Pramāṇa Vol. 18, No. 3, March 1982, pp. 249-259. © Printed in India

Heat capacity of $MnBr_2 \cdot 4H_2O$ near the antiferromagnetic transition temperature

S N BHATIA
Department of Physics, Indian Institute of Technology, Bombay 400 076, India

MS received 13 November 1980; revised 8 February 1982

Abstract. Heat capacity of $MnBr_2 \cdot 4H_2O$ has been measured in the critical region around the Neel temperature. The data can be fitted, over a restricted range of $|t| \leqslant 10^{-2}$, to the asymptotic power law. The critical exponents and the amplitudes A and A' are not consistent with any theoretic predictions. However when scaling constraints are imposed, their values agree with the parameters of Ising model. Corrections to scaling are necessary to extend the range of the fit to $|t| > 10^{-2}$. The correction terms are asymmetric giving $-1{\cdot}15 \pm 0{\cdot}25$ as the ratio of the amplitudes of the lowest order correction terms, D and D' above and below T_c. This value is in agreement with the recent predictions of the renormalisation group theory.

Keywords. Heat capacity; critical phenomenon; scaling; renormalisation group theory.

1. Introduction

There has been a lot of interest in the study of the phase transitions particularly of the magnetic systems (de Jongh and Miedema 1974). In the neighbourhood of the transition temperature T_c, the various thermodynamic quantities describing these transitions have been represented by power laws. The specific heat as an example has been described as

$$\left.\begin{aligned} C_p &= \frac{A}{\alpha}|t|^{-\alpha} + B, \quad T > T_c, \\ C_p &= \frac{A'}{\alpha'}|t|^{-\alpha'} + B', \quad T < T_c, \end{aligned}\right\} \tag{1}$$

where $|t|$ is the reduced temperature defined as

$$|t| = \frac{T - T_c}{T_c}.$$

The emphasis has been on the determination of the critical exponents only (such as α and α' for C_p), paying little attention to the amplitudes A and A' and the constant terms B and B'. Theoretic understanding of the phenomena started with the hypothesis of scaling (Kadanoff 1966; Widom 1965) which essentially stated that the

Gibb's potential of the system was a (generalised) homogeneous function of its arguments. This hypothesis related the various exponents to each other (called the scaling laws) (Kadanoff 1971; Stanley *et al* 1971) leaving only two exponents as fundamentally unknown. Further the specific heat exponents below and above T_c, α' and α were found to be equal and also the constant terms B and B' were found to be equal *i.e.* $\alpha' = \alpha$ and $B' = B$ implying thereby a basic symmetry in the singularity about T_c.

Recently, the high temperature series expansion technique (HTSE) (Domb and Green 1976) has made good progress. Long series extending from ten to twelve terms have been available for some thermodynamic quantities and it has become possible to predict their critical behaviour accurately. At the same time renormalisation group technique (RGT) (Wilson 1971, 1972a, b; Domb and Green 1976) has proved to be very powerful in the same region. In addition to providing strong support to the scaling laws, with these techniques it has been possible for the first time to make predictions about the amplitudes of the singular terms. The critical exponents, amplitude ratio for the specific heat A/A' and certain other parameters have been found to be universal (Kadanoff 1971, 1967) in the sense that they depend only upon a small number of parameters of very general type, which determine the symmetry of the system. For the magnetic materials dominated by short range interactions, the dimensionality d of the system and the effective number of spin degrees of freedom n determine the universality class and within a given class the actual value of the spin or the exchange interaction between them, therefore, play an insignificant part in determining the exponents or the amplitude ratio.

The universal classes of three dimensional systems of particular interest here are those having $n = 3$ the Heisenberg class of magnets having isotropic interaction, $n = 2$ the planar class and the anisotropic Ising class with $n = 1$. The calculated properties of these systems in the critical region are listed in table 1.

Most magnetic materials however do not belong to any one universality class, due to the presence of anisotropies of different kinds. Consequently near T_c, the Heisenberg-like behaviour is expected to cross over (Pfeuty *et al* 1974; Surjit Singh and Jasnow 1975; Fisher 1974) to either the planar or the Ising-like behaviour depending upon the planar or the axial nature respectively of the anisotropy present. The precise temperatures of this cross over (both below and above T_c) are not known but the cross over region is expected to scale roughly with the relative magnitudes of the anisotropy to the exchange energy.

