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Analysis of Specific Heat Data in the Critical Region of Magnetic Solids

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A detailed analysis of specific heat data in the critical region of magnetic solids is presented. An inverse power law, whose strength is measured by the exponent α, is used to describe the temperature dependence of the magnetic specific heat. Other parameters used include the power law coefficient A, the critical temperature T_c, and a constant background term B. Advanced techniques of data analysis suitable for estimation of nonlinear parameters and their errors under conditions of realistically weighted experimental data were used to obtain the dependence of α, T_c, A, and B on the range of data points included in the fit. Those exponents and parameters that provide the best overall fit to the data have been found. Literature references to 49 experiments from 1935 to 1971 are given. We present in tabular form the values of α, A, and B for 24 different magnetic crystals. With some exceptions, the best fits to the data suggest that in the temperature range studied the magnetic specific heat is not symmetric; the exponent α depends on the range of data included in the fit, varies widely from material to material, and in many cases is definitely negative below the critical temperature; and that there is little evidence that the asymptotic region is being adequately sampled by experiment. These results have the implication that until such time as we can adequately account for departures from the expected sharp peak in the data at T_c (data rounding) and corrections to asymptotic scaling, then comparisons between magnetic specific heat experiments and lowest order scaling predictions are to this date still tenuous.

Key words: Critical exponents; critical phenomena; data analysis; magnetic solids; nonlinear least-squares; phase transitions; specific heat; static scaling.

1. Introduction

Near the critical point of real physical systems various thermodynamic anomalies occur that are usually characterized by power laws involving experimentally determined critical exponents. For example, the specific heats of a paramagnetic-ferromagnetic transition, an alloy order-disorder transition and a liquid-gas transition just above the critical temperature all behave as $C \propto A\,|\,T-T_c\,|^{-\alpha}$ in which T_c is the critical temperature, α is the specific heat critical exponent and A is the power law coefficient. Below T_c, the specific heat behaves similarly, though perhaps with different numerical values for A and α, which are then denoted by A' and α'. Likewise, the isothermal compressibility K_T for the gas-liquid transition and the isothermal susceptibility χ_T for the paramagnetic-ferromagnetic transition near the critical point also obey power laws of the form $(T-T_c)^{-\gamma}$ for $T>T_c$ and $|T-T_c|^{-\gamma'}$ for $T<T_c$. As a final example, the liquid-gas density difference $\rho_L-\rho_G$ and the analogous magnetic quantity, the zero field magnetization M, both vanish as $|T-T_c|^{\beta}$ as the critical temperature is approached from below. The scaling hypothesis of Widom-Kadanoff-Domb [1][1], which maintains that the thermodynamic potentials (e.g. the Gibbs potential) are generalized homogeneous functions of their independent variables, characterizes critical point thermodynamic behavior by relating the diverse anomalies through scaling relations among the exponents. For example, the scaling relation prediction for the exponents of the thermodynamic quantities cited above is $\alpha'+2\beta+\gamma'=2$. Scaling theory also predicts that primed $(T<T_c)$ and unprimed $(T>T_c)$ critical exponents are equal: $\alpha'=\alpha$ and $\gamma'=\gamma$; and that for the case $\alpha'=\alpha=0$, the specific heat coefficients A' and A are equal. (For reviews of critical phenomena see refs. [2–10].)

In this paper we present a detailed analysis of specific heat data in the critical region of magnetic crystals. Our original intention was to subject to experimental verification certain of the above conclusions drawn from the static scaling hypothesis and also conclusions from detailed model Hamiltonian calculations that may be applicable to these data. In particular, we intended to determine (1) if existing data support the scaling predictions that the specific heat critical exponents α' and α, and the coefficients A' and A for the case $\alpha'=\alpha=0$, are equal below and above the critical temperature and (2) if the data predict exponents in agreement with applicable Ising and Heisenberg model calculations. To this end we examined the results of 49 magnetic specific heat experiments out of which the exponents of 24 different materials could be obtained. From available data, we carefully determined the dependence of the exponents and parameters on the range of data included in the fits for 16 different materials. Another original purpose of our analysis was to correlate the experimentally observed exponents with specific characteristics of the

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[1] Figures in brackets indicate literature references at the end of this paper.

materials: ferromagnetic versus antiferromagnetic, anisotropic as opposed to isotropic interactions, exchange as opposed to dipolar interactions, and metallic versus insulating properties are comparisons we considered.

