sumably does not absorb efficiently except when the neutron velocities have become small, makes it seem as likely that their results actually indicate a greater absorption coefficient for paraffin than for the other substances which they studied. There are, however, so many factors involved, the slowing down, the scattering, and the capture of neutrons, that it is highly desirable that new experiments be made to ascertain the actual absorption coefficient of hydrogen in its various compounds. These experiments are crucial for, if the capture of neutrons by hydrogen is determined solely by

energy levels in the deuterium nucleus, it could in no way depend upon the particular chemical compound in which the hydrogen is bound.

Note added August 14. In experiments which have just been carried out in this laboratory by W. F. Libby and E. A. Long, two remarkable results have been obtained, first, at 20°K there is a great increase either in the slowing of neutrons, or their absorption, or both, when liquid hydrogen is replaced by paraffin. Second, the slowing of neutrons by cold paraffin continues down to temperatures at which there is no mechanism now known to account for this phenomenon. These experiments indicate very strongly that there are processes involved which concern the molecule as a whole and not merely the nucleus.

The Magnetic Anisotropy of Copper Sulphate Pentahydrate, CuSO₄·5H₂O, in Relation to Its Crystal Structure. Part I

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The magnetic anisotropy of the triclinic crystal $CuSO_4 \cdot 5H_2O$ has been measured. The crystal is found to be nearly uniaxial magnetically, i.e., has an axis of approximate magnetic symmetry, the susceptibility along the axis being less than that along perpendicular directions by about 300×10^{-6} c.g.s. e.m.u. per gram molecule at 26°C. The above axis is inclined at 156°, 65°, and 52°, respectively, to the 'a', 'b' and 'c' axes of the crystal. These results are discussed in relation to the known arrangement of the water molecules and oxygens round the Cu^{++} ions and the resulting crystalline electric fields acting on the latter.

1. INTRODUCTION

IN some recent papers Van Vleck and his collaborators[1] have discussed theoretically the magnetic behavior of some of the Tutton salts of the iron group of metals, particularly in relation to the influence of the strong internal electric fields which are acting on the paramagnetic ions in the crystals. The two copper salts $CuSO_4 \cdot K_2SO_4 \cdot 6H_2O$ and $CuSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O$ have been studied in detail by Jordahl[2] and by Janes,[3] and they conclude from the magnetic data that the crystalline electric field acting on the Cu^{++} ion in these crystals has monoclinic symmetry. The field can be split up into two parts, one with cubic symmetry, which is found to be very predominant, and the other

with rhombic symmetry, which is much feebler; the over-all Stark separations of the energy levels of Cu^{++} produced by these two fields are about 18,000 cm⁻¹ and 350 cm⁻¹, respectively. This predominantly cubic symmetry of the field is a natural consequence of the octohedral arrangement[4] of the six water molecules in the crystal round each Cu^{++} ion, the disposition of the SO_4^{--} and the K^+ or NH_4^+ ions, which are at a greater distance from Cu^{++}, probably producing the feeble rhombic field.

The magnetic susceptibility of the triclinic crystal $CuSO_4 \cdot 5H_2O$ has been measured in the *powder state* over an extensive range of temperatures by de Haas and Gorter,[5] and from these susceptibility data, both Jordahl and Janes concluded that in this crystal also, the crystalline

[1] See Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford (1932), Chapter XI.
[2] Jordahl, Phys. Rev. 45, 87 (1934).
[3] Janes, Phys. Rev. 48, 78 (1935).

[4] Regarding the structure of the Tutton salts see Hofmann, Zeits. f. Krist. 78, 319 (1931).
[5] de Haas and Gorter, Leiden Comm. 210 d (1930).

fields acting on Cu^{++} should be predominantly cubic. This result too has recently been shown to be in conformity with the structure of the crystal, by Beevers and Lipson;[6] they find that each Cu^{++} ion in the crystal is at the center of an approximate octohedron formed by four water molecules and two oxygens.

Whether this crystalline field is wholly cubic, or whether there is also a feeble rhombic component, as in the Tutton salts, it is not possible to decide, since the mean susceptibility of the crystal, for which alone experimental data are at present available, is not sensitive to such feeble superposed fields. Measurements on the magnetic anisotropy of the crystal will however give us much information on this point. We have therefore made measurements on the anisotropy of this crystal at different temperatures. In Part I of this paper we give an account of the measurements at room temperature, and discuss the results in relation to the structure of the crystal. Measurements at low temperatures will be dealt with in Part II.

2. EXPERIMENTAL

Copper sulphate pentahydrate crystallizes in the triclinic system, in the space group C_i^1. An x-ray analysis of the crystal has recently been made by Beevers and Lipson.[7] The unit cell has the dimensions

$a =$ 6.12A,	$\alpha =$ 82° 16',
$b =$ 10.7,	$\beta =$ 107° 26',
$c =$ 5.97,	$\gamma =$ 102° 40',

and it contains 2 molecules of $CuSO_4 \cdot 5H_2O$.

