

## Heat Capacity of $K_3Fe(CN)_6$ and $CuK_2(SO_4)_2 \cdot 6H_2O$ below $1^\circ K^*$

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Measurements of the heat capacity of potassium ferricyanide for  $0.075 \leq T \leq 0.5^\circ K$  and of copper potassium Tutton salt for  $0.021 \leq T \leq 0.28^\circ K$  are presented. A structured heat-capacity peak was found for the ferricyanide around  $0.130^\circ K$ . A  $\lambda$ -type heat-capacity peak was found for the Tutton salt, with  $T_\lambda \approx 0.029^\circ K$ . Entropy calculations, a discussion of the results, and a comparison with previous data are also presented.

### I. INTRODUCTION

THE heat capacities of potassium ferricyanide [ $K_3Fe(CN)_6$ ] and copper potassium Tutton salt [ $CuK_2(SO_4)_2 \cdot 6H_2O$ ] below  $1^\circ K$  have been measured using the method developed by Vilches and Wheatley.<sup>1</sup> This technique has been used successfully to give the dependence of the heat capacity and entropy on the absolute temperature for salts exhibiting magnetic cooperative phenomena at low temperatures.<sup>2,3</sup> The purpose of this work is to study the magnetic-ordering transitions in these materials at temperatures very near their critical points and to measure the heat capacities over as wide a temperature range as could be obtained with this technique.

Potassium ferricyanide was chosen for this work because workers at Leiden<sup>4,5</sup> had observed an anomaly in the heat capacity at  $0.129^\circ K$  as well as some interesting structure in the heat capacity above  $T_c$ . Also, there existed a discrepancy between the heat-capacity results of the Leiden group and the entropy measured by Ohtsuka<sup>6</sup> concerning the qualitative behavior of this salt relatively far above  $T_c$ . The critical point for this transition occurred in an ideal temperature region for our measuring technique and we expected to be able to make a precise determination of the temperature

dependence of the heat capacity near  $T_c$ . Moreover, we hoped that the effective spin being  $\frac{1}{2}$  would facilitate theoretical analysis of the results.

Copper potassium Tutton salt has been studied extensively for many years<sup>7-11</sup> with widely varying results. The only direct calorimetric measurements were done by Rayne<sup>10</sup> and went no lower than  $0.1^\circ K$ . Miedema suggested on the basis of adiabatic demagnetization experiments<sup>9,11</sup> that major decreases in entropy occurred both at about  $0.05^\circ K$  and at about  $0.007^\circ K$ . The entropy apparently decreased by about  $\frac{1}{2}R \ln 2$  in this salt in the region of each temperature. The magnetic ions have effective spin  $\frac{1}{2}$ . These entropy changes were not understood. They would correspond to two heat-capacity peaks. We therefore felt that it would be interesting to study this Tutton salt, at least to  $20 m^\circ K$ , where the present measuring technique begins to fail.

### II. EXPERIMENTAL METHOD AND RESULTS

The method of measurement is identical to that described by Vilches and Wheatley.<sup>1</sup> The only important modification was the use of a magnetic thermometer containing about 5.5 g of cerium magnesium nitrate (CMN) instead of the 1.1-g CMN thermometer used in their work. This gave about a factor of 5 improvement in temperature sensitivity. Further details concerning the extraction of heat capacities from the measurements are given by Abel, Anderson, Black, and Wheatley.<sup>12</sup>

#### A. Potassium Ferricyanide

$K_3Fe(CN)_6$  is a low-temperature antiferromagnet in which the  $Fe^{3+}$  ion has an effective spin of  $\frac{1}{2}$ . The

<sup>7</sup> D. de Klerk, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XV, p. 38.

<sup>8</sup> E. Ambler and R. P. Hudson, *Rept. Prog. Phys.* **18**, 251 (1955).

<sup>9</sup> C. G. B. Garrett, *Proc. Roy. Soc. (London)* **A203**, 375 (1950).