Table 1. Theoretical estimates for 3-dimensional model systems

n	$\alpha = \alpha'$	A/A'	D/D'
1	$0{\cdot}110 \pm 0{\cdot}004$[a]	0·55[b]	1·25[c]
2	$-0{\cdot}007 \pm 0{\cdot}006$[a]		1·17[c]
3	$-0{\cdot}115 \pm 0{\cdot}009$[a]	1·36[b]	1·14[c]

[a] Le Guillou and Zinn Justin (1980)
[b] Aharony and Hohenberg (1976)
[c] Chang and Houghton (1980). The values given have been obtained by constructing Pade approximants

Experimentally, verification of the power laws is very difficult because the data are marked by the onset of 'rounding' in the temperature region very close to T_c, where the power laws are expected to hold. The rounding probably arises due to the sample inhomogenieties which produce a distribution of the transition temperatures. Outside this asymptotic region, however, corrections to scaling (Wegner 1972; Brezin *et al* 1973; Saul *et al* 1975; Camp and van Dyke 1975; Camp *et al* 1976; Baker *et al* 1976) arise and the power laws get modified. In particular for the heat capacity (1) is modified to

$$\begin{aligned} C_p &= (A/\alpha)\,|t|^{-\alpha}\,[1 + D\,|t|^{x} + \ldots] + B, \quad T > T_c, \\ &= (A'/\alpha')\,|t|^{-\alpha'}\,[1 + D'\,|t|^{x'} + \ldots] + B', \quad T < T_c, \end{aligned} \tag{2}$$

where D and D' are the amplitudes of the lowest order correction terms. These correction terms were first seen [Ahlers and Kornblit (1975); Kornblit and Ahlers (1973, 1975)] in the heat capacity data of He^4 and subsequently by others in the C_p of some magnetic compounds. Wegner (1972), however, was the first to study them in the context of RGT. He showed that the corrections arose through the dependence of the thermodynamic functions on the fields associated with the irrelevant operators. The leading correction came from the leading irrelevant operator. The exponent x is not strongly dependent on the spin dimensionality or lattice type and both the RGT and HTSE (Camp and van Dyke 1975; Saul *et al* 1978; Le Guillou *et al* 1977) calculations are consistent with $x = x' = 0{\cdot}5 \pm 0{\cdot}2$. No estimates of D or D' were available. Only recently Chang and Houghton (1980) have extended the ϵ-expansion to order ϵ^2 and shown that:

$$\begin{aligned} \frac{D}{D'} = 1 + \epsilon\left[\frac{n+8}{2\,(n+2)} - \tfrac{1}{2}\ln 2\right] + \\ \epsilon^2\left[\frac{3n^3 - 22n^2 - 88n + 152}{4\,(n+8)\,(n+2)^2} - \zeta(2) - \frac{9I}{2\,(n+8)}\right. \\ \left. - \frac{3(5n+22)}{(n+8)\,(n+2)}\,\zeta(3) - \frac{1}{4}\left(\frac{n^2 - 8n - 68}{(n+8)^2} + \frac{n+8}{n+2}\right)\ln 2 + \frac{1}{8}\ln^2 2\right], \end{aligned} \tag{3}$$

where ζ's are the Rieman zeta-functions and $I = -2{\cdot}349$. These calculations of A/A' are consistent with the previous calculations for A/A' upto the order ϵ^2. The values of the ratios predicted for the various universality classes are listed in table 1. Since the series converges slowly, Pade' approximants have been constructed to estimate the contribution of the higher order terms of the series.

To test these predictions, we have measured the heat capacity of manganese bromide tetrahydrate near its Neél temperature. Similar measurements have previously been reported by Hemstead and Mochel (1973), Kreps and Friedberg (1977) and Rives and Landau (1978). The first two of these measurements were analysed for α and α' in the light of asymptotic power law. Rives and Landau (1978) did take into consideration the correction terms but their analysis gave $D = -D'$. Our data gives significantly different results and they are in accord with the predictions of RGT (Chang and Houghton 1980).

2. Experimental

The calorimeter which permitted the heat capacity measurements with high temperature resolution, was of the conventional design. A pot filled with liquid He^4 was used as refrigerator. Its temperature was controlled by controlling the pressure of the helium vapours above the liquid level. A sample chamber was attached to its bottom. The sample was suspended with a nylon string inside this chamber and supported a wire-wound heater and a thermometer on its opposite ends. The nylon string together with a bellows operated from the outside acted as a mechanical heat switch. The sample was pulled up to touch the bottom of the refrigerator to cool it and was released when the desired temperature was attained. No exchange gas was used to cool the sample. High vacuum was maintained in the sample chamber and a small temperature difference between the sample and the chamber was maintained (typically $\simeq 0{\cdot}1$ K) to keep the heat exchange of the sample with the environment minimal. The whole assembly was isolated by a vacuum jacket and then placed in liquid helium bath.

