E.P.R. INVESTIGATION ON ORTHORHOMBIC g—TENSORS IN COPPER RUBIDIUM SULPHATE HEXAHYDRATE, COPPER CESIUM SULPHATE HEXAHYDRATE AND COPPER THALLIUM SULPHATE HEXAHYDRATE

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ABSTRACT. Electron paramagnetic resonance technique has been employed to determine precisely the orthorhombic g-tensors and their orientations in the unit cell in three copper tutton salts, namely, copper rubidium sulphate hexahydrate, copper cesium sulphate hexahydrate and copper thallium sulphate hexahydrate. The results have been compared with those of other Tutton salts reported earlier (Bose et al, 1964 ; Ghosh et. al., 1965). The comparison brings out clearly appreciable variation in the nature of the ligand field from salt to salt, presumably due to the long range effect arising from distant neighbours outside the primary ligand cluster.

INTRODUCTION

In previous communications (Bose et al, 1964; Ghosh et al, 1965) it has been shown that the e.p.r. method can be conveniently utilized in probing the three orthorhombic axes of the magnetic complex and finding the three principal ionic g-values in the single crystals of copper tutton salts. The results of application of the method to the case of copper potassium sulphate hexahydrate, copper ammonium sulphate hexahydrate, copper potassium selenate hexahydrate and copper ammonium selenate hexahydrate have been reported in that connection. The same method has been adopted to three other tutton salts, copper rubidium sulphate hexahydrate, copper cesium sulphate hexahydrate and copper thallium sulphate hexahydrate; and the results are discussed in the present paper.

METHOD OF MEASUREMENT

In all these salts variation of g-values was studied at room temperature in four natural planes of the crystals, namely $c(001)$ plane, $b(010)$ plane, $q(011$ or $0\bar{1}1)$ plane and $p(110$ or $1\bar{1}0)$ plane with the help of 1.2cm transmission type e.p.r. spectrometer (Ghosh et al, 1963). Actually measurements in three planes are sufficient for determining the $G_t s'$ denoting the principal ionic g-values and their orientations, but the measurement in an additional plane has been used to make a check on the final results.

As already described in the previous papers (Bose *et al*, 1964; Ghosh *et al*, 1965) for any setting of the crystal two values of g in a general plane containing the r.f. and the static magnetic field for two inequivalent ions in the unit cell are obtained at correspondingly different magnetic fields. The crystal is rotated in a given plane at intervals of $10°$ (sometimes $5°$) and the g^2-values have been plotted against the angular rotations. The general equation of the g^2-ellipsoid as shown earlier (Bose *et al*, 1964) is

$$\zeta_{11}X^2 + \zeta_{22}Y^2 + \zeta_{33}Z^2 + 2\zeta_{12}XY + 2\zeta_{23}YZ + 2\zeta_{13}XZ = 1,$$

where

$$\zeta_{11} = \sum_{i=1}^{3} G_i{}^2\alpha_i{}^2, \quad \zeta_{22} = \sum_{i=1}^{3} G_i{}^2\beta_i{}^2, \quad \zeta_{33} = \sum_{i=1}^{3} G_i{}^2\gamma_i{}^2$$

$$\zeta_{12} = \sum_{i=1}^{3} G_i{}^2\alpha_i\beta_i, \quad \zeta_{13} = \sum_{i=1}^{3} G_i{}^2\alpha_i\gamma_i, \quad \zeta_{23} = \sum_{i=1}^{3} G_i{}^2\beta_i\gamma_i.$$

in which α_i, β_i, γ_i represent the direction cosines of G_i relative to the orthogonal $X(a)$, $Y(b)$ and $Z(c')$ axes of the crystal respectively.

RESULTS AND DISCUSSION

From the above measurements the six independent coefficients $\zeta_{ij}s$ defining the g^2-ellipsoid have been determined. These are given in table 1.

Table 1

	ζ_{11}	ζ_{22}	ζ_{33}	ζ_{12}	ζ_{13}	ζ_{23}
$Cu(RbSO_4)_2.6H_2O$	5.217	4.995	4.210	0.600	0	−0.125
$Cu(CsSO_4)_2.6H_2O$	5.215	5.016	4.487	0.655	0.209	−0.029
$Cu(TlSO_4)_2.6H_2O$	5.211	5.002	4.407	0.682	0.234	−0.193

By the method of matrix diagonalisation, from these six coefficients in each of these salts the principal g-values and their orientations have been obtained. The principal g-values and their orientations are shown in table 2 and table 3 respectively. The experimental data for other tutton salts reported elsewhere (Bose *et al*, 1964; Ghosh *et al*, 1965) are also included in tables 2 and 3 for comparison.

