[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity and Magnetic Properties of Single Crystal Copper Sulfate Pentahydrate from 0.25 to 4°K.[1]

BY T. H. GEBALLE AND W. F. GIAUQUE

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Copper sulfate pentahydrate has been studied at temperatures down to 0.25°K. by adiabatic demagnetization. The sample was in the form of an ellipsoid of revolution, cut from a crystal, and with the major axis coincident with the direction of maximum susceptibility at higher temperatures. The vacuum apparatus was made of methyl methacrylate polymer. Measurements of heat capacity were made by direct energy input. The temperature was determined by means of the exact thermodynamic relationship between entropy and heat content. A carbon thermometer was used as a secondary temperature reference. The temperature change and differential magnetic susceptibility were measured as a function of magnetic field along constant entropy paths. The magnetic processes were shown to be highly reversible and there was no remanent magnetism. The intensity of magnetization, heat content and entropy have been determined as a function of magnetic field and temperature. It is shown experimentally that the magnetic system orients under the restraining influence of directional crystal forces thus causing changes in internal energy. The heat capacity joins well with data of Duyckaerts who covered the range above 2°K. The heat capacity curve has a maximum at 1.35°, a minor maximum at 0.75°, and shows evidence of a third maximum below 0.25°K. The entropy associated with the ^2S magnetic system should be R in 2 and one-half of this amount has been lost at 0.25°K. in zero field. The over-all shape and size of the heat capacity curve corresponds approximately to a Schottky curve for one-half mole of ^2S ions. Since the crystal structure analysis of Beevers and Lipson has shown that there are two different classes of copper ions in $CuSO_4 \cdot 5H_2O$ the above facts are taken to indicate that one-half of the ions lose the entropy associated with their ^2S states at near 1°K. whereas the other half retains its entropy to temperatures well below 0.25°K.

This paper reports thermodynamic and magnetic measurements on single crystal copper sulfate pentahydrate principally at temperatures below 4°K. The interpretation of magnetic data at very low temperatures is so difficult that it seemed desirable to avoid the use of randomly oriented small crystals. An ellipsoid of revolution was cut from a crystal and investigated in a homogeneous field directed along the major axis of the ellipsoid.

It was decided to have the major axis of the ellipsoid correspond to the direction of maximum susceptibility as found by Krishnan and Mookerji[2] between 90°K. and ordinary temperatures. Such a procedure would ordinarily be quite arbitrary since at very low temperatures energy levels can undergo alterations in their populations with temperature or magnetic field. However divalent copper has a single unbalanced spin and such a simple case has a good chance of maintaining nearly the same axis of maximum susceptibility to very low temperatures.

Beevers and Lipson[3] showed, by means of X-ray analysis, that two different kinds of cupric ion exist in equal proportions in the lattice. Each is surrounded by a group of six oxygen atoms, four from water molecules and two from sulfate groups. The spatial configuration of each group of oxygen atoms is similar, being roughly an octahedron elongated in the direction of the sulfate oxygens. The various distances involved in $CuSO_4 \cdot 5H_2O$, which is triclinic, have been calculated by Taylor and Klug.[4] The unique directions associated with each octahedral group, and hence with each ion, *i.e.*, the directions called Z_1 and Z_2 by Krishnan and Mookerji differ by 82°. Bagguley and Griffiths[5] have suggested on the basis of magnetic resonance measurements at ordinary temperatures that the angle is more nearly 90°. Krishnan and Mookerji[2b] have emphasized that the tetragonal symmetries are only approximate and Bagguley and Griffiths' analysis assumes that a portion of the contributing magnetic moment is fixed within the crystal. Without more detailed knowledge the 8° discrepancy cannot be taken very seriously, especially since the resonance work was not done at low temperatures.

Krishnan and Mookerji found that the direction of maximum magnetic susceptibility, their "gamma" axis, bisects the angle between Z_1 and Z_2. While differing values of the coefficient of expansion in different directions must make minor alterations in the direction of the maximum susceptibility at lower temperatures there is no reason to believe that there would be much change in direction until very low temperatures are reached.

Preparation of Copper Sulfate and the Crystal of Copper Sulfate Pentahydrate.—Copper sulfate was prepared by starting with material of low iron content and further purifying it by adding 0.02 g. of KOH per liter of nearly saturated solution. After two weeks it was filtered through a fiber glass filter with a pore diameter of 5 to 15 microns. The filtrate was refiltered after heating to 90° with evaporation until some $CuSO_4 \cdot 5H_2O$ crystallized in addition to a basic salt. The liquid was then cooled rapidly and the crystals freed of mother liquor by filtering under suction. 15.5 kilograms of salt as pentahydrate was prepared. Analysis showed 0.002 mole % iron, "Iron group" sulfides other than iron 0.001 mole %, alkali and alkaline earths were not detected. (The accuracy was 0.04% as K_2SO_4.) Two samples of clear sections of the crystal used for the experiments were dehydrated by heating to about 400° for 56 hours. The samples were weighed after 12 hours and after the completion of heating. No weight was lost after 12 hours. The losses in weight were 36.03 and 36.04%, respectively, compared to the theoretical 36.08% for $CuSO_4 \cdot 5H_2O$. A section of crystal which contained imperfections lost 36.21%.

The crystal used was grown from a seed which was rotated alternately clockwise and counter-clockwise through nearly 360° with eight reversals per minute. The 12 liters of copper sulfate solution was gradually cooled from 55.3 to 34.5° over a period of 35 days. The crystal weighed about 1400 g.

The sections of the crystal formed by the solid angle subtended by the opposing $\bar{1}11$ and $1\bar{1}\bar{1}$ faces at the crystal

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[1] This research was supported in part by the Office of Naval Research, U. S. Navy.

