Heat Capacity of RbMnF$_3$ near the Antiferromagnetic Transition Temperature

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Precision measurements of the heat capacity C_p of the isotropic Heisenberg system RbMnF$_3$ near the antiferromagnetic transition temperature $T_c = 83.08$ K are reported. The measurements are for $76 \leq T \leq 88$ K. The results are in every respect consistent with predictions based upon recent theories of critical phenomena. They imply that C_p is finite and continuous at T_c. Under certain assumptions about the functional form of C_p, the critical exponents $\alpha = \alpha' = -0.14 \pm 0.01$ and the amplitude ratio $A/A' = 1.40 \pm 0.04$ are obtained. These parameters are believed to be characteristic of systems with short-range interactions and three degrees of freedom in the order parameter. A comparison with thermal-expansion measurements yields $dP/dT_c = 1.69 \times 10^3$ bar K^{-1} and $dS/dT_c = 0.51$ J mole^{-1} K^{-2}.

I. INTRODUCTION

There has been considerable theoretical progress recently towards the understanding of the behavior of systems near critical points.[1-4] In particular, new theoretical calculations of critical exponents[1,2] and of the equation of state[3] by means of an expansion in the dimensionality d of the system have yielded results in agreement with scaling,[5,6] and with the concept of universality[7] of critical-point parameters within a given symmetry class of the order parameter. In addition to the validity of the various scaling laws,[4-6] it is expected that critical exponents and certain other parameters will be universal in the sense that they are identical for apparently vastly different systems, provided the physical dimensionality d and the number of degrees of freedom n of the order parameter are the same, and provided the interactions have a sufficiently short range. In the three-dimensional systems commonly accessible to laboratory investigations one thus expects to encounter only three distinct sets of critical-point parameters for systems with short-range interactions, corresponding to three different values of n. For systems where the order parameter is a scalar, one has $n = 1$. Typical for this case are Ising magnets with negligible dipolar interactions, liquid-gas critical points, β-brass-type order-disorder transitions, and phase separations in liquid mixtures. When the order parameter may have more than one component, one expects different parameters. Thus, for instance, magnetic systems with two "easy axes," and the superfluid transition in liquid helium where the order parameter is complex and therefore has a magnitude and a phase, correspond to $n = 2$. They are expected to have exponents which may differ, for instance, from the liquid-gas exponents. Representative of $n = 3$ are Heisenberg magnetic systems with isotropic interactions, where the order parameter is a vector with dimensionality n equal

to the physical dimensionality $d = 3$ of the system. However, for Heisenberg ferromagnets there may be appreciable contributions to the interaction from dipolar forces; and these systems therefore do not necessarily show the critical behavior which is expected for systems with short-range forces.[8] Dipolar forces are negligible, however, for antiferromagnets; and isotropic antiferromagnets may therefore be regarded as the prime example of the case $d = 3$, $n = 3$ with short-range interactions. Possibly the best example of this class is the antiferromagnet RbMnF$_3$.[9,10] Although a variety of experimental measurements have been reported for this system near the antiferromagnetic ordering temperature T_c,[11-15] there are as yet no measurements for any system with $n = 3$ which are as accurate as some of the results for critical-point parameters corresponding to $n = 2$[16,17] or $n = 1$.[18] In addition, the results which are available for the specific heat C_p[11] and for the thermal-expansion coefficient α_p[14,15] of RbMnF$_3$ have usually been interpreted to imply a violation of the predictions of scaling which require equal exponents for C_p and α_p above and below T_c. Many of these difficulties are attributable to often very severe materials problems which made it impossible to obtain sufficiently homogeneous samples for measurements very near T_c. We wish to report in this paper two sets of measurements of C_p which were made on two very homogeneous samples of RbMnF$_3$. We find that our results agree with scaling in that the exponents which are derived from the measured C_p above and below T_c are equal. The common value of these exponents is negative, implying that C_p is finite at T_c. Our exponent is in agreement with numerical calculations for the Heisenberg system,[19,20] with results obtained from an expansion of the exponent in the dimensionality of the system,[2] and with the trend as a function of n provided by measurements for $n = 1$ and $n = 2$ and exact theoretical results for $n = \infty$.

Preliminary results of this work were reported

before, together with results for the Heisenberg ferromagnet EuO.[21] Since the transition region in EuO exhibited appreciable "rounding" because of sample inhomogeneities, additional measurements will be made on other samples and the results will be published in a separate paper.

The experimental details of the specific-heat measurements will be described in Sec. II. In Sec. III we report our results for RbMnF$_3$. An extensive analysis of these results will be reported in Sec. IV. A comparison of our data with other experiments will be presented in Sec. V. A comparison with theoretical predictions is given in Sec. VI and a brief summary is provided by Sec. VII.

II. APPARATUS AND METHODS

A. Calorimeter

1. General

The calorimetric apparatus is shown schematically in Fig. 1. It was designed for experiments covering various temperature ranges from 0.3 to 100 K.

The sample was glued with a minute amount of GE-7031 varnish to a sample holder, and the holder was suspended by nylon threads inside an isothermal shield. Thermal contact between the shield and the sample holder could be made by means of a mechanical heat switch. The shield was thermally isolated from the main bath, except for radiation heat exchange and for conduction along certain stainless-steel tubes. These tubes were used for the heat switch and for the pumpline of an inner bath, and provided physical sup-

port for the shield. The inner bath was thermally an integral part of the isothermal shield. It could be used as a He^3 stage with liquid He^4 in the outer bath in order to attain temperatures near 0.3 K. In the present case, however, it was partially filled with nitrogen, and liquid nitrogen at the normal boiling point was used in the outer bath. The refluxing nitrogen in the inner bath pumpline provided an efficient cooling mechanism for the isothermal shield. After the shield was cold, the nitrogen was removed from the inner bath. Slow cooling of the isothermal shield by radiation heat exchange was then still possible if desired. The system was enclosed in a vacuum can, and immersed in the main bath. The vacuum can contained near its bottom some Linde type 13X molecular-sieve pellets. The vacuum which had initially been established at room temperature was therefore improved considerably upon transfer of liquid nitrogen to the main bath. Although for the present work the main bath was maintained at the normal boiling point, the measurements on EuO mentioned previously and to be reported in detail elsewhere required lower temperatures, and were made with the main bath under reduced pressure and regulated near 64 K. The electrical leads were brought down through the vacuum line and were thermally attached to the bath and then to the isothermal shield. They consisted of 1.3 $\times 10^{-2}$-cm-diam manganin wire with quadruple Formvar insulation.

