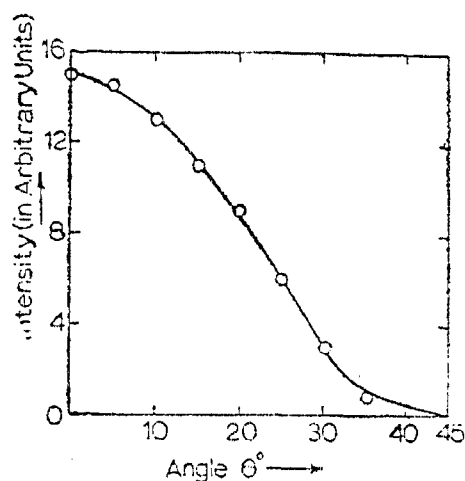


FIG. 4. Angular dependence of the $m_l = -3/2$ line of spectrum I.

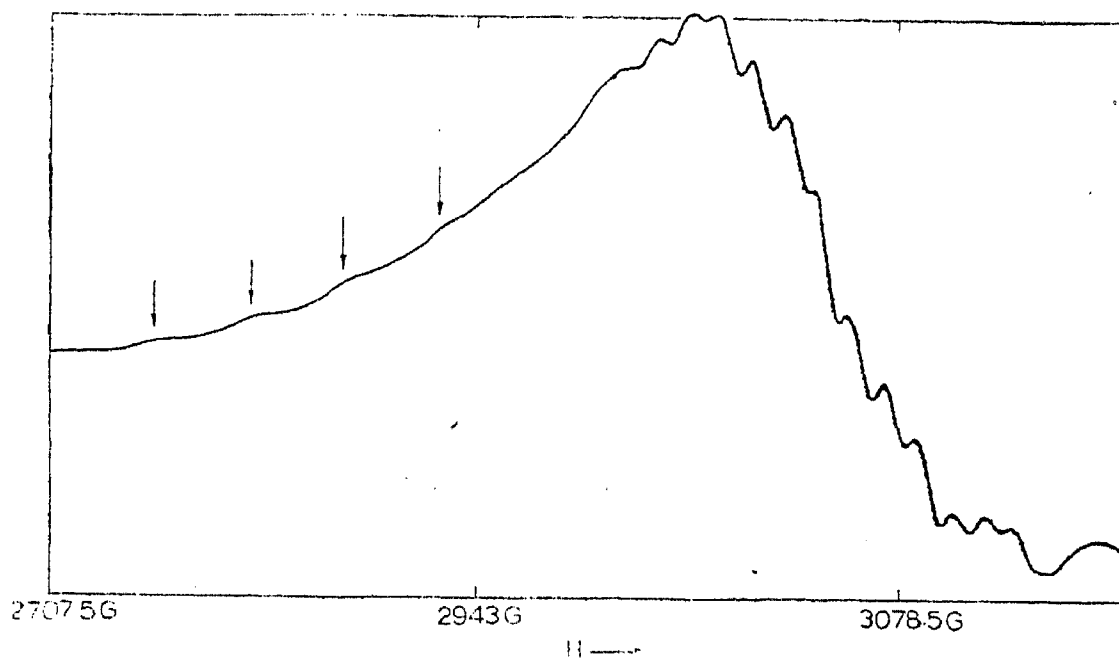


FIG. 5. Part of the EPR spectrum of Cu^{2+} in NH_4Br at room temperature with $\text{H} // [100]$. Arrows indicate the weak spectrum II_1 .

approximate values of the constants obtained by using the equations (2a) are given in Table 1.

