

## CHAPTER V

### OPTICAL AND ELECTRON SPIN RESONANCE STUDIES OF DIVALENT $3d^9$ ION DOPED IN $\text{CsCdCl}_3$

We could not grow  $\text{Ti}^{2+} : \text{CsCdCl}_3$  crystals; so we proceeded with the measurement of  $\text{CsCdCl}_3 : \text{Cu}^{2+}$ .

#### RESULTS AND DISCUSSION

##### I. Optical Studies

Divalent copper with electronic configuration  $[\text{A}] 3d^9$  has the ground state  ${}^2D$ . In an external crystalline electric field of  $O_h$  symmetry, the five-fold orbitally degenerate ground state splits up into two sets, one upper orbital triplet set  ${}^2T_{2g} (\Gamma_5)$  and another lower orbital non-degenerate doublet set  ${}^2E_g (\Gamma_3)$  lying about  $\sim 12000 \text{ cm}^{-1}$  below the upper triplet (Fig. 19). The orbital degeneracy can be removed completely only with the superimposition of an orthorhombic field on the predominant cubic field. The trigonal field as occurs in  $\text{CsCdCl}_3 : \text{Cu}^{2+}$  due to a small distortion along the three-fold axis of the octahedron, does not split the lower doublet  ${}^2E_g$ , but it splits the upper triplet into a singlet and a doublet. If one considers only spin-orbit coupling ( $\lambda \cdot \bar{L} \cdot \bar{S}$ ) term, the ground level remains orbitally degenerate and is, therefore, susceptible to a dynamic Jahn-Teller distortion<sup>151,55</sup>. The degeneracy, however, can be removed by the combined action of

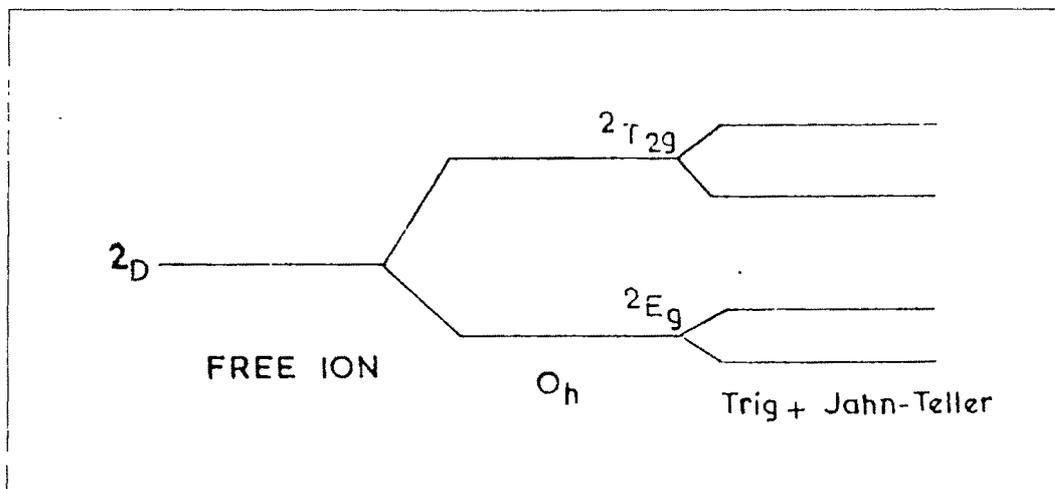


Fig.19. Splitting of  $2D$  term of  $Cu^{2+}$  in  $CsCdCl_3$ .

trigonal field and spin-orbit coupling. The total distortion of the cluster around  $\text{Cu}^{2+}$  in  $\text{CsCdCl}_3$  will comprise of two parts : (1) Small trigonal distortion along the c-axis already present in  $\text{CsCdCl}_3$  and (2) a comparatively larger J-T distortion along the 4-fold octahedral axes and the magnitude of distortion is large, compared to  $\text{CsCdCl}_3$  crystal itself.