2. Isothermal Shield

The isothermal shield consisted of an upper platform with the inner bath, and of a heavy-walled can which completely surrounded the sample space. It was made primarily of copper, and the can was thermally attached to the platform by bolts which compressed an indium gasket. Attached to the inside of the shield were three copper rods from which the sample could be conveniently suspended by nylon strings. The strings were held under tension by springs at the shield end. The jaws of the heat switch (Fig. 1) were indium coated, and were thermally attached to the shield with copper braid. The shield temperature T_S could be raised and maintained above the main bath temperature by either of two heaters wound one each around the inner bath and along the entire length of the shield can. By means of either platinum[22] or germanium[23] thermometers located at the shield platform, T_S could be measured. At the temperature of the present experiment the 2 kg of copper in the shield provided a large thermal mass, and the heat losses to the main bath (mostly radiation) were sufficiently small to result in shield-bath relaxation times of about 10 h. Internal relaxation times within the shield were
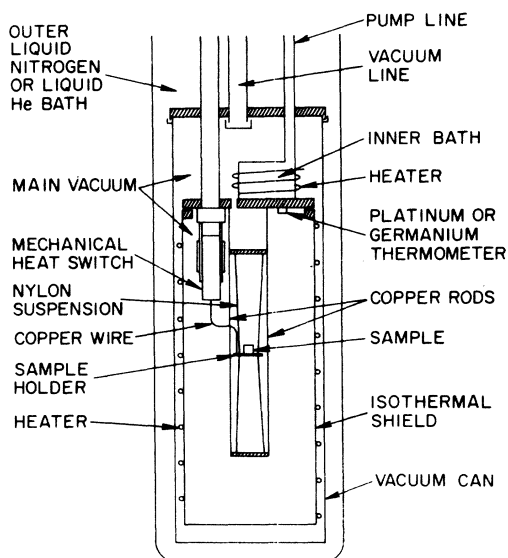

FIG. 1. Schematic diagram of the calorimeter.

at most a few seconds. Under these circum-
stances a good isothermal environment over the
duration of a heat-capacity measurement (≈ 10
min) could be provided by adjusting a steady-state
heat input to an appropriate level after the desired
shield temperature was established.

3. Sample Holder

The sample holder was made of a copper disk
which was 18 mm in diameter and 0.2 mm thick.
A 0.075-cm-diam copper wire was soldered to the
disk, and its free end was placed between the heat-
switch jaws so that thermal contact could be made
between the sample holder and the isothermal
shield. A flat heater was varnished to the bottom
of the sample holder, using GE-7031 varnish. Its
resistance was nominally 5770 Ω and it was made
of 0.0038-cm-diam Karma[24] wire. The heater
was provided with two current and two potential
leads. The current leads between the sample
holder and the top of the isothermal shield had a
total resistance of approximately 10 Ω, half of
which was included in the heater resistance for
calculating the heater power. A thermistor[25]
which was also varnished to the bottom of the same
holder was used as the temperature sensor. The
total weight of this system was about 0.8 g, and
at 83 K it had a heat capacity of 0.15 J/K. Ther-
mal relaxation times with a typical RbMnF$_3$ sample
glued in place were at most a few seconds.

B. Thermometry

The temperature scales used in this experiment
were maintained on three platinum thermometers[22]
which were mounted on the isothermal shield (Sec.
II A 2). All platinum thermometer resistances
were measured by a four-lead direct-current po-
tentiometric technique. The temperature scale
used for the first sample (RbMnF$_3$-I, see Sec. IIC)
was based on a calibration supplied by the ther-
mometer manufacturer,[22] whereas the work on the
second sample employed a calibration by Cryocal,
Inc.[26] The two temperature scales differed from
each other by no more than 0.03 K for T near 83
K. We estimate that the difference between these
two temperature scales may cause differences of
perhaps 1% in the derived specific heat; but this
difference should be nearly constant over the nar-
row range of T involved in this work, and should
not affect the singular temperature dependence of
C_p and the crucial critical-point parameters de-
rived from the data.

The temperature increments used in the specific-
heat measurements were determined with the
thermistor[25] which was mounted on the sample
holder (Sec. IIA 3). The thermistor resistance
was measured using an ac-bridge technique de-
scribed elsewhere.[27] It was calibrated against the

platinum thermometers by closing the heat switch
and by adjusting the sample temperature until it
was constant in time. The precision of this pro-
cedure was much greater than the accuracy of the
original platinum-thermometer calibrations and
calibration points could readily be obtained with a
scatter of $\pm 10^{-3}$ K. The simple polynominal

$$T = A + B \ln R + C \, (\ln R)^2 \tag{1}$$

was fitted to the calibration data by a least-squares
procedure, and represented them within the ran-
dom scatter of about $\pm 10^{-3}$ K over the temperature
interval of the measurements. We preferred Eq.
(1) for our purposes over certain others[28] because
of its simplicity and its linearity in the parameters.
Within the resolution of our comparison of the
working thermometer with the platinum thermom-
eters, the thermistor maintained its calibration
for weeks as long as it was not thermally cycled.
Thermal cycling to room temperature could result
in calibration changes of 0.1 K.

The temperature resolution of the thermistor
measurements were about 2×10^{-5} K near 83 K.
This enabled us to measure C_p to $\pm 1\%$ when $|t|$
$\equiv |1 - T/T_c| \gtrsim 3 \times 10^{-5}$, and to $\pm 0.1\%$ when $|t| \gtrsim 3$
$\times 10^{-4}$.

C. Samples

The samples used were two single crystals, to
be referred to as I and II, of RbMnF$_3$. RbMnF$_3$-
II was the same sample that was used by Golding[14,15]
for thermal-expansion measurements. RbMnF$_3$-
I was cut from the same main sample that yielded
RbMnF$_3$-II. RbMnF$_3$-I weighed 3.331 g, and
RbMnF$_3$-II weighed 2.510 g. Both samples were
approximately cubic in shape. The results for
RbMnF$_3$-I are those reported briefly previously.[21]

D. Procedure

After liquid nitrogen was transferred to the outer
bath, nitrogen gas was admitted to the inner bath
until cooling of the isothermal shield by refluxing
of nitrogen in the pumpline started. The heat
switch was left open so that the sample was cooled
slowly by thermal radiation. This was done in
order to minimize the stresses to which the sam-
ple would be exposed because of a different rate of
contraction for the sample holder.[29] After 18 h
the temperature was near 100 K. The heat switch
was closed and the nitrogen in the inner bath was
pumped out. The thermistor was then calibrated
against the platinum thermometer (Sec. II B).

The heat-capacity measurements were made by
a conventional technique. The isothermal shield
was kept at a constant temperature T_S near the
sample temperature T. Power was dissipated in
the heater for a measured length of time, and
foredrifts and afterdrifts of the sample tempera-

ture could be extrapolated linearly to the middle of the heating time interval to determine the temperature step ΔT. Initial relaxations after the heater was turned off lasted no longer than a few seconds, and were ignored. The heat capacity was first measured with $\Delta T \cong 0.2$ K. These results yielded an approximate transition temperature; and then data points with smaller ΔT were taken in the transition region. The smallest ΔT which we used as approximately 4 mK.

