

Letters to the Editor

Polarised absorption spectrum of Co^{2+} doped in CsCdCl_3 at 77°K and 20°K .

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The energy levels of Co^{2+} have been studied extensively in octahedral field of oxides, (Low 1959) in tetrahedral fields of oxides, sulfides and halides (McClure 1957, Pappalardo & Dietz 1961, Cotton *et al* 1961) and also in cubic field of fluorides (Stahl-Brada & Low 1959). In order to study the ligand field provided by a distorted octahedron of Cl^- we have grown single crystals of CsCdCl_3 doped with Co^{2+} from the melt at about 485°C in an inert atmosphere by the Stock-Berger method and recorded the polarised spectrum at 77°K and 20°K . (Gruen & McBeth 1963)

Crystals of CsCdCl_3 are hexagonal as grown from melt. The structure has been reported by Siegel & Gebert (1964) (Space Group C_6/mmm C, $Z = 6$). Six Cl^- ions form a trigonally distorted octahedron around the central metal ion.

Figure 1 shows the low resolution spectrum at 77°K . A high resolution polarised spectrum for the visible region at the liquid hydrogen temperature was photographed in a Zeiss PGS 2 grating spectrograph with Kodak

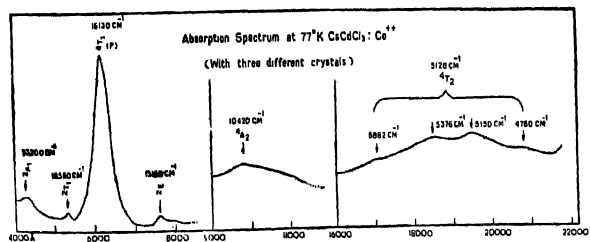


Figure 1

103 A-E film. Figures 2a and 2b reproduce the microphotometer tracing of the photographs taken at 20°K .

The ground term 4F of Co^{2+} splits in the octahedral field into 4T_1 , 4T_2 and 4A_1 with 4T_1 lying lowest. We have assigned the band at 5128 cm^{-1} to the ${}^4T_1 \rightarrow {}^4T_2$ transition and calculated D_q to be $\sim 640 \text{ cm}^{-1}$. This low value of D_q is presumably due to the large Cd-Cl distance (2.59 \AA average) and the large difference in ionic radii of Cd^{2+} (1.03 \AA) and of Co^{2+} (0.80 \AA).

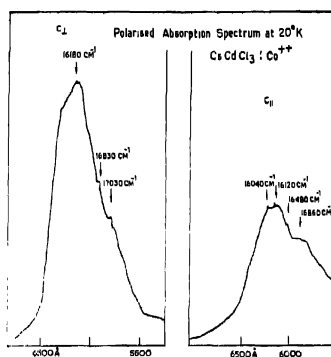


Figure 2a

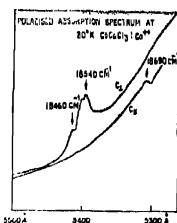


Figure 2b

The observed band at 10420 cm^{-1} is ascribed to ${}^4T_1 \rightarrow {}^4A_1$ transition. The band is weak compared to the ${}^4T_1 \rightarrow {}^4T_2$ transition, for it corresponds to a two electron jump. The observed band at 16130 cm^{-1} is ascribed to the ${}^4T_1 \rightarrow {}^4T_1$ (4P) transition. The energy separation between 4F and 4P is calculated to be 12410 cm^{-1} which is less than the free ion value 14500 cm^{-1} . The sharp band at 18550 cm^{-1} is assigned to a spin forbidden transition to the doublet state (2T_1) arising from the 3G state. The high intensity is presumably due to the mixing with the 4P quartet state. The 2T_2 term may be somewhere around the 2T_1 term. The band

at 23200 cm^{-1} may be identified as the ${}^4T_1({}^6P) \rightarrow {}^3A_1({}^2G)$ transition. The ${}^3E({}^2G)$ term has been located at 13160 cm^{-1}

The observed humps at 5376 cm^{-1} , 5150 cm^{-1} and 4760 cm^{-1} probably correspond to the components of the 4T_2 state split by the spin-orbit and the trigonal field interactions. From the observed fine structure at 17030 cm^{-1} , 16830 cm^{-1} and 16180 cm^{-1} in C_{\perp} spectrum and at 16480 cm^{-1} , 16120 cm^{-1} and 16180 cm^{-1} at C_{\parallel} spectrum (figure 2a) at 20°K we calculated λ_s (spin-orbit coupling for 4P) to be 120 cm^{-1} and Δ (trigonal field splitting) $\sim 140\text{ cm}^{-1}$. The observed fine structure at 18540 cm^{-1} and 18460 cm^{-1} in C_{\perp} spectrum and at 18690 cm^{-1} in C_{\parallel} spectrum at 20°K gives the value of $\lambda_G \sim 105\text{ cm}^{-1}$ and Δ to be $\sim 150\text{ cm}^{-1}$ (corresponding values for 3G state)

Theoretical and experimental details of the energy level pattern along with the magnetic susceptibility and anisotropy of the crystal will be reported shortly in details.

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The crystal structure of potassium salt of homophthalic acid

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As part of a programme for studying the structures of simple organic acids and their salts and the scheme of hydrogen bonding in these structures, we have been studying for sometime homophthalic (α -2-toluene dicarboxylic) acid $\text{C}_8\text{H}_8\text{O}_4$ (Gupta & Bose 1969). We thought it worthwhile to get the skeletal arrangement of the homophthalate group itself by the well-known heavy atom technique in crystallography. Our preliminary results are interesting and are being reported here.