[2] K. S. Krishnan and A. Mookerji, *Phys. Rev.*, [a] **50**, 860 (1936); (b) *ibid.*, **54**, 533 (1938); (c) *ibid.*, **54**, 841 (1938).

[3] C. A. Beevers and H. Lipson, *Proc. Roy. Soc.* (*London*), **146**, 570 (1934).

[4] T. I. Taylor and H. P. Klug, *J. Chem. Phys.*, **4**, 601 (1936).

[5] D. M. S. Bagguley and J. H. E. Griffiths, *Proc. Roy. Soc.* (*London*), **A201**, 366 (1950).

center were optically diffuse, but the rest of the crystal was clear. The faces were essentially uniform planes and the angles agreed with those given by Groth[6] within the limits of accuracy of the Penfield contact goniometer used. It was evident that the substance was a single crystal.

Preparation of the Ellipsoid.—In order to cut the crystal with the major axis of the ellipsoid of revolution coincident with the axis of maximum susceptibility, it was necessary to find the relationship between the desired direction and the external geometry of the triclinic crystal. We are indebted to Professor A. Pabst of the Department of Mineralogy for the solution of this problem. He found that Krishnan and Mookerji's experimentally determined "gamma" axis is inclined 1°42′ from the $(\bar{1},1,1)$ face and its projection on that face makes an angle of 16°16′ with the $(\bar{1}11, \bar{1}10)$ edge of the crystal.

The crystal was given a thin protective coating of cellulose acetate cement, and cemented to a brass matrix with Albastone, a dental cement made by the S. S. White Dental Mfg. Co. The brass matrix was mounted on a Gorton 3-L pantograph machine. A brass ellipse of major axis 24 cm. and minor axis 5 cm. was used as a template and the machine set for a reduction of 2.2 to 1. A Norton W-154 mounted grinding wheel was used as a cutter. The stylus diameter had a ratio of 2.2 to 1 for the cutter diameter in order to reproduce the contour of the template properly. The finished ellipsoid measured 10.87 cm. in length and 2.26 cm. in diameter. The major axis corresponded to the axis of maximum susceptibility within one or two degrees.

After the machining several small cracks were apparent and there were a few places where minor chipping had occurred. It is quite probable that the cracking was caused by the small amount of heat developed in the dental cement, which should have been applied as a number of thin coats. The density of a clear crystal of $CuSO_4 \cdot 5H_2O$ was measured and found to be 2.279 g. cm.$^{-3}$ at 24.3°. The actual weight of the ellipsoid was 66.233 g. *in vacuo* when it was placed in the calorimeter. The difference between the observed and calculated weights was probably due to the original inclusion of solution in the diffuse region. The excess water in this solution probably evaporated through the imperfections which appeared to be long thin channels. There was no evidence of any remaining solution inclusion when the diffuse region was cut during the machining. The volume of the ellipsoid was measured by weighing in air and kerosene and found to be 29.34 cc. instead of the 29.20 cc. calculated from the dimensions. The voids should have little effect on the results since all calculations are based on the amount present. This corresponds to 0.2653 mole using a molecular weight of 249.69.

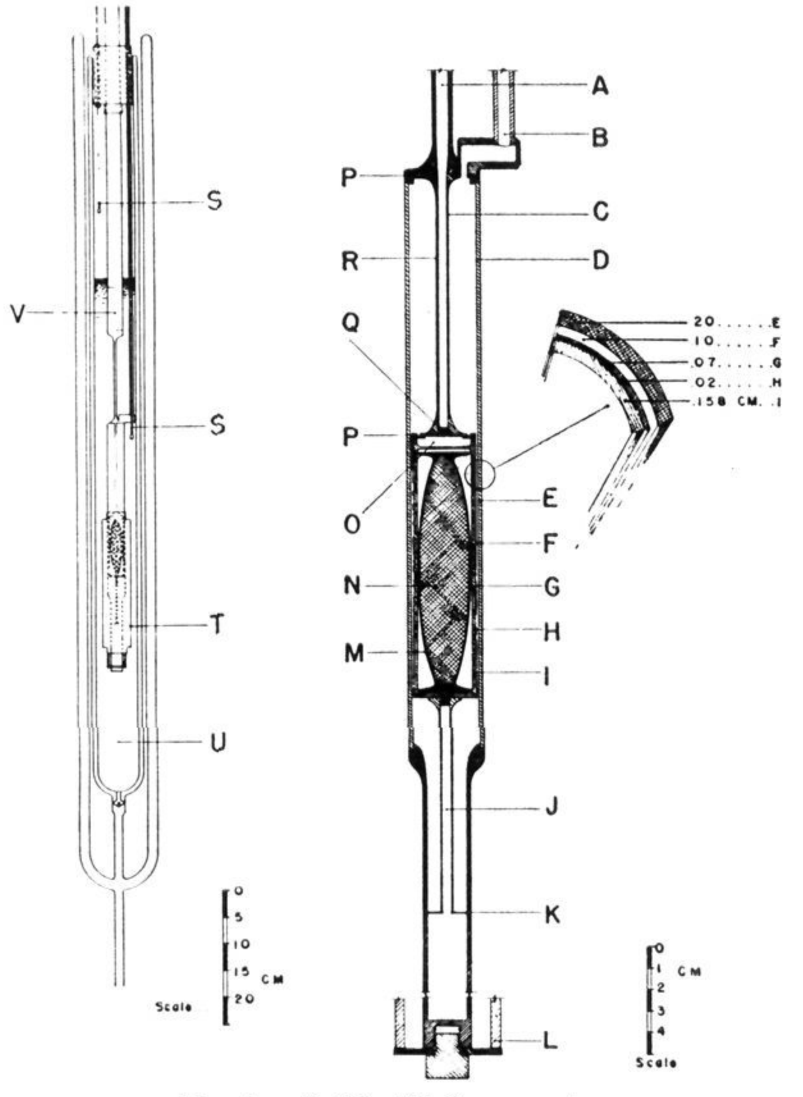

Fig. 1.—$CuSO_4 \cdot 5H_2O$ apparatus.