As the crystal is triclinic, the direction of none of its magnetic axes is known directly from considerations of symmetry, as in the other crystal systems. We have therefore to determine experimentally these directions as well.

The experimental procedure adopted is as follows. The crystal is suspended at the end of a calibrated quartz fiber, in a uniform horizontal magnetic field, with some natural face of the crystal horizontal, or some edge in it vertical. The upper end of the fiber is attached axially to a graduated torsion-head. The movements of

[6] Beevers and Lipson, Proc. Roy. Soc. **A146**, 570 (1934).
[7] See reference 6. See also Tutton, *Crystallography and Practical Crystal Measurement*, Vol. 1 (Macmillan, 1927), p. 297.

the crystal are watched through a telemicroscope, whose axis has been adjusted to be horizontal and normal to the direction of the field.

In the first place the torsion-head is rotated suitably so as to make the torsion on the fiber nothing when the crystal takes up its equilibrium orientation in the magnetic field. We shall call this position of the torsion-head as its zero position. We require now to determine (1) the directions of the maximum and minimum susceptibilities of the crystal in the horizontal plane, i.e., the directions which set themselves along and perpendicular to the magnetic field; (2) the difference between the maximum and minimum susceptibilities in the horizontal plane, i.e., the anisotropy in the horizontal plane. The latter is determined by finding the angle α_0 through which the torsion-head has to be rotated from its zero position in order to make the crystal *just* to turn round in the field.[8] The anisotropy $\Delta\chi$ per gram molecule is then given by the relation

$$\Delta\chi = (2Mc/mH^2)(\alpha_0 - \pi/4), \qquad (1)$$

where c is the torsional constant of the fiber, H is the magnetic field, m is the mass of the crystal and M is the gram molecular weight.

To determine the directions of the magnetic axes in the horizontal plane we proceed as follows. When the crystal has taken up its equilibrium orientation in the field under zero torsion of the fiber, let some horizontal edge, or some vertical face of the crystal make a small angle $\varphi(<\pi/4)$ with the direction of observation, i.e., with the direction of the normal to the field. Let α be the angle through which the torsion-head has to be rotated from its zero position in order to bring the above edge or face exactly along the direction of observation. Evidently

$$\sin 2\varphi = (\alpha - \varphi)/(\alpha_0 - \pi/4), \qquad (2)$$

from which φ is known. By finding the inclination φ of two such edges or faces, to the normal to the field, the two magnetic axes in the horizontal plane are fixed uniquely.

The crystal is resuspended so as to make other convenient crystal directions successively vertical, and for each suspension the directions of the

[8] See Phil. Trans. **A234**, 265 (1935).

TABLE I. *Magnetic anisotropy of* $CuSO_4 \cdot 5H_2O$ *at* $26°C$.

Serial number	Mode of suspension	Orientation in the field	$\Delta\chi$ $(\times 10^6)$	θ	$\Delta\chi/\sin^2\theta$ $(\times 10^6)$
1	'c' ax. vert.	($\bar{1}00$) at 25° to the field and ($\bar{1}\bar{1}0$) at 51° to it.	183	52°	295
2	'a' ax. vert.	(011) at $2\frac{1}{2}$° to field and (021) at $17\frac{1}{2}$° to it.	55	$24\frac{1}{2}$°	320
3	($\bar{1}00$) and ($\bar{1}11$) vert.	($\bar{1}00$) at $45\frac{1}{2}$° to field and ($\bar{1}11$) at 14° to it.	261	86°	262
4	($\bar{1}\bar{1}0$) and ($\bar{1}11$) vert.	($\bar{1}\bar{1}0$) at 60° to field and ($\bar{1}11$) at 12° to it.	263	79°	273
5	(100) horiz.	'c' ax. at $59\frac{1}{2}$° to field and intersection of ($\bar{1}00$) and ($\bar{1}11$) at $7\frac{1}{2}$° to it.	163	45°	326
6	(110) horiz.	'c' ax. at 44° to field, and intersection of ($\bar{1}\bar{1}0$) and ($\bar{1}11$) at 12° to it.	220	61°	288
7	($\bar{1}10$) horiz.	'c' ax. at 90° to field and intersection of ($\bar{1}10$) and ($\bar{1}11$) at $2\frac{1}{2}$° to it.	113	38°	298
8	($\bar{1}11$) horiz.	Intersection of ($\bar{1}11$) and ($\bar{1}00$) at 22° to field, and intersection of ($\bar{1}11$) and ($\bar{1}\bar{1}0$) at 47° to it.	26	16°	342

magnetic axes in the horizontal plane, and the corresponding anisotropy $\Delta\chi$, are determined in the above manner.

3. RESULTS

The experimental results obtained at room temperature are collected together in Table I. The second column gives the manner of suspension of the crystal, and the third the observed orientation of the crystal in the magnetic field; the fourth column gives the value of the anisotropy. The room temperature fluctuated about a mean value of 26°C by a few degrees, and all the values of $\Delta\chi$ have been reduced for uniformity to this temperature by assuming that $\Delta\chi$ varies inversely as the square of the temperature. This temperature correction is small. The last two columns in the table will be explained in the next section.