Carbon resistors were used as thermometers, care being taken in their choice so as to have large dR/dT. Thermometers were calibrated *in situ* against the vapour pressure of He^4 at the end of each run. Resistance was measured by a transformer-coupled a.c. wheatstone bridge operating at 400 Hz. A PAR model HR-8 lock-in detector was used at the output stage of the bridge.

The sample was heated continuously at a low rate (typically 5-10 ergs/sec), and the off-balance voltage of the lock-in was recorded on a tape at regular intervals of 2 seconds. The bridge was calibrated with standard resistors and the voltage *vs.* time data was thereby changed to resistance *vs.* time. By using the thermometer calibration this was further changed to temperature *vs.* time from which $\dot{T}$ at different temperatures could be obtained. Specific heat is obtained from

$$\dot{Q} = m\, C_p\, \dot{T},$$

where $\dot{Q}$ is the heating rate. Heating is disrupted frequently to determine the heat exchange of the sample with the environment from the drift rate of the sample temperature. C_p can thus be determined to an accuracy of 1%. The heat capacity of the sample holder (addenda) is measured separately and subtracted from the C_p of the sample. The resulting heat capacity of $MnBr_2 \cdot 4H_2O$ is shown in figure 1. Earlier C_p of this compound was measured by Kapadnis and Hartmans (1956) over a wide range of temperature 1 — 20 K. Agreement with our results in the overlapping temperature range is not good. In the high temperature region they have estimated a lattice contribution of aT^3 with $a = 9{\cdot}36 \times 10^{-4}$ J/mole-K^4. This contribution was subtracted from our data.

3. Analysis

One serious handicap of the analysis of all data in the critical region is that there is a large number of parameters (some eight to ten) whose values are to be determined from a single set of data. Usually this presents great difficulties and introduces

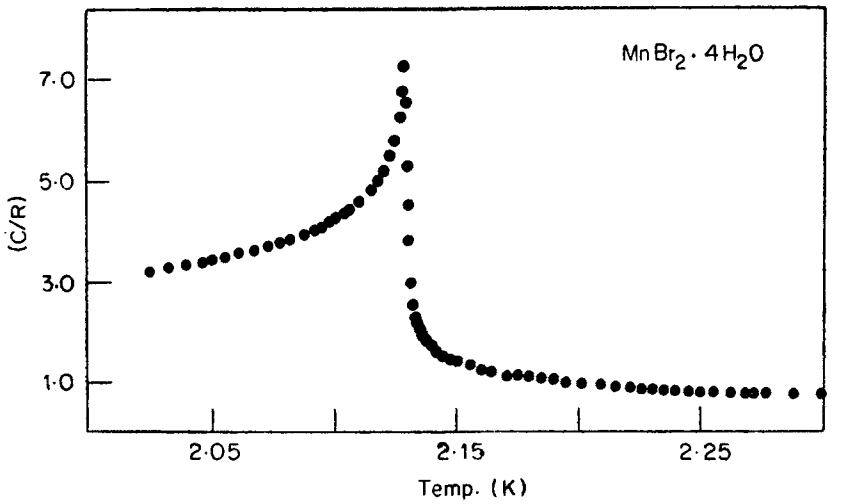

Figure 1. Specific heat of $MnBr_2 \cdot 4H_2O$ near the transition temperature. Every third data point is plotted for the sake of clarity.

large errors in the values of the parameters thus determined. A recourse is taken therefore to reduce this number. We adopted a similar approach. We analysed the data in different stages raising the number of unknown parameters in each stage.

First the data for $|t| \leqslant 5 \times 10^{-3}$ were analysed for the asymptotic power law. *A priori* there is no reason to take this value of $|t|$ as the end of the asymptotic region, but the C_p— analysis of other compounds supports this choice. Differentiation of (1) with respect to T gives:

$$\frac{dC_p}{dT} = A\,|t|^{-(\alpha+1)}, \tag{3}$$

so that a log-log plot of dC_p/dT *vs.* $|t|$ should yield the values of α (from the slope) and A (from the intercept). A linear least square analysis of (1) can then give B and B'. Since T_c is also unknown it can be determined here by repeating the above procedure for different T_c's and taking the longest range of $|t|$ over which the log-log graph is linear as the criterion for the correct choice of T_c. Since no constraints can be imposed here, it is expected that the scaling conditions will show up in the final results.

