

MAGNETIC STUDIES ON CUPRIC IONS IN CRYSTALS

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ABSTRACT. Magnetic anisotropy and principal susceptibilities of few alkali cupric halides have been measured and the results are discussed in relation to crystal structure and Van Vleck's theory. The relative orientations of the paramagnetic units in cupric Tutton salts have been calculated.

I. INTRODUCTION

The magnetic behavior of cupric ions in single crystals of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ has been studied by K. S. Krishnan and the present writer (1936, 1938). It was shown that the electric field in the neighbourhood of the Cu^{++} ion has tetragonal symmetry, imparting on the crystal a uniaxial magnetic symmetry. The magnetic data combined with the known fine structure of the crystal reveals that the magnetic moment for directions normal to the axis of symmetry of the paramagnetic unit has the spin-only value, while the moment for direction along the axis of symmetry gets some contribution from the orbital angular momentum over the spin-only value.

Cupric alkali halides, for which X-ray data are available will provide interesting magnetic studies of single crystals as there is the possibility of calculating the directional magnetic properties of the paramagnetic unit in these crystals and compare them with those of copper sulphate pentahydrate. In this communication are presented the results of a systematic study of some of these crystals as well as of cupric acetate monohydrate as it is a less hydrated crystal, is therefore magnetically more concentrated than the other copper salts and thus may show interesting magnetic behavior quite different from the above salts and the cupric Tutton salts.

II. EXPERIMENTAL

The method adopted for the measurement of the anisotropy is that of Krishnan and Banerji (1934). The crystal is suspended at the end of a calibrated quartz fibre in the centre of a homogeneous magnetic field with known directions vertical. The direction in the crystal which sets along the field and the difference between the maximum and the minimum susceptibility in this plane were determined.

By suspending the crystal separately in any convenient vertical direction and allowing it to take up its natural orientation in a non-homogeneous magnetic field, one of the principal susceptibilities of the crystal was determined by the magnetic balancing method of Krishnan and Banerji (1937), which, combined with the anisotropy measurements, gave the principal susceptibilities.

III. RESULTS

Results of measurements are collected in Tables I and II and expressed in the usual units, *i.e.*, 10^{-6} of a c.g.s. electromagnetic unit. For the tetragonal crystals the gram molecular susceptibilities along the axis of symmetry of the crystal and for directions normal to it are denoted by χ_a and χ_t respectively; for monoclinic crystals χ_3 is the gm. mol. susceptibility along the 'b' axis, while greater of the two in the (010) plane is denoted by χ_1 and the smaller by χ_2 . θ is the angle which the 'a' axis makes with the χ_2 axis. Effective magnetic moments (μ_i) are calculated by using the expression $\mu_i = 2.84 \sqrt{\chi'_i T}$ where $i=1, 2, 3$ or \perp and χ'_i is the principal susceptibility corrected for diamagnetism (for both cation and anion). Mean effective moment ($\bar{\mu}$) is given by

$$\frac{\sqrt{\mu_1^2 + \mu_2^2 + \mu_3^2}}{3} \text{ or } \frac{\sqrt{\mu_a^2 + 2\mu_t^2}}{3}$$

The diamagnetism of Cu^{++} ion was calculated to be -14.8×10^{-6} by the method of Slater as modified by Angus (1932). The following diamagnetic corrections for the different groups as given in Stoner's book ("Magnetism and Matter," page 470) were adopted.

NH_4^+	K^+	Rb^+	Cs^+	Ti^+	Cl^-	SO_4^{--}	SeO_4^{--}	$\text{CH}_3(\text{COO})_2^-$
-22.1	-18.5	-27.2	-41	-40	-20.1	-33.0	-41.4	-28.6

TABLE I

Temperature = 30 C

Crystal	Crystallographic data	Mode of suspension	Orientation in the field	Magnetic Anisotropy 10^6 CGS. Units
$\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$	Tetragonal $z=2$ $a=7.58$ $c=7.95$	Tetragonal axis horizontal	Tetragonal axis normal to the field.	$\chi_t - \chi_a = 258$
$\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$	Tetragonal $z=2$ $a=7.45$ $c=7.88$	Tetragonal axis horizontal.	Tetragonal axis normal to the field	$\chi_t - \chi_a = 263$
$\text{CuCl}_2 \cdot 2\text{RbCl} \cdot 2\text{H}_2\text{O}$	Tetragonal $z=2$ $a=7.81 \text{ \AA}$ $b=8.0 \text{ \AA}$	Tetragonal axis horizontal.	Tetragonal axis normal to the field	$\chi_t - \chi_a = 262$
$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	Moncl. prism $z=8$ $a=13.18$ $b=8.46$ $c=13.89$ $\beta=117^\circ 6'$	'b' axis vertical. 'a' axis vertical. (001) pl. horiz.	$\theta = 2.2$ 'b' normal to the field. 'b' ax. par ^l to the field.	$\chi_1 - \chi_2 = 198$ $\chi_1 - \chi_3 = 132$ $\chi_3 - \chi_2 = 66$

