

Letters to the Editor

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ANISOTROPY OF WATER CLUSTER ABOUT THE Cu^{+1} ION

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The ground state of Cu^{+1} ion ($3d^9 \ ^2D_{5/2}$) in octahedrally co-ordinated salts under the influence of the usual type of cubic crystalline electric field with positive coefficient (Van Vleck, 1932, Schlapp and Penney, 1932 and Gorter, 1942) splits into an orbital doublet and triplet above it.

Beevers and Lapson (1934) have shown that the water cluster about the Cu^{+1} ion has the approximate tetragonal symmetry and hence according to the theories of Polder (1942), Abragam and Pryce (1951), Bleaney *et al.* (1955) and Bose *et al.* (1957) the ionic magnetic anisotropy of the Cu^{+1} ion is given by

$$K_{\parallel} - K_{\perp} - \Delta K = \frac{2N\beta^2}{kT} (\lambda + kT) \cdot D' - \frac{2N\beta^2}{kT} (\lambda + kT) \cdot D f^2$$

where K_{\parallel} and K_{\perp} are the ionic susceptibilities parallel and normal to the tetragonal axis respectively; $D = \left(\frac{4}{E_{\parallel}} - \frac{1}{E_{\perp}} \right)$, where E_{\parallel} and E_{\perp} are the energy differences of the lowest basic doublet and the two tetragonal levels respectively of the triplet, and f^2 is the covalency factor (Owen, 1955).

Our measurements of the absorption spectra of Cu^{++} ion in copper sulphate in aqueous solution at first sight show that there is only one band having maximum at $12,400 \text{ cm}^{-1}$, but a closer examination of the absorption curves (fig. 1) shows that there is another maximum at about $12,000 \text{ cm}^{-1}$. The second maximum is directly noticeable, though it is not very prominent. There is a great deal of experimental evidences (Ballhausen and Jorgensen, 1954) that the absorption

curves of cupric ion in aqueous solution in different amino copper complexes consist of at least two discernible bands

If this separation is taken to be due to the tetragonal component of the crystal field then one can calculate D , which when substituted in the above expression will give $\Delta K/f^2$. Now according to Owen's findings and also of ours (Mookherji and Chhonkar, 1959) f^2 in CuSO_4 aqueous solution is 0.85 which gives directly ΔK in solution state for the water cluster about the Cu^{++} ion. Since we have found in our studies of nickel salts (Mookherji and Chhonkar, in course of publication) ΔK in state of solution and in crystalline state does not differ appreciably and hence our evaluated value of ΔK in case of CuSO_4 solution should agree with that of crystal value of ΔK (Bose *et al.* 1957) provided that our optical findings are correct. $\Delta K = 548.4 \times 10^{-6}$ at 300°K as obtained by Bose *et al.* (1957) from magnetic studies agrees well with our calculated value of $\Delta K = 548 \times 10^{-6}$ at the same temperature and hence we conclude that the first and second maxima are due to tetragonal splitting.

Since our assignment agrees well with the magnetic findings we have calculated f^2 evaluating ΔK from our optical measurements and utilising Bose *et al.* (1957) magnetic ΔK - values. They are given in Table I. We find that f^2 -values are of the right order and almost the same for all the salts studied in agreement with the suggestions of Bose *et al.* (1957) for these salts.

TABLE I

Sulphate series					
Pentahydrate	K	NH_4	Rb	Ti	Zn-K
0.85	0.88	0.76	0.875	0.81	0.88
Selenate series					
Pentahydrate	K	NH_4			
0.865	0.88	0.83			

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