In the present case however, a unique T_c could not be obtained by the above procedure as straight segments could not be identified clearly in the log-log plots and also the error functions of the least square analysis were not very steep functions of T_c. These shallow curves gave a T_c spread over about 1 mK. The exponents and other parameters were all dependent on T_c and varied very rapidly with it. α and B' both decreased while α' and B both increased in their values when T_c was increased. However a T_c could be picked where each of the scaling constraint could be satisfied separately *viz.* for $T_c \simeq 2{\cdot}130250$ K, $\alpha \simeq \alpha' = 0{\cdot}065 \pm 0{\cdot}005$ and for $T_c \simeq 2{\cdot}130500$ K, $B \approx B' = -5{\cdot}95 \pm 0{\cdot}05$ but both the constraints could not be satisfied for the same T_c.

Both these values of T_c are greater than T_{max} — the temperature where C_p attains a maximum. A larger value of T_c than T_{max} is consistent with the argument of Gaunt and Domb (1968) who attribute the difference to rounding. Assuming a gaussian dis-

tribution of T_c's and taking 2·130500 K as the middle of the distribution, a value of Γ (half-width of the distribution) $\approx$ 0·7 mK was obtained from the data.

Although simple in application, the above technique usually fails to predict the correct results because in the asymptotic region, due probably to large fluctuations, the uncertainties in measuring C_p and hence in determining dC_p/dT are large. From the dC_p/dT plots, it was not possible to determine the beginning of the rounded region. It was taken as $|t| \simeq 2\Gamma$. Outside this region, fluctuations in C_p are comparable to the normal errors of measurement. Therefore, data for $|t| \leqslant 2\Gamma$ were not included into the subsequent analysis. Data are similarly rejected for other specimens also, the amount rejected varying with the quality of the crystal. The remaining data were subjected to a non-linear least square analysis with the two scaling constraints imposed. The parameters A, A', B and α were computer varied, and the analysis repeated for the various T_c's determined above. For $T_c = 2{\cdot}130250$ K, a significant reduction in the statistical error was achieved giving $\alpha \simeq 0{\cdot}118$, $B = -2{\cdot}35$, and $A/A' \simeq 0{\cdot}5$.

These values of α and B are significantly different from their corresponding values determined above. Both the results are however consistent with (1) which allows a smaller (negative) B for a larger α as determined here. To extend the analysis further, the power law in the full form *i.e.* (2) was used. Two additional constraints $x = x'$ and $D = -D'$ were imposed. x was set equal to its predicted value 0·5 and D was allowed to be varied. The range of the fit was gradually increased to larger $|t|$ values until the end of the data was reached. Only minor adjustments in the values of the parameters were required. For $|t| > 10^{-3}$ the entire data could be fitted to the values

$$A/A' = 0{\cdot}5 \pm 0{\cdot}05;\ B = B' = -2{\cdot}40 \pm 0{\cdot}05;\ D = D' = 0{\cdot}3 \pm 0{\cdot}1.$$

These parameters did not change appreciably when x was varied between 0·4 to 0·6. Outside these limits, the fits deteriorated. These values of A/A', B and D agree with those reported by Rives and Londau (1978) for $MnBr_2 \cdot 4H_2O$.

As a last step the final constraint $D = D'$ was also removed. An appreciable improvement in the fit was observed. The improvement was more in the data for $T > T_c$ than for $T < T_c$. This is shown in figure 2, where the normalized deviation of each data point from the fitted value is plotted both for $D = -D'$ and $D \neq -D'$. Since this result is appreciably different from that of Rives, it was checked for some ' possible accidents ' that might have occurred while the data was being taken. Thus the relative temperature scales of the data $T > T_c$ and $T < T_c$ was shifted by as much as $\pm$ 1 mK. This always had the effect of increasing the ratio D/D'. Similarly the addenda correction and the lattice contribution when doubled had little effect on the value of D/D'.

Comparison of (1) and (2) shows that a plot of $\log (C - B)$ *vs* $\log |t|$ should be a straight line within the asymptotic region and that the corrections to the power law (1) should also show up as deviations from the straight lines, the magnitude of the deviations being proportional to the correction amplitudes, D and D'. Such a plot of our data with the final fitted values is shown in figure 3. The deviations from the dashed lines representing the asymptotic behaviour are clearly different for the data above and below T_c implying thereby $D > D'$. It may also be noted that the deviations attain observable values only above $|t| > 10^{-2}$, justifying thereby, our use of the asymptotic law for $|t| \leqslant 10^{-2}$.