The specific heat near the critical point is one of the weakest of the various thermodynamic anomalies. Since the associated exponent α may be quite close or equal to zero, the anomaly is often obscured by background effects and becomes difficult to characterize accurately by experiment. From the results of various model calculations, it is felt that at the critical point the specific heat should either diverge ($\alpha \geqslant 0$) or show a finite cusp ($\alpha < 0$). In fact, though, high resolution experiments reveal that considerable rounding off of the data occurs which obscures the expected sharp peak. Our efforts to realize the above intentions were frustrated by the presence of rounding in the experimental data and the lack of a firm theory to account for it. The rounding prevents sampling the temperature dependence of the specific heat beyond $\sim 10^{-4}$ in reduced temperature, $\epsilon = |T/T_C - 1|$ and, as pointed out by Gaunt and Domb [11] using Ising model calculations, makes tenuous any comparisons between experimentally determined exponents and those describing the theoretical asymptotic behavior. An alternative to comparing exponents is to display in a straightforward graphical manner the experimental data and the theoretical curve for those situations where a reliable theoretical prediction for the specific heat temperature dependence exists. This more fundamental procedure has been utilized by Gaunt and Domb [11] and by Wielinga [9, 12], but with the result that a really impressive agreement over more than a decade in reduced temperature occurs in very few instances.

The above considerations forced us to modify our original intentions to one in which we seek those exponents and parameters that provide the best overall fit to the data based on a model equation given below, and study how they depend on the range of data included in the fit. With a few notable exceptions, we obtained for the large majority of materials the following results:

a. The best fits to the data and the behavior of the exponents on the range of data included in the fits suggest the temperature dependence of the magnetic specific heat is not symmetric about the transition point in the temperature range studied.

b. Most of the materials are best accommodated by negative exponents below the transition and positive exponents above.

c. The exponents providing the best fits are relatively insensitive to the specific characteristics of the materials listed above.

d. Many of the exponent values reported in the literature for a particular material can be substituted by a number of other equally likely values. Given the usual amount of scatter, most specific heat data can accommodate an uncomfortably large range of critical exponents. In the next section, we describe the types of constraints placed on the data analysis to restrict the range of possible exponents. The methods used and the assumptions made in our analysis of the data are discussed in section 3. Our results are given in section 4, and a discussion of these results is contained in section 5. The principal results in terms of evaluated data are contained in tables 1 and 2 (at the end of section 5). In table 1 literature references to 49 experiments from 1935 to 1971 are given. Table 2 lists for 24 different magnetic crystals the values of α', α, A', A, B', and B obtained from our analysis and/or reported in the literature.

2. Role of Constraints

It is well established that an unambiguous experimental determination of the magnetic specific heat critical exponents α' and α is very difficult. In addition to scatter in the data, the problem basically involves the presence of rounding in the experimental data, which makes the range of critical behavior and the position of the critical temperature hard to establish prior to least square adjusting the data to a model equation of the temperature dependence. The techniques used to deal with this problem usually result in the introduction of more disposable parameters into the data analysis. If no constraints are imposed, the consequence is that the data can be fit equally well with a wider range of alphas. Some constraints must then be involved to narrow down the range. For example, when the critical temperature is made a fit parameter, its adjusted value determined from the data below the transition is usually different from that using the data above the transition. One constraint used at this point is to accept for consideration only those alphas leading to the same critical temperature. Often this results in increasing the standard deviation of the fit. The data of Skalyo and Friedberg [13] on $CoCl_2 \cdot 6H_2O$ illustrate a possible effect of this constraint. When T_N is made adjustable the fit below the transition for $2.1029 \leqslant T \leqslant 2.2813$ shows an absolute minimum standard deviation of about 0.04 J/mol K indicating the relative specific heat accuracy is about 1/3 percent. This minimum occurs at $\alpha' = -0.25$. But α' can be varied to as low as -0.50 and as high as $+0.30$ before the deviation of the fit equals twice the absolute minimum standard deviation (2/3%). If in addition, we restrict T_N to the rounded region, the range in which the deviation of the fit is still less than 2/3 percent becomes $-0.50 \leqslant \alpha' \leqslant -0.20$. Finally, if T_N is fixed at 2.2885 K, the similarly determined range narrows to about $-0.35 \leqslant \alpha' \leqslant -0.15$, but the absolute minimum standard deviation increases by about 25 percent.

