

ELECTRON PARAMAGNETIC RESONANCE OF CU²⁺ ION IN CsCl SINGLE CRYSTALS

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ABSTRACT

Electron paramagnetic resonance spectrum of the Cu²⁺ ion in CsCl is studied at different temperatures. The local symmetry at the Cu²⁺ site is found to be tetragonal. A model of substitutional Cu²⁺ ion associated with a first neighbour cation vacancy is proposed to explain the observed spectrum.

INTRODUCTION

WHEN divalent impurity cations are placed substitutionally for monovalent ions of the host lattice, the excess of charge that results from the substitution is to be compensated. The charge compensation usually takes place by forming cation vacancies in the lattice. It has been found¹⁻⁶ from the paramagnetic resonance of Mn²⁺ in alkali halides having f.c.c. or NaCl type structure that the Mn²⁺ ions go substitutionally at cation sites and that some of them are associated with nearby cation site vacancies showing thereby orthorhombic or tetragonal site symmetries while others, being too far away from cation vacancies, exhibit cubic site symmetry. A fairly large amount of EPR work⁷⁻²⁰ has been done on transition metal ions doped in crystals of CsCl, CsBr, NH₄Cl and NH₄Br which are known to have b.c.c. structure. Since all these have the same type of structure it is expected that the immediate environment of the paramagnetic ion impurities in these crystals will be similar. However, the EPR studies of Mn²⁺ and Cu²⁺ in NH₄Cl^{8, 12, 13} and Mn²⁺ in CsCl¹⁷ indicate that the paramagnetic ions are

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incorporated interstitially between four anion ions with water molecules replacing two neighbouring cations (NH_4^+ or Cs^+) in the $\langle 100 \rangle$ direction while the studies of Mn^{2+} in CsBr ¹⁸ indicate that Mn^{2+} ion is incorporated substitutionally in the lattice associated with a first neighbour cation vacancy. It has been found that in NH_4Br , Mn^{2+} ions¹⁹ go in substitutionally at cation sites with remote charge compensation sites while Cu^{2+} ions^{19, 20} go predominantly in interstitial positions, the site symmetry being the crystallographic $\langle 100 \rangle$ direction, with only a few of them going in substitutional positions at room temperature. The present paper reports the EPR study of Cu^{2+} in CsCl single crystals.

Trappeniers and Hagen¹³ in their paper on EPR of Cu^{2+} in NH_4Cl give for comparison the constants obtained by them for Cu^{2+} doped in CsCl crystal which was grown from a solution containing ammonia. The crystals of CsCl grown in the present experiments are grown without the presence of ammonia and the spectrum obtained is entirely different from that obtained by Trappeniers and Hagen. Further comments in this connection will be made in the latter part of the paper.

EXPERIMENTAL DETAILS AND RESULTS

Single crystals of CsCl doped with Cu^{2+} are obtained by slow vaporization at room temperature of aqueous solution of CsCl to which 0.9 per cent by weight of CuCl_2 has been added. The crystals are yellowish in colour but clear and transparent. Spectra were recorded on a Varian V-4502 EPR spectrometer with 100 Kc/s modulation at X-band frequencies. The resonance line of DPPH was used as a reference.

The free Cu^{2+} ion has a $3d^9$ configuration with a ground state 2D .²¹ When subjected to a cubic crystalline field this five-fold orbital degenerate state splits into a doublet (2E) and a triplet (2T) and the orbital degeneracy is further removed in the presence of a tetragonal or an orthorhombic component in the crystalline field leaving an orbital singlet as the ground state. The nuclear spin of copper is $3/2$ and the hyperfine interaction gives a four line spectrum. Figure 1 shows the EPR spectrum taken when the direction of magnetic field is parallel to a $\langle 100 \rangle$ axis of the crystal. The angular variation of the spectrum reveals that the local symmetry about Cu^{2+} ion is tetragonal with $\langle 100 \rangle$ axis as the symmetry axis. There are three geometrically equivalent positions of the symmetry axes, due to the equivalence of the three crystallographic $\langle 100 \rangle$, $\langle 010 \rangle$ and $\langle 001 \rangle$ axes. But they are magnetically inequivalent, giving three different spectra at any arbitrary orientation. Figure 2 shows the angular variation of the g-tensor in a $\langle 001 \rangle$

