

MAGNETIC ANISOTROPY OF SINGLE-CRYSTAL CuSO_4 IN THE ANTIFERROMAGNETIC STATE

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The magnetic anisotropy of a single crystal of anhydrous copper sulfate has been measured between 1.5° and 300°K. The transition to the antiferromagnetic state has been found to be accompanied by an anomalous growth of χ_{\perp} , while the parallel susceptibility varied in the usual way. A quadratic temperature dependence has been established for χ_{\parallel} . A possible magnetic structure of CuSO_4 is discussed.

1. INTRODUCTION

THE magnetic susceptibility of anhydrous copper sulfate was first measured, down to hydrogen temperatures, by Gorter and de Haas in 1931.¹ They performed the measurements on a polycrystalline specimen at nitrogen and hydrogen bath temperatures. They found that at nitrogen temperatures and above, the Curie-Weiss law $\chi = c/(T - \Theta)$ holds, with $\Theta = -77.5^\circ$. At hydrogen temperatures, the value of the susceptibility is considerably greater than that calculated by the Curie-Weiss law and is independent of the temperature. In 1941 Stout² observed in anhydrous copper sulfate at $T = 34.8^\circ\text{K}$, a heat-capacity anomaly characteristic of a second-order phase transition. The data indicated above, together with our magnetic investigations³ of a group of anhydrous sulfates of Ni^{++} , Cl^{++} , Fe^{++} , and Cu^{++} , suggest that the anhydrous copper sulfate, like the other foregoing compounds, is antiferromagnetic.

The temperature dependence of the magnetic susceptibility of a polycrystalline specimen of CuSO_4 , which we have obtained in a previous investigation,⁴ show that at $T = 34.5^\circ\text{K}$ this substance experiences a transition and apparently becomes antiferromagnetic below this temperature. The transition itself is unusual and is distinguished by an anomalously rapid growth of the susceptibility near $T = 34.5^\circ\text{K}$. To explain the character of the observed anomaly and to investigate in greater detail the behavior of the susceptibility below the temperature of this anomaly, we have undertaken to measure of the temperature dependence of the susceptibility in a single crystal CuSO_4 . The results are reported in this paper.

2. APPARATUS AND SPECIMENS

The magnetic susceptibility was measured by the Faraday method with apparatus analogous to that previously described.⁵ This apparatus made it possible to cover without a broad continuous band of temperatures from 1.3 to 300°K. The temperature was measured in the 1.3 to 4.2°K range by determining the vapor pressure of a helium bath, from 4.2 to 20°K by determining the resistance of a carbon thermometer, and from 20 to 300°K by determining the resistance of a copper thermometer calibrated with a standard platinum resistance thermometer.⁶ The carbon thermometer was calibrated by the Clement and Quinell method.⁷

The susceptibility was measured at several magnetic field intensities between 12.5 and 13.5 kilooersteds. The susceptibility was measured in various directions in a plane perpendicular to the line of suspension of the specimen. The error in the absolute value of the susceptibility did not exceed $\pm 1 \times 10^{-4}$ per mole; the relative error did not exceed 2 to 6% in the various temperature ranges. The relative errors were somewhat higher than in previous investigations, owing to the smallness of the specimens. A correction was introduced for the diamagnetism of the SO_4^{--} ion.⁸ Single-crystal specimens of anhydrous copper sulfate were used in the investigations. These specimens were obtained* from a solution of cuprous oxide in molten ammonia sulfate.⁹ The $(\text{NH}_4)_2\text{SO}_4$ decomposes, above 360°C and the anhydrous copper sulfate drops

*The author is very grateful to N. N. Mikhailov for permitting him to grow crystals in his laboratory and for constant interest in this work.

out as a crystalline precipitate. Preliminary investigations have shown that the size and quality of the resultant crystals depend, firstly, on the rate of decomposition of the $(\text{NH}_4)_2\text{SO}_4$ and, secondly, on the value and constancy of the temperature during the entire process. If the process is carried out at ~ 390 or 400°C , an intermediate compound of the type $[\text{Cu}(\text{MH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ is first formed and is then transformed into CuSO_4 , but not in form of crystals but in the form of a powder. If a higher temperature, approximately 500°C , is maintained during the entire process, the CuSO_4 may decompose after the removal of the decomposition products of $(\text{NH}_4)_2\text{SO}_4$. We therefore chose an intermediate temperature of 430°C , which was maintained accurate to 2 or 3° . At this temperature, the entire process was completed in 20 hours. The optimum initial proportion was one part CuSO_4 four parts of $(\text{NH}_4)_2\text{SO}_4$ (by weight).