When the direction of the magnetic field is along the $[110]$ axis of the crystal, a fairly well resolved spectrum (spectrum II_2) shown in Fig. 6 is obtained but it does not reveal the presence of any superhyperfine structure. It may be mentioned that when H is parallel to $[110]$ direction, two-thirds of the species I are expected to give a four-line spectrum centred at $g = 2.1$ corresponding to $\theta = 45^\circ$, while one-third of the species I are expected to

TABLE I

Spin-Hamiltonian constants of the spectra obtained in BCC and tetragonal phases of NH₄Br doped with Cu²⁺

Designation of the spectrum	Description of the complex	g	A (Gauss)	$(A_x - A_y)$ (G)
I	Interstitial Cu ²⁺ ions with planar co-ordination of 4 Br ⁻ ions at room temperature	$g_{11} = 2.0036 \pm 0.005$ $g_{\perp} = 2.217$	$A = 182.6$ $B \sim 0$	21.1 ± 0.8
I (L.T.)	Interstitial Cu ²⁺ ions with planar co-ordination of 4 Br ⁻ ions at -130° C.	$g_{11} = 2.032 \pm 0.001$	$A = 164.0$	12.6 ± 0.1
II ₁	Cu ²⁺ ions at lattice sites associated with 1st neighbour cation vacancies at room temperature	$g = 2.34$	$A \sim 31$..
III ₁	Cu ²⁺ ions at lattice sites associated with 1st neighbour cation vacancies at -130° C.	$g_{11} = 2.367 \pm 0.005$ $g_{\perp} = 2.152 \pm 0.003$	$A = 70.0$ $B = 68.4$..
II ₂	Cu ²⁺ ions at lattice sites associated with 2nd nearest neighbour cation vacancies at room temperature	$g_x = 2.301 \pm 0.001$ $g_y = 2.15 \pm 0.001$	$A_x = 46.0$ $A_y = 49.0$..
III ₂	Cu ²⁺ ions at lattice sites associated with 2nd neighbour cation vacancies at -130° C.	$g_x = 2.101 \pm 0.001$ $g_y = 2.07 \pm 0.001$ $g_z = 2.67 \pm 0.005$	$A_x = 100.2$ $A_y = 97.0$ $A_z = 61.4$..

give probably an unresolved spectrum at $g = 2.22$ corresponding to $\theta = 90^\circ$. The intensity of the former ($\theta = 45^\circ$) will be zero (see Fig. 4) and is therefore not observed, while the latter ($\theta = 90^\circ$) is probably overlapped by the spectrum due to species II₂ and adds to the general broadness of the spectrum in Fig. 6. The spectrum II₂ is very likely due to Cu²⁺ ions

at the ammonium sites associated with second nearest neighbour cation vacancies lying on the $[110]$ axis. The quartet marked $\Pi_2(\perp)$ represents the 90° part of the spectrum Π_2 , *i.e.*, it corresponds to the Cu^{2+} ions associated with the 2nd nearest neighbour cation vacancies in the plane perpendicular to the magnetic field or the $[110]$ axis of crystal. When $H//[110]$, two-thirds of this type of species Π_2 make an angle of 60° with the direction of the magnetic field, and their spectrum ($\theta = 60^\circ$) is expected to be too weak (*see* Fig. 4) to be distinctly observed. The expected angular parts of the spectrum due to this type of complex which H is parallel to $[100]$ appear to be obscured by spectrum I, which can probably be seen to some extent in the region marked II in Figs. 3 and 1. Spectrum Π_2 is analysed using the equations obtained by Bleaney *et al.*¹¹ appropriate for the orthorhombic symmetry. The principal axes of the g -tensor X, Y and Z, lie along $[001]$ and the mutually orthogonal $[110]$ and $[\bar{1}10]$ axes of the crystal respectively. The spin-Hamiltonian constants are given in Table I.