The experimental measurements yield the ratio $\Delta Q/\Delta T$; but after applying a curvature correction and subtracting the sample-holder heat capacity we get C_p of $RbMnF_3$. The pressure is of course equal to zero. In most cases the curvature correction did not exceed 0.1% of the total heat capacity. The data were converted to a molar basis, using a molecular weight of 197.40 g.

E. Heat Capacity of Sample Holder

The heat capacity of the sample holder was measured separately with random errors of less than 0.1%. It never exceeded 10% of the total heat capacity. A linear function of T was adequate to represent the sample-holder heat capacity in the pertinent temperature range.

III. RESULTS

The results for $RbMnF_3$-II are shown in Figs. 2 and 3. Those for $RbMnF_3$-I were published in graphical form previously, and are very similar to the data in Fig. 3. The slight difference between the two sets of measurements is attributable to differences in the temperature scales (Sec. II B).

Over our temperature range from 76 to 88 K, the results could be represented well by the equation

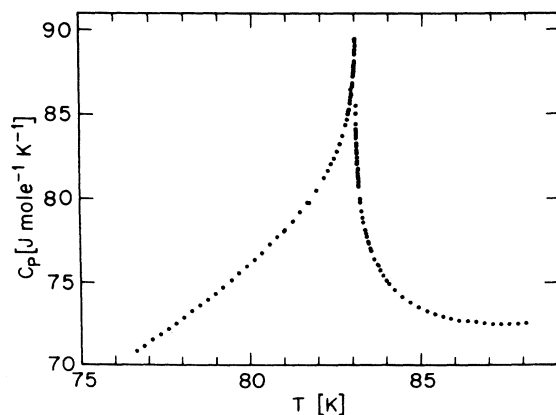$$C_p = (A/\alpha)(|t|^{-\alpha} - 1) + B + Et , \qquad (2)$$

where

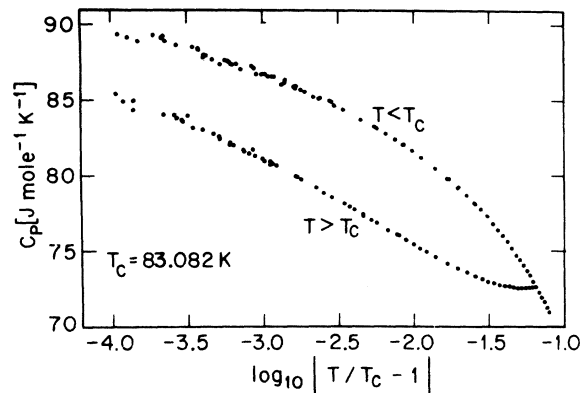FIG. 2. Specific heat of $RbMnF_3$-II as a function of T.

FIG. 3. Specific heat of $RbMnF_3$-II as a function of $\log_{10}|T/T_c - 1|$.

$$t \equiv (T - T_c)/T_c \qquad (3)$$

and where T_c is the transition temperature. Since some of the parameters in Eq. (2) will generally be different above and below T_c, the ones that pertain to $T < T_c$ are identified by a prime. In fitting our data to Eq. (2), A and B were permitted to be different above and below T_c; but α, E, and T_c could be forced to be identical on the two sides of the transition without any significant sacrifice in the quality of the fit. The parameters for the two samples are given in Table I. We believe that all differences in parameters between the two samples can reasonably be attributed to the different temperature scales. It is particularly gratifying that of all the parameters the result for $\alpha = \alpha'$ is least sensitive to the temperature scales. In absolute terms, we believe that the results for $RbMnF_3$-II yield a C_p somewhat closer to the true C_p than those for $RbMnF_3$-I.

The deviations of our data in percent from Eq. (2) and Table I are shown in Fig. 4 for $RbMnF_3$-II. It is evident that the function is a good representation of the results. However, for the smallest $|t|$ departures from Eq. (2), although they remain less than 1%, are probably significant and may be attributable to sample inhomogeneities. The range of t over which these inhomogeneities are

TABLE I. Parameters for Eq. (2).

Parameter	$RbMnF_3$-I	$RbMnF_3$-II
$\alpha = \alpha'$	-0.1406	-0.1416
A [J mole^{-1} K^{-1}]	6.154	6.305
A' [J mole^{-1} K^{-1}]	4.493	4.496
B [J mole^{-1} K^{-1}]	54.811	53.248
B' [J mole^{-1} K^{-1}]	68.174	67.123
$E = E'$ [J mole^{-1} K^{-1}]	89.833	76.638
$T_c = T_c'$ [K]	83.048	83.082

noticeable is similar to that deduced by Golding[15] from thermal-expansion measurements on the same sample, and is an order of magnitude smaller than the range of t over which sample inhomogeneities were noticeable in previous C_p measurements. [11]

A deviation plot of the results for RbMnF₃-I does not differ significantly from Fig. 4, and will not be shown.

IV. ANALYSIS

A. The Function

The theoretical predictions about critical phenomena with which we would like to compare our results pertain to the asymptotic behavior of C_p. Since experimental results necessarily are obtained at some nonzero value of $T_c - T$, it is by no means trivial to extract from them reliable estimates of parameters which can be compared with the predictions. This problem has been dealt with in detail for the case of C_p near the superfluid transition in liquid helium, and we refer the interested reader to Sec. V of Ref. 30. We will proceed here by comparing the measured C_p with the function

$$C_p = (A/\alpha)(|t|^{-\alpha} - 1)(1+D|t|^x)+B+Et \qquad (4)$$

for $T > T_c$, and with the same function with primed parameters for $T < T_c$.[31] The term $(A/\alpha)|t|^{-\alpha}$ represents the leading contribution to the singularity of C_p. If $\alpha > 0$, C_p becomes infinite at T_c; but for $\alpha < 0$, C_p remains finite and has the value $B - A/\alpha$ or $B' - A'/\alpha'$ at T_c. We will insist that $x > 0$; and then the term $D|t|^x$ will vanish at T_c and will represent a singular contribution to C_p which is of higher order than the leading singularity. It is known both from experiment[16,17,30] and theory[32] that such terms generally must be considered in the data analysis.