Figure 1 shows the diagram of the equipment used to grow single crystals of CuSO_4 . Approximately 10 g of a mixture of CuSO_4 and $(\text{NH}_4)_2\text{SO}_4$ were placed in cup 1. The decomposition products were removed through test tube 2. A feature of this equipment is that the optimum rate of decomposition can be chosen for any specified temperature. Smooth variation of the mounting height of test tube 2 regulates the gap between the bottom of test tube 2 and cup 1, thus regulating the speed of removal of the decomposition products.

The temperature of the oven 3 was regulated with a platinum resistance thermometer 4, connected in a dc bridge circuit. The null device of the bridge was a type MRShchPr-54 regulating millivoltmeter which controlled the operation of the oven. This circuit maintained the oven temperature accurate to 2 or 3° . The platinum resistance thermometer served only to regulate the temperature. The oven temperature was measured with a copper-constantan thermocouple attached to the upper part of test tube 2. The thermocouple readings were recorded by an automatic millivoltmeter.

The foregoing procedure has yielded single crystals of anhydrous copper sulfate measuring $3 \times 1 \times 0.2$ mm and weighing 1 to 2 mg (see reference 4). These crystals are transparent and have a weak gray color. Unlike the polycrystalline CuSO_4 , obtained by roasting in vacuum, they can be exposed to air for a sufficiently long time (approximately 15 days) without absorbing any moisture. Most crystals are elongated prisms with rhombic cross section, terminating in most cases with quadrilateral pyramids. The angles between

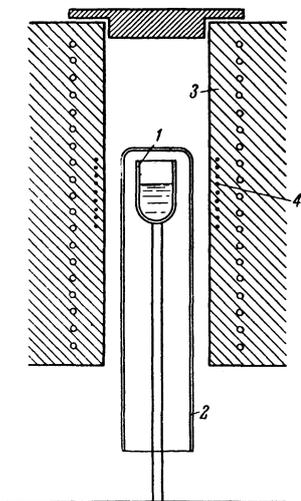
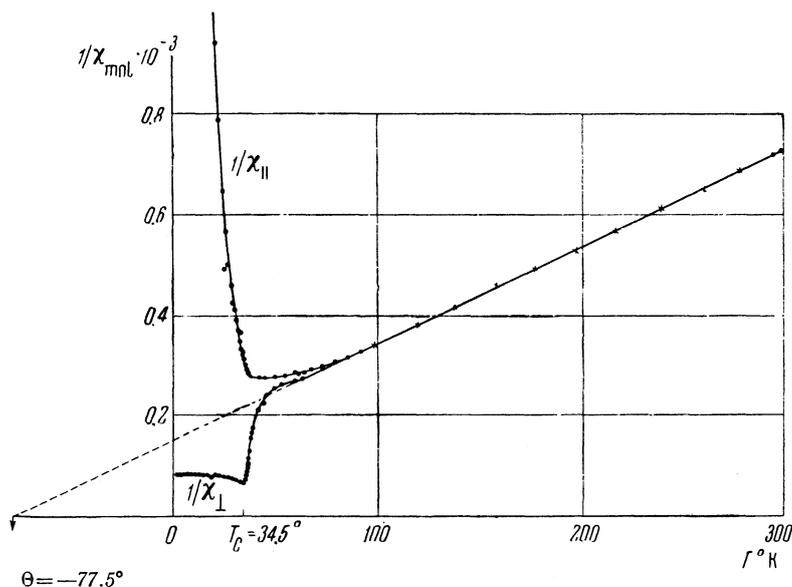


FIG. 1. Diagram of the equipment used to grow single crystals of CuSO_4 .