The observed spectra at room temperature (Fig. 20a dotted line) showed a broad band from  $11600 \text{ cm}^{-1}$  to  $8350 \text{ cm}^{-1}$ . Fixing the peak of the absorption at  $10200 \text{ cm}^{-1}$ , we ascribe this to  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  transition and ignoring the effect of spin-orbit coupling the value of  $Dq$  is found to be  $1020 \text{ cm}^{-1}$ . In addition to this broad band there is also a very sharp and strong band at  $23750 \text{ cm}^{-1}$  with high extinction coefficient, which is electron-transfer band and will be discussed later on.

At  $77^\circ\text{K}$  the broad band shows a two-fold structure (Fig. 20 solid line). In addition to the strong absorption peak at  $10525 \text{ cm}^{-1}$ , there is a shoulder in the absorption band located at  $8695 \text{ cm}^{-1}$ . These two peaks may be ascribed to transitions to two components of the upper  ${}^2\text{T}_{2g}$  states, split by lower symmetry field. It would appear that the total lower-symmetry field splitting of the upper  ${}^2\text{T}_{2g}$  state is larger in the present case than in the case of other transition ions doped in  $\text{CsCdCl}_3$ , supporting our contention that there is additional large distortion arising from the Jahn-Teller effect. Further, the lack of appreciable polarization of the bands (Fig. 20) indicate that this additional tetragonal distortion