The constant B may contain a contribution associated with the phase transition, and therefore need not have the same value above and below T_c. The major contribution to B in the case of RbMnF₃ will, however, be from other degrees of freedom of the system which make regular contributions to C_p. Foremost amongst these are of course the lattice degrees of freedom. These regular contributions will be a function of the temperature; and in order to take this T dependence into account, we have included the term Et in Eq. (4). In order to assure that this term is indeed regular at T_c, we shall always impose the constraint

$$E = E' . \qquad (5)$$

Since most of the contribution to B comes from regular terms, one would expect E not to be much larger than B. Indeed, it is already apparent from Table I that B and E are of about the same size.

Our approach to dealing with the regular contribution is somewhat different from that of some previous workers.[10,11,14,15] Often, a "lattice contribution" to thermodynamic properties has been estimated for instance by comparison with isomorphic materials which have no phase transitions. This contribution is then subtracted, and only the "magnetic" part is considered and analyzed without inclusion of terms which are regular functions of T. This latter approach may lead to difficulties for two reasons. First, it is not clear that subtraction of a regular background based on isomorphic materials eliminates all regular contributions to C_p, because some of these contributions may be associated with the phase transition. Second, even if in principle a reliable estimate of the regular contributions were possible, then in practice this estimate would be subject to some uncertainty, equivalent to an uncertainty for E in Eq. (4). Since the parameters in Eq. (4) are correlated, the
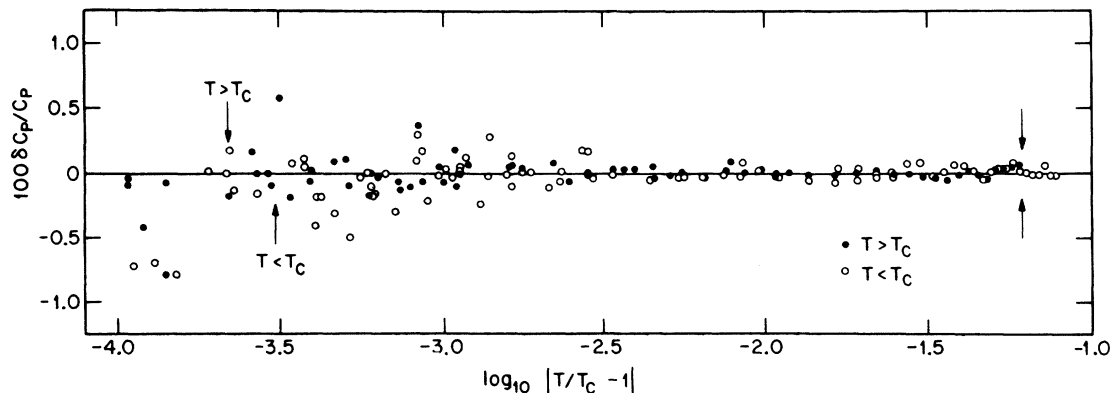

FIG. 4. Deviation of the data from the best fit. The arrows mark the $|T/T_c-1|$ corresponding to the t_{MIN} and t_{MAX} used in the fit (sample II).

uncertainty in the regular terms may have a sizable effect upon the uncertainty of the other parameters. Simply setting E equal to zero after subtraction of a lattice estimate is equivalent to assuming that this estimate is exact, and may lead to unrealistically small errors for the other parameters. Of course, if the range of $|t|$ is extremely narrow ($|t| \lesssim 10^{-3}$, for instance), then the correlation of the other parameters in Eq. (4) with E is small, and the regular terms must not be known very accurately. On the other hand, if the range of $|t|$ is too large we would expect to have to include terms in our analysis which vary as t^2.

B. Method

Various methods have been employed to fit specific-heat measurements to functions like Eq. (4).[33] Most of them were devised because of the computational difficulties involved in nonlinear-least-squares problems. These difficulties are now largely removed because of the availability of satisfactory computer programs and adequate computational facilities. We therefore used the Marquardt maximum-neighborhood method[34] to obtain least-squares fits of Eq. (4) to the data with various constraints on the parameters. Each fit yielded the best parameters for Eq. (4), as well as their standard errors. It is perhaps worth emphasizing at this point that the computed errors take into account the correlation between the parameters, and that the errors therefore are strongly dependent upon some of the constraints which are imposed. All the data used in the fits were assigned a weight which was inversely proportional to our best a priori estimate of the square of the random probable error. We used the smaller of

$$W_i = (2 \times 10^{-5} C_p / \Delta T)^{-2} \qquad (6a)$$

or

$$W_i = (10^{-3} C_p)^{-2} \qquad (6b)$$

for the ith data point. The number 2×10^{-5} in Eq. (6a) is the estimated temperature resolution in K, and 10^{-3} in Eq. (6b) corresponds to a minimum random error in C_p of 0.1% which is assumed present when the temperature resolution does not limit the precision of the data.

Because of sample inhomogeneities (see Sec. III), it is difficult to interpret measurements extremely near T_c.[35] Certainly, data affected by inhomogeneities should not be fit to Eq. (4) without some modification. We discarded such data entirely, and used in the analysis only measurements for which $|t| \geq t_{\text{MIN}}$, where

$$t_{\text{MIN}} \equiv |T - T_0| / T_0 . \qquad (7)$$

For T_0, a constant temperature rather close to the least-squares result for T_c was chosen. We used

83.05 and 83.08 K for samples I and II, respectively. It was not possible to use T_c itself as a reference temperature for the elimination of data because T_c is least-squares adjusted, and the number of data points used in the fit would vary upon successive iterations. Since the range of t over which inhomogeneities are important is not known initially, the data were usually analyzed for several t_{MIN}. We also sometimes eliminated data from the fit if $t > t_{\text{MAX}}$ in order to test whether the neglected higher-order regular terms (t^2, etc.) are important. For the definition of t_{MAX} we also used T_0; but of course, $|T_0 - T_c|/T_0 \ll t_{\text{MAX}}$ and the definition of the reference temperature is not as important.

C. Results for Parameters

Equation (4) without any constraints contains 14 adjustable parameters (7 for each side of the transition, including T_c and T_c'). With such a large number of parameters it is very difficult to obtain convergence of the iterative nonlinear least-squares procedure; and if convergence is obtained, then the errors for the parameters are so large that no particularly useful information about the asymptotic behavior of C_p can be obtained. However, it is not unreasonable to impose certain constraints upon Eq. (4), and to inquire whether these constraints and the data yield parameters with errors which are consistent with theoretical predictions. Some of these constraints may indeed be predicted by theory, and their imposition yields a test of the over-all consistency of theory and experiment together.