<sup>10</sup> J. Rayne, *Phys. Rev.* **95**, 1428 (1954).

<sup>11</sup> A. R. Miedema, thesis, Leiden University, 1960 (unpublished).

<sup>12</sup> W. R. Abel, A. C. Anderson, W. C. Black, and J. C. Wheatley, *Physics (N.Y.)* **1**, 337 (1965).

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<sup>1</sup> O. E. Vilches and J. C. Wheatley, *Rev. Sci. Instr.* **37**, 819 (1966).

<sup>2</sup> O. E. Vilches and J. C. Wheatley, *Phys. Rev.* **148**, 509 (1966).

<sup>3</sup> Martin Rayl, O. E. Vilches, and J. C. Wheatley, preceding paper, *Phys. Rev.* **165**, 692 (1968).

<sup>4</sup> H. Van Kempen, thesis, Leiden University, 1965 (unpublished).

<sup>5</sup> W. T. Duffy, Jr., J. Lubbers, H. Van Kempen, T. Haseda, and A. R. Miedema, in *Proceedings of the Eighth International Conference on Low Temperature Physics* (Butterworths Scientific Publications Ltd., Washington, 1963), p. 245.

<sup>6</sup> T. Ohtsuka, *J. Phys. Soc. Japan* **16**, 1549 (1961); *J. Phys. Soc. Japan*, Suppl. B-1, 472 (1962).

magnetic structure is discussed by Ohtsuka.<sup>6</sup> His principal conclusion is that the interacting ions are arranged in relatively isolated linear chains.

We have measured the heat capacity of this salt for  $0.075 \leq T \leq 0.5^\circ\text{K}$  and attempted to find the detailed behavior of the heat capacity near  $T_c$  for two samples under a variety of experimental conditions. Both samples consisted of small crystals grown from aqueous solutions of analytical reagent (AR) grade  $\text{K}_3\text{Fe}(\text{CN})_6$ . The first sample consisted of 11.48 g of crystals selected on the basis of accepting those which passed through a sieve with 1-mm squares and did not pass through one with 0.5-mm squares. The second sample was selected by applying the same size criterion to crystals which had been accepted only after examination under a microscope for optical clarity and correct shape. Crystals exhibiting some flat surfaces as well as surfaces with the expected facets were accepted if they were optically clear. The second sample weighed 9.42 g and was packed in 0.37 g of cotton to prevent crystal motion. We do not show our results for sample 1 except for some points at high temperature because they are of less precision than our work with sample 2 and, within the experimental scatter, are identical to those for sample 2.

Our resulting heat-capacity curve (Fig. 1) includes a correction, negligible at lower temperatures, applied

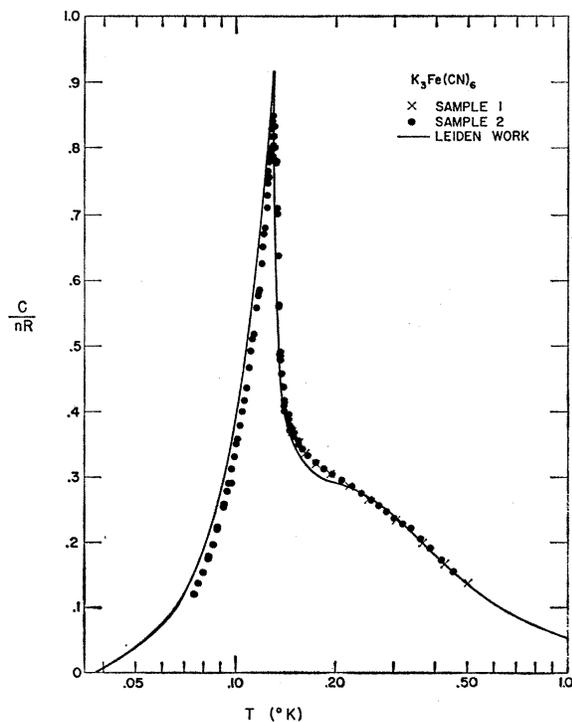


FIG. 1. Heat capacity of  $\text{K}_3\text{Fe}(\text{CN})_6$ . The data are corrected for the heat capacity of the  $\text{He}^4$  used as thermal contact agent. The temperature scale is logarithmic.

