Letters to the Editor

The Board of Editors does not hold itself responsible for opinions expressed in the letters published in this section. The notes containing short reports of original investigations communicated to this section should not contain many figures and should not exceed 500 words in length. The contributions reaching the Secretary by the 15th of any month may be expected to appear in the issue for the next month. No proof will be sent to the author.

20

A PRELIMINARY NOTES ON MAGNETIC SUSCEPTIBILITY AND ANISOTROPY IN TETRAHEDRALLY CO-ORDINATED Co^{++} ION †

S. KUMAR*, S. MITRA and R. RAI

Magnetism Department, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-32

(*Received August* 14, 1964)

The double chlorides $CoCs_2Cl_4$ and $CoCs_3Cl_5$ both have a slightly distorted tetrahedron of four Cl^- ions with the Co^{2+} at the centre. The Co^{2+} may be considered to be under a predominantly cubic ligand field of the type T_d, which splits the $3d^7$ ^4F ground state of Co^{++} into an orbital singlet $^4A_2$ and two triplets $^4T_2$ and $^4T_1$ each with fourfold degeneracy due to spin so long as the small distortion is neglected. The $^4A_2$ level lies lowest with $^4T_2$ and $^4T_1$ successively at energies 3500 cm^{-1} and 6300 cm^{-1} above it (Cotton *et al*. 1961). Spin-orbit coupling has non-vanishing matrix elements between $^4T_2$ and $^4A_2$ and in the presence of the small tetragonal field, caused by the abovementioned distortion taking place along a line joining the opposite edges of the tetrahedron (Powell and Wells, 1935), splits up the $^4A_2$ level into two Kramer's doublets with separation of the order of 9 cm^{-1}. (Bowers and Owen, 1955). No mixing of $^4T_1(F)$ and $^4T_1(P)$ levels with $^4A_2$ comes directly except in a very high order through $^4T_2$, which can therefore be neglected.

Calculation upto second order of magnetic perturbation $\beta H(L+2S)$ yields the expression for principal magnetic susceptibility K_i ($i = \parallel$ or $\perp$ to the tetragonal axis of the ion) which explains well (Table I) the magnetic measurements of mean susceptibility and anisotropy in the range 300°K to 90°K by one of us (S.M.). on $CoCs_3Cl_5$. It is seen that the spin-orbit coupling parameters parallel

† A part of the work has been submitted for both reading and publication to the International Conference on magnetism—1964 Nottingham (U.K.) communicated on 8-2-64.

*Present address—The Patent Office, Calcutta-17.

and perpendicular to the tetragonal axis of the ion ($\zeta_\parallel$ and $\zeta_\perp$) are reduced to -140 cm^{-1} and -120 cm^{-1} respectively, from the free ion value of -180 cm^{-1} (Laporte, 1928). The corresponding values of orbital reduction factors are $\kappa_\parallel = 0.92$ and $\kappa_\perp = 0.98$. The cubic field coefficient Dq is 350 cm^{-1}; Δ, the tetragonal field separation of the excited $^4T_2$ level varies from 322 cm^{-1} at 90°K to 980 cm^{-1} at 300°K.

The values of the parameters taken here are consistent with the paramagnetic resonance measurements (Bowers and Owen, 1953) and spectroscopic fine structure results (Cotton *et al*, 1961).

The anisotropic reduction in ζ is (1) due to an anisotropic overlap of the surrounding ligands *s*- and *p*-charge clouds with the central *d*-charge clouds (Bose *et al*, 1960) and also (2) due to the $3d$–$4p$ configurational interaction arising from the non-centrosymmetry of the complex (Bose *et al*, 1964) The increase in Δ from 322 cm^{-1} at 90°K to 980 cm^{-1} at 300°K is due to the thermal expansion or relaxation effects of the lattice. Details of the experimental and theoretical results will be published shortly along with those on $CoCs_2Cl_4$ which have also been completed by us.

TABLE

$D_q = 350$ cm^{-1} $\zeta = -140$ cm^{-1} $\zeta_\perp = 120$ cm^{-1}, $\kappa_\parallel = 0.92$, $\kappa_\perp = 0.98$

Temp °K	cm^{-1}	$p_\parallel^2$	$(p_\parallel^3 - p_\perp^2)$	g values	zero field splitting cm^{-1}
300°K	980	21.84 (21.81)	1.55 (1.56)		
200°	630	21.16 (21.26)	1.73 (1.72)		
90°K	322	19.96	2.34	$g_\parallel = 2.30$ (2.32 ± .04)	8.5
		(20.00)	(2.34)	$g_\perp$ 2.28 (2.27 ± .04)	(9.0)

Values in parantheses are the experimental values.

ACKNOWLEDGMENT

The authors are grateful to Prof. A. Bose for his guidance and suggestions, and also to Mr. S. Ray for helpful discussions. One of us (S.K.) is grateful to the Controller-General of Patents, Designs & Trade Marks for permitting him to do part-time research work and to The Director of the Indian Association for the Cultivation of Science for providing laboratory facilities.

REFERENCES

Bowers, K. D. and Owen . J., *Rep. Progr. Phys.*, **18**, 304.
Bose, A., Chakravarty, A. S. and Chattrji, R., 1960, *Proc. Roy. Soc.*, **A255**, 145.
Bose, A., Rai, R. and Mitra, S., 1964, *Proc. Phys. Soc.*, (communicated)
Cotton, F. A., Goodgame, D. M. L. and Goodgame M., 1961, *J. Amer. Chem. Soc.*, **83**, 4690.
Laporte, O., 1928, *Z. f. Krist.*, **47**, 761.
Powel, H. and Wells A. P., 1935, *J. Chem. Soc*, 359.