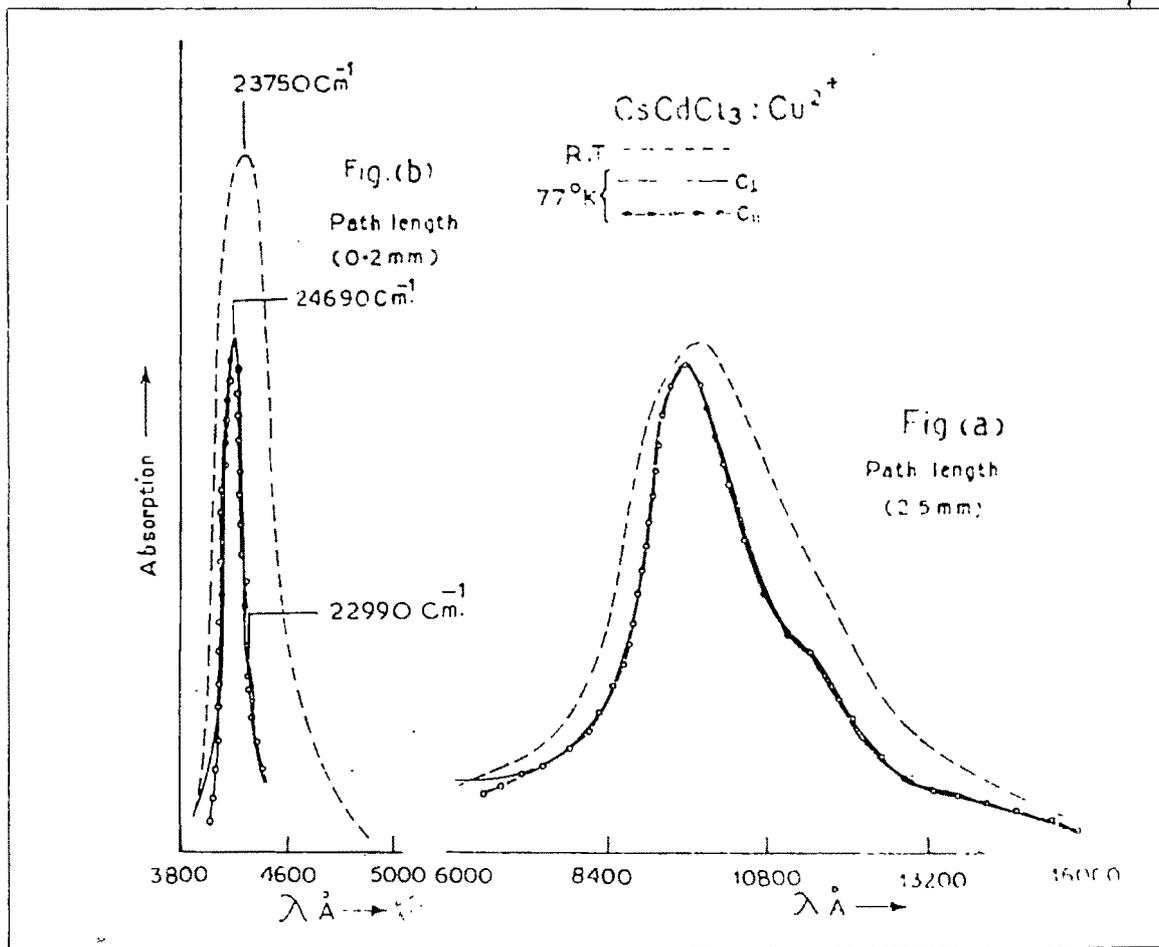


Fig. 20. Absorption spectrum of  $\text{Cu}^{2+}$  in  $\text{CsCdCl}_3$ . The dotted line is the unpolarized room temperature spectrum. The chain and solid line is the polarized spectrum taken at  $77^\circ\text{K}$ . Fig.(a) shows the d-d band and that Fig.(b) the charge-transfer band.

(whose axis do not coincide with trigonal axis) due to the Jahn-Teller effect is in fact sufficiently large to mask the polarization effect of the small trigonal field. Spin-orbit coupling is another cause which might give mixed polarization of bands.

The electron-transfer band has also been observed to be split into two components at 77°K (Fig. 20b) which again do not show any polarization effect. Looking at the molecular orbital diagram for octahedral complexes (cf. page 113a) the observed charge transfer band at 23750 cm<sup>-1</sup> may be ascribed to t<sub>2u</sub> (ligand)

→ e<sub>g</sub> (metal) orbital. The splitting of this band at 77°K into two components (24690 and 22990 cm<sup>-1</sup> which is very near to 19800 cm<sup>-1</sup> and 24600 cm<sup>-1</sup> observed in CsCuCl<sub>3</sub><sup>119</sup>) is probably due to asymmetric field splitting of t<sub>2u</sub> (ligand) orbital. Alternatively, the weak shoulder might be ascribed to forbidden t<sub>1g</sub> (ligand) → e<sub>g</sub> (metal) transition. A third possibility is that the splitting represents the separation between <sup>2</sup>P<sub>1/2</sub> and <sup>2</sup>P<sub>3/2</sub> state of chlorine atom in the charge-transfer excited state - somewhat similar to the two equally strong C-T bands of pyridine methiodide<sup>151a</sup>. It is difficult to make a choice between the above three alternatives, but we can possibly discount the third alternative on the ground that the observed bands are of unequal intensity and because of the improbability of complete electron transfer in the present case.

## II. Electron Spin-Resonance at Room Temperature

We have measured the electron-spin-resonance spectrum of CsCdCl<sub>3</sub> : Cu<sup>2+</sup> with the X-band e.p.r. spectrometer of the Fertilizer Corporation of India, Sindri, in planes containing the C-axis and normal to it. The spectra in both orientations appear to be the same, with single symmetric line of peak to peak derivative line-width 75.5 gauss (Fig. 21). The practically isotropic g-value is found to be 2.1954 ( g<sub>||</sub> = 2.1956, g<sub>⊥</sub> = 2.1952). The isotropy of the g-value of Cu<sup>2+</sup> in CsCdCl<sub>3</sub> at room temperature is a direct consequence of the presence of