As already mentioned, we have always imposed the constraint Eq. (5). In addition, it was assumed initially that $D = D' = 0$; i.e., that singular higher-order corrections to the leading singularity are negligible. The nine parameters A, A', B, B', α, α', T_c, T_c', and $E = E'$ were allowed to vary freely, and data over the range $t_{\text{MIN}} \leq |t| \leq 6.25 \times 10^{-2}$ were used in the fit. For sample I, this resulted in the values for α, α', T_c, and T_c' which are shown in Fig. 5 for several values of t_{MIN}. It is apparent from these data that the measurements readily permit $T_c = T_c'$. The same conclusion is obtained from an analysis of the results for sample II. If the constraint $D = D' = 0$ had not been imposed, all error bars in Fig. 5 would be larger; but the error bars for T_c and T_c' would still overlap. The results for α and α' indicate that these exponents are both negative, and are consistent with the scaling prediction $\alpha = \alpha'$.

Since the data permit the constraint $T_c = T_c'$, and since this constraint is reasonable on physical grounds, the data were analyzed next by using Eq. (4) and $D = D' = 0$, $E = E'$, and $T_c = T_c'$. The remaining eight parameters were least-squares ad-
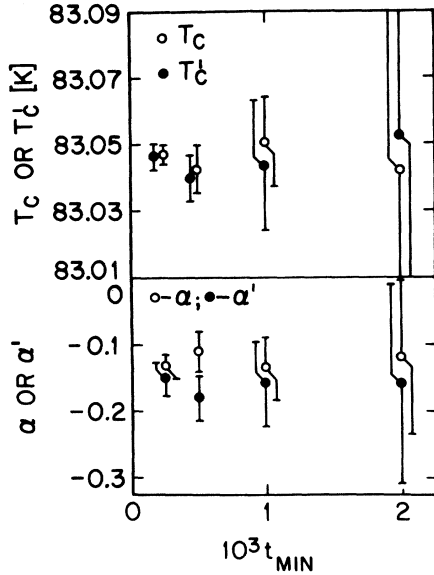
FIG. 5. α, α', T_c, and T_c' obtained from a fit of the data to Eq. (4) for different ranges of t with the constraints $E=E'$, $D=D'=0$ (sample I).

justed. The results for α and α' are shown as open and solid circles in Fig. 6(a) for several t_{MIN}, and those for $T_c=T_c'$ are given in Fig. 7(a) as open circles. The values given in Figs. 5 and 6 were obtained from sample II; but the results for sample I are very similar and in part have already been given in Fig. 2 of Ref. 21 as open and solid circles. Figure 6 shows that even with the constraint $T_c=T_c'$ the results are consistent with $\alpha=\alpha'$, and the exponents are again negative.

Since $\alpha=\alpha'$ is permitted by the data, and since this relation is predicted by scaling, we next imposed this constraint on the data analysis. This yields the best value of α and α' consistent with the assumption that scaling is valid. In addition, we retained $D=D'=0$, $E=E'$, and $T_c=T_c'$. The remaining seven parameters were least-squares adjusted, and the solid squares in Figs. 6(a) and 7(a) were obtained for $\alpha=\alpha'$ and $T_c=T_c'$ for sample II with several t_{MIN}. Additional results for sample I can be found in Fig. 2 of Ref. 21. Numerical values for all parameters and both samples were given already in Table I for $t_{MIN}=2\times10^{-4}$. Both $\alpha=\alpha'$ and $T_c=T_c'$ are found to be independent of t_{MIN} within their rather small uncertainties. The standard errors obtained for $\alpha=\alpha'$ from the least-squares fit is only about ± 0.002 if $t_{MIN}=2\times10^{-4}$. On the basis of this analysis, we estimate that $\alpha=\alpha'$ and A/A' probably lie in the ranges -0.14 ± 0.01 and 1.40 ± 0.04, respectively, if the amplitudes of singular corrections to the asymptotically dominant behavior are small.

Since the regular contribution to C_p had been

approximated in the above analysis by a constant and a term proportional to t, we next varied t_{MAX} at constant t_{MIN} in order to see if the neglect of terms of order t^2 and higher had yielded systematic errors. Figures 6(b) and 7(b) show the results corresponding to the last two sets of constraints (8 and 7 parameter fits). It is evident that the derived parameters do not depend upon t_{MAX}.

With the seven-parameter fit and the widest range of t, the errors of the parameters were sufficiently small that some of the constraints imposed so far could be relaxed. We therefore permitted D and D' to be different from each other, imposed $x=x'$, and retained $T_c=T_c'$, $\alpha=\alpha'$, and $E=E'$. This ten-parameter fit for $t_{MIN}=2\times10^{-4}$ yielded $\alpha=\alpha'=-0.14\pm0.06$, $x=x'=0.46\pm0.37$, $D=-1.1\pm1.0$, and $D'=0.1\pm2.1$ for sample II. We conclude that with our resolution we cannot establish the existence of singular correction terms to C_p of RbMnF₃. Imposing in addition the theoretically predicted value[32] $x=x'\cong0.5$, which is supported by other experiments,[17] yielded $D=-1.1\pm0.6$ and $D'=-0.1\pm0.4$. These results also do not really rule out the possibility that $D=D'=0$. The additional constraint $x=x'=0.5$ considerably reduces the uncertainty in the leading exponent, and results in $\alpha=\alpha'=-0.134$ with a standard error of 0.005. This nine-parameter fit left an appreciable uncertainty in the amplitude ratio, however, because of a large correlation between A and D, and between A' and D'. It gave $A/A'\cong1.2\pm0.2$.

The negative exponent which is obtained for C_p implies that the heat capacity is finite at T_c. When C_p is finite, it is of interest to inquire whether it is continuous at T_c; for a discontinuity would correspond to an exponent equal to zero and would therefore in some sense be the leading singularity. The finite value of Eq. (4) at T_c is equal to $B-A/\alpha$ or $B'-A'/\alpha'$. With the constraints $\alpha=\alpha'$, $T_c=T_c'$,
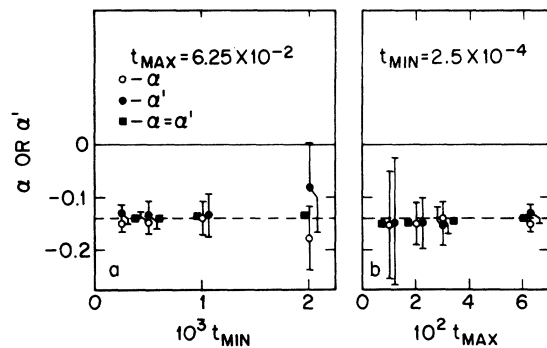

FIG. 6. Exponents α and α' obtained from a fit of the data to Eq. (4) for different ranges of t. The constraints are $T_c=T_c'$, $E=E'$, $D=D'=0$. Results are given with and without the additional constraint $\alpha=\alpha'$.
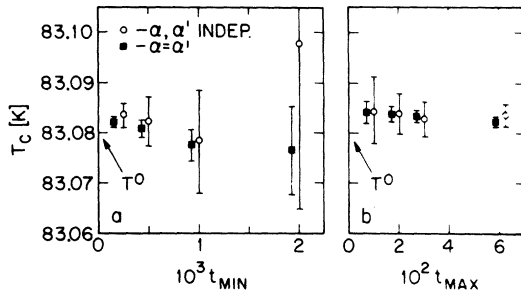
FIG. 7. $T_c = T_c'$ obtained from a fit of the data to Eq. (4) for different ranges of t. The constraints are the same as those of Fig. 6.

$E = E'$, and $D = D' = 0$ we obtained $B - A/\alpha = 97.78 \pm 0.43$ J mole^{-1}K^{-1} and $B' - A'/\alpha' = 98.87 \pm 0.26$ J mole^{-1}K^{-1} for sample II. Although the probable errors do not quite overlap, the difference is only 1.5 times the sum of the standard errors, and should not be regarded as significant. For sample I the values and errors were similar, and likewise were consistent with a continuous C_p. If singular correction terms are allowed (i.e., D and D' not equal to zero), the errors are larger, and the values are still consistent with a continuous C_p.

V. COMPARISON WITH OTHER EXPERIMENTS

A. Specific Heat

It is difficult to compare our measurements directly with previous results for C_p[11] because in the past only the magnetic heat capacity was reported and the subtracted lattice contribution was not given. However, Teaney et al.[11] interpreted their C_p in terms of a logarithmic divergence for $T > T_c$, corresponding to $\alpha = 0$. For $T < T_c$, their C_p appeared to approach a finite value, implying $\alpha' < 0$. Although this seems contrary to the results reported here, the difference may be largely one of interpretation. In the earlier work, T_c was arbitrarily chosen to be very near the temperature where C_p reaches a maximum. If we arbitrarily impose the constraint $\alpha = 0$ (i.e., insist on a logarithmic divergence for $T > T_c$) in the analysis of our data, then we also obtain a T_c very near the maximum of C_p. Deviations from the fit will of course not be random since our data do not really allow $\alpha = 0$. In Fig. 8 we present on linear scales our results for sample II very near T_c. The temperature indicated by the vertical bar labeled A is the T_c corresponding to $\alpha' \neq \alpha = 0$. For α' this analysis yields the value -0.28. Although this procedure does not yield a statistically satisfactory fit to our results, and although it is not justifiable for any a priori reason or on any fundamental grounds, it does yield parameters

which are not in disagreement with the earlier work and indicates a certain degree of consistency between the experimental results. Our best estimate of T_c is also shown in Fig. 8 and labeled B.

B. Thermal Expansion

1. Exponents

The isobaric volume thermal-expansion coefficient α_p (not to be confused with the exponents α and α') is an asymptotically linear function of C_p (see Sec. VB2). It follows that α_p should have the same asymptotic dependence upon t as C_p. Therefore the exponents α and α' can also be obtained from measurements of α_p and an analysis in terms of an equation equivalent to Eq. (4).

The linear thermal-expansion coefficient β_p of RbMnF$_3$ was measured by Golding[14,15] on the same sample which yielded the C_p data labeled RbMnF$_3$-II. For a cubic crystal like RbMnF$_3$, β_p differs from α_p only by a multiplicative constant which is independent of t; and therefore β_p should also reveal the same asymptotic behavior as C_p. Golding obtained[15] from his results the exponents $\alpha = 0.007 \pm 0.02$ and $\alpha' = -0.10 \pm 0.03$. These values and their errors do not seem to permit $\alpha = \alpha'$, and therefore suggest a violation of scaling. However, the exponents were obtained on the basis of the assumption that a pure power law [$D = D' = 0$, $E = E' = 0$ in Eq. (4)] could be used in the analysis. Inclusion of singular correction terms, and of terms which are regular functions of T, would increase the statistical errors considerably and would permit equal exponents above and below T_c for β_p. Golding subtracted from his data the "lattice expansivity," and therefore felt that the constraint $E = E' = 0$ was justified. However, his estimated lattice expansivity corresponds to the true regular contributions to β_p only within certain errors (see also Sec. IV A); and in principle $E = E'$ should be
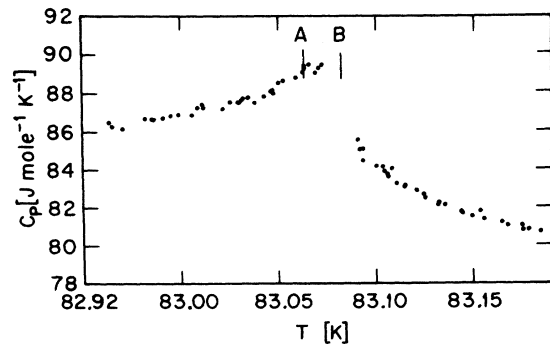

FIG. 8. Specific heat near the transition. A: T_c obtained when $\alpha \neq \alpha'$ with the constraints $\alpha = 0$. B: T_c obtained by the least-squares fit with the constraints $\alpha = \alpha'$, $E = E'$, $D = D' = 0$ (sample II).

permitted to vary over the range determined by
these errors when the uncertainties of the other
parameters are determined. Since we are unable
to estimate the uncertainty in $E = E'$ for Golding's
data, we have not pursued this problem further;
but one must keep in mind that the assumption
$E \equiv E' \equiv 0$ may lead to unrealistically small errors.
We reanalyzed the expansivity data over about the
same range of t that was used in the original work,[15]
and used the constraints $\alpha = \alpha'$, $E = E' = 0$, $T_c = T'_c$,
and $x = x' = 0.5$. Permitting nonzero values for
D and D' was sufficient to allow the constraint α
$= \alpha'$, and we obtained $\alpha = \alpha' = -0.12 \pm 0.23$ from
the data when equal exponents were assumed. The
rather large uncertainty is attributable primarily
to the narrow range of t spanned by the data. For
the amplitudes of the correction terms we have
$D = 1.9 \pm 2.3$, and $D' = 1 \pm 5$. It appears on the basis
of this analysis that the thermal-expansion mea-
surements are consistent with the results for C_p.

2. Pippard Relation

The total differential of the entropy

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT , \tag{8}$$

the Maxwell relation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, and
the definition $C_p = T(\partial S/\partial T)_P$ yield

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_t + VT\left(\frac{\partial P}{\partial T}\right)_t \alpha_p . \tag{9}$$

Here the derivatives at constant t usually approach
a finite value at $t = 0$, and for sufficiently small t
are very nearly equal to the derivatives along the
transition line. Relations like Eq. (9) are often
referred to as Pippard[36] relations. Equation (9)
implies that C_p is an asymptotically linear function
of α_p, and thus in the cubic case also of β_p. A
plot of β_p vs C_p should therefore yield a single
straight line for results both above and below T_c,
provided $|t|$ is small enough. If the data do not
at least approach a unique straight line as $|t|$
vanishes, they must be regarded as thermodynam-
incally inconsistent with each other. This appar-
ently straightforward comparison is difficult in
practice, however, unless β_p and C_p are measured
simultaneously, at the same T, and on the same
temperature scales [see for instance Sec. IV B
of Ref. 30, where simultaneous measurements
for C_v and $(\partial P/\partial T)_v$ were compared]. In the pres-
ent case, the temperature scales are of course
different, and the results cannot be compared
directly. Therefore, we compared the pairs of
values β_p and T obtained by Golding with smoothed
values of C_p. We obtained the smooth C_p by first
choosing a T_c appropriate to Golding's β_p and on
his temperature scale. From this T_c and his set
of T's we obtained values of t. For these t, C_p

was evaluated, using Eq. (2) and the parameters
in Table I for RbMnF₃-II. The experimental β_p
was then plotted against this C_p. The result for
the $T_c = 83.0425$ K quoted by Golding is shown in
Fig. 9(a). From this figure it seems that the
two sets of measurements are quite inconsistent
with each other. However, when $T_c = 83.0530$ K
is chosen, we obtain the results in Fig. 9(b).
Although the results in Fig. 9(b) are not repre-
sented perfectly by the solid straight line, the fit
does seem fairly reasonable. A T_c of 83.0530 K
is not consistent, however, with a pure power-
law fit to Golding's data, and is permitted by these
data only if singular or regular correction terms
are included in an analysis. If T_c is fixed at
83.0530 K, singular corrections to the asymptotic
behavior are allowed, and $\alpha = \alpha'$ is assumed, then
the β_p yield $\alpha = \alpha' = -0.15 \pm 0.16$. Thus, when con-
sistency between C_p and β_p in terms of Eq. (9) is
obtained by adjusting the choice of T_c, then the
two sets of data also yield the same exponents.
From the straight line in Fig. 9(b), one has $dS/dT_c = 0.51$ J mole⁻¹K⁻² and $dP/dT_c = 1.69 \times 10^3$ bar
K⁻¹ if a molar volume of 45.52 cm³ is used.[37]

It might be remarked that consistency of β_p with
C_p could have been obtained also by adjusting T_c
for C_p, and by adhering to Golding's choice of T_c
for β_p. This procedure would, of course, lead
to $\alpha \neq \alpha'$.

C. Neutron Scattering and Scaling

The properties of RbMnF₃ near T_c have been
investigated[12,13] by neutron scattering. These
measurements were interpreted to yield the ex-
ponents[4]

$$\beta = 0.316 \pm 0.008 , \tag{10a}$$

$$\nu = 0.724 \pm 0.008 , \tag{10b}$$

$$\gamma = 1.397 \pm 0.034 , \tag{10c}$$

$$\eta = 0.067 \pm 0.01 . \tag{10d}$$

The interpretation[12,13] was made on the assumption
of pure-power-law behavior even for rather large
t. The exponent ν, for instance, was derived
from data with $10^{-3} \leq t \leq 0.2$ without permitting
singular or regular correction terms. If these
assumptions are valid for RbMnF₃, then the above
exponents may be compared with α and with the
predictions of scaling; but in case of any appar-
ent departures from scaling we must remember
that the error estimates quoted in Eqs. (10) are
very optimistic. We will compare the results
Eqs. (10) with the estimate $\alpha = \alpha' = -0.14 \pm 0.01$
which we believe to pertain if singular corrections
are small.

From scaling, we have the exponent relation

$$\nu = \tfrac{1}{3}(2 - \alpha) . \tag{11}$$

Our C_p result yields $\frac{1}{3}(2 - \alpha) = 0.713 \pm 0.003$, which is in good agreement with the value of ν given in Eq. (10b). However, it is also predicted by scaling that

$$2\beta + \gamma = 2 - \alpha . \tag{12}$$

For $2 - \alpha$, we obtain 2.14 ± 0.01. Contrary to this value, the neutron scattering results, Eqs. (10a) and (10c), give 2.03 ± 0.04 for $2\beta + \gamma$. We note, however, that the values of β and γ are also inconsistent with the result Eq. (10b) for ν; for Eq. (11) predicts that $2 - \alpha = 3\nu$. Equation (10b) gives 2.172 ± 0.024 for 3ν, which also differs from $2\beta + \gamma$. It appears likely that the errors of β or γ or both have been underestimated.

D. Other Heisenberg Systems

On the basis of universality arguments[7] and of the expansion of exponents in the dimensionality of the system[1-3] it is expected that all phase transitions characterized by an order parameter with three degrees of freedom in materials with short-range forces should have identical exponents. We therefore expect all isotropic antiferromagnets to yield the same α and α' as that found here for RbMnF$_3$; but unfortunately there are no other examples of this group for comparison.

Other phase transitions with three degrees of freedom in the order parameter are those occurring in some ferromagnets; but is has been pointed out recently by Fisher and Aharony[8] that for these materials dipolar long-range interactions will modify the behavior and will result in different asymptotic exponents. However, for ferromagnets with relatively high transition temperatures the difference in behavior due to the different range of interaction will be noticeable only extremely
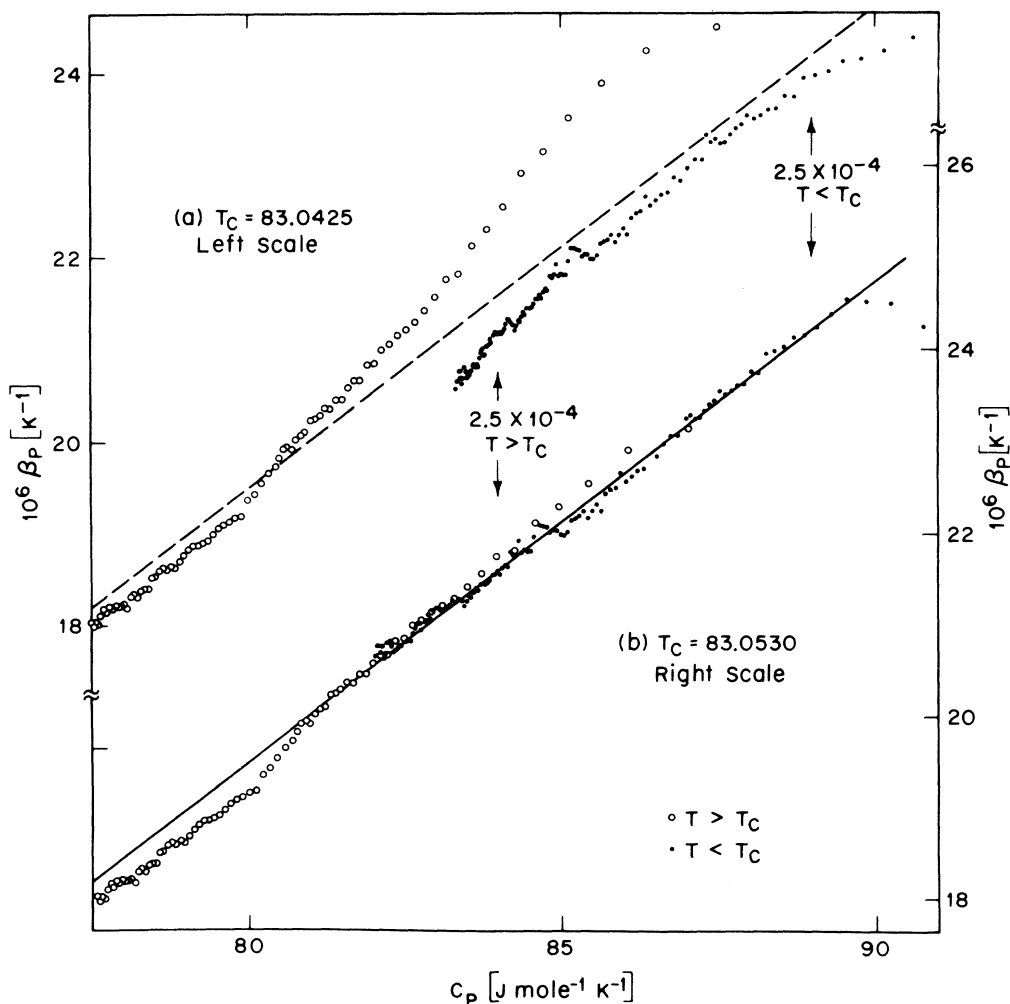