Another effect which enters to disturb the perfection of an ellipsoid cut at ordinary temperatures is due to unequal contraction with temperature along the several crystal axes. A preliminary attempt to measure the coefficient of expansion in several directions failed due to too rapid cooling. This cracked the crystals used in these experiments except one which was a long thin section in the direction of the *c*-axis. In this case $(1/L)\mathrm{d}L/\mathrm{d}T$ averaged less than 10^{-6} deg.$^{-1}$ over the range 77 to 290°K. The effect of temperature distortion of the ellipsoid should be very small in any case and the measurements were discontinued.

Apparatus and Methods of Measurement.—The apparatus was somewhat similar to that described by Fritz and Giauque,[7] and by Lyon and Giauque[8] except that it was made of methyl methacrylate plastic (Plexiglas) instead of Pyrex glass. The various problems such as vacuum tightness, sealing of electrical leads, etc., connected with the use of plastic apparatus at low temperatures have been discussed by Giauque, Geballe, Lyon and Fritz.[9] A carbon thermometer of the type described by Giauque, Stout and Clark[10] was used as an intermediate reference. A more recent and general discussion of the use of carbon blacks for this purpose, including "Molacco Black" which was used in this research, has been given by Geballe, Lyon, Whelan and Giauque.[11]

The magnetic susceptibility was measured by means of a fluxmeter described by Giauque, Fritz and Lyon.[12]

The apparatus is shown in Fig. 1. All parts were machined from 1.5-in. rods of methyl methacrylate polymer. A and B are tubes leading to high vacuum systems. C is a thin walled vacuum line supporting the sample tube. O is a 1.9-cc. chamber in which helium can be liquefied and pumped through a hole, Q, 0.061 cm. in diameter for cooling below bath temperature in the liquid helium II range. J is a thin tube and K a six-pointed support of low heat conductivity for centering the sample tube. L shows three legs for supporting and centering the fluxmeter coils shown at T. D indicates the vacuum jacket. Electrical leads pass through the plastic at points P and P, and were fastened along the side of the tube C as indicated at R. The carbon thermometer was placed in a milled groove 2 cm. wide on the sample case jacket I and covered by a vacuum tight cover G. F shows the insulating vacuum space and E its enclosing wall. N shows the ellipsoidal sample and M two thin walled half ellipsoidal shells which were designed to keep the crystal aligned in case it cracked during cooling. Fortunately this did not occur. The 16-cc. gas space within the sample tube was filled to 1 atmosphere at 295°K. with a mixture of nitrogen and 1.8 cm. pressure of helium. S,S are liquid helium vapor pressure thermometers, U the liquid helium or hydrogen bath and V a large diameter vacuum line brought close to the apparatus. The total weight of Plexiglas in thermal contact with the crystal was 42.1 g.

The electrical leads were made from Leeds and Northrup No. 1106 galvanometer suspension ribbon made of 14 k. gold. Where these leads were brought into contact with the carbon thermometer they were beaten out until they were about 0.0008 cm. thick and 0.05 cm. wide. The contact area was 0.15 cm.^{2} per lead.

The solenoid magnet used has been described by Giauque and MacDougall.[13]

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(6) P. H. Groth, "Chemische Krystallographie," Vol. 2, W. Englemann, Leipzig, 1908, p. 419.

(7) J. J. Fritz and W. F. Giauque, THIS JOURNAL, **71**, 2168 (1949).

(8) D. N. Lyon and W. F. Giauque, *ibid.*, **71**, 1647 (1949).

(9) W. F. Giauque, T. H. Geballe, D. N. Lyon and J. J. Fritz, *Rev. Sci. Instruments*, **23**, 169 (1952).

(10) W. F. Giauque, J. W. Stout and C. W. Clark, THIS JOURNAL, **60**, 1053 (1938).

(11) T. H. Geballe, D. N. Lyon, J. M. Whelan and W. F. Giauque, to be published.

(12) W. F. Giauque, J. J. Fritz and D. N. Lyon, THIS JOURNAL, **71**, 1657 (1949).

(13) W. F. Giauque and D. P. MacDougall, *ibid.*, **57**, 1175 (1935).

The fluxmeter coils were calibrated with the coils and the vacuum jacket of the sample tube immersed in liquid helium but with the sample held at 50°K. where its susceptibility involved the application of only a small correction.

Temperature Scale.—The carbon thermometer was calibrated in terms of vapor pressures of helium and hydrogen, and below 1°K., by means of the thermodynamic equation

$$T = \left(\frac{\partial H}{\partial S}\right)_{\mathrm{H}} \qquad (1)$$

and data to be described below. H = heat content, S = entropy and H = magnetic field strength. Between 4.4 and 1.6°K. the data of Schmidt and Keesom,[14] and from 1.6 to 0.9°K. the data of Bleaney and Simon[15] were used.

The equation of Martinez and Onnes[16] was used for liquid hydrogen, and that of Giauque, Johnston and Kelley[17] was used for solid hydrogen.