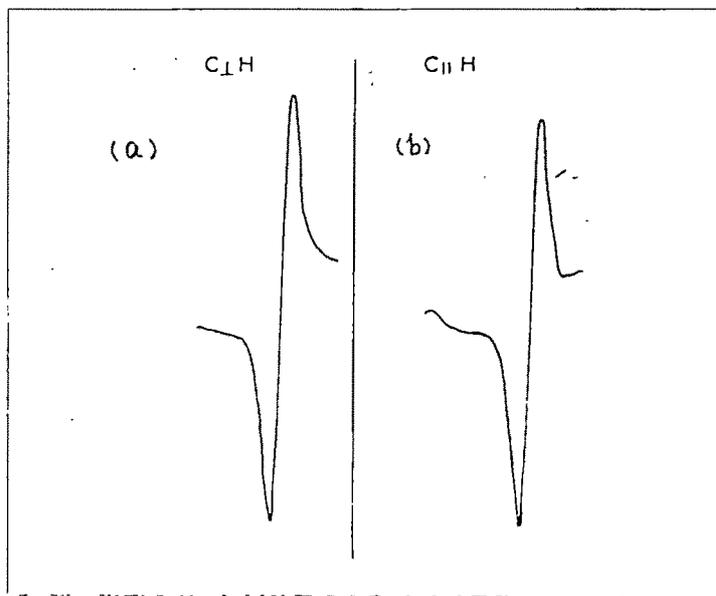


Fig.21. E.S.R. spectrum of  $\text{Cu}^{2+}$  in  $\text{CsCdCl}_3$  at room temperature.

- (a) C-axis  $\perp$  to the magnetic field
- (b) C-axis  $\parallel$  to the magnetic field.

Jahn-Teller distortion, i.e. of the complex resonating between the three equivalent minimum configurations corresponding to minimum value of J-T potential energy, which corroborates our optical findings. Writing the wavefunction corresponding to the minimum potential energy as

$$\Psi = \Psi_1 \sin \alpha + \Psi_2 \cos \alpha \quad (113)$$

where  $\Psi_1$  and  $\Psi_2$  are the wavefunctions of the lowest doublet and  $\alpha$  is a parameter corresponding to which the configuration can have the same minimum value of the molecular potential energy, Abragam and Pryce<sup>55</sup> calculated the g-values of  $\text{Cu}^{2+}$  for trigonal symmetry. For each value of  $\alpha$  they calculated

$$\begin{aligned} g_1 &= 2 + 2\mu (\cos \alpha - \sqrt{3} \sin \alpha)^2 \\ g_2 &= 2 + 2\mu (\cos \alpha + \sqrt{3} \sin \alpha)^2 \\ g_3 &= 2 + 8\mu \cos^2 \alpha \end{aligned} \quad (114)$$

where  $\mu = -(\lambda/10Dq)$ . Averaging over  $\alpha$ ,  $g_1 = g_2 = g_3 = 2 - \frac{4\lambda}{10Dq}$ . With the observed  $Dq = 1020 \text{ cm}^{-1}$  from spectral studies at room temperature, and  $g$  values from e.s.r. the value of  $\lambda$ , the spin-orbit coupling constant is found to be  $\sim -515 \text{ cm}^{-1}$ , which is close to that of  $\text{CsCuCl}_3$  ( $\sim 600 \text{ cm}^{-1}$ ) by Rinneberg et al<sup>152</sup>. This is very much less than the free ion value of  $-829 \text{ cm}^{-1}$ . Of course the large width of the band prevents an accurate calculation of the parameter but the magnitude is right and the reduction due to charge overlap is in the right direction as observed with other compounds of copper.<sup>153</sup>

We could not measure the magnetic susceptibility and anisotropy of  $\text{CsCdCl}_3 : \text{Cu}^{2+}$  as the small paramagnetism due to the very low percentage ( $\approx 1.5$  moles %) of  $\text{Cu}^{2+}$  ion in the doped crystals is not sufficient to show itself clearly above the large diamagnetism of the host lattice  $\text{CsCdCl}_3$ . The diamagnetism of the doped crystal decreases with the fall of temperature, though it is still diamagnetic even at  $80^\circ\text{K}$ , showing the latent paramagnetism of the  $\text{Cu}^{2+}$  ion in the lattice. The results are however only of qualitative order and it is not possible to corroborate the spectral data from the magnetic measurements.