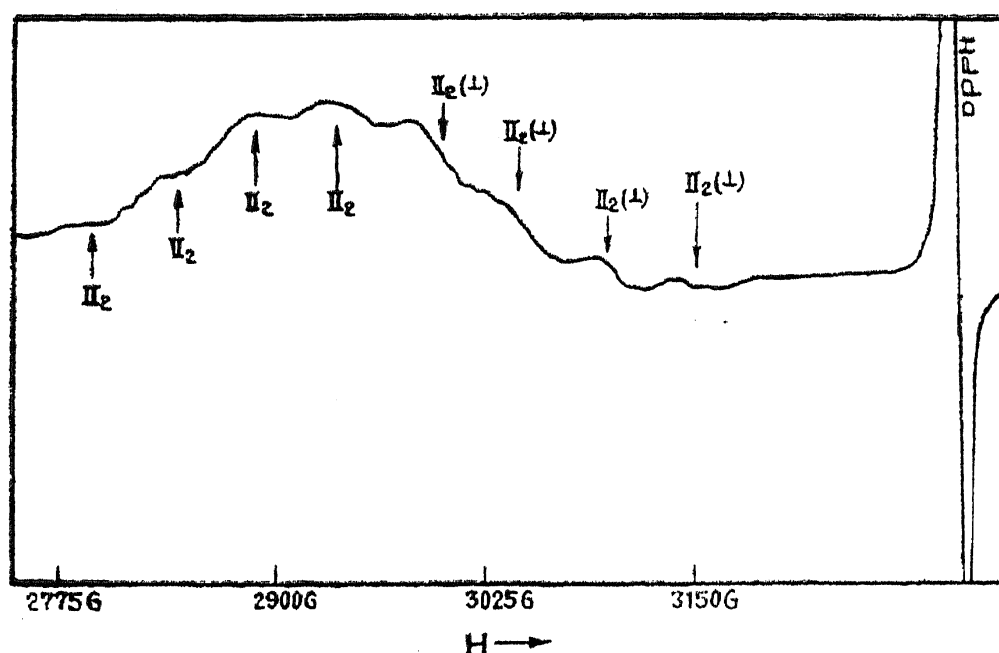


FIG. 6. EPR spectrum of Cu^{2+} in NH_4Br at room temperature with $[110]$ axis parallel to H . Lines marked $\Pi_2(\perp)$ are the 90° parts of the spectrum Π_2 for $H//[110]$.

B. Tetragonal phase

As mentioned earlier NH_4Br is said to have a λ -point transition at -38.1°C . below which it goes to an ordered tetragonal phase. In the present study the transition temperature is found to be -45°C . and not -38.1°C ., the change being probably due to the presence of the copper impurity in the crystals used. The spectra are recorded down to -130°C ., both by keeping $[100]$ and $[110]$ axes of the crystal parallel to the direction of the magnetic field. The spectrum I that is obtained at room temperature

showing superhyperfine structure persists at low temperature with a reduced intensity and is shown in Fig. 7. [Called for convenience spectrum I (L.T.)].