4. THE MAGNETIC AXES AND THE ANISOTROPY OF THE CRYSTAL

It is convenient to study the experimental data obtained in the previous section with the help of the stereographic projection. For any given suspension of the crystal, there is one plane which is horizontal (which need not necessarily be a natural or a possible crystallographic plane). In Table I we have numbered the different crystal suspensions for which we have made magnetic observations, serially from (1) to (8). In the stereographic projection (see Fig. 1) the poles of the corresponding horizontal planes are denoted by the same numbers. Thus point 1 in the figure is the pole of the plane which would be horizontal when the crystal suspension is 1; and so on.

From each of these poles a great circle is drawn to represent the direction of maximum susceptibility in the particular plane, i.e., the direction which sets itself along the field in the corresponding suspension of Table I. (To be more precise, this great circle is the locus of the poles of all the tautozonal planes which have the above direction of maximum susceptibility as the zone axis.) Only relevant portions of these great circles are shown in the figure.

As will be seen from the figure, all these great circles pass very close to a certain point M which we have marked by a small circle with a central dot. This indicates (1) that the crystal has an axis of approximate magnetic symmetry, namely along the normal to the plane which has M as its pole; this axis is found to make with the a, b and c axes of the crystal the angles 156°, 65° and 52°, respectively: (2) that the susceptibility of the crystal along the above axis is less than that along perpendicular directions; denoting the two susceptibilities by χ_{II} and $\chi_{\perp}$, respectively, χ_{II} should be less than $\chi_{\perp}$.

If the above conclusion regarding the approximate uniaxial symmetry of magnetism of the

crystal is correct, then the anisotropy $\Delta\chi$ for a given plane should be given by the relation

$$\Delta\chi = (\chi_\perp - \chi_{11})\sin^2\theta, \qquad (3)$$

where θ is the angle between the normal to the plane and the axis of symmetry; in other words, $\Delta\chi/\sin^2\theta$ should be nearly constant.

The value of θ corresponding to any given suspension can be directly read from the stereographic projection. The values entered in Table I were obtained in this manner. It will be seen from the last column of the table that except for suspension (8), for which θ is very small (16°), the values of $\Delta\chi/\sin^2\theta$ are near about 300×10^{-6}.

The variations of the individual values of $\Delta\chi/\sin^2\theta$ from the mean offer a rough estimate of the deviation from perfect axial magnetic symmetry. On close examination we find that the values of $\Delta\chi/\sin^2\theta$ are largest for the suspensions (2) and (5), and smallest for (3) and (4), which suggests that the direction of the greater of the two almost equal susceptibilities in the plane M is nearly perpendicular to the planes (3) and (4).

5. THE CRYSTALLINE FIELD AND ITS AXES

The above value for the magnetic anisotropy of $CuSO_4\cdot5H_2O$, namely $\chi_\perp - \chi_{11} = 300\times10^{-6}$ c.g.s. e.m.u. per gram molecule, points definitely to the existence of a rhombic component in the crystalline field, of nearly the same magnitude as in the Tutton salts of copper.

This small rhombic field is indeed to be expected from the disposition of the water molecules and the oxygens round the Cu^{++} ions in the crystal. From the x-ray analysis by Beevers and Lipson it is found that though each copper ion is at the center of an octohedron formed by four water molecules and two oxygens, the octohedron is only an approximate one; the four water molecules being much closer to Cu^{++} than the two oxygens. The crystalline field acting on Cu^{++}
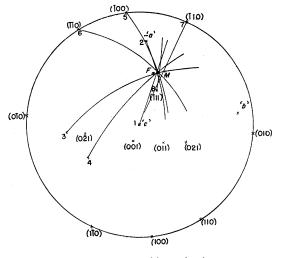

FIG. 1. Stereographic projection.

along directions in the plane of the water molecules, should therefore differ slightly from that along the normal to the plane of the water molecules.

There are two Cu^{++} ions in the unit cell, which we shall differentiate by the subscripts I and II. On calculating the orientations of the square of water molecules surrounding Cu_I and that surrounding Cu_{II}, from the parameters given by Beevers and Lipson, we find that the two squares are nearly perpendicular to each other (actually at 82°), and that they are both parallel to a direction F which makes with the a, b and c axes of the crystal the angles 155°, 68° and 50°, respectively. This direction F, as will be seen from the stereographic projection, is very close to the magnetic symmetry axis M, which is inclined at 156°, 65° and 52°, respectively, to the same crystallographic axes.

This coincidence of the magnetic and the crystalline field axes is significant; it points to the asymmetry of the crystalline field acting on the paramagnetic ion as the ultimate cause of the magnetic anisotropy of the crystal, as contemplated in Van Vleck's theory.