The function

$$(T/\mathrm{H})^2\ \Delta\mathrm{R}/\mathrm{R}_{\mathrm{H}=0} \qquad (2)$$

where $\mathrm{R}_{\mathrm{H}=0}$ is the resistance in zero magnetic field and $\Delta\mathrm{R} = \mathrm{R}_{\mathrm{H}} - \mathrm{R}_{\mathrm{H}=0}$, at temperature T, used by Fritz and Giauque[7] was again found to be a slowly varying function of temperature. It was used for extrapolating the effect of magnetic field on resistance below 1°K. by assuming that the function became zero at 0°K. It is estimated that the maximum error involved in this extrapolation would not exceed 0.001° and that this would occur near 0.8°K. The thermometer characteristics are given in Table I.

TABLE I

EFFECT OF MAGNETIC FIELD ON CARBON THERMOMETER

T, °K.	R, ohms	H, oersteds	ΔR, ohms	$(T/\mathrm{H})^2/(\Delta\mathrm{R}/\mathrm{R}_{\mathrm{H}=0}) \times 10^{10}$
20.32	47800	8816	2.3	2.4
13.92	50916	8815	9	3
4.211	66633	2351	4.8	2.3
		6089	35.5	2.55
		6807	43.8	2.52
		8489	71.8	2.55
1.166	131509	2441	109	1.89
		5959	668	1.94
		6857	862	1.87
		8620	1254	1.74

TABLE II

TEMPERATURE SCALE BELOW 1°K.

T, °K.	R, ohms	$-\mathrm{d}R/\mathrm{d}T$ ohm deg.$^{-1}$
1.076	140000	109000
0.849	170000	182000
.649	240000	550000
.456	425000	1108000
.235	800000	3850000

It would have been more convenient and more accurate had the temperature coefficient of resistance been much smaller numerically. This can easily be done by using a carbon black of larger particle size.[11] Molacco Black has an average diameter of 8×10^{-6} cm. The high resistance in the present case made insulation of considerable importance. The insulation was better than 10^9 ohms between parallel wires and between wiring and ground. The numerically large temperature coefficient of this thermometer may not be typical of Molacco Black. Another Molacco thermometer on Plexiglas had approximately the same characteristics as a Molacco thermometer on glass[11] which has been designated "Thermometer W and G." It is possible that the thermometer was affected by the plastic cement used to cement the ends of the cover, G, Fig. 1. The solvent vapor had access to the thermometer.

The Initial Molal Magnetic Susceptibility.—The turn area of the fluxmeter coils in liquid helium was determined by having the sample at 50°K. at the start of the experiment and 27°K. at the end. The corrections for the presence of the sample at these temperatures was made by extrapolating the equation of Krishnan and Mookerji[2c]

$$\chi_{\mathrm{molal}} = \frac{0.486}{T + 1.8} \qquad (3)$$

The two results agreed to 0.01%. Since the determination of susceptibility depends on the difference between an observation and the above determination, the 0.01% can make a considerable error in the case of a substance with a small magnetic moment. An error of 0.01% leads to an uncertainty of 1.1% in the susceptibility at 1.2°K. and 3% at 4.2°K. in the case of cupric ion. The data are given in Table III. The observations marked with asterisks were made with helium in the insulating vacuum space during temperature calibrations. The others were made with the sample isolated by a vacuum.

TABLE III

THE INITIAL MOLAL MAGNETIC SUSCEPTIBILITY OF $\mathrm{CuSO_4 \cdot 5H_2O}$

T, °K.	χ_M	$\chi_M T$	T, °K.	χ_M	$\chi_M T$
0.222	1.332	0.296	2.523*	0.147	0.371
.270	1.032	.279	2.709	.138	.374
.278	0.962	.268	2.920*	.130	.380
.307	.886	.272	3.502*	.113	.396
.543	.580	.315	3.787	.106	.401
.564	.554	.312	4.211*	.0966	.407
.575	.538	.309	4.221*	.0962	.406
.701	.418	.293	5.01	.083	.42
.849	.342	.290	5.26	.080	.42
1.091	.280	.305	6.70	.064	.43
1.103	.278	.307	8.05	.055	.44
1.158*	.269	.312	8.13	.055	.45
1.162*	.269	.313	8.85*	.052	.46
1.166*	.266	.310	9.26	.050	.46
1.332	.238	.317	10.33	.046	.47
1.408*	.230	.324	11.19	.043	.48
1.630	.202	.333	12.55	.040	.50
1.688*	.200	.338	13.84	.035	.48
1.844*	.187	.345	13.92*	.033	.46

The data are illustrated in Fig. 2 which shows the decrease in the Curie product, χT, in the liquid helium region.

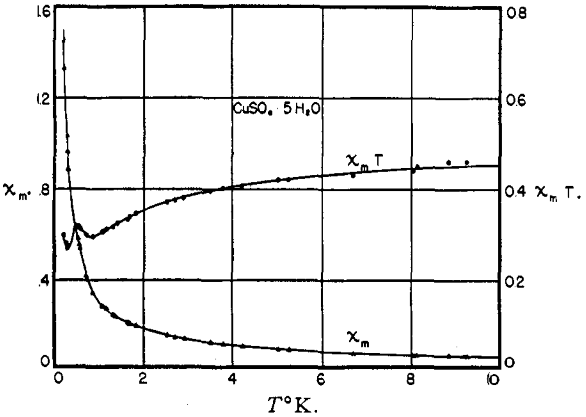

Fig. 2.—Initial susceptibility of $\mathrm{CuSO_4 \cdot 5H_2O}$

The Adiabatic Differential Susceptibility.—The adiabatic differential susceptibility, $(\partial \mathrm{I}/\partial \mathrm{H})_S$, was measured with a low temperature fluxmeter as described previously.[12] In all cases the measurements were taken in the order of increasing fields to minimize the effect of heat leak. The re-

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[14] G. Schmidt and W. H. Keesom, *Comm. Phys. Lab. Univ. of Leiden*, No. 250 (1937).