The value of α obtained above does not agree with the predictions of any of the models listed in table 1 although it comes close to that of the Ising model. It must be pointed out that this value of α ($= 0{\cdot}110$) is a relatively recent prediction for this model and has not been verified experimentally, for any magnetic substance as yet. $\alpha = 0{\cdot}125$ was predicted for this model on the basis of much shorter series (Guttman 1975) and experimentally was found to be obeyed by many materials (de Jongh and Miedema 1974) even though only the asymptotic form of the power law was used for the entire critical region. To see which of these values of α suits our data better, the above analysis was repeated first by fixing α at 0·125 and then at 0·110. For both values of α the fit deteriorated slightly, the rms error increased from $3{\cdot}96 \times 10^{-3}$ to

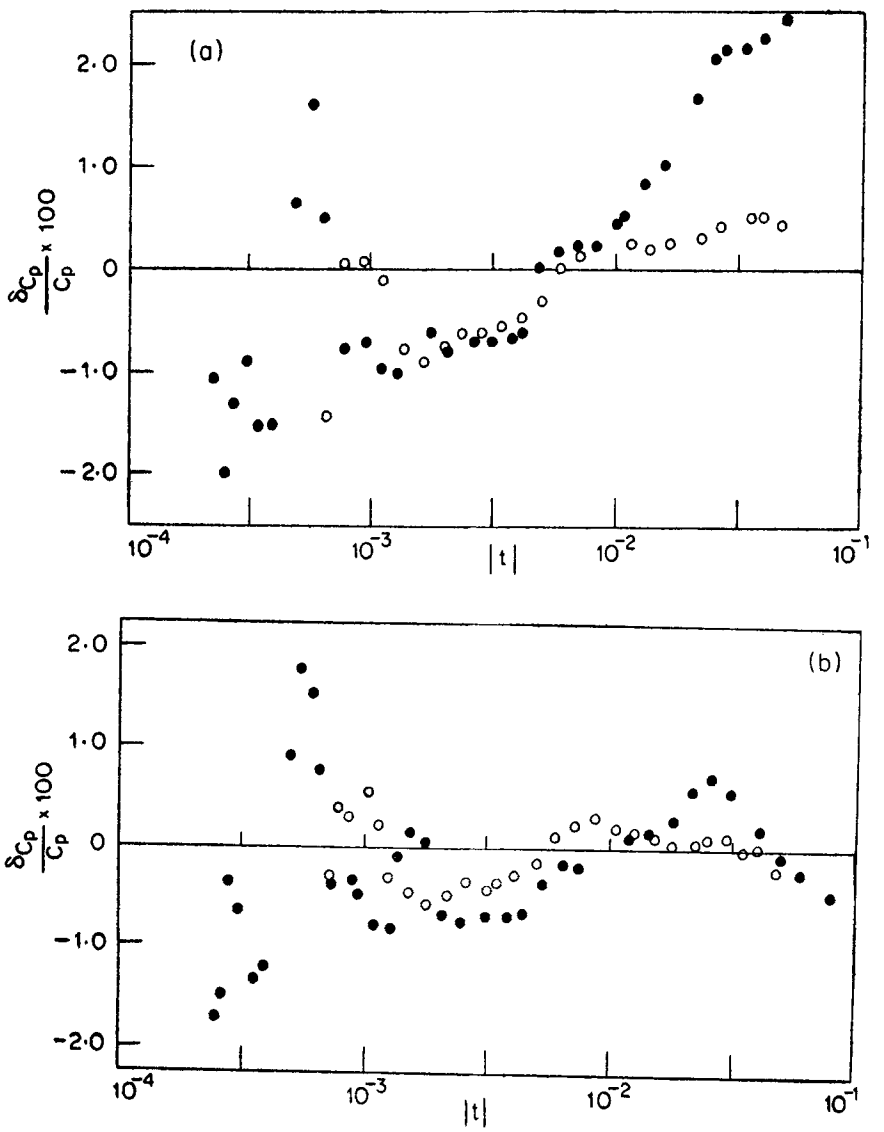

Figure 2. Deviations of the data from the best fit (a) the constraint $D = -D'$ imposed and (b) when the constraint was removed. The open and closed circles correspond to $T < T_c$ and $T > T_c$ respectively.