Another possible constraint is to require that $\alpha' = \alpha$ [14]. Figure 1(a) shows lines of minimum standard deviation for Ni [14] taken from our analysis of the Ni data. Along these lines the standard deviation is locally minimized for the given range of α' and α as a function of possible critical temperatures in a physically acceptable range. The filled dot on each line represents the parameters giving the smallest standard deviation. In our analysis we have made sure that this smallest standard deviation is in fact the absolute minimum. For the data of Connelly et al. [14] these lines intersect at a plausible value for the critical temperature and at a pair of alphas not significantly different from those yielding the absolute minimum standard deviation. Within the heavy portions of the lines values of the standard deviation on either side of the minimum are considered not to be significantly different than the smallest values. But not all data allow the crossover to admit the possibility that $\alpha' = \alpha$ is very likely. Figure 1(b) for Gd [15] suggests that $\alpha' \neq \alpha$. Indeed, the crossover may be completely outside the range of physically acceptable critical temperatures.

Another method used to narrow the range of possible alphas is to associate the rounding with a Gaussian distribution in critical temperatures T_c in which the width d and mean T_o of the distribution become fit parameters [15–19]. The distribution is convoluted over T_c with a particular form $C\ (T,\ T_c,\ \alpha,\ .\ .\ .)$ of the ideal temperature dependence to yield $C\ (T,\ T_o,\ d,\ \alpha,\ .\ .\ .)$. The range of alphas is narrowed down by constraining the calculated maximum specific heat $C\ (T_m,\ T_o,\ d,\ \alpha,\ .\ .\ .)$ to coincide with the data at a temperature T_m at which the data exhibit a maximum C_{MAX}. The method requires that for N data pairs each with variance σ_i^2 we minimize

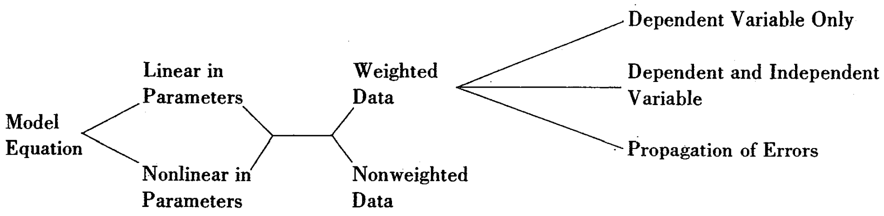
$$\sum_{i=1}^{N} \sigma_i^{-2}[C_i - C(T, T_o, d, \alpha, \ .\ .\ .\ ]^2 + \lambda[C_{\text{MAX}} - C(T_m, T_o, d, \alpha, \ .\ .\ .].$$

Lagrange's multiplier λ can be eliminated analytically and the fit parameters $(T_o,\ d,\ \alpha,\ .\ .\ .)$ determined by iteration methods. It is known that this may change the values of α' and α [15, 20], but since data in the rounding enter the constraint equation the effect on alpha is suspect insofar as alpha is to represent the asymptotic temperature dependence.