FIG. 9. Linear thermal-expansion coefficient (Ref. 15) as a function of C_p for two choices of T_c (see text for detail). The two sets of points are displaced vertically with respect to each other, and the two straight lines are identical and are provided as references.

near T_c. Therefore, it is not unreasonable to expect the ferromagnet nickel with a transition temperature of about 631 K to yield the same exponents as those found for RbMnF$_3$, provided the measurements do not extend too near the transition. Indeed, results for C_p have been interpreted to imply $\alpha = \alpha' = -0.10 \pm 0.03$[38]; although another set of measurements has been used to assert that $\alpha' < \alpha \cong 0$.[39] The result $\alpha = \alpha' = -0.10 \pm 0.03$ for nickel is of course consistent with our result for RbMnF$_3$ and with our expectations; but this interpretation also yielded a C_p which is discontinuous at T_c. A discontinuous C_p is not expected from theory, and differs from our conclusion for RbMnF$_3$.

The ferromagnet EuO has a transition temperature of only 69 K, and therefore should reveal the behavior characteristic of long-range dipolar interactions over a much wider range of $|t|$. Indeed, EuO appears to have $\alpha = \alpha' \cong -0.04$, which seems to be significantly different from the result for RbMnF$_3$.[21]

VI. COMPARISON WITH THEORY

We saw already in Sec. V C that the experimental results for RbMnF$_3$ largely satisfy the predictions of scaling. The relations $\alpha = \alpha'$ and $\nu = \frac{1}{3}(2 - \alpha)$ are obeyed well within the experimental uncertainty; and although the scaling law $2\beta + \gamma = 2 - \alpha$ seems to break down, the departures from it are probably attributable to underestimates of uncertainties for the asymptotic exponents.

In addition to comparing α and α' with other experimentally determined exponents through the scaling laws, one can also compare the value of $\alpha = \alpha'$ with theoretical estimates. For $T > T_c$, the properties of the Heisenberg systems have been studied repeatedly[19,20,40-44] by numerical techniques. Some of the most recent results are $\alpha = -0.14 \pm 0.06$,[19] and $\alpha = -0.09 \pm 0.04$.[20] Both of these are in agreement with our experimental value of -0.14 ± 0.01.

Recently, estimates of exponents have also become available from the known exact result in four dimensions and from an expansion in the dimensionality d about $d = 4$.[1,2] In terms of the expansion parameter $\epsilon \equiv 4 - d$, one has to second order in ϵ[45]

$$\alpha = \alpha' = -\frac{n-4}{2(n+8)}\epsilon - \frac{n^3 + 32n^2 + 116n + 112}{4(n+8)^3}\epsilon^2 + \cdots .$$

(13)

Here n is the number of degrees of freedom of the order parameter, or the so-called spin dimensionality. For the present case of $n = 3$ and in three dimensions ($\epsilon = 1$), one obtains $\alpha = \alpha' \cong -0.10$. It is difficult to estimate the uncertainty which arises from the neglect of higher-order terms in Eq. (13); but the result obtained from the expansion to second order is obviously in quite good

agreement with the experimental value.

Equation (13) suggests that α and α' should be given by a smooth function of n. It is therefore interesting to compare the best estimates of α for systems with various values of n. Such a comparison already was presented elsewhere,[30] and it was demonstrated that the values of α for $n = 1$, 2, 3, and ∞ can be represented by a smooth function of $1/n$ which has the theoretically predicted slope near $1/n = 0$. In addition, the results for the amplitude ratio A/A' were also shown to be consistent with a smooth function of $1/n$, and with the scaling predictions[5,6] $A/A' = 1$ when $\alpha = \alpha' = 0$.

VII. SUMMARY

In this paper we described an isothermal calorimeter which is suitable for specific-heat measurements over the temperature range 0.3--~100 K. We gave details of the procedure used to determine C_p of RbMnF$_3$ samples which weighed a few grams over the temperature range 76-88 K. During this work, special emphasis was given to high-resolution measurements very near the antiferromagnetic transition temperature $T_c = 83.08$ K. Two sets of results obtained on two separate samples were found to be consistent with each other. The data were analyzed in terms of power laws, with appropriate consideration given to singular higher-order and regular correction terms to the asymptotically dominant singularity. They strongly support the result $\alpha = \alpha' \cong -0.14$, with the amplitude ratio $A/A' \cong 1.40$. The negative exponents imply that C_p is finite at T_c. We also find that within our resolution C_p is continuous at T_c.

The parameters should be representative of systems with three degrees of freedom for the order parameter and with short-range interactions. We compared our results with other C_p measurements, with a determination of the thermal-expansion coefficient, and with neutron scattering experiments and scaling. We generally find consistency between the various experiments, although the differences in interpretation have at times yielded sets of parameters which appear to disagree with each other. We also compared our experimental parameters for C_p with theoretical predictions based upon numerical calculations, and upon the Wilson expansion in the dimensionality of the system. We found good agreement with the predictions.

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