TABLE II

Crystal	Direction along which susceptibility was measured	Temp. °C	Density of the crystal	Vol. susceptibility (10 ⁻⁶ C.G.S. units)	Gm. mol. susceptibility (10 ⁻⁶ C.G.S. units)	Mean susceptibility at 30°C	Effective moment at 30°C			
							μ_1	μ_2	μ_3	
<chem>CuCl2.2NH4Cl.2H2O</chem>	Along X ₁ axis	28.7	2.004	0.980	1,380	1,290	1.77	1.91	1.88	
<chem>CuCl2.2KCl.2H2O</chem>	Along X ₁ axis	31.3	2.430	10.16	2,340	1,250	1.73	1.91	1.85	
<chem>CuCl2.2RbCl.2H2O</chem>	Along X ₁ axis	30.0	2.504	8.074	1,330	1,240	1.74	1.92	1.86	
<chem>Cu(CH3COO)2.H2O</chem>	Along 'b' axis	32.5	1.968	7.355	748	770	μ_1 1.54	μ_2 1.25	μ_3 1.43	1.41

IV. MAGNETIC ANISOTROPY IN RELATION TO CRYSTAL STRUCTURE

We proceed to discuss the results obtained in the previous section in relation to X-ray data concerning the paramagnetic unit in the crystal.

CuCl2.2KCl.2H2O—This crystal has been analysed by X-ray methods by Hendricks and Dickinson (1927) and Chrobak (1934). It is assigned a space group D_4h^{14} with two molecules in the unit cell. Chrobak finds after detailed Fourier analysis that Cu^{2+} ion is at the centre of an octahedron formed by two oxygen atoms at opposite corners and four chlorines, the diagonal joining the two oxygens being along 'c' axis. The two oxygen distance (Cu-O) from the central Cu^{2+} ion is 1.97Å . Two chlorines are in the same plane as Cu^{2+} ion and oxygens are at a distance (Cu-Cl₁) of 2.32Å . The other two chlorines which are located centrally above and below this plane are at a distance (Cu-Cl₂) of 2.95Å . There are two such groups in the unit cell of the crystal and are parallel to each other. Let the gm. mol. susceptibility along (Cu-Cl₂) be represented by K_2 and that along (Cu-O) by K_1 ; K_2 should be greater than K_1 . Evidently χ_2 along the 'c' axis of the crystal should be equal to K_1 and χ_1 equal to K_2 . As a result χ_1 should be greater than χ_2 which is observed experimentally. We have then $K_2 - K_1 = \chi_1 - \chi_2 = 265 \times 10^{-6}$ and $\frac{K_2 + K_1}{3} = \frac{\chi_2 + 2\chi_1}{3} = 1250 \times 10^{-6}$ at 30°C. Hence the anisotropy of the individual group is about 21% as against 40% for that in the crystal of CuSO4.5H2O (Krishnan and Mookherjee, 1938).

CuCl2.2NH4Cl.2H2O—This crystal has also been studied in detail by Chrobak (1934). Two alternative structures are proposed. According to the first Cu^{2+} ion is at the corners of an octahedron formed by two oxygens at opposite corners and four chlorines similar to the potassium salt, 'c' axis being parallel to the diagonal joining the two oxygens. According to the second

structure Cu^{++} ion should be at the centre of a cube formed by eight chlorine atoms. The centres of opposite faces are occupied by oxygen atoms and the line joining them is parallel to 'c' axis.

From the available X-ray data it was not possible to decide between the two. Krishnan and Mookherjee (1938) showed that magnetic anisotropy measurements favoured the first structure, *i.e.*, same as the potassium salt. Since the two paramagnetic units in the unit cell of the crystal are parallel to each other χ_1 should be greater than χ_2 as before. This was also observed.

Evidently $\chi_1 - \chi_2 = K_2 - K_1 = 258 \times 10^{-6}$ and $\frac{2\chi_1 + \chi_2}{3} = \frac{K_2 + 2K_1}{3} = 1290$ at 30°C ; so that the anisotropy of the unit is about 20%, almost the same as the potassium salt.

$\text{CuCl}_2 \cdot 2\text{RbCl} \cdot 2\text{H}_2\text{O}$ —For this salt no detailed X-ray data are available. There are two molecules. If the disposition of the chlorine and oxygen atoms about the Cu^{++} ion is the same and if the orientation of the groups is the same which is very much to be expected the anisotropy of the paramagnetic unit will be about 21%, almost the same as the other two halides.

Cupric Tutton Salts—Krishnan and Mookherji (1937) made measurements on a large number of Tutton salts at room temperature. The distribution of the oxygen atoms surrounding the cupric ion if taken to be the same as in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystal, *i.e.*, four of the oxygens contributed by four water molecules, form a square with Cu^{++} ion at the centre; the other two which are contributed by the SO_4^{--} groups lie centrally above and below the square, but at a much larger distance than the other four oxygens, one should expect the anisotropy of the paramagnetic unit to be at most the same as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Tutton salts have been studied by X-ray methods by Hofmann (1931). There are two molecules in the unit cell of the crystal. Let the symmetry axes of these two units be represented by Z_1 and Z_2 . All the crystals are monoclinic and the (010) plane is a symmetry plane; so the principal magnetic axes and susceptibilities of one of the units can be obtained from those of the others by reflection in the (010) plane of the crystal. Since the paramagnetic unit possesses uniaxial magnetic symmetry χ_2 should be the direction normal to the plane containing Z_1 and Z_2 ; χ_1 should be the internal bisector of the angle 2ψ between Z_1 and Z_2 .

Evidently $\chi_1 = K_2 \cos^2\psi + K_1 \sin^2\psi$; $\chi_2 = K_1$; $\chi_3 = K_2 \sin^2\psi + K_1 \cos^2\psi$.

$$\cos 2\psi = \frac{\chi_1 - \chi_3}{K_2 - K_1} \quad \text{and} \quad (\chi_1 + \chi_2 + \chi_3)/3 = (K_2 + 2K_1)/3.$$

Using the above equations we have calculated the relative orientations (2ψ) of the two paramagnetic units and their principal susceptibilities K_2 and K_1 as shown in Table III. It is found that the values of $(K_2 - K_1)$ compare well with that of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ($K_2 - K_1 = 550$). The variation of $K_2 - K_1$ from 640 to 500 is very much to be expected as the distances of oxygen atoms from the Cu^{++} ion should not be exactly the same in all cases.

Unlike $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Tutton salts have six oxygen atoms from six water molecules for the formation of the octahedron hence one might say that these octahedrons should be regular and not drawn-out ones as is supposed. But this dissymmetry in the unit is very much to be expected because of the well known Jahn-Teller Theorem (1937).

TABLE III

Data refer to 30°C

Crystal	$K_{\parallel} - K_{\perp}$	2ψ	K_{\parallel}	n_{\parallel}	n_{\perp}	\bar{n}
$\text{CuRb}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	600	80.4	1,710	2.17	1.81	1.93
$\text{CuCs}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	564	78.3	1,720	2.19	1.84	1.97
$\text{CuTl}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	495	81.9	1,670	2.16	1.86	1.97
$\text{Cu}(\text{NH}_4)_2(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	586	78.4	1,750	2.20	1.84	1.97
$\text{CuK}_2(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	639	79.3	1,870	2.24	1.86	2.02
$\text{CuRb}_2(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	630	82.9	1,740	2.21	1.81	1.95
$\text{CuTl}_2(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	580	82.9	1,690	2.18	1.80	2.06

n_{\parallel} and n_{\perp} denote the effective magnetic moments of the paramagnetic unit when the applied magnetic field is along and perpendicular respectively to the symmetry axis of its crystalline field and \bar{n} is the corresponding mean magnetic moment.

V. MAGNETIC BEHAVIOUR OF CUPRIC IONS IN CRYSTALS

Cupric Alkali Halides—As revealed by X-ray studies the paramagnetic units of these crystals are made up of octahedrons of four chlorine and two oxygen atoms with copper at the centre. Two oxygens and two chlorines form a square about the cupric ion; the other two chlorines lie centrally above and below this square. This octahedron is not a regular one. But the line joining the two chlorines above and below the square is drawn out. As a result the crystalline electric field acting on Cu^{++} ion in the crystal should have approximate tetragonal symmetry like $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The potential of an electron placed at the point x, y, z is then given by $\phi = D(x^4 + y^4 + z^4) + A(x^2 + y^2 - 2z^2)$ and the susceptibility along z -axis, *i.e.*, the tetragonal axis should be greater than along directions normal to it. Van Vleck (1932) has shown that the orbital moment is conserved only along the symmetry axis while along other directions it is of high frequency type. Consequently along axes other than the symmetry axis the magnetic moment should have the spin-only value. On referring to Table II we find that μ_{\parallel} which in this case evidently corresponds to n_{\parallel} , the moment along the symmetry axis of the paramagnetic unit, varies from 1.91 to 1.94 while μ_{\perp} which corresponds to n_{\perp} , the moment along the normal to the symmetry axis, varies from 1.77 to 1.73. Now the magnetic moment for one spin only is $1.73[\mu = 2\sqrt{s(s+1)}, s = \frac{1}{2}]$. Thus there is fair agreement of the experimental findings with the prediction of the theory.

In case of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ it was found that n_{\parallel} was equal to 2.13 and $n_{\perp} = 1.80$. The distance between the Cu^{++} ion and the oxygen atoms centrally

above or below the square 2.4 A. U. and is smaller than the distance (Cu—Cl_{II}) 2.93 A. U. in potassium halide. One naturally expects that n_{11} for CuSO₄·5H₂O should be smaller than n_{11} for potassium cupric halide, symmetry of the crystalline electric field being the same. But reverse is the case as is found in Table II. This is not difficult to understand, for going through various interatomic distances in these two crystals one finds that the symmetry axis of the paramagnetic unit in CuCl₂·2RbCl₂·2H₂O is not so symmetrical as that of the paramagnetic unit in CuSO₄·5H₂O. So the orbital contribution along this axis is more than for that of the halides. This also explains why the mean moment in alkali halides is nearer the spin-only value than in the case of CuSO₄·5H₂O.

Tutton Salts As shown in Table II these salts behave similarly as CuSO₄·5H₂O. One can therefore say that the disposition of oxygen atoms about Cu⁺⁺ ion in the paramagnetic unit is almost the same and their symmetry axes enjoy the same degree of symmetry as that of CuSO₄·5H₂O.

One direct consequence of such magnetic behaviour is that all the three copper halides should follow simple Curie Law more closely than CuSO₄·5H₂O and the Tutton Salts.

Cu(CH₃COO)₂·H₂O—Only the space group and the number of molecules in the unit cell is available from X-ray data for this crystal, so it is not possible to evaluate the relative orientations of the paramagnetic units and thence to calculate n_{11} and n_{12} . Even then the mean moment of the unit is much lower than the spin-only value. This is also very much smaller than those of the other cupric salts. Cupric bromide (CuBr₂) has almost the same susceptibility as this salt.

This low value of the effective magnetic moment of this crystal can be due to (i) concentrations of the magnetic particles being very large, exchange interactions between the neighbouring moments may be appreciable, destroying magnetism, (ii) splitting of the ground state asymmetric electric field due to its neighbours might take place in such a manner that there might be a non-magnetic level somewhere at about 300 cm⁻¹, so that as we come down to room temperature the number of electrons in this level increases and so the moment decreases.

The first point can be decided by diminishing the concentrations of Cu⁺⁺ ions in this salt, *i.e.*, by diluting it with some isomorphous diamagnetic salt and studying the magnetic moment. n should reach the value of other cupric salts when it is sufficiently diluted.

For the second point measurements on temperature variation of the magnetic moment, specially at high temperature, is required. Magnetic moment should increase with the increase of temperature and should reach the spin-only value at a temperature at which the non-magnetic level is completely depopulated of electrons.

Whatever may be the cause of this low magnetic moment one point stands out clearly that since the magnetic moment does not agree with the value

calculated theoretically for the Cu^{++} ion there should be a complicated temperature variation, *i.e.*, the crystal should not follow simple Curie Law like the other cupric salts. This salt has a moment almost equal to cupric bromide, so its temperature variation may be expected to be similar. μ should decrease rapidly with the fall of temperature as is found in case of cupric bromide (Stoner, *Magnetism and Matter*, page 482).

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REFERENCES

- Angus, W. R. (1932), *Proc. Roy. Soc.*, **136A**, 560.
 Chrobak, L. (1934), *Z. Kristallogr.*, **88A**, 35.
 Jahn, H. A. (1937), *Proc. Roy. Soc.*, **164A**, 117.
 Jahn, H. A. and Teller, H. (1937), *Proc. Roy. Soc.*, **161A**, 220.
 Hendricks, S. B. and Dickenson, R. G. (1927), *J. Amer. Chem. Soc.*, **49**, 2149.
 Hofmann (1931), *Z. Kristallogr.*, **78A**, 279.
 Krishnan, K. S. and Banerjee, S. (1934), *Phil. Trans.*, **234A**, 265.
 Krishnan, K. S. and Mookherji, A. (1936), *Phys. Rev.*, **60**, 860.
 " " " (1937), *Phil. Trans.*, **237A**, 135.
 " " " I (1938), *Phys. Rev.*, **34**, 533.
 " " " II (1938), *Phys. Rev.*, **54**, 841.
 Krishnan, K. S. and Mookherjee A and Bose A. (1938), *Phil. Trans.*, **238A**, 125.
 Van Vleck, J. H. (1932), "The Theory of Electric and Magnetic Susceptibilities."