In the light of the paucity of accurate theoretical predictions valid for real materials, many of these constraints used to establish exponents are, though certainly reasonable, still somewhat arbitrary. Thus, we did not build them into our numerical analysis techniques. In the next section we describe the techniques we have used and how they were employed to obtain exponents giving the best overall fit to the data.

3. Data Analysis

The various numerical analysis considerations taken into account to obtain critical parameters are indicated below.



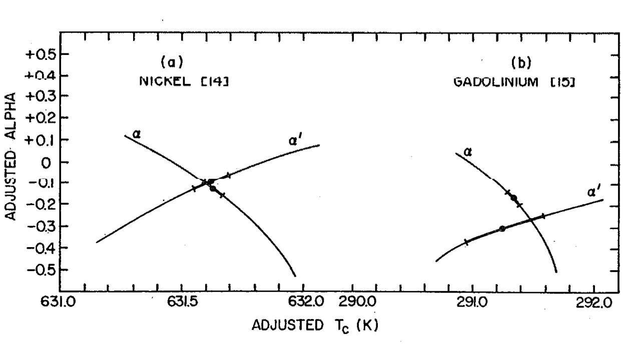


FIGURE 1. Lines of locally minimized standard deviation projected onto the $\alpha - T_c$ plane. The filled dot locates the absolute minimum standard deviation. Within the heavy portions of the lines the standard deviation of the fit is compatible with the quoted experimental accuracy of the parameters, the deviation of the fit is still random with no systematic trends and the adjusted critical temperatures are physically plausible. (a) Results of our analysis for Ni [14] and (b) for Gd [15].

The model equation used in this analysis for the temperature dependence of the magnetic specific heat is that suggested by Fisher [3a]:

$$C(T) = (A/\alpha)[|T/T_c - 1|^{-\alpha} - 1] + B,\ T > T_c. \quad (1)$$

When primed quantities (α', etc.) appear they refer to $T < T_c$. When eq (1) refers to antiferromagnets T_N replaces T_c. The exponent α is usually in the range ± 0.3, e.g., $\alpha = +\ 0.125$ for the 3-dimensional Ising model, $-\ 0.16$ for the Heisenberg model, zero for 2-dimensional Ising model, and from $+\ 0.04$ to $+\ 0.10$ for many real fluids [10]. For $\alpha < 0$, the model equation describes a finite cusp, $\alpha > 0$ corresponds to a power law singularity and $\alpha = 0$ gives a logarithmic divergence. Eq (1) is nonlinear in the parameters α and T_c and linear in A and B. We assume the data do not fix T_c accurately and take it to be a fit parameter. The nonlinear presence of α

and T_c precludes an analytic closed form expression for the parameters and their errors. For many cases non-weighted data are sufficient. It is only for reduced temperatures $\epsilon = |T/T_c - 1| < 10^{-3}$ that we find the reported temperature error σ_{T_i} propagated through eq (1) will drive the weight below that represented by the error σ_{C_i} in the measurement of the specific heat itself (fig. 2). But it is also for $\epsilon < 10^{-3}$ that data show rounding and the propagated part of the error derived from eq (1) fails to estimate the true experimental error in this region. However, to accommodate exceptions we have written our computer programs to minimize the reduced chi-square of eq (1) with the data C_i:

$$\chi_\nu^2(\alpha, T_c, A, B) = \nu^{-1} \sum_{i=1}^{N} W_i[C_i - C(T_i)]^2, \qquad (2)$$

where the number of degrees of freedom ν is equal to the number of data pairs N minus the number of parameters (= 4). When minimized with respect to the parameters eq (2) gives the estimated experimental variance or the square of the standard deviation of the fit if the weight W_i is set equal to unity, but when W_i is properly constructed, χ_ν^2 should be approximately one.