plane. In Fig. 1 the lines marked I_{\parallel} are those due to the magnetic complex of Cu^{2+} ion whose site symmetry axis is parallel to the direction of magnetic field and the lines marked I_{\perp} are those due to the magnetic complexes of Cu^{2+} ion whose site symmetry axes are perpendicular to the direction of

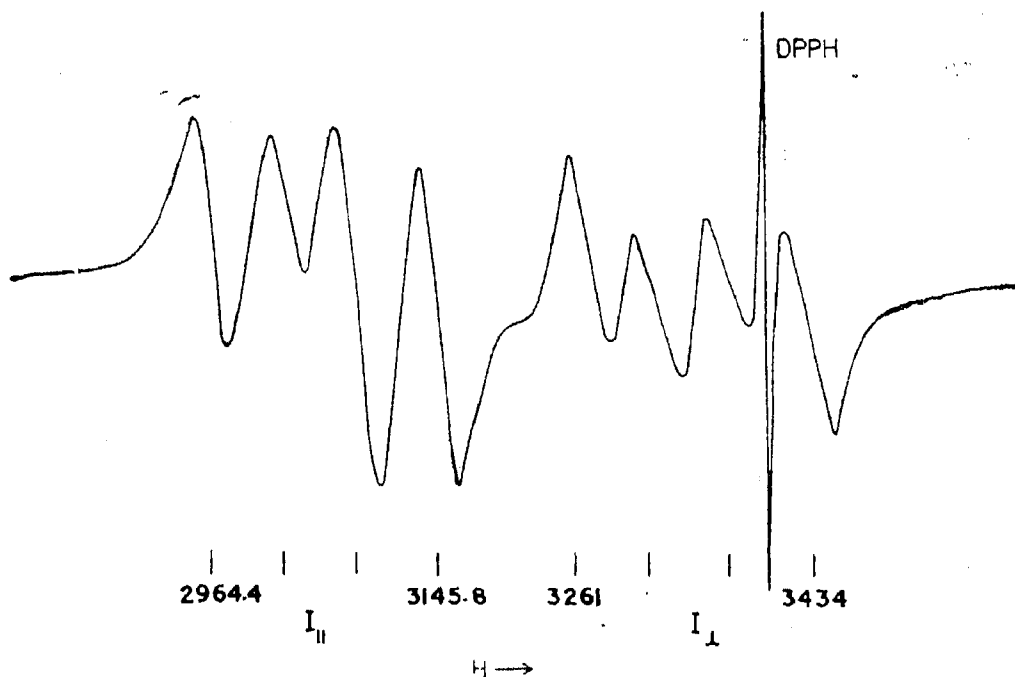


FIG. 1. EPR spectrum of Cu^{2+} doped CsCl single crystals with H parallel to $\langle 100 \rangle$ axis in the (001) plane at room temperature.

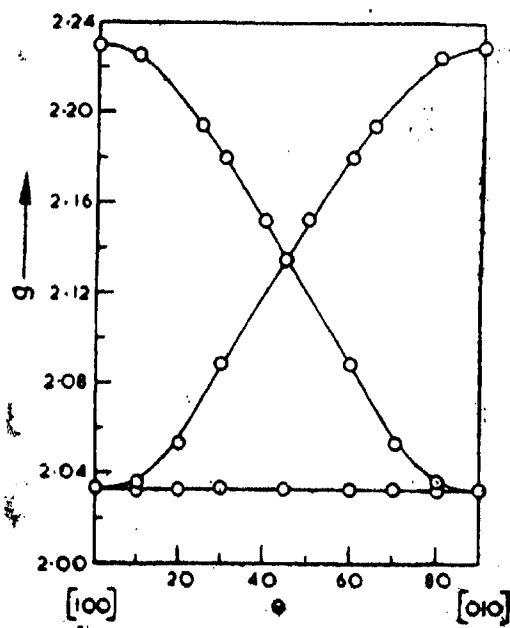


FIG. 2. Angular variation of g -tensor in the (001) plane

the magnetic field. Each line in the spectrum marked I_{\perp} shows the expected splitting due to the non-equivalence of the two complexes in the perpendicular plane when the magnetic field 'H' deviates from the $\langle 100 \rangle$ direction in a (001) plane or a (010) plane (see Fig. 3). It may be noted here that copper has two isotopes Cu^{63} and Cu^{65} with 69.09% and 30.91% natural abundance respectively and one would expect a doubling of the hyperfine structure lines. However, in the present experiments the hyperfine lines due to different isotopes could not be observed separately. The reason for this might be the fact that the magnetic moments are not much different from one another (2.2206 and 2.3790 nuclear magnetons²² respectively) while the line widths (peak-to-peak derivative widths) are of the order of 25 gauss.

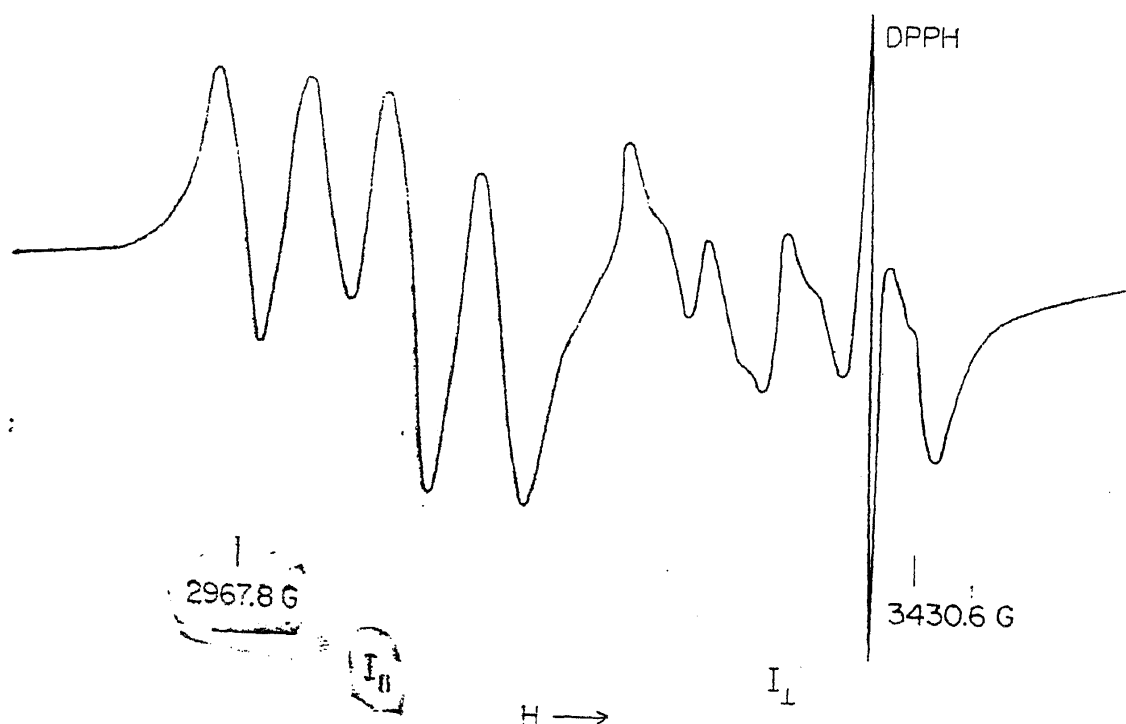


FIG. 3. EPR spectrum of Cu^{2+} doped CsCl single crystal with H making an angle of 10° with $\langle 100 \rangle$ axis in the (001) plane at room temperature.

DISCUSSION

When the Cu^{2+} ion is incorporated in CsCl it can go substitutionally to a Cs^+ site and the charge neutrality can be maintained by producing a cation vacancy. If it substitutes for Cs^+ and is associated with a first neighbour cation vacancy, the Cu^{2+} ion will have a tetragonal site symmetry with $\langle 100 \rangle$ axis as the site symmetry axis. If the cation vacancy is at a second nearest neighbour site the site symmetry of the magnetic ion will be orthorhombic with the symmetry axis along a $\langle 110 \rangle$ direction of the crystal. As the

angular variation of the spectrum (see Fig. 2) shows that the local symmetry about Cu^{2+} is tetragonal the latter type of charge compensation is to be given up in favour of the first. However, there is a second possible way of incorporating Cu^{2+} ion in the lattice, still the local site symmetry being tetragonal as observed. The Cu^{2+} ion can go at an interstitial position, *i.e.*, in the plane of four Cl^- ions and for the compensation of extra positive charge the two first neighbour Cs^+ ions lying along the four-fold axis get removed, thereby giving rise to a tetragonal symmetry. Existence of this type of complex was observed earlier in the case of Mn^{2+} doped NH_4Cl ^{8, 12} and CsCl ¹⁷ and Cu^{2+} doped NH_4Cl ^{13, 15} and NH_4Br ²⁰ where in two water molecules are supposed to occupy the positions of the action (NH_4^+ or Cs^+). Since both the interstitial and substitutional models lead to EPR spectra with the same symmetry properties it is not possible to say definitely what is the position of the paramagnetic ion unless one has some additional features in the spectrum. Foreman and van Wyk¹⁷ observed superhyperfine structure from the neighbouring nuclei in the case of Mn^{2+} doped CsCl when Mn^{2+} is incorporated interstitially in the lattice. Superhyperfine structure due to the halogen nuclei has also been observed in the EPR of Cu^{2+} in $\text{Cu}^{2+}:\text{NH}_4\text{Br}$ ²⁰ and $\text{Cu}^{2+}:\text{ND}_4\text{Cl}$ ¹³ crystals where Cu^{2+} goes in interstitially in the $\langle 100 \rangle$ direction. The absence of such structure from the neighbouring nuclei in the present experiments suggests that Cu^{2+} is not interstitial in the CsCl lattice. It may also be noted that the optical absorption spectrum of the crystal did not reveal any water absorption. Thus in all it appears that Cu^{2+} goes substitutionally in the crystal and is associated with a first neighbour alkali vacancy.

The spin Hamiltonian which describes the spectrum ($S = \frac{1}{2}$, $I = 3/2$) is given by^{9, 15}

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

where the terms have the usual meanings. The quadrupole terms are neglected as no quadrupole effects are seen in the spectrum. The magnetic field positions of the resonance lines for $H \parallel Z$ axis are given by

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

while those for $H_{\perp z}$ axis are

$$H_{\perp}(m) = H_0 - Bm - \frac{A^2 + B^2}{4H_0} [I(I+1) - m^2]$$

where $H_0 = (h\nu/g\beta)$, ν being the microwave frequency. The parameters obtained from the analysis of the observed spectrum are $g_{\parallel} = 2.229 \pm 0.003$, $g_{\perp} = 2.033 \pm 0.003$, $A = 62.9 \pm 1 \times 10^{-4} \text{ cm.}^{-1}$ and $B = 54.7 \pm 1 \times 10^{-4} \text{ cm.}^{-1}$. These may be compared with the following values obtained by Trappeniens and Hagen¹³ for Cu^{2+} in CsCl grown in the presence of ammonia: $g_{\parallel} = 2.0132 \pm 0.0006$, $g_{\perp} = 2.217 \pm 0.002$, $A = 143.9 \pm 0.5 \times 10^{-4} \text{ cm.}^{-1}$ and $B \approx 0 \times 10^{-4} \text{ cm.}^{-1}$. The fact that the value of B obtained in the present experiments for Cu^{2+} is $54.7 \times 10^{-4} \text{ cm.}^{-1}$ while that obtained by Trappeniens and Hagen is ~ 0 shows clearly that the spectra in the two cases are different. It may be mentioned here Trappeniens and Hagen reported that the spectrum obtained by them for Cu^{2+} in NH_4Cl crystal grown in the presence of ammonia is different from that in crystals grown under different other conditions and suggested that Cu^{2+} is probably associated with one (or two) ammonia molecule (s) situated in the place of a neighbouring $(\text{NH}_4)^+$ vacancy (or vacancies) in the $\langle 100 \rangle$ direction. If this suggestion is extended to Cu^{2+} in CsCl grown in the presence of ammonia, the spectrum obtained by Trappeniens and Hagen could be due to Cu^{2+} which substitutes a Cs^+ ion but is associated with a neutral ammonia molecule in the place of a first neighbour alkali vacancy.

The spectrum is recorded at different temperatures in the range of 300° K to 77° K and it is found to be practically independent of temperature.

ACKNOWLEDGEMENT

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REFERENCES

1. Schneider, E. E. and Caffyn, J. E. "Defects in crystalline solids," *Report of 1954 Bristol Conference*, Physical Society, London, 1955, p. 74.
2. Forrester, P. A. and Schneider, E. E. *Proc. Roy. Soc. (London)*, 1956, **69 B**, 833.
3. Morigaki, K., Fujimoto, M. and Itoh, J. *J. Phys. Soc. Japan*, 1958, **13**, 1174.
4. Watkins, G. D. *Phys. Rev.*, 1959, **113**, 79.
5. Shrivastava, K. N. and Venkateswarlu, P. *Proc. Ind. Acad. Sci.*, 1966, **63 A**, 284.
6. Jagannadham, A. V. and Venkateswarlu, P. *Ibid.* (To be published).

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7. Abe, H. and Shirai, H. .. *J. Phys. Soc. Japan*, 1960, 15, 1711.
8. Seed, T. J. .. *J. Chem. Phys.*, 1964, 41, 1486.
9. Zaripov, M. M. and Chirkin, G. K. *Soviet Physics, Solid State* (English Translation), 1964, 6, 1290.
10. ——— and Chirkin, G. R. *Jour. Structural Chem.* (English Translation), 1964, 5, 29.
11. ——— and Chirkin, G. K. *Soviet Physics, Solid State* (English Translation), 1965, 7, 74.
12. ——— .. *Ibid.*, 1966, 7, 2391.
13. Trappeniers, N. J. and Hagen, S. H. *Physica*, 1965, 31, 122.
14. ——— .. *Ibid.*, 1965, 31, 251.
15. Pilbrow, J. R. and Spaeth, J. M. *Phys. Stat. Sol.*, 1967, 20, 225 and 237.
16. Foreman, A. and Wyk, J. A. van *J. Chem. Phys.*, 1966, 44, 73.
17. ——— .. *Can. J. Phys.*, 1967, 45, 3381.
18. Iri, T. and Kwabara, G. .. *J. Phys. Soc. Japan*, 1967, 23, 536.
19. Sastry, M. D. .. "EPR of transition metal ions in ammonium halide crystals," *Ph.D. Thesis*, Indian Institute of Technology, Kanpur, India, 1967.
20. ——— and Venkateswarlu, P. .. *Proc. Ind. Acad. Sci.*, 1967, 66, 208.
21. Low, W. .. *Paramagnetic Resonance in Solids*, Academic Press, New York, 1960.
22. Pople, J. A., Bernstein, H. J. and Schneider, W. G. *High Resolution Nuclear Magnetic Resonance*, McGraw-Hill Book Co., Inc., New York, 1959.