FIG. 2. Temperature dependence of the reciprocal molar susceptibility $1/\chi_{\text{mol}}$ of single-crystal CuSO_4 . ●) data of present work, ×) data of reference 4.



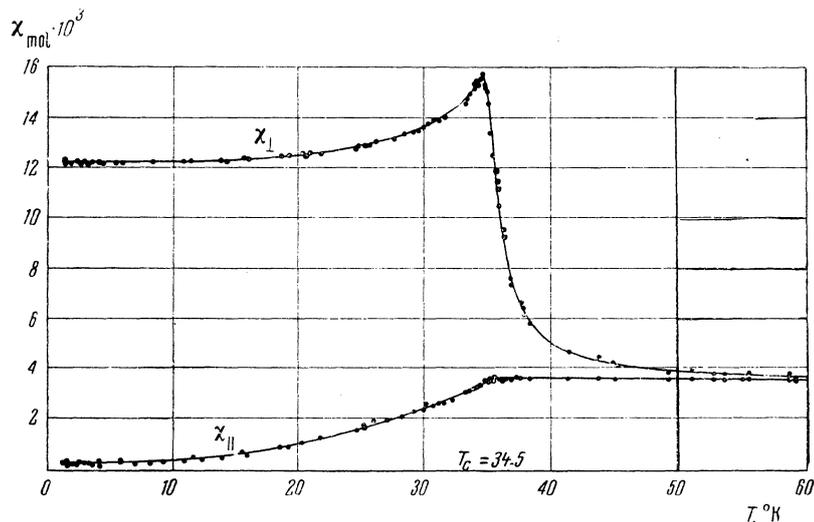


FIG. 3. Temperature dependence of the molar magnetic susceptibility χ_{mol} of single-crystal CuSO_4 .

the prism faces are approximately 66 and 114° respectively.

The structure of anhydrous copper sulfate has not yet been thoroughly studied. Hammel¹⁰ has obtained x-ray diffraction patterns of anhydrous sulfates of transition metals by the powder method. He has established that the lattice of these compounds is apparently rhombic with four molecules in each elementary cell. For CuSO_4 he obtained the following lattice parameters: $a = 4.88 \text{ \AA}$, $b = 6.66 \text{ \AA}$, and $c = 9.32 \text{ \AA}$.

Preliminary x-ray structural investigations, made by Porai-Koshitz* with single crystals of CuSO_4 produced by us, have confirmed Hammel's data. Hammel has found later that the principal plane forming the prism is $\{120\}$ and that the c axis coincides with the long edge of the prism, while axes a and b lie along the long and short diagonals of the rhombic section of the prisms, respectively. According to these data, the angles between the faces of the prism should be $60^\circ 30'$ and $111^\circ 30'$ respectively, which is in good agreement with our data.

3. MEASUREMENT RESULTS

The susceptibility was measured with two single-crystal CuSO_4 specimens weighing 0.95 and 1.1 mg . The susceptibility was measured in the first specimen in the ab plane (c axis directed along the suspension line), and in the second specimen in the planes ab (c axis along the suspension line) and ac (b axis along the suspension line). In the entire investigated temperature range, the susceptibility component χ_c in the c direction coincides

with the component χ_b along the b axis. We denote henceforth $\chi_\perp = \chi_b = \chi_c$ and $\chi_\parallel = \chi_a$.

Figure 2 shows the temperature dependence of the reciprocal of the molar susceptibility of CuSO_4 . In the temperature range from 300 to 85°K , within the limits of experimental accuracy, χ_\perp coincides with χ_\parallel and with the susceptibility values obtained by us with polycrystalline CuSO_4 .⁴ Figure 2 shows therefore, for this range of temperatures, the data obtained for a polycrystalline specimen, which are more accurate. The diagram shows that the Curie-Weiss law holds in the temperature interval from 300 to 85°K . The constants are $C = 0.517$ and $\Theta = -77.5^\circ$. The value of the g factor, calculated from these data, is 2.38 .