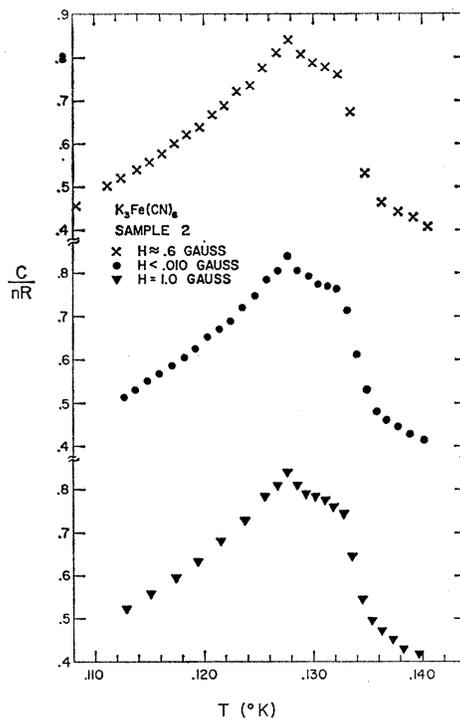


FIG. 2. Data showing the peak of the heat-capacity curve for  $\text{K}_3\text{Fe}(\text{CN})_6$ , sample 2, in various small magnetic fields. The figure has three vertical scales.

to all of the data for  $T > 0.160^\circ\text{K}$  for the heat capacity of the liquid  $\text{He}^4$  in the measuring cell. The solid curve represents smoothed results of the Leiden group.<sup>5</sup> The agreement between the two experiments is quite good, especially above the peak. The Leiden workers have compared their experiment with a calculation<sup>5</sup> based on a theory due to Stout and Chisholm<sup>13</sup> which assumes Ising linear chains coupled by an interchain molecular field. The agreement below the peak is better for our data than for theirs. Above the peak, agreement is poor in both cases.

The heat capacity was measured with special care very near the heat-capacity peak shown in Fig. 1. The result of eleven runs for the two samples under varying conditions of heat leak, heating rate, size of temperature intervals, and small external magnetic fields is the structured peak 5 m°K in width shown in Fig. 2. The vertical scales are shifted for the three runs shown in the figure since the runs are indistinguishable when plotted on the same curve. Hence no field dependence of the peak is observable for the small fields used. The agreement is within 1% from run to run. No evidence was obtained for a large change in heat capacity over a very small ( $\approx 10^{-4} T_c$ ) temperature

<sup>13</sup> J. W. Stout and R. C. Chisholm, *J. Chem. Phys.* **36**, 979 (1962).

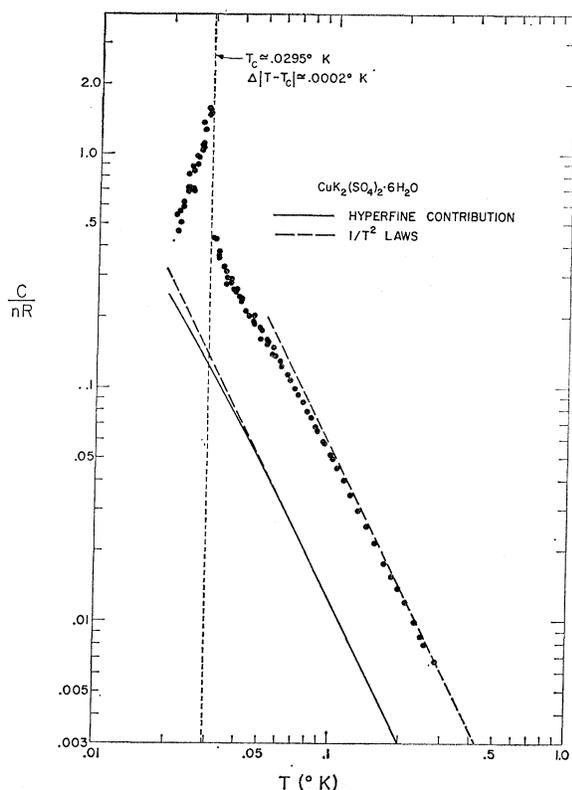


FIG. 3. Heat capacity of  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The data are corrected for the heat capacity of the  $\text{He}^4$  used as thermal contact agent.

range as we observed<sup>3</sup> in manganese ammonium Tutton salt. It appears from our work that  $C(T)$  is continuous, although it is possible that  $dC/dT$  may be discontinuous at the peak. Using this method of measurement, we were unable to resolve the structure of the peak further. We are not aware of a theory which predicts or explains the type of structured heat-capacity peak observed here. It is possible, however, that the structure results from two closely separated ordering transitions. In this connection a combined study of magnetic and thermal properties would be quite interesting.

#### B. Copper Potassium Tutton Salt

The  $\text{Cu}^{2+}$  ion in  $\text{CuK}_2$  Tutton salt has an effective spin of  $\frac{1}{2}$ . Miedema discusses the magnetic structure in his thesis.<sup>11</sup> It is expected to be a canted ferromagnet at low temperature.

We have measured the heat capacity of one sample of this salt for  $0.021 \leq T \leq 0.28^\circ\text{K}$ . The sample consisted of small crystals grown from an aqueous solution of stoichiometric amounts of the component sulfates (AR grade). The size distribution was between 0.17 and 0.5 mm, as small crystals result in relatively

low thermal equilibrium times at very low temperature. The sample consisted of 10.48 g of crystals which were clear and of the right shape upon examination under a microscope. The external magnetic field was typically 0.6 G and directed roughly along the axis of the cryostat.

The results of three runs (Fig. 3) indicate that  $T_c = 0.0295^\circ\text{K}$  for the only transition observed in the range of our measurements. It is interesting that in the magnetic measurements of Garrett<sup>9</sup> he found a Curie-Weiss  $\Delta$  of  $0.034^\circ\text{K}$ , rather close to the value of  $T_c$  measured in the present work. Experimental difficulties arising principally from the long thermal equilibrium times near the  $\lambda$  point prevented us from making observations closer than  $\pm 0.2\text{m}^\circ\text{K}$  from the transition temperature. Similar difficulties occurred in the work with ferric alum,<sup>2</sup> for which  $T_c$  is  $0.026^\circ\text{K}$ . The estimated error in our data below  $0.031^\circ\text{K}$  is  $\pm 10\%$ , again owing to the long thermal equilibrium times. The lowest temperature for which we were able to obtain results of sufficient accuracy was  $0.021^\circ\text{K}$ . It was not possible to measure heat capacities as close to the transition as we did in our manganese ammonium Tutton salt work,<sup>3</sup> although a sudden change in the temperature-time curve similar to that observed in the manganese Tutton salt experiments was observed each time we heated the sample through the transition. Measurements above  $0.031^\circ\text{K}$  were considerably easier to make and much more precise (roughly 2% error) than those at lower temperatures. Measurements were not extended above  $0.3^\circ\text{K}$ , where the background heat capacity of the  $\text{He}^4$  became comparable to that of the sample. All of our data for  $T > 0.05^\circ\text{K}$  are corrected for the heat capacity of the  $\text{He}^4$ . The corrected data are plotted in Fig. 3 and are given in the appendix.

### III. DISCUSSION

#### A. Potassium Ferricyanide

This salt was originally chosen for study since we had hoped that it would be a simpler example of magnetic critical phenomena than manganese ammonium Tutton salt, a material with a similar magnetic-ordering temperature. By simple magnetic critical behavior we refer to a dependence of heat capacity on reduced temperature  $\epsilon \equiv (T - T_c)/T_c$  given by an equation of the type

$$C_{\pm} = A_{\pm} |\epsilon|^{-\alpha_{\pm}} + B_{\pm}, \quad (1)$$

where  $\pm$  refers to  $\epsilon \geq 0$ ,  $A$  and  $B$  are constants, and  $\alpha$  are constants in the range 0 to 0.2. A dependence of heat capacity on  $\epsilon$  given by Eq. (1) was indeed observed over certain relatively wide ranges of  $\epsilon$  in the case of the manganese Tutton salt ( $T_c \approx 0.176^\circ\text{K}$ ), and a critical temperature  $T_c$  could be defined precisely. Perhaps the most puzzling qualitative feature of the

measurements on the ferricyanide is that no critical temperature could be defined, so that unambiguous values of  $\epsilon$  could not be assigned to the heat-capacity points. An analysis in terms of Eq. (1) would thus appear to be meaningless. In searching for qualitative differences between the two salts we note that the magnetic unit in the ferricyanide is an example of what is called<sup>14</sup> a strongly bound complex. The ground state of the complex has effective spin  $\frac{1}{2}$  and is highly anisotropic. It is possible that the properties of the complex might be rather easily altered by lattice strains and that this might result in inhomogeneities in  $T_c$  which could smooth out an otherwise sharp transition. An argument against this view is that it is hard to see qualitatively how the structure in the heat-capacity curve (Fig. 2) could be explained by random strains. In distinction with the ferricyanide, the magnetic properties of manganese Tutton salt can be described in terms of  $Mn^{2+}$  ions in  $S$  states with effective spin  $\frac{5}{2}$ . Interaction with the surroundings is much weaker than in the ferricyanide. The ground-state splitting is caused by higher-order effects, though the magnitude of the splitting is comparable to  $T_c$  in this salt. We suggest that if a smoothing out of an otherwise sharp transition were to be caused by lattice strains or imperfections, then it seems more likely that the ferricyanide would be more strongly affected than the manganese Tutton salt.

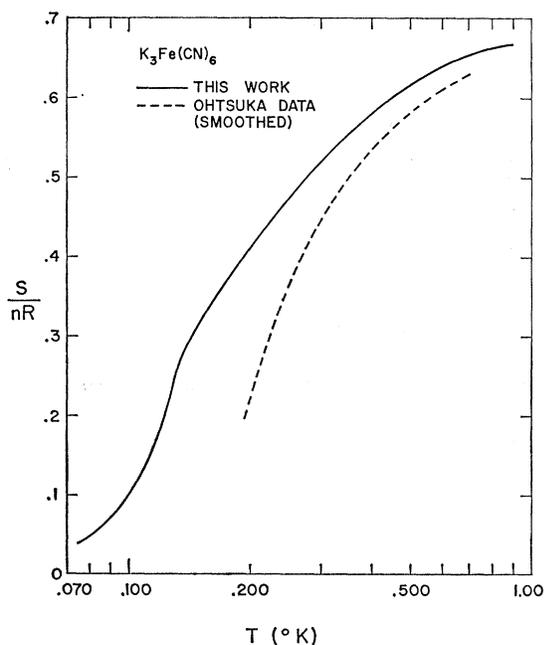


FIG. 4. Magnetic entropy of  $K_3Fe(CN)_6$ .

<sup>14</sup> K. D. Bowers and J. Owen, Rept. Prog. Phys. **18**, 304 (1955).

The entropy of potassium ferricyanide has also been computed from the data. Since  $CT^2/nR$  was still increasing at the highest temperature ( $0.5^\circ K$ ) of the present measurements, we used the value  $b \equiv CT^2/nR = (0.04 \pm 0.01) (\text{°K})^2$  given by McKim and Wolf<sup>15</sup> to give the asymptotic behavior of this quantity. The computed entropy is shown on Fig. 4, where it is compared with the work of Ohtsuka. There is qualitative disagreement, though the source of the disagreement is not known. The entropy near the transition may also be compared with the work of Domb and Miedema,<sup>16</sup> who relate the entropy at the transition with the lattice structure and with models of magnetic cooperative behavior. We find that  $S/nR = 0.265$  at  $T = 0.133^\circ K$ , the high-temperature edge of our peak, or  $S/nR = 0.234$  at  $T = 0.128^\circ K$ , the temperature of our highest heat capacity. An entropy  $S_c/nR = 0.265$  is expected by Domb and Miedema<sup>16</sup> for a honeycomb lattice (coordination number  $q = 3$ ) and an Ising model with spin  $\frac{1}{2}$ . Ohtsuka<sup>6</sup> expected that the magnetic complexes would be arranged in linear chains with relatively weak coupling between chains, though this does not seem to be borne out either by the qualitative aspects of the heat capacity or by the entropy at the heat-capacity peak.

### B. Copper Potassium Tutton Salt

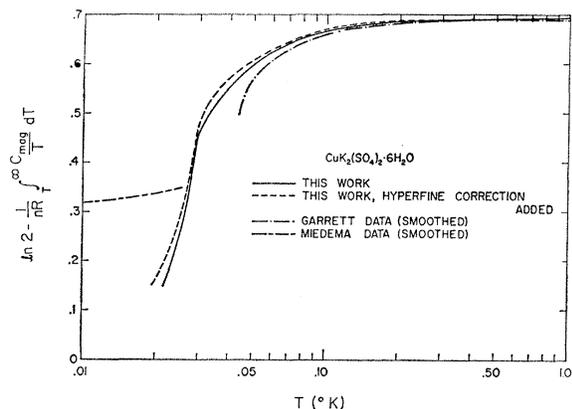
As discussed in II, we found that experimental difficulties caused by the low value of  $T_c$  for this salt prevented our making precise heat-capacity measurements very near  $T_c$ . In terms of reduced temperatures, it was not possible to obtain data for  $|\epsilon| < 10^{-2}$ . This value of  $\epsilon$  is probably too large to permit our making any meaningful analysis of the data near  $T_c$ . However, the data are tabulated in the appendix.

Our heat-capacity data (Fig. 3) indicate that  $CT^2/nR$  is still increasing with increasing temperature at our highest measured temperature. This quantity is  $5.4 \times 10^{-4} (\text{°K})^2$  at  $0.283^\circ K$ , in reasonable agreement with a probable limiting value of  $6.0 \times 10^{-4} (\text{°K})^2$  from early work discussed by deKlerk.<sup>7</sup> The only calorimetric data for this salt which overlap our work are those of Rayne,<sup>10</sup> which are apparently<sup>7</sup> unreliable above  $0.65^\circ K$ . Rayne's data fall somewhat above ours, following the relation  $CT^2/nR = (5.8 \pm 0.2) \times 10^{-4} (\text{°K})^2$  in the range  $0.1 \lesssim T \lesssim 0.65^\circ K$ .

Since the  $Cu^{2+}$  ion has nuclear spin  $\frac{3}{2}$  in addition to its electronic spin of  $\frac{1}{2}$ , there is a contribution of hyperfine splitting to the heat capacity.<sup>14</sup> This contribution, the solid curve in Fig. 3, departs from a  $T^{-2}$  law in the same way as does the measured heat

<sup>15</sup> F. R. McKim and W. P. Wolf, Proc. Phys. Soc. (London) **B69**, 1231 (1956).

<sup>16</sup> C. Domb and A. R. Miedema, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1964), Vol. 4, p. 296.

FIG. 5. Magnetic entropy of  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

capacity. The limiting value of  $C_{\text{hfs}}T^2/nR$  is  $1.3 \times 10^{-4} (\text{°K})^2$  as calculated by Benzie and Cooke.<sup>17</sup> We have verified their computation. We note from Fig. 3 that the hyperfine contribution is about  $\frac{1}{4}$  of the total heat capacity above  $T_c$  and apparently a considerably larger fraction below  $T_c$ .

