

Polarised absorption spectrum of Fe^{2+} doped in CsCdCl_3 at 77°K

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In order to study the energy levels of Fe^{2+} in a ligand field provided by an octahedron of chloride ions, we have grown a single crystal of Fe^{2+} -doped CsCdCl_3 from melt at 485°C by Stock-Berger's method. The crystal structure of CsCdCl_3 has been reported by Siegel and Gebert (1964). The space group is C_6/mmc , $Z = 6$. Six Cl^- ions form a trigonally distorted octahedron around the central metal ion. The polarised absorption spectrum of the doped single crystal, cooled to 77°K in a cold-finger type dewar, was measured with Zeiss VSU-2 spectrophotometer.

The electronic ground term 5D of Fe^{2+} , which incidentally is the only quintet term for the d^6 configuration, splits under the octahedral crystalline field into an upper doublet 5E_g and a lower triplet ${}^5T_{2g}$ state. The separation between them gives the measure of $10 Dq$. The small trigonal field present in CsCdCl_3 splits the lower triplet further into a singlet ${}^5A_1(C_{3v})$ and a doublet ${}^5E(C_{3v})$ leaving the upper ${}^5E_g(O_h)$ unsplit (figure 1). The upper state might be split by the spin-orbit interaction or by the combined action of the trigonal field and spin-orbit interaction, but such splittings should be small ($<100 \text{ cm}^{-1}$, Low 1960). A large splitting of the upper E_g state, may, however, be caused by tetragonal Jahn-Teller distortion through the vibronic mechanism. Figure 2 shows the recorded polarised spectrum at 77°K .

We have assigned the absorption band at 6452 cm^{-1} to the ${}^5T_{2g} \rightarrow {}^5E_g$ transition and calculated the observed Dq to be $\sim 645 \text{ cm}^{-1}$. This is low in comparison with the Dq observed with Fe^{2+} in oxide ($\sim 1030 \pm 20 \text{ cm}^{-1}$, Low 1960) and in OH^- complex ($\sim 1080 \text{ cm}^{-1}$, Cotton & Mayers, 1960). This low value of Dq is obviously due to the large Od-Cl distance in our case (2.59 \AA) and the difference in the ionic radii of Fe^{2+} (0.83 \AA) and Cd^{2+} (1.03 \AA). It is interesting to note that the present octahedral value of Dq is comparable to the tetrahedral $Dq \sim 510 \text{ cm}^{-1}$ observed for FeCl_4^{2-} in chloride melt (LiCl-KCl , Gruen and McBeth 1962).

The absorption spectrum at 77°K (figure 2) shows that ${}^5T_{2g} \rightarrow {}^5E_g$ band splits into two components at 5210 cm^{-1} and 6370 cm^{-1} . This splitting is presumably due to the Jahn-Teller distortion of the upper 5E_g state. The lack of polarisation of the bands agrees with this assignment. The separation of 1160 cm^{-1} of the components, which measures the magnitude of the Jahn-Teller distortion, is less than that observed for Fe^{2+} surrounded by an octahedron of $(\text{OH})^-$ ions (~ 2000 ; cm^{-1} Liehr & Ballhausen 1958). This is in conformity with the low strength of the crystal field in the present case.

In addition, we have observed a band at 25040 cm^{-1} with high extinction coefficient. This is ascribed to the charge-transfer transition involving transfer of an electron from the Cl-ligand to the metal ion. In the molecular orbital scheme it is assigned to the transition (figure 3) t_{2u} (ligand) \rightarrow t_{2g} (metal). The direct product of $t_2 \times t_2$ breaks into T_1, T_2, A_1, A_2 . Under C_{3v} symmetry there should be three transitions polarised perpendicular to C and one transition polarised along C . From the observed polarised spectrum at 77°K (figure 2) it is seen that there are two transitions in the C_{\perp} direction at 25160 cm^{-1} and 24390 cm^{-1} and there is one transition at 25565 cm^{-1} in the C_{\parallel} direction. The magnitude of the trigonal field splitting is estimated to be nearly 400 cm^{-1} .

The authors have undertaken the magnetic susceptibility and anisotropy measurement to corroborate the above finding.

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Statistically linear mass relation of elementary particles and its representation by a polynomial curve fitting equation

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It is found that when the atomic weights of elements are plotted against the atomic numbers, a parabolic curve is obtained for the first 86 elements which however does not hold for the rest of the elements (figure 1). In the case of elementary