Figure 3 shows the results of the measurement of the magnetic susceptibility below 60°K , plotted in coordinates χ_{mol} and T° . When $T \approx 35^\circ\text{K}$, χ_\perp increases sharply, almost tripling in value within approximately 2.5° , reaching a maximum at $T = 34.5^\circ\text{K}$. It then drops to three quarters of its maximum. From 12 or 14°K down to 1.5°K χ_\perp does not change with temperature. Below 60°K χ_\parallel is almost constant down to 36°K , below which it diminishes practically to zero. The small remanent value of χ_\parallel , observed at $T = 1.3^\circ\text{K}$, may be due to an imperfectly accurate mounting of the crystal and corresponds to a 1° deviation from the crystallographic direction. The maximum value of χ_\parallel corresponds to approximately one quarter of the maximum value of χ_\perp . A dependence of χ_\perp on the magnetic field is observed in the transition region. Qualitatively this dependence is similar to that observed in polycrystalline specimens,⁴ in that the susceptibility decreases with increasing magnetic field, and its maximum shifts towards the lower temperatures.

Quantitatively this dependence is difficult to

*The author is deeply grateful to M. A. Porai-Koshitz for supplying him with data on the structure of CuSO_4 and for much valuable advice.

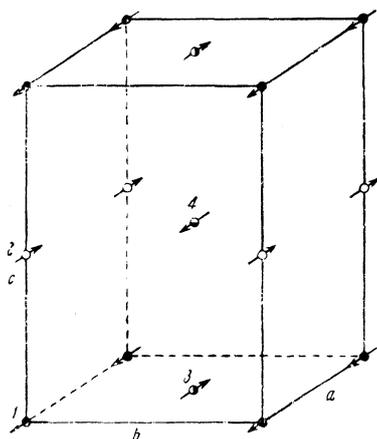


FIG. 4. Assumed magnetic structure of CuSO_4 . $a = 4.88 \text{ \AA}$, $b = 6.66 \text{ \AA}$, $c = 9.32 \text{ \AA}$.

estimate for a single-crystal specimen, since the susceptibility can be measured only in strong magnetic fields, owing to the smallness of the specimen. No field dependence was observed at all for χ_{\parallel} . We did not find within the limits of the measurement accuracy, the dependence of the susceptibility on the field, observed by de Haas and Wiersma¹¹ at hydrogen temperatures, or the residual moment observed by Schultz et al.¹² at the same temperatures in a polycrystalline specimen.

4. DISCUSSION OF RESULTS

Our measurements of the temperature dependence of the magnetic susceptibility of anhydrous copper sulfate in a single-crystal specimen show that at 34.5°K the substance experiences a transition, below which it becomes antiferromagnetic. While it was difficult to conclude the character of the observed transition (whether it is a first-order or second-order transition), from the data for the polycrystalline specimen of CuSO_4 , the behavior of $\chi_{\parallel}(T)$ in a single-crystal specimen is unequivocal evidence of a second-order transition. This conclusion is also confirmed by Stout's² data on the heat capacity of CuSO_4 .

According to the observed temperature dependences for χ_a , χ_b , and χ_c in the antiferromagnetic state, the CuSO_4 in the antiferromagnetic state is uniaxial in the magnetic sense. The direction of least magnetization coincides with the a axis.

As indicated above, we still do not know the exact crystalline structure of CuSO_4 . However, from data on the crystalline structure of NiSO_4 ¹³ and from preliminary results on the x-ray structural investigation of CuSO_4 made by Porai-Koshitz, we may assume that the arrangement of the Cu^{++} ions in the elementary cell of CuSO_4 is as shown in Fig. 4.

Let us attempt to ascertain what type of ordering of the magnetic moments is the most likely for

the structure we are investigating. Following the theory of the molecular field,^{14,15} we divide the initial lattice into four simple sublattices, as indicated in Fig. 4. Let M_i be the mean magnetization per unit volume of the i -th sublattice. We consider only interactions between ions that are 4.0 to 5.0 \AA apart, and introduce the following symbols: A — interaction constant between ions inside each sublattice, Γ_1 — constant of the interaction between ions of sublattices I and II and sublattices III and IV, Γ_2 — constant of interaction between ions of sublattices I and III and sublattices II and IV. For the mean moments of the four sublattices we can write the following equations:

$$\begin{aligned} M_1 &= \frac{C}{4T} [H - 2AM_1 - 2\Gamma_1 M_2 - 4\Gamma_2 M_3]; \\ M_2 &= \frac{C}{4T} [H - 2\Gamma_1 M_1 - 2AM_2 - 4\Gamma_2 M_4]; \\ M_3 &= \frac{C}{4T} [H - 4\Gamma_2 M_1 - 2AM_3 - 2\Gamma_1 M_4]; \\ M_4 &= \frac{C}{4T} [H - 4\Gamma_2 M_2 - 2\Gamma_1 M_3 - 2AM_4]. \end{aligned} \quad (1)$$