[15] B. Bleaney and F. E. Simon, *Trans. Faraday Soc.*, **35**, 1205 (1939).

[16] J. P. Martinez and H. Kamerlingh Onnes, *Comm. Phys. Lab., Univ. of Leiden*, No. 156b (1922).

[17] W. F. Giauque, H. L. Johnston and K. K. Kelley, THIS JOURNAL, **49**, 2367 (1927).

TABLE IV

CONSTANT ENTROPY VALUES OF DIFFERENTIAL SUSCEPTIBILITY, MOLAL MAGNETIZATION, MOLAL HEAT CONTENT AND TEMPERATURE AS FUNCTIONS OF MAGNETIC FIELD

S = cal. deg.$^{-1}$ mole^{-1}, H = cal. mole^{-1}

	$H = 0_{(\text{start})}$	$H = 408$;	$H = 1000$;	$H = 2400$;	$H = 6200$;	$H = 8500$;	$H = 0_{(\text{end})}$
Isentrope $S - S_{1°\text{K.}} = -0.254$							
$(\partial/I\partial H)_S$	1.332	0.950	0.540	0.265	0.140	0.124	
I	0	...	870	1384	2112	2425	
$H - H_{1°\text{K.}}$	−0.157	...	−0.168	−0.210	−0.369	−0.494	
T, °K.	0.222	...	0.292	0.497	0.737	0.852	0.232
Isentrope $S - S_{1°\text{K.}} = -0.225$							
$(\partial I/\partial H)_S$	0.930	0.820	0.529	0.280	0.140	0.124	
I	0	...	754	1273	2012	2326	
$H - H_{1°\text{K.}}$	−0.149	...	−0.159	−0.194	−0.346	−0.466	
T, °K.	0.286	...	0.366	0.560	0.777	0.902	0.296
Isentrope $S - S_{1°\text{K.}} = -0.155$							
$(\partial I/\partial H)_S$	0.554	0.524	0.449	0.305	0.170	0.140	
I	0	...	512	1030	1881	2232	
$H - H_{1°\text{K.}}$	−0.118	...	−0.125	−0.151	−0.287	−0.400	
T, °K.	0.564	...	0.595	0.664	0.897	1.038	0.576
Isentrope $S - S_{1°\text{K.}} = -0.101$							
$(\partial I/\partial H)_S$	0.418	0.412	0.383	0.304	0.175	0.144	
I	0	...	407	885	1759	2119	
$H - H_{1°\text{K.}}$	−0.0838	...	−0.0888	−0.110	−0.235	−0.341	
T, °K.	0.700	...	0.718	0.769	1.016	1.140	0.707
Isentrope $S - S_{1°\text{K.}} = -0.0434$							
$(\partial I/\partial H)_S$	0.342	...	0.324	0.280	0.175	0.144	
I	0	...	334	737	1611	1972	
$H - H_{1°\text{K.}}$	−0.0406	...	−0.0444	−0.0620	−0.173	−0.271	
T, °K.	0.849	...	0.862	0.918	1.138	1.259	0.850
Isentrope $S - S_{1°\text{K.}} = +0.0251$							
$(\partial I/\partial H)_S$	0.280	...	0.274	0.248	0.174	0.144	
I	0	...	278	643	1448	1811	
$H - H_{1°\text{K.}}$	+0.0263	...	+0.0230	+0.0076	−0.0898	−0.180	
T, °K.	1.090	...	1.098	1.137	1.306	1.430	1.089
Isentrope $S - S_{1°\text{K.}} = +0.160$							
$(\partial I/\partial H)_S$	0.205	...	0.204	0.198	0.160	0.140	
I	0	...	205	485	1169	1512	
$H - H_{1°\text{K.}}$	+0.231	...	+0.229	+0.217	+0.141	+ 0.067	
T, °K.	1.603	...	1.611	1.629	1.779	1.901	1.586
Isentrope $S - S_{1°\text{K.}} = +0.245$							
$(\partial I/\partial H)_S$	0.168	...	0.168	0.166	0.136	0.120	
I	0	...	168	400	986	1276	
$H - H_{1°\text{K.}}$	0.391	...	0.389	0.380	0.304	0.253	
T, °K.	2.092	...	2.099	2.123	2.276	2.407	2.080

sults at high fields are relatively insensitive to changes in energy content. The results are given in Table IV.

It will be noticed that the final temperatures in the first five series are slightly higher than the initial temperatures by small amounts showing that the entropy was nearly but not quite constant during the series. The bath temperature was above the sample temperature during almost all of these measurements. In the last three series the final temperatures are slightly lower than the initial temperatures because the sample was above the bath temperature. It may be seen by noting the slow rate of change of $(\partial I/\partial H)_S$ with temperature at high fields that the change in entropy which occurs before the last measurements are made leads to trivial error, as discussed by Giauque and MacDougall.[18]

Thermometer observations along an adiabatic curve could have been made intermittently with the adiabatic differential susceptibility measurements; however, this was not done because the time required, though short, would have allowed a small additional heat leak. When taken in sequence the temperature measurements require considerably less time than the susceptibility observations. The temperature was measured along almost the same adiabatic paths used for susceptibility determinations and a small correction was applied.

When measurements of $(\partial I/\partial H)_S$ are made with the fluxmeter used here, or by some alternating current method, the entropy, S, in the expression applies to the substance, and perhaps for exactness we should say it applies to the portion of the magnetic system that responds during the time allowed. If the calorimetric vessel has heat capacity it will not be in equilibrium during a measurement and, when the field is increased rapidly, there will be an irreversible flow of heat between the substance and the calorimeter with a consequent increase in the entropy of the system. Even if the field were increased slowly enough to keep the change reversible, any increase in entropy of the container must result in a decrease in the entropy of the substance.

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(18) W. F. Giauque and D. P. MacDougall, THIS JOURNAL, **60**, 376 (1938).

Fortunately the sample container used here had a negligible heat capacity below a few degrees absolute. Evidence of reversibility, to be discussed below, shows that the above adiabatics may be taken as at constant entropy.

Calculation of the Thermodynamic Temperature.—The data are sufficient to determine the temperature on the Kelvin absolute scale without any extra thermodynamic assumptions.

$$T = (\partial H/\partial S)_{\mathbf{H}} \qquad (1)$$

where

$$H = E - \mathbf{HI} \qquad (4)$$

and H represents the heat content.

$$\mathbf{I} = \int_0^{\mathbf{H}} \left(\frac{\partial \mathbf{I}}{\partial \mathbf{H}}\right)_S \mathrm{d}\mathbf{H} \qquad (5)$$

and for magnetization at constant entropy

$$\int_0^{\mathbf{H}} \mathrm{d}H = -\int_0^{\mathbf{H}} \mathbf{I}\,\mathrm{d}\mathbf{H} = -\int_0^{\mathbf{H}}\int_0^{\mathbf{H}} \left(\frac{\partial \mathbf{I}}{\partial \mathbf{H}}\right)_S \mathrm{d}\mathbf{H}\,\mathrm{d}\mathbf{H} \qquad (6)$$

When $\mathbf{H} = 0$, $H = E$ and the difference in heat content between the several isentropes at $\mathbf{H} = 0$ was found by direct calorimetric energy input. The resistance of the uncalibrated carbon thermometer was used as a reference for the variation of energy content. An arbitrary reference point was used for heat content and the values computed at all points along the several isentropes.

The above calculation for I requires a determination of remanent magnetism, if any, since this quantity would appear as a lower limit. As will be shown below, there was no remanent magnetism.

The calculation also requires that evidence be obtained to show that the measurements of adiabatic differential susceptibility are actually reversible, *i.e.*, that the adiabatic curves are also isentropes. Evidence for reversibility will be presented below.

The change in entropy between the members of the family of isentropic curves was calculated from the equation

$$\Delta S = \int \frac{1}{T}\,\mathrm{d}H \qquad (7)$$

which must be applied at constant magnetic field.

Since absolute values of $1/T$ are required the first stages of the calculation were confined to the region above 1°K. where the temperatures were known. After the temperatures were extended somewhat below 1°K. by using the isentropes at higher temperatures in combination with equation 1, so that all the isentropic curves could be connected, the temperatures at all points on isentropes were computed.

The data for eight isentropes are summarized in Table IV which has been given above.

The Energy Change Which Accompanies Magnetization.—When an ideal paramagnetic substance is magnetized at constant temperature, all of the magnetic work done during the process is evolved as heat. There is no change in internal energy. There is, of course, a very small energy increase due to the diamagnetic component which is associated with any system of charged particles but at low temperatures this may be ignored in comparison with paramagnetic effects.

If there is interaction of any sort between the magnetic ions or between these ions and the electric fields of adjacent water or other molecules or ions an energy change can be expected to accompany isothermal magnetization. The thermodynamic equation

$$T\mathrm{d}S = \mathrm{d}E - \mathbf{H}\mathrm{d}\mathbf{I} \qquad (8)$$

leads to the result

$$\left(\frac{\partial E}{\partial \mathbf{I}}\right)_T = -T^2\left(\frac{\partial \mathbf{H}/T}{\partial T}\right)_{\mathbf{I}} \qquad (9)$$

In the ideal case $(\partial E/\partial \mathbf{I})_T = 0$ and $\mathbf{H}/T$ has a definite value corresponding to each value of I regardless of the conditions under which I has been produced.

Values of I along the isentropic curves are plotted against $\mathbf{H}/T$ in Fig. 3, which also includes a calculated curve for the case of one electron "spin" free of all lattice restraint as it orients in the magnetic field.

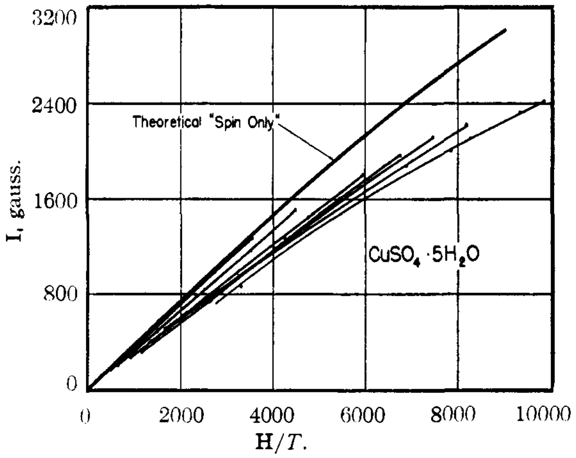

Fig. 3.—Intensity of magnetization of $CuSO_4 \cdot 5H_2O$. Points are on isentropes.

It is evident from Fig. 3 that the cupric ions in $CuSO_4 \cdot 5H_2O$ are subject to directing influences of internal forces associated with the crystal structure. Since the isentropes at lower values of temperature lie toward the right, it is evident that $(\partial E/\partial \mathbf{I})_T$ is positive as would be expected if the magnetic field is required to orient the magnetons against a restraining force.

Values of ΔE for isentropic magnetization may be calculated by means of the equation

$$\Delta E = \int_0^{\mathbf{H}} \mathbf{H}(\partial \mathbf{I}/\partial \mathbf{H})_S\,\mathrm{d}\mathbf{H} \qquad (10)$$

and these values combined with the calorimetric energy differences between the isentropes at zero field will permit the evaluation of ΔE for isothermal magnetization. An alternative, and preferable method in the present case, is to use the data in Table IV with the equation

$$\Delta E = H_{\mathbf{H}} + \mathbf{HI}_{\mathbf{H}} - H_{\mathbf{H}=0} \qquad (11)$$

Reversibility of the Magnetic Measurements.—The thermodynamic equations used above assume that the magnetic measurements combined with them are reversible. There are two kinds of evidence which indicate that the measurements were made slowly enough to be equilibrium values.

A 60-cycle current of 243 root mean square oersteds was imposed on the magnet for ten minutes when the sample had initial temperatures of 0.24 and 0.41°K. in zero field. At the maximum of each sine wave the substance has received the energy $\Delta E = \chi H^2_{\max}/2 = \chi H^2_{\text{rms}}$. This has assumed that χ is constant in small fields. The total exchange over ten minutes is $\Delta E = 36000 \times 2\chi H^2_{\text{rms}}$ = 122 cal. mole^{-1} at 0.24° and 73 cal. mole^{-1} at 0.41°. When the current was turned off it was found that the crystal had retained 2.3 × 10^{-4} cal. mole^{-1} or about 2 parts in a million at 0.24°K. The experiment at 0.41°K. gave an energy dissipation of 5 parts in a million.

It has been pointed out previously[12] that the readings on a fluxmeter of the type used here can be used to detect irreversibility. Any serious lag in the building up of induction in the sample would be noted on the sensitive galvanometer used in the null point balance, since timing as well as magnitude of the balancing effects is essential. This method would not show up a completely irreversible component of the magnetic system but such a condition could hardly be attained at very low temperatures without detection of its intermediate stages at higher temperatures.

No Remanent Magnetism.—In addition to the above observations the sample was warmed from 0.25 to 1.45°K. in a small residual field of about 2.0 oersteds, over a period of 10 minutes, with a sensitive galvanometer connected to the coils about the sample. This method[18] showed a small e.m.f. in the coil consistent with the change in the initial susceptibility. There was no evidence of remanent magnetic moment. The accuracy was about 0.05% of the moment which existed prior to demagnetization. The same arrangement was used to observe the sample for several minutes after demagnetization from a full field to 0.22°K. No e.m.f. was generated in the coil.

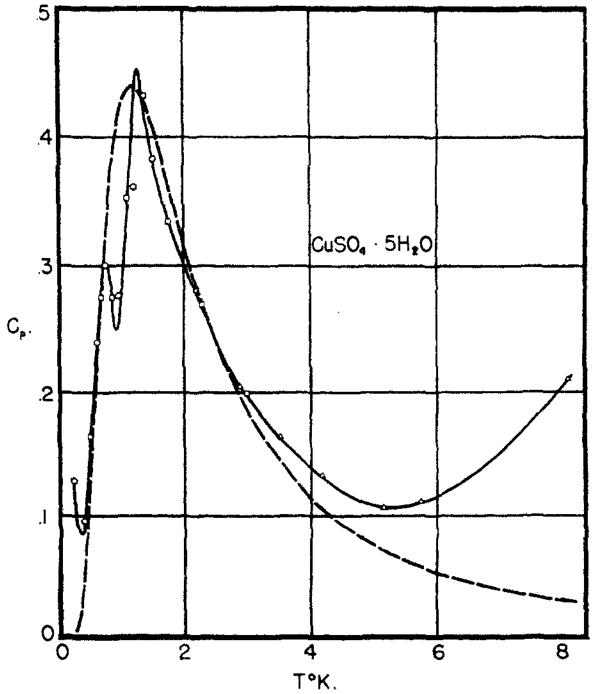

Fig. 4.—Heat capacity of $CuSO_4 \cdot 5H_2O$ in calories per mole per degree: O, series I; □, series II; Δ, Duyckaerts; — - — — —, theoretical Schottky function.

The Heat Capacity of $CuSO_4 \cdot 5H_2O$.—The heat capacity was measured in the ordinary manner. However, it was necessary to record dH/dR until the absolute temperature could be determined. Before the first series of measurements helium gas was pumped from the insulating vacuum space at 1.17°K. When heat capacity measurements above 2°K. were made after demagnetization, it was evident from the heat leak that conducting helium gas was present, presumably due to deadsorption above the cleanup temperature even though the McLeod gage indicated a pressure of 10^{-6} mm. or less. Thus all results above 1.5°K. in series 1 were discarded.

Before series 2 the helium gas was pumped out at 4.2°K. and subsequent cooling before demagnetization was accomplished by condensing liquid helium in the small chamber, O, Fig. 1, at the top of the sample tube. The results of series 2 were discarded above 4°K. because they could not be accepted as reliable above the temperature at which helium had been pumped from the insulating vacuum space.

The data are given in Table V and are shown in Fig. 4 along with the results of Duyckaerts.[19]

TABLE V

HEAT CAPACITY OF $CuSO_4 \cdot 5H_2O$, CAL. DEG.$^{-1}$ MOLE^{-1}

	Series 1			Series 2	
T, °K.	ΔT	C	T, °K.	ΔT	C
0.243	0.025	0.128	0.535	0.122	0.164
.436	.214	.097	.689	.152	.276
.630	.102	.240	.876	.200	.276
.764	.092	.302	1.101	.232	.353
.975	.222	.277	1.378	.314	.432
1.221	.236	.362	1.763	.467	.334
1.510	.353	.383	2.297	.628	.270
			2.997	.864	.199

The results join well with those of Duyckaerts who covered the range 2 to 20°K. Duyckaerts' results are also in fair agreement with unpublished results of Stout[20] whose measurements at higher temperatures extend down to 14°K.

The outstanding features of the heat capacity curve, as shown in Fig. 4, are a pronounced maximum near 1.37°K., a small maximum at 0.75°K., a low minimum near 0.4°K., and the beginning of a rise which must lead to another maximum well below 0.25°K.

Ashmead[21] demagnetized $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot K_2SO_4 \cdot 6H_2O$ from a field of 35,000 oersteds and measured warming curves to 1°K. for each salt. The experiment gives results proportional to heat capacity on a curie temperature scale. His curve for $CuSO_4 \cdot 5H_2O$ shows a decrease from 1°K. to a minimum near 0.3° curie, it rises steeply in the region below 0.25° curie, and becomes very steep near 0.1° curie. Ashmead's curve for $CuSO_4 \cdot K_2SO_4 \cdot 6H_2O$ is near zero at 1°K., rises very slowly until the region below 0.25° curie where it eventually develops into a very steep rise at about 0.05° curie. Ashmead has commented on the great difference

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(19) G. Duyckaerts, *Societe Royal des Sciences de Liege*, **10**, 284 (1941).

(20) J. W. Stout, personal communication.

(21) J. Ashmead, *Nature*, **143**, 853 (1939).

in the characteristics of the two salts since the ^2S state in each one would be expected to behave very similarly except for a minor difference due to the greater concentration of copper ions in the copper sulfate pentahydrate.

In the preliminary treatment of our data we attempted to eliminate the small maximum near 0.75°K. as due to some sort of error but this proved to be impossible. An attempt to draw a simple curve through the points near 0.75°K. made it impossible to make calculations which were consistent with constant entropy differences between the several isentropes.

The most important characteristic of the main curve is that it agrees surprisingly well with a Schottky curve for two states

$$C = \frac{Rx^2}{(e^{x/2} + e^{-x/2})}$$

where $x = \epsilon/kT$, except that it corresponds to one-half mole of ions per mole of $CuSO_4 \cdot 5H_2O$. The theoretical heat capacity maximum for this case is 0.44 cal. deg.$^{-1}$ (half-mole)$^{-1}$, whereas the observed maximum is about 0.45 cal. deg.$^{-1}$ mole^{-1} of $CuSO_4 \cdot 5H_2O$. The agreement on the high temperature side is quite good although the experimental curve is slightly more concave than the theoretical one just below the maximum. On the low temperature side the theoretical curve passes through the middle of the small maximum and drops to a very low value near the minimum in the heat capacity curve near 0.4°K.

The total entropy decrease under the experimental curve is especially significant.

The amount of entropy lost by the magnetic system in the region above 4°K. is only 0.07 cal. deg.$^{-1}$ mole^{-1}, assuming the dotted Schottky curve shown in Fig. 4. When the Schottky curve is subtracted from the results of Duyckaerts the difference is approximately proportional to T^3 as might be expected for the lattice energy. The total entropy due to lattice vibrations below 4°K. is less than 0.01 cal. deg.$^{-1}$ mole^{-1}. The amount of entropy removed from the magnetic system down to 0.40°K. is 0.64 cal. deg.$^{-1}$ mole^{-1} of copper sulfate pentahydrate and 0.70 cal. deg.$^{-1}$ mole^{-1} at 0.22°K., the lowest temperature reached during the present measurements. The theoretical amount for one-half mole of copper ions in a ^2S state is $R/2 \ln 2 = 0.69$ cal. deg.$^{-1}$.

Since Beevers and Lipson[3] have shown that alternate copper ions have different environments in $CuSO_4 \cdot 5H_2O$ the above facts suggest that the environment of one type makes it behave like the copper ions in $CuSO_4 \cdot K_2SO_4 \cdot 6H_2O$, whereas the other type is split into levels which are about 2 cm.$^{-1}$ apart in zero magnetic field.

If the unsymmetrically placed atoms surrounding each copper ion had a unidirectional influence, the crystal should have a magnetic moment corresponding to the lining up of the magnetic moments of one-half the copper ions at the lower temperatures. This is not the case since, as mentioned above, there is no residual magnetic moment.

The fact that the heat capacity curve is close to the Schottky type would indicate that there is not much interaction between adjacent copper ions and if this were to be assumed it would be necessary to assume that the copper ions with the energy splitting environment have directing influences which are ordered mirror images in equal proportions, to eliminate residual magnetic moment and satisfy the entropy change. The alternative, and probably most acceptable, explanation is to assume some unknown exchange effect which couples the ions into anti-ferromagnetic domains in such a way as to produce only minor alterations in an ideal Schottky curve. The experimental curve is somewhat narrower and the maximum is slightly higher than the ideal Schottky curve. These are characteristics of coöperative phenomena but the deviation is usually much more pronounced. The small maximum at 0.75° is a type of fine structure which requires something more than a simple Schottky picture for the over-all process. A careful examination of Ashmead's curve discloses a small maximum at 0.75°K. It is much less pronounced than the one in the present work as would be expected since such details become blurred by a warming rate technique.

The fact that energy dissipation was only a few parts in a million for magnetization with a 60-cycle field of 243 r.m.s. oersteds at 0.24°K. proves that the magnetization process is one of the most reversible we have found. This indicates that the ions are acting in a simple manner under the influence of the field. Their actions are either of a nearly individual nature or their orientations do not require complex reorganizations of any groupings or extensive domains which may exist.

We thank Drs. D. N. Lyon, J. M. Whelan, R. H. Busey and J. E. Kunzler for assistance with the experimental measurements. The coöperation of the above group during week-long periods of continuous experiment made this investigation possible. We also thank Professor A. Pabst of the Department of Mineralogy for calculating the relationship between the direction of maximum susceptibility and the exterior crystal faces.

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