

Letters to the Editor

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LIGHT ABSORPTION IN PARAMAGNETIC Co^{++} IONS IN STATE OF SOLUTION

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In a recent paper Chakravarty and Chatterji (1959) assuming an approximate tetragonal axis of symmetry for the octahedron of water cluster about Co^{++} ion and following the method of Abragam and Pryce (1951) have developed general expressions for the magnetic susceptibilities along and normal to the axis of symmetry of the water cluster about Co^{++} ion in crystal in terms of the tetragonal splitting Δ , the effective Lande-splitting factor and the spin-orbit coupling coefficient. In order to get a fit with the experimentally observed data of magnetic susceptibility measurements by Bose (1948), they required a small value of Δ varying with temperature and a value of the coefficient of spin-orbit coupling which is the same as that for the free ion, for the salts studied.

An examination of the energy level expressions Owen (1955) shows that if Δ is small, then the number of absorption bands of Co^{++} ion salts in crystalline state or in state of solution will be limited to three instead of six. Absorption measurements of about fifteen cobalt salts in state of aqueous solution by us, show a single band at about $19,550 \text{ cm}^{-1}$ and two discernable bands at about $20,900 \text{ cm}^{-1}$ and $21,800 \text{ cm}^{-1}$ which point out clearly that Δ should be extremely small in them, in agreement with the theoretical findings of Chakravarty and Chatterji. The second findings by these authors that the spin-orbit coupling coefficient in crystalline state is the same as the free ion value, will mean that the covalent overlap of $3d$ -orbitals and the s - and p -orbitals of water cluster about Co^{++} ion can be neglected (Owen 1955). Consequently the term separation E for the free ion will be the same as E' , that for the crystal. From our optical absorption

measurements we have evaluated E' for about a dozen of Co^{++} salts in state of aqueous solution. We find that $E'/E \sim 0.95$ which is in complete agreement with the findings of Chakravarty and Chatterji.

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