Using these equations, we determine the Curie temperature T_C in the following cases:

1. $M_2 = -M_1$; $M_3 = -M_1$; $M_4 = M_1$;
 $T_{C1} = \frac{C}{2} (\Gamma_1 + 2\Gamma_2 - A)$;
2. $M_2 = -M_1$; $M_3 = M_1$; $M_4 = -M_1$;
 $T_{C2} = \frac{C}{2} (\Gamma_1 - 2\Gamma_2 - A)$;
3. $M_2 = M_1$; $M_3 = -M_1$; $M_4 = -M_1$;
 $T_{C3} = \frac{C}{2} (2\Gamma_2 - \Gamma_1 - A)$.

It is obvious that the most probable order corresponds to the maximum T_C . To estimate T_C we first estimate the magnitudes of the interactions A , Γ_1 , and Γ_2 . Assuming that the exchange interaction between the magnetic ions increases with diminishing distance between them, we obtain

$$\Gamma_2 > \Gamma_1 > A. \quad (3)$$

Using (3) to estimate T_C in (2) we find that the most likely type of ordering is the first one, i.e., $M_2 = -M_1$, $M_3 = -M_1$, $M_4 = M_1$ (see Fig. 4).

From the data obtained for the susceptibility of a single-crystal of CuSO_4 we can draw certain conclusions regarding the temperature dependences for χ_{\parallel} and χ_{\perp} below the Curie point. It is seen from Fig. 5, which is plotted in coordinates χ_{\parallel} and T^2 , that $\chi_{\parallel} = a + b(T/T_C)^2$ from ~ 15 to 34°K . This result agrees with the general deductions of the theory of spin waves.¹⁶⁻¹⁹ The presence of the constant a may be due to an incorrect allowance for the diamagnetic correction for the SO_4^{--} ion. No

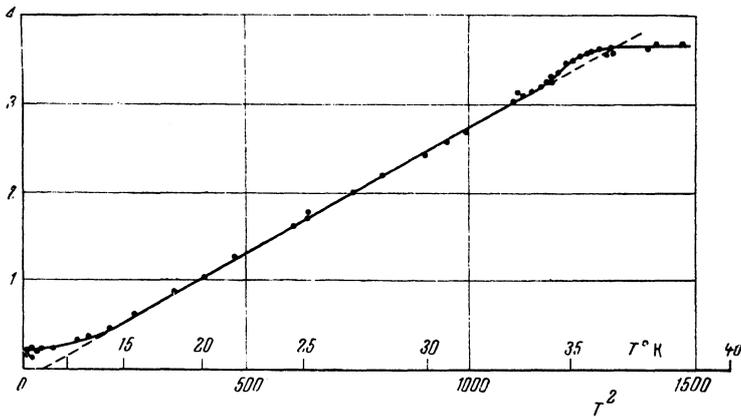


FIG. 5. Temperature dependence of the parallel magnetic susceptibility of a single crystal of CuSO_4 below the Curie point.

simple power-law approximation could be found for χ_{\perp} .

The most interesting is the anomalous increase in anisotropy, which we observed in the narrow region of the transition point. Since the exchange interaction is isotropic, we must assume that the establishment of antiferromagnetic ordering is accompanied by a change in the spin-orbit interaction. Attention should be called to the fact that the value of the g factor in CuSO_4 is considerably greater than 2. This is evidence that in the splitting of the orbital levels by the crystal field, the distance between the lower levels becomes relatively small. One can assume that the exchange interaction leads to a further change in the splitting picture. We made no numerical calculations, but qualitatively such a scheme could explain the anomalous increase in the anisotropy.

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