In this analysis we do not define χ_ν^2 using data weighted in the dependent and independent variables of eq (1). To do so would require [21] that instead of eq (2) we minimize

$$\nu^{-1} \sum_{i=1}^{N} [W_{C_i} (\Delta C_i)^2 + W_{T_i} (\Delta T_i)^2],$$

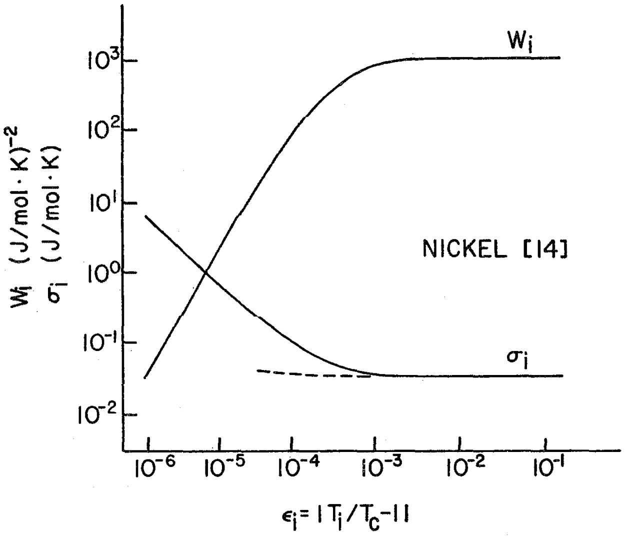


FIGURE 2. The dependence of the weight W_i [See eq (4b)] and the standard deviation $\sigma_i = W_i^{-1/2}$ of a data point on reduced temperature for Ni [14] based on eq (1). The weight is fairly constant down to $\epsilon \sim 5 \times 10^{-4}$. The dashed line indicates what appears to be the experimental standard deviation in the rounding region where eq (1) does not describe the data.

with $W_{C_i} = \sigma_{C_i}^{-2}$, $W_{T_i} = \sigma_{T_i}^{-2}$, and where $\Delta C_i = C_{i_{OBS}} - C_{i_{\mathrm{ADJ}}}$, $\Delta T_i = T_{i_{\mathrm{OBS}}} - T_{i_{\mathrm{ADJ}}}$ are respectively the differences between the least square adjusted values and the observed measured values of C and T. Using the calculus of variations, the parameters would then be given by a solution of

$$W_{C_i}\Delta C_i + \lambda_i = W_{T_i}\Delta T_i \pm (A/T_c)\epsilon_i^{-\alpha-1}\lambda_i = 0, \qquad (3a)$$

$$\Sigma(A/\alpha^2)[\epsilon_i^{-\alpha}(1 - \ln \epsilon_i^{-\alpha}) - 1]\lambda_i$$
$$= \Sigma(A/T_c)\epsilon_i^{-\alpha-1}(\epsilon_i \pm 1)\lambda_i 0, \qquad (3b)$$

$$\Sigma\alpha^{-1}(\epsilon_i^{-\alpha} - 1)\lambda_i = \Sigma\lambda_i = 0, \qquad (3c)$$

subject to the constraint that $C_{i_{\mathrm{ADJ}}} = (A/\alpha\ [|T_{i_{\mathrm{ADJ}}}/T_c - 1|^{-\alpha} - 1] + B$. The naive approach to eqs (3) would be to solve eqs (3a) for the adjusted values $C_{i_{\mathrm{ADJ}}}$, $T_{i_{\mathrm{ADJ}}}$ and substitute into the constraint equation yielding an expression for the Lagrange multipliers λ_i in terms of the observed values and the parameters. Then the right hand member of eq (3a) can be solved for $T_{i_{\mathrm{ADJ}}}$ this time just in terms of the observed values and the parameters. Substituting $T_{i_{\mathrm{ADJ}}}$ and λ_i into eqs (3b, c) would give four (intractable) equations involving only the observed data and α, T_c, A, B. The occurrence of nonlinear algebraic equations (like eqs (3)) is not due solely to the nonlinear presence of parameters in the model equation, but will occur whenever we separately weight the dependent and independent variables, even when the model equation is linear in the parameters [22, 23]. Since eqs (3) are so difficult to solve efficiently we will ascribe all the uncertainties to the dependent variable. This is effected by treating ΔT_i as zