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High-Resolution Specific Heat of $CoCl_2 \cdot 6H_2O$†

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The specific heat of a single crystal of $CoCl_2 \cdot 6H_2O$ has been measured with high resolution near $T_N = 2.29$ K. The data were fitted to the usual asymptotic form $C = A\epsilon^{-\alpha} + B$, where $\epsilon = |1 - T/T_N|$, using several different techniques. An examination of the gradient $\partial C/\partial T$ showed that the critical region was limited to $\epsilon \lesssim 7\times10^{-2}$ and that for $\epsilon \lesssim 4\times10^{-3}$ the specific heat was rounded. The data were found to fit the asymptotic form for $4\times10^{-3} \lesssim \epsilon \lesssim 7\times10^{-2}$ with $\alpha' = -0.19 \pm 0.04$ for $T < T_N$ and $\alpha = 0.34 \pm 0.05$ for $T > T_N$. It was also found that the observed rounding could be predicted by treating the sample as a system of microcrystals having a finite distribution of ordering temperatures. It was thus possible to produce a reasonable fit to all the data for $\epsilon < 7\times10^{-2}$ using the above values of α' and α which were determined from the data in the "unrounded critical region." It was further found that the results of a previous experiment in another laboratory could also be fitted over the entire critical region using the above values of α' and α with a somewhat broader distribution of ordering temperatures.

I. INTRODUCTION

Recent theoretical advances[1] in the description of critical-point behavior of simple models have prompted numerous experimental studies of many different systems. Within the critical region, the specific heat of a system is expected to obey the asymptotic form

$$C/R = A\epsilon^{-\alpha} + B \ , \qquad (1)$$

where $\epsilon = |1 - T/T_N|$ and A', α', and B' below T_N (where T_N is the Néel temperature) may differ from the corresponding constants A, α, B above T_N. The values of α' and α which have been determined experimentally have shown a wide variation in magnitude.[2] In all cases the specific heat was observed to be "rounded" very near to the ordering temperature and in some cases [3,4] significant differences in the behavior of two different single crystals of the same material have raised questions concerning the possibilities of actually determining the intrinsic critical-point behavior.

The thermal and magnetic properties of $CoCl_2 \cdot 6H_2O$ have been investigated extensively, [5–16] and the nature of the magnetic interactions is fairly well known. At liquid-helium temperatures the Co^{2+} ions have an effective spin $S' = \frac{1}{2}$ with the nearest-neighbor interactions dominated by anisotropic exchange and with weaker exchange coupling between more distant neighbors. Dipolar interactions are not negligible but the ordered struc-

ture[10] is not the one favored by the dipolar coupling. In fact, in the actual ordered configuration the dipolar energy is only a few percent of the total energy determined from specific-heat measurements.[5]

Previous high-resolution specific-heat measurements on a polycrystalline sample have been reported by Skalyo and Friedberg.[8] Their results showed considerable rounding, which we believe was at least partially due to the polycrystalline nature of the specimen. The present investigation was initiated primarily to try to find out to what extent the rounding could be attributed to the presence of a polycrystalline specimen. For this purpose a large nominal single crystal was used. As we shall show below, the rounded region is significantly smaller than that found by Skalyo and Friedberg, but is nonetheless an order of magnitude larger than that found earlier[3,4,17,18] on several different systems. We shall show, however, that a simple phenomenological description of both our sample and that of Skalyo and Friedberg is sufficient to explain the rounding in both cases. (A preliminary account of this work was presented at the Sixteenth Annual Conference on Magnetism and Magnetic Materials.)

II. EXPERIMENTAL TECHNIQUES

A. Sample Preparation

The samples of $CoCl_2 \cdot 6H_2O$ used in this investigation were grown from aqueous solution by slow temperature reduction from saturation. The starting material used was the reagent grade of $CoCl_2 \cdot 6H_2O$ manufactured by Fisher Scientific Company, which contains 0.001 wt% Cu, 0.002 wt% Fe, and 0.08 wt% Ni. No efforts were made to increase the chemical purity. However, ultrapure water and millipore filtering were used in preparing the solutions. Nominal single crystals having a mass of 1–2 g can be easily grown, but larger samples become increasingly difficult to obtain owing to the high solubility and dark purple color of the solution. An analysis of the sample using an electron-probe microscope, with a resolution of 0.1% by weight in $3d$-ion content, failed to detect any impurities.

B. Specific-Heat Apparatus

The apparatus used in this investigation is a modified version of the one used by Dixon and Rives.[17] A small ($\sim 0.25l$) "pot" of He^4, surrounded by a 4.2-K helium bath, is held at fixed temperature near the ordering temperature of the sample. A mechanical heat switch is used to bring the sample into contact with the He^4 pot and thus cool it. The sample is isolated thermally by simply opening the heat switch. The sample was mounted to the heat switch by means of copper and phosphor-bronze clamps, and Apiezon J oil was used to improve thermal contact. The heater and thermometer clamps were at opposite ends so that the transient behavior of the sample could be observed. The sample had a mass of 1.46 g. Standard ac thermometry was employed with an Allen-Bradley 220-Ω, $\frac{1}{2}$-W resistor forming one arm of a 400-Hz transformer coupled modified Wheatstone bridge. Detection was made with a P.A.R. HR-8 lock-in amplifier and the ultimate temperature sensitivity was $\pm 1\ \mu$K. The off-balance signal was recorded by a digital voltmeter and printer; near the specific-heat maximum, consecutive points were about 7 μK apart. The power dissipated in the thermometer during the measurements was between 1.4×10^{-8} W and 3.2×10^{-8} W. This amount did not produce self-heating. Absolute calibration of the thermometer was made by introducing helium gas into the calorimeter and then comparing the resistance with the vapor pressure of liquid helium in a small bulb within the refrigerator.

The specific-heat measurement was made by the continuous heating method[19] in which a constant heating rate $\dot{Q}$ is applied to the sample. Since

$$\Delta Q = m C \Delta T\ , \tag{2}$$

where m is the molar fraction of material, the specific heat per mole C is related to the total rate of heat input by

$$\begin{aligned} C &= \dot{Q}/m\dot{T} \\ &= (\dot{Q}_0 + \dot{Q}_1)/m\dot{T}, \end{aligned} \tag{3}$$

where $\dot{Q}_0$ is the heat leak to the sample, $\dot{Q}_1$ is the external heating rate of the sample, and $\dot{T}$ is the time rate of change of temperature. $\dot{Q}_1$ is measured with a potentiometer, corrected for heat lost to the thermal ground,[20] and $\dot{Q}_0$ is determined with the usual drift technique. $\dot{T}$ is related to the change in resistence R of the thermometer by

$$\dot{T} = \frac{\partial T}{\partial R}\,\frac{\partial R}{\partial V}\,\dot{V}, \tag{4}$$

where $\partial T/\partial R$ is found from the temperature calibration, $\partial R/\partial V$ is obtained from a bridge calibration, and $\dot{V}$ is the time rate of change of the off-balance voltage of the bridge. During a run at least 10 determinations of $\dot{Q}_0$ and $\dot{Q}_1$ were made and care was taken to eliminate transient data resulting from changing the heating rate or rebalancing the bridge. The residual heat leak was less than 0.5 erg/sec (usually $\dot{Q}_0 < \frac{1}{10}\dot{Q}_i$) and could be determined to about $\pm 5\%$. The residual error due to these effects is 0.6%. Estimates of the temperature gradient produced in the sample were made using previously measured values of the thermal con-

ductivity[9] and specific heat.[8] These estimates indicated that the thermal gradient was a maximum of 5 μK and almost certainly much less than this. In fact, experimental results showed no dependence on the heating rate (within the limits described here). The heat capacity of the lattice and the addenda was negligible over the entire range of measurement.

III. EXPERIMENTAL RESULTS

The experimental results for several runs using a heating rate of 5.8 erg/sec are shown in Fig. 1. Results obtained using other heating rates (varying from 2.7 to 10.7 erg/sec) are identical to those shown. Significant differences between our data and those of Skalyo and Friedberg[8] are immediately obvious. Although the two sets of measurements are in good agreement far from T_N, our data reach a maximum value about 7% higher than the previous results, and the peak is significantly narrower.

The data have been analyzed in a number of different ways which are outlined below.

A. Computer Least-Squares Fits to C/R

The asymptotic form of Eq. (1) was used to fit the data in the range $2\times10^{-3} \lesssim \epsilon \lesssim 10^{-1}$ using the technique described by van der Hoeven *et al.*[21] Sets of values for T_N and α are chosen for $T < T_N$ and $T > T_N$ and then a linear least-squares fitting routine is used to pick the best values of A and B. Plots of the error as a function of α, T_N are examined and the values of α, T_N which produce the least error in the fitting procedure are assumed to be the "best" values. From separate analyses below and above T_N we find $\alpha' = -0.20 \pm 0.04$,

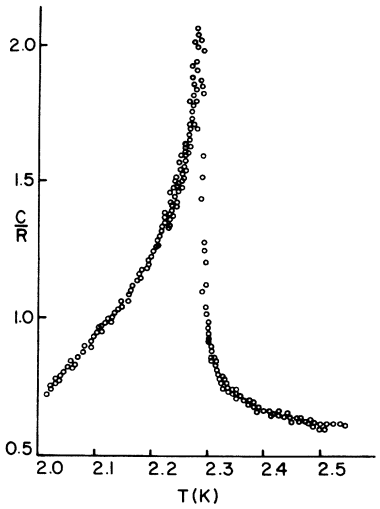

FIG. 1. Magnetic specific heat of $CoCl_2 \cdot 6H_2O$ vs temperature near T_N. Several runs were included with heating rates varying from 2.7 to 10.7 erg/sec.

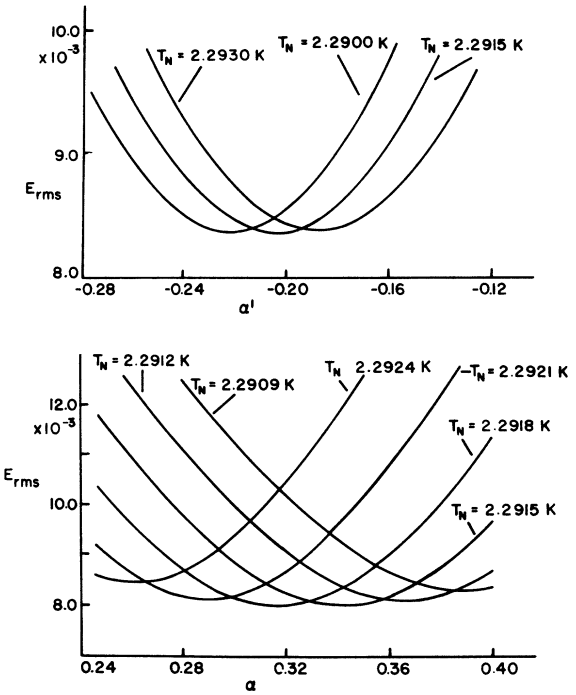

FIG. 2. Results of least-squares fits to Eq. (1). Values of α, T_N or α', T_N were chosen and A, B determined by a linear least-squares routine.

$\alpha = 0.33 \pm 0.05$ (see Fig. 2). The minimum in the sum of the squares of the deviations shown in Fig. 2 defines α clearly and also gives a distinct value for T_N. On the low-temperature side, however, α' and T_N are very poorly defined, and when one considers the uncertainty in the extent of the data to be fitted, it becomes clear that the error bars will be very large indeed. The difference between the "optimum" ordering temperatures T_N^+, T_N^- determined from the analyses above and below T_N respectively, was $(T_N^+ - T_N^-) \approx 0.3$ mK. The coefficients A and B were less sensitive to changes in T_N and we found $A' = -3.5 \pm 0.3$, $B' = 3.1 \pm 0.4$ and $A = 0.10 \pm 0.03$, $B = 0.40 \pm 0.04$. The rms errors of the fits were $\sim \pm 0.8\%$ both below and above T_N. It should be emphasized again that these results were dependent on the range of data included in the fitting procedure. This was particularly noticeable when data within the rounded region were included. Several different fits were made for different ranges of data outside of the obvious rounded region; all the values of α, α' obtained lie within the stated error limits.

B. Analysis of the Derivative of the Specific Heat

One of the difficulties inherent in the analysis presented in Sec. III A was the large number of unknown parameters as well as lack of knowledge about the entry into the critical region and the

onset of rounding. Much of the difficulty can be removed by examining the derivative of the specific heat.[18,22] From Eq. (1) we can see that in the critical region

$$\frac{\partial C/R}{\partial T} = \frac{\alpha A}{T_N} \epsilon^{-(\alpha+1)} \quad . \tag{5}$$

A log-log plot of $\partial C/\partial T$ vs ϵ will then be linear with a slope of $-(1+\alpha)$. Deviations from linearity for large ϵ will be present when the system is no longer in the critical region. (Since this region is very insensitive to the choice of T_N the entry into the critical region is unambiguous.) For small ϵ, deviations from linear behavior arise due to rounding. The choice of T_N is the value which produces the greatest range of linearity of $T < T_N$ and $T > T_N$ simultaneously.

The gradient of the specific heat was determined in two ways. First the data over a small temperature interval were graphically fitted to a straight line. In the second, and we believe superior, method, data over small temperature intervals were least-squares fitted to the asymptotic form given in Eq. (1) taking several different fixed values of α, T_N, and allowing A and B to be determined by the fitting procedure. The results turned out to be insensitive to the choice of α used to find the derivatives, except quite close to T_N (see Fig. 3). In all cases, however, the rounding became obvious before the dependence on α did. From these plots we find that the critical region begins at at $\epsilon \sim 7\times10^{-2}$ and that rounding sets in for $\epsilon \lesssim 4 \times10^{-3}$. It should be emphasized that the rounding determined in this way covers a region about twice as wide as the "obvious rounding" deduced from direct inspection of the specific-heat results. In the unrounded critical region this procedure produced $\alpha' = -0.18 \pm 0.03$, $A' = -3.6 \pm 0.4$, $B' = 3.3 \pm 0.5$; $\alpha = 0.35 \pm 0.06$, $A = 0.09 \pm 0.02$, $B = 0.41 \pm 0.06$, $T_N = 2.291 \pm 0.001$. The "best-fit" results are shown in Fig. 3. As expected, the onset of rounding is clearly indicated on this plot. Data outside the critical region have been suppressed. The results obtained from the first method were virtually identical to those yielded by the more complex computer fit outlined above and thus were not reported separately.

IV. DISCUSSION

Although the values which we have determined for α' and α may be correct for a real sample, they might not be the parameters which would typify an ideal, pure, incompressible $CoCl_2 \cdot 6H_2O$ lattice. In fact, random impurities and magnetoelastic effects could renormalize the critical exponents.[23-25] In such a case it is thought the specific heat would not be broadened but the "critical form" would be altered and the singularity could be converted to a cusp. Indeed, both techniques of data analysis described above produced a negative value for α' leading to a cusp as the temperature approaches the ordering temperature from below. It is not clear, however, why renormalization appears to occur only below T_N. The possibility that the rounding is due to the random hyperfine fields cannot be excluded; it should be noted, however, that in $MnCl_2 \cdot 4H_2O$ the rounded region is $1\frac{1}{2}$ orders of magnitude less than is found here, even though the hyperfine constants are much the same.[26] It therefore appears highly unlikely that the hyperfine interaction plays a major role in altering the critical specific heat in $CoCl_2 \cdot 6H_2O$ as determined in our experimental results.

We believe the rounding which was observed

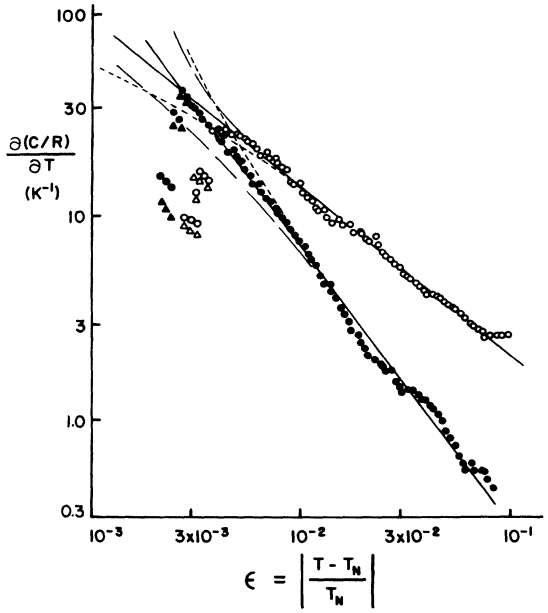

FIG. 3. Derivative of the specific heat $\partial C/\partial T$ vs temperature. The choice of $T_N = 2.2910$ K produced the greatest range of linearity on this plot. The data were fitted to Eq. (1) by choosing values of α, α' T_N and determining A, B by a linear least-squares technique. The derivatives were then calculated by using Eq. (5). The results below T_N are given by open symbols and above T_N by closed symbols. Very different values of α, α' could be used in the original fitting procedure and still not alter the result obtained from this plot. Fixed values chosen for the original fits were $T_N = 2.291$ K and for data above T_N, $\alpha = 0.3$, closed circles, $\alpha = 0.4$, closed triangles, for $T < T_N$, $\alpha = -0.10$, open triangles, $\alpha = -2.0$, open circles. In both cases the effect of using different values for α, α' to fit the data is negligible outside of the rounded region. The dotted lines show the effect of decreasing T_N by 2 mK, and the dashed lines show the effect of increasing T_N by 2 mK. From the fits we find $\alpha' = -0.18 \pm 0.03$, $\alpha = 0.35 \pm 0.06$.

here can be explained in the same manner as results for other systems have been explained.[22,27-30] If the system is subdivided into a number of microsystems then a distribution of ordering temperatures will exist. The specific heat of the entire sample would then be given by

$$C(T, T_N) = \sum_i C(T, T_{Ni}) f(T_N, T_{Ni}) / \sum_i f(T_N, T_{Ni}), \quad (6)$$

where $C(T, T_{Ni})$ is the asymptotic specific heat at T for the ith region and $f(T_N, T_{Ni})$ is the distribution function giving the fraction which orders at T_{Ni}. Accordingly we have calculated the specific heat of a system using a Gaussian distribution of ordering temperatures with half-width Γ. For the case at hand the asymptotic form found in Sec. III B was used for $C(T, T_{Ni})$. The value of the Gaussian half-width Γ was varied to produce the best fit to the data over the entire critical range, that is, for $\epsilon < 7 \times 10^{-2}$. The comparison between the calculated specific heat and our experimental data is shown in Fig. 4, with $\Gamma = 5$ mK. The agreement is quite satisfactory. Of course, the choice of a Gaussian distribution in treating the microcrystals is quite arbitrary. If it were possible to predict a more realistic distribution no doubt the fit could be improved still more. Nonetheless in view of this distribution of ordering temperatures it is not surprising that the least-squares fitting procedure mentioned in Sec. III A produced values of T_N differing by 0.3 mK for data above and below T_N.

The rather surprising success of Eq. (6) in fitting the rounding led us to try the same procedure on the previous results of Skalyo and Friedberg.[8] In order to determine the true significance of the procedure, the same values of α' and α used above were again used in $C(T, T_{Ni})$. Again the value of the half-width was varied to produce the best fit to their data, and the results are included in Fig. 4 with $\Gamma = 13$ mK. Thus the results from two different samples having significantly different behavior in the critical region can be related. From Fig. 4 we can see that the region which appears clearly "rounded" from first inspection is only ~5 mK wide. Our experimental specific heat actually deviates from the asymptotic form over a region ~14 mK wide. Thus, the "region of broadening" is actually much broader than one might have first guessed from a casual look at the data.

It is not clear why the observed rounding in this case is at least an order of magnitude larger than that observed previously in several other single-crystal investigations.[3,4,17,18] From the above discussion and the fact that the rounding is significantly less than that observed in a polycrystalline sample of the same material, it is quite possible that the crystal contains a large number of imperfections (grain boundaries, etc.) which effectively separate the "single" crystal into a fairly large number of microcrystals. The sizes of the microcrystals which produced the fit shown in Fig. 4 were not significantly different from the sizes of the polycrystals used in the earlier determination[8] and therefore no measurable size effect is expected within the resolution of this experiment.

V. CONCLUSION

The specific heat of $CoCl_2 \cdot 6H_2O$ has been measured with high resolution near T_N. By examining

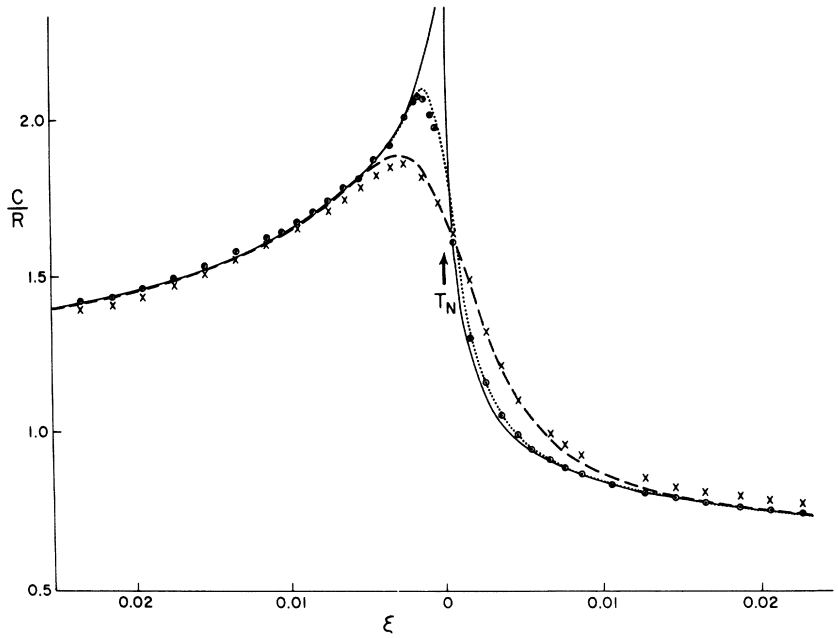

FIG. 4. Magnetic specific heat of $CoCl_2 \cdot 6H_2O$ vs temperature near T_N. Circled dots are experimental results reported here, crosses are experimental results of Skalyo and Friedberg, solid line is theoretical asymptotic critical form, dotted line is theoretical rounded form with $\Gamma = 5$ mk, and dashed line is theoretical rounded form with $\Gamma = 13$ mK.

the derivative of the specific heat, $\partial C/\partial T$, we were able to define the "unrounded critical region" in which the usual asymptotic law was obeyed. The critical exponents found from our analysis are $\alpha' = -0.19 \pm 0.04$ and $\alpha = 0.34 \pm 0.05$. By considering the sample to be made up of an array of microcrystals having a distribution of ordering temperatures we were able to describe the observed rounding; moreover, by choosing two different halfwidths for the distribution of ordering temperatures we were able to reproduce both our results and those of Skalyo and Friedberg using exactly the *same* asymptotic law.

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[30]D. C. Mattis and W. P. Wolf [Phys. Rev. Letters 16, 899 (1966)] have shown that the anisotropic hyperfine interaction $A_z I_z S_z$ will not broaden the transition and only the residual terms $A_x I_x S_x + A_y I_y S_y$ could appreciably affect the specific-heat peak (in fact Mattis and Wolf suggested that these terms in the Hamiltonian could be the source of the rounding in the results of Skalyo and Friedberg). Results on several different hydrated salts containing Co^{2+} and Mn^{2+} (see Ref. 26) show that A_x, A_y are about the same for the two ions and therefore the effect of the hyperfine interactions in $CoCl_2 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$ should be similar. Since the rounding in the latter salt is less than 0.3 mdeg it appears highly unlikely that the hyperfine interaction could account for the rounding in this case. Unfortunately there are no naturally abundant cobalt isotopes with zero nuclear spin and it is thus impossible to eliminate hyperfine coupling.