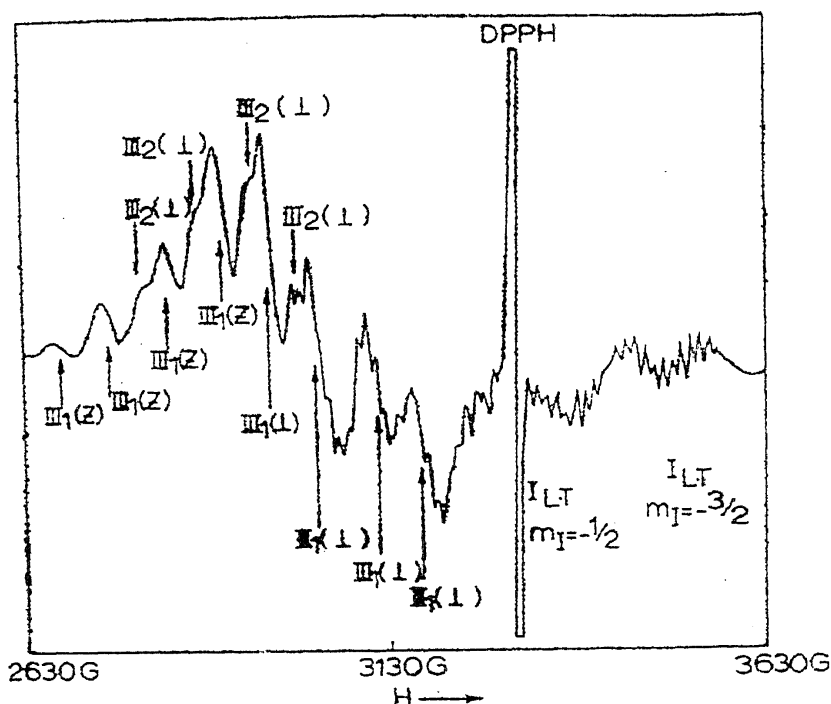


FIG. 7. EPR spectrum of Cu^{2+} in tetragonal NH_4Br at -130°C . [100] axis parallel to H . Spectra marked $\text{III}_1(\perp)$ and $\text{III}_2(\perp)$ are the 90° angular parts of the spectra III_1 and III_2 respectively. Lines marked I(L.T.) correspond to the spectrum I at low temperature.

This reduction in the intensity is probably because a number of Cu^{2+} ions originally in the interstitial position get readjusted to the lattice sites after phase transformation, the readjustment becoming more prominent at low temperatures. Two superhyperfine sets of spectra I (L.T.) are clearly seen in Fig. 6 towards the high field side of the spectrum and two other sets are superposed on $\text{III}_1(\perp)$ lines. The spectra marked III_1 , $\text{III}_1(\perp)$ and $\text{III}_2(\perp)$ are the additional spectra that came up in the tetragonal phase and they will be discussed clearly in the next para. The spectrum I (L.T.) is analysed using the equations (2a) and the constants obtained are included in Table I and are found to be smaller than the corresponding values at the room temperature. It is further studied at different temperatures and the values of hyperfine constants A are plotted against temperature as shown in Fig. 8. Unlike in NH_4Cl^6 the hyperfine constant A decreases with the lowering of temperature after transition. This is probably because of the anomalous lattice expansion of NH_4Br at low temperatures.¹⁹ The 90° parts of spectrum I (L.T.) are not clearly seen in Fig. 7 and probably they are responsible for the broad absorption on which spectra III_1 , etc., are superposed.

As mentioned earlier, additional spectra marked III_1 , $\text{III}_1(\perp)$ and $\text{III}_2(\perp)$ have come up at low temperatures, when the direction of the magnetic field is parallel to $[100]$ axis, and these spectra did not reveal the presence of any superhyperfine structure. Two more intense quartets are obtained