The entropy of copper potassium Tutton salt has also been computed from our data (Fig. 5) using the value  $b = CT^2/nR = 6.0 \times 10^{-4} (\text{°K})^2$  to give the asymptotic behavior of the specific heat. The entropy, computed both with and without the hyperfine contribution, is compared in Fig. 5 with the entropies found by Garrett<sup>9</sup> and Miedema.<sup>11</sup> There is qualitative disagreement between their results and the present work, although the source of this disagreement is not known. We find that more than 78% of the magnetic entropy of the  $\text{Cu}^{2+}$  ions is lost in ordering above  $0.0215 \text{°K}$ , in contradiction with Miedema's work. Our data do not exclude the possibility of another heat-capacity peak at much lower temperature, but, if such a peak is found and is due to the ordering of the electronic spins of the  $\text{Cu}^{2+}$  ions, the corresponding entropy loss will be much less than  $\frac{1}{2} R \ln 2$ .

The entropy near the transition may again be compared with the work of Domb and Miedema.<sup>16</sup> We

find that  $(S_\infty - S_c)/nR = 0.243$  using the total heat capacity or, using the electronic heat capacity only,  $(S_\infty - S_c)/nR = 0.226$ . According to the work quoted by Domb and Miedema,<sup>16</sup> an fcc Heisenberg ferromagnet has  $(S_\infty - S_c)/nR = 0.265$ . This figure is rather close to the value of 0.226 found for  $(S_\infty - S_c)/nR$  in the present case. Hence our result implies that the properties of  $\text{CuK}_2$  Tutton salt may be similar to those of a Heisenberg ferromagnet.

## APPENDIX

TABLE I. Corrected data for  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

$T(\text{m°K})$	$C/nR$	$T(\text{m°K})$	$C/nR$	$T(\text{m°K})$	$C/nR$
25.0	0.689	21.4	0.464	21.1	0.544
25.7	0.968	21.9	0.504	21.8	0.565
27.0	1.06	22.4	0.589	22.6	0.618
29.0	1.49	23.5	0.814	23.6	0.713
32.2	0.379	24.1	0.711	24.7	0.840
34.6	0.322	24.8	0.705	25.6	0.973
36.4	0.290	26.6	1.02	26.9	1.35
38.4	0.262	27.2	1.11	23.4	0.682
40.6	0.238	28.6	1.56	24.4	0.883
46.0	0.202	30.7	0.430	25.6	0.901
48.7	0.179	31.9	0.363	26.5	1.09
52.0	0.159	34.6	0.275	27.6	1.26
55.5	0.148	36.4	0.279	28.5	1.45
59.6	0.128	38.3	0.259	30.6	0.433
64.1	0.113	40.2	0.231	32.2	0.356
69.2	0.0988	43.3	0.201	33.7	0.327
74.8	0.0856	45.8	0.186	35.1	0.293
80.7	0.0741	48.8	0.167	37.2	0.260
86.5	0.0649	52.2	0.152	39.3	0.242
92.1	0.0583	56.6	0.136	42.0	0.212
98.4	0.0514			45.2	0.191
105.6	0.0449			49.2	0.174
112.7	0.0399			52.6	0.156
120.9	0.0344			56.4	0.138
130.7	0.0296			60.5	0.124
141.9	0.0253			65.5	0.108
154.1	0.0216			71.3	0.0927
168.8	0.0176			77.8	0.0784
182.2	0.0155			84.8	0.0675
195.6	0.0137			92.6	0.0576
209.7	0.0120			100.6	0.0493
211.4	0.0119				
228.5	0.00985				
245.6	0.00855				
253.5	0.00790				
283.4	0.00673				

<sup>17</sup> R. J. Benzie and A. H. Cooke, *Nature* **164**, 837 (1949).