$4{\cdot}85 \times 10^{-3}$ and $4{\cdot}95 \times 10^{-3}$ respectively with the individual deviations still remaining within the precision of experimental measurements. However both these values of α had marked effect on the correction term where the amplitude ratio D/D' increased to $-2{\cdot}30$ for $\alpha = 0{\cdot}125$ and decreased to $-0{\cdot}5$ for $\alpha = 0{\cdot}110$. A and A' remained essentially unchanged while B decreased and increased for the two respective α's. This behaviour is understandable from (2) from where we see an increase in α leading to a decrease of the asymptotic contribution to C_p, the decrease being taken up by the correction and the regular terms. Addition of another higher order term Et with the constraint $E = E'$ to keep it non-singular at T_c, (Kornblit and Ahlers 1973) did not improve the situation. E could be varied over a wide range from approximately $-B$ to $+B$ with the corresponding changes in D, D' and B. Thus it can be concluded that all the values of α between the range 0·110 to 0·125 are acceptable to the data, with perhaps a slight preference for the upper end of this range. The other parameters for the best fit, shown in table 2, agree with the prediction of the three-dimensional Ising model.

There is enough evidence from thermal measurements that the exchange in $MnBr_2{\cdot}4H_2O$ is isotropic (Gijsman *et al* 1959) and that the exchange field (Schmidt and Friedberg 1967) (H_E) is 17·7 kOe and J the exchange constant (Miedema *et al* 1965) is $0{\cdot}08\ k_B$. However information about the anisotropy field (H_A) is not available. H_A can be determined from the spin-flop field measurements. Unfortunately the only measurement of this type made on this salt (Becerra *et al* 1975) cannot be used here as the fields have not been measured along the preferred axis. Miedema *et al* (1965) had earlier measured the C_p of $MnCl_2{\cdot}4H_2O$ and $MnBr_2{\cdot}4H_2O$ in the 0·3 to 1 K range. Whereas the magnetic specific heat of the chloride salt was analysed for the anisotropy, no such analysis was attempted for the bromide salt. We have therefore attempted to determine H_A from the perpendicular susceptibility, using the molecular field theory. When anisotropy is present, this theory gives at $T = 0$°K

$$\chi_\perp = \frac{1}{A + K/2M_0^2} = \frac{M_0}{AM_0 + K/2M_0}$$
$$= \frac{M_0}{(AM_0 + \frac{1}{2}H_A)}, \tag{4}$$

where M_0 is the sublattice magnetisation at 0°K. A and K are the molecular and anisotropy field constants and AM_0 and K/M_0 therefore the molecular-exchange and anisotropy fields respectively. $\chi_\perp$ does not change with temperature and equals the

Table 2. Experimental values of parameters for $MnBr_2{\cdot}4H_2O$

1	$\alpha = \alpha'$	$0{\cdot}118 \pm 0{\cdot}007$	
2	A	$0{\cdot}256 \pm 0{\cdot}02$	$A/A' = 0{\cdot}53 \pm 0{\cdot}05$
3	A'	$0{\cdot}484 \pm 0{\cdot}02$	
4	D	$0{\cdot}19 \pm 0{\cdot}02$	$D/D' = -1{\cdot}15 \pm 0{\cdot}25$
5	D'	$-0{\cdot}17 \pm 0{\cdot}02$	
6	$B = B'$	$-2{\cdot}39 \pm 0{\cdot}05$	
7	$x = x'$	$0{\cdot}5 \pm 0{\cdot}1$	
8	T_c	$2{\cdot}130370 \pm 0{\cdot}250$	
9	$E = E'$	$0{\cdot}0 \pm 2{\cdot}5$	

maximum susceptibility which occurs near T_c. From the measured susceptibility of this salt (Schellang and Friedberg 1969) $\chi_\perp$ therefore is 0·95 cgs/mole. Using the above value of H_E, (4) gives 6 kOe for H_A. A similar calculation for the chloride salt gives 5·5 kOe for H_A, which is about twice the value obtained from the spin-flop measurements (Rives *et al* 1975). Near equality of H_A for the two salts was anticipated as they are isostructural (Groth 1908). Further the bromide salt will also have axial anisotropy as the chloride salt does (Rives and Benedict 1975). This is adequately supported by bromide NMR in this salt (Swuste and Kopinga 1972). A change (Pfeuty *et al* 1974; Fisher 1974) from the Heisenberg to Ising like behaviour is then expected to occur at

$$t_{co} \simeq \left(\frac{\text{anisotropy energy}}{\text{exchange energy}}\right)^{-\phi}$$

where ϕ is the anisotropy cross-over exponent and has been estimated for the $d = 3$, Heisenberg spins by Pfeuty *et al* (1974) to be 1·25. With the above estimates of H_A and H_E we get t_{co} to be 3×10^{-1}. Allowing for the correction factor in molecular field calculations we get t_{co} as 2×10^{-1}. Thus it is expected that for $|t| < 2 \times 10^{-1}$ $MnBr_2 \cdot 4H_2O$ should be Ising like while for $|t| > 2 \times 10^{-1}$ it should correspond to the Heisenberg model. From figure 3 we find that the whole of the present data is restricted to $t < t_{co}$. A comparison of the determined values of α, A/A' and D/D' with the calculated values of these quantities (tables 1, 2) shows them closer to the

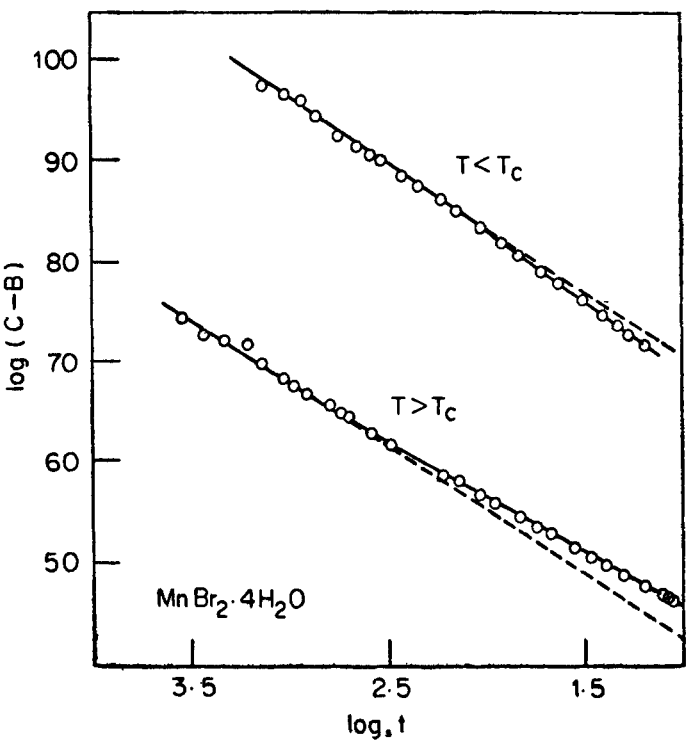

Figure 3. Comparison of the data with the theoretical fits. The dashed line is the asymptotic fit and the solid curve is the best fit including corrections to the scaling. Parameters for the fit are listed in the table.

values for $n = 1$. Thus $MnBr_2 \cdot 4H_2O$ behaves like an Ising system within this temperature range. Further since the fit is smooth over the whole range of $|t|$ without showing any signs of any break anywhere, therefore our estimates of t_{co} are reasonably correct.

4. Conclusions

The present analysis suggests that in the critical region $5 \times 10^{-3} \leqslant t \leqslant 10^{-1}$ $MnBr_2 \cdot 4H_2O$ behaves like an Ising system. From other thermal data it is known to behave like a Heisenberg magnet outside this region. It is unfortunate that the present data does not extend to far enough temperatures to actually see this cross-over. The observed values of A/A' and D/D' agree with the corresponding values predicted by theory. Such an agreement for A/A' has been reported for many magnetic systems (Rives *et al* 1977; Rives and Landau 1978; Domb and Green 1976). However as mentioned earlier, not much attention appears to have been paid to the ratio D/D' in the analysis of the heat capacity data of the anisotropic systems as the asymptotic law has invariably been used over the entire critical region. There are very few systems for which the power law in the full form has been used, and these give the ratio varying over a wide range. Thus D/D' is $-1{\cdot}0$ for $MnCl_2 \cdot 4H_2O$ (Rives and Landau 1978), $-0{\cdot}37 \pm 0{\cdot}05$ for $Cu(NH_4)Br_2 \cdot 4H_2O$ (Rives *et al* 1977) and 2 ± 2 for EuO (Kornblit *et al* 1975). The present data appears to accept the new value of α although the accord is seen to be better with the old value 0·125. So far the new value of α *viz.* 0·110 has been found to be satisfactory only in explaining the critical behaviour of the refractive index of some non-magnetic liquids (Beysens and Bourgau 1979). The present data appears to be the first example of an anisotropic magnetic system accepting the value $\alpha = 0{\cdot}110$. Mueller *et al* (1976) obtained $-0{\cdot}026 \pm 0{\cdot}004$ and $-0{\cdot}016 \pm 0{\cdot}002$ for α from the thermal expansion coefficient and the heat capacity of He^4 respectively as against the predicted value of $\alpha = -0{\cdot}007 \pm 0{\cdot}006$ for the $n = 2$ systems. They obtain $1{\cdot}29 \pm 0{\cdot}25$ and $1{\cdot}2 \pm 0{\cdot}6$ for the ratio D/D' from the two respective measurements. The accuracy of our results compares favourably with theirs.