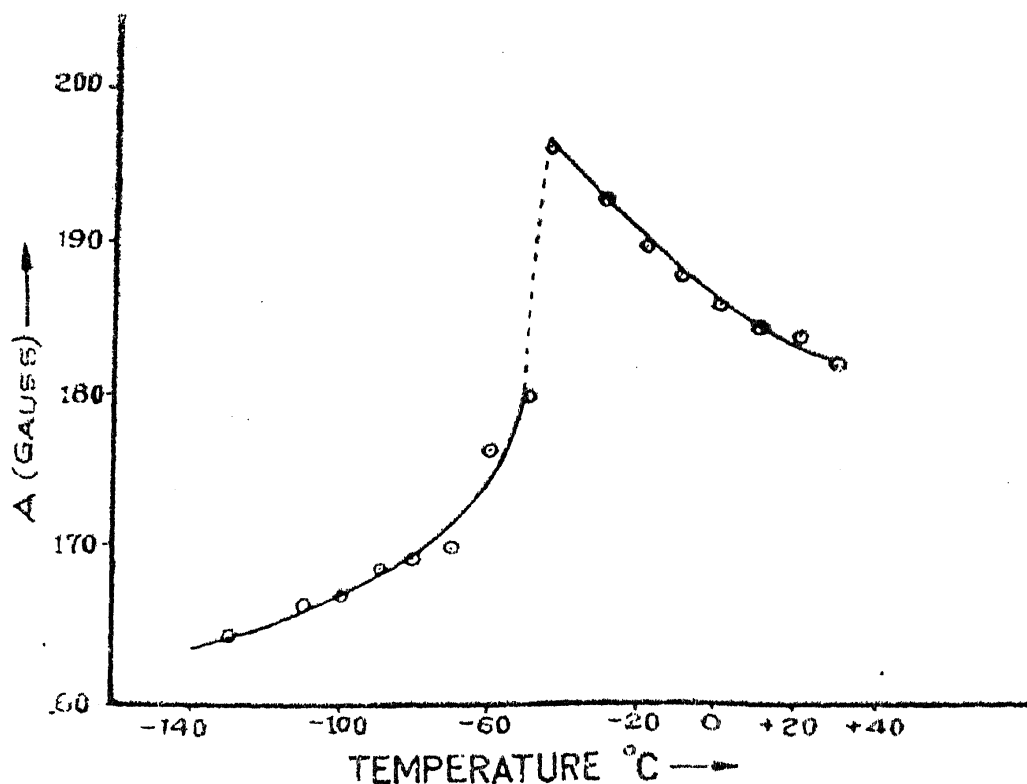


FIG. 8. Variation of hyperfine constant A with temperature for the spectrum I.

[marked III_2 and $\text{III}_2(\text{T})$] with H parallel to $[110]$ and are shown in Fig. 9, and again these quartets also did not reveal the presence of any superhyperfine structure. The spectra III_1 and III_2 are very likely due to Cu^{2+} ions

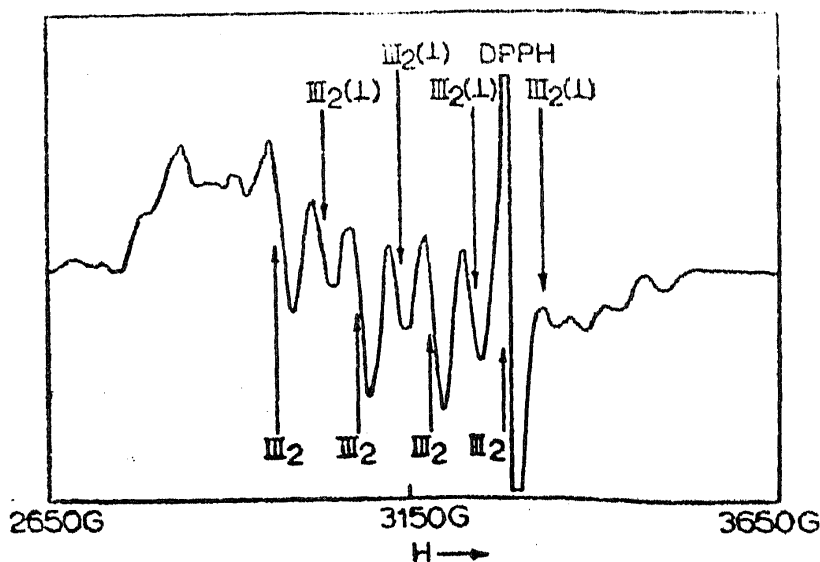


FIG. 9. EPR spectrum of Cu^{2+} in NH_4Br at -130°C ., with $[110]$ axis parallel to H. Lines marked $\text{III}_2(\perp)$ are the 90° parts of spectrum III_2 for this orientation.

which are in substitutional positions and which are associated with the first and second neighbour cation vacancies respectively. Apparently, the bulk of the Cu^{2+} ions which are originally in the interstitial positions in the room temperature phase of the crystal get readjusted to the lattice sites in the low temperature phase. The spectra marked $\text{III}_1 (\perp)$ and $\text{III}_2 (\perp)$ are the 90° angular parts of the spectra III_1 and III_2 respectively. The spectrum III_1 is analysed using the equations (2a) and (2b) and the constants are included in Table I. For this spectrum Z-axis coincides with 4-fold tetragonal axis, X and Y axes coincide with the other two crystallographic axes. The spectrum III_2 is analysed using the spin-Hamiltonian (3) appropriate for orthorhombic symmetry. The principal axes of the g-tensor X, Y and Z lie along [001] and the mutually orthogonal [110] and $[\bar{1}10]$ axes of the crystal respectively. In the analysis of all the spectra in the present study, the quadrupole terms are neglected as they do not play an important role $\Delta m = 0$ transitions.

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