It will be seen from table 2 that the g^2-ellipsoids in all these salts are of definitely orthorhombic symmetry. It will be seen by examining table 3 that the angle, the G_3-axis makes with the symmetry axis of the monoclinic crystal (i.e. b-axis) is nearly the same for all the salts. On the other hand, all other angles vary appreciably for the different salts. This is perhaps due to the fact that in all the salts G_3 axis coincides with the approximate tetragonal axis of the paramagnetic complex and the difference in orientations in the different salts arise from a distribution of alkali atoms or acid radicals, which vary from salt to salt,

9

Table 2

	G_1	G_2	G_3
$Cu(KSO_4)_2 . 6H_2O$*	2.05_5	2.15_7	2.38_4
$Cu(NH_4SO_4)_2.6H_2O$*	2.05_3	2.20_8	2.35_8
$Cu(Rb\ SO_4)_2.6H_2O$	2.04_8	2.12_7	2.39_2
$Cu(Cs\ SO_4)_2.6H_2O$	2.07_5	2.14_9	2.40_7
$Cu(Tl\ SO_4)_2.6H_2O$	2.02_7	2.17_0	2.40_6
$Cu(KSeO_4)_2.6H_2O$†	2.07_5	2.16_4	2.35_7
$Cu(NH_4SeO_4)_2.6H_2O$†	2.05_2	2.12_3	2.39_6

*Bose *et al*, 1964,   †Ghosh *et al*, 1965.

Table 3

	$\cos^{-1}\alpha_1$	$\cos^{-1}\beta_1$	$\cos^{-1}\gamma_1$	$\cos^{-1}\alpha_2$	$\cos^{-1}\beta_2$	$\cos^{-1}\gamma_2$	$\cos^{-1}\alpha_3$	$\cos^{-1}\beta_3$	$\cos^{-1}\gamma_3$
$Cu(KSO_4)_2.6H_2O$	$72°.8$	$106°.9$	$24°.5$	$54°.1$	$134°.1$	$114°.4$	$41°.1$	$49°$ $(48°.6)$*	$92°$
$Cu(NH_4SO_4)_2.6H_2O$	$109°.9$	$115°.7$	$33°.5$	$41°.9$	$131°.8$	$92°.2$	$54°.9$	$52°.7$ $(49°.6)$*	$56°.6$
$Cu(KSeO_4)_2.6H_2O$	$108°.9$	$104°.5$	$23°.6$	$49°$	$139°$	$89°.4$	$46°.5$	$52°.6$ $(50°.7)$*	$66°.5$
$Cu(NH_4SeO_4)_2.6H_2O$	$92°.2$	$128°$	$38°.1$	$36°.6$	$119°.3$	$109°.9$	$53°.5$	$51°.9$ $(51°.)$*	$59°$
$Cu(RbSO_4)_2.6H_2O$	$98°.5$	$75°.1$	$17°.3$	$51°.2$	$136°.3$	$73°$	$40°.1$	$50°.1$ $(49°.8)$*	$93°.1$
$Cu(CsSO_4)_2.6H_2O$	$121°.5$	$59°.4$	$46°.8$	$67°.5$	$125°.3$	$43°.8$	$40°.3$	$50°.3$ $(50°.9)$*	$83°.8$
$Cu(TlSO_4)_2.6H_2O$	$118°.2$	$58°.9$	$44°.5$	$63°.9$	$124°.3$	$45°.6$	$40°.2$	$49°.9$ $(49°.7,$*	$87°.8$

*Angular values within parentheses are the angles obtained from magnetic anisotropy experiments (Bose *et al*, 1957) on the assumption of approximate tetragonal symmetry about the G_3 axis.

packed about the equatorial plane of the complex without affecting appreciably the relative orientations of the symmetry axis. The orientation angles do not appear to bear any strict sequence to the ionic radii of the alkali atoms or the acid radicals. It appears that the NH₄ and Tl sulphate salts which do not strictly belong to those of the alkali metal series K, Rb and Cs, have decidedly a more pronounced orthorhombicity of the ligand field. Their angular orientations except

$\cos^{-1} \beta_3$ also do not fit in the sequence of the other three sulphate salts. In the selenate salts, however, this larger orthorhombicity appears to be largely compensated by the presence of SeO_4^{-2} ion.

Variation in the g-tensor in the isomorphous Tutton salts indicates very clearly that the ligand field, especially its anisotropic part, is not only dependent on the primary ligand cluster but also upon what are the more distant neighbours and how they are situated, in short what is their effect upon the Cu^{2+} ion directly or indirectly through the immediately neighbouring water dipoles, since in the isomorphous series of salts it is only some of these distant neighbours which are different. The information, however, is as yet far from complete and situation is too complex to render an accurate explanation of the said difference in anisotropy behaviour.

ACKNOWLEDGMENT

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