References

Aharony A and Hohenberg P C 1976 *Phys. Rev.* **B13** 3081
Ahlers G 1973 *Phys. Rev.* **A8** 530
Ahlers G and Kornblit A 1975a *Phys. Rev.* **B12** 1938
Baker G A, Nickel B G, Green M S and Meiron D I 1976 *Phys. Rev. Lett.* **36** 1351
Becerra C C, Paduan Filho A and Oliveira N F 1975 *Solid State Commun.* **16** 791
Beysens D and Bourgau A 1979 *Phys. Rev.* **A19** 2407
Brezin E, Le Guillou J C and Zinn-Justin J 1973 *Phys. Rev.* **B8** 5330
Brezin E, Le Guillou J C and Zinn-Justin J 1977 *Phys. Rev. Lett.* **39** 95
Camp W J and van Dyke J P 1975 *Phys. Rev.* **B11** 2579
Camp W J, Saul D M, van Dyke J P and Wortis M 1976 *Phys. Rev.* **B14** 3990
Chang M and Houghton A 1980 *Phys. Rev.* **B21** 1881
Domb C and Green M S 1976 *Phase transitions and critical phenomena* Vol. 3 for HTSE and Vol. 6 for RGT (New York: Academic Press)
Fisher M E 1974 *Rev. Mod. Phys.* **46** 597

Gaunt D S and Domb C 1968 *J. Phys.* **C1** 1038
Gijsman H M, Poulis N J and vanden Handel J 1959 *Physica* **35** 954
Groth P 1908 *Chem. Krystallogr.* **I**
Guttman A J 1975 *J. Phys.* **A8** 1249
Hemstead R D and Mochel J M 1973 *Phys. Rev.* **B7** 287
de Jongh L J and Miedema A R 1974 *Adv. Phys.* **23** 1
Kadanoff L P 1966 *Physics* **2** 263
Kadanoff L P *et al* 1967 *Rev. Mod. Phys.* **39** 395
Kadanoff L P 1971 *Proceedings of the international school 'Enrico Fermi'* (New York: Academic Press)
Kapadnis D G and Hartmans R 1956 *Physica* **22** 181
Kornblit A and Ahlers G 1973 *Phys. Rev.* **B8** 5163
Kornblit A and Ahlers G 1975 *Phys. Rev.* **B11** 2678
Kreps L W and Friedberg S A 1977 *J. Low Temp. Phys.* **26** 317
le Guillou J C and Zinn-Justin J 1977 *Phys. Rev. Lett.* **39** 95
le Guillou J C and Zinn-Justin J 1979 *J. Phys.* **40** 969
le Guillou J C and Zinn-Justin J 1980 *Phys. Rev.* **B21** 3976
Miedema A R, Wielinga R F and Huiskamp W J 1965 *Physica* **31** 835
Mueller K H, Ahlers G and Pobell F 1976 *Phys. Rev.* **B14** 2096
Pfeuty P, Jasnow D and Fisher M E 1974 *Phys. Rev.* **B10** 2088
Rives J E and Benedict V 1975 *Phys. Rev.* **B12** 1908
Rives J E, Landau D P, Lung H I and Chandrasekhar H S 1977 *Physica* **B86-88** 568
Rives J E and Landau D P 1978 *Phys. Rev.* **B17** 4426
Saul D M, Wortis M and Jasnow D 1975 *Phys. Rev.* **B11** 2571
Schelleng J H and Friedberg S A 1969 *Phys. Rev.* **185** 728
Schmidt V A and Friedberg S A 1967 *J. Appl. Phys.* **38** 5319
Stanley H E, Hankey A and Lee M H 1971 *Proceedings of the international school 'Enrico Fermi'* (New York: Academic Press)
Surjit Singh and Jasnow D 1975 *Phys. Rev.* **B12** 493
Swuste C H W and Kopinga K 1972 *Physica* **60** 415
Wegner F J 1972 *Phys. Rev.* **B5** 4529
Widom B 1965 *J. Chem. Phys.* **43** 3892, 3898
Wilson K G 1971 *Phys. Rev.* **B4** 3174, 3184
Wilson K G 1972a *Phys. Rev. Lett.* **28** 548
Wilson K G 1972b *Phys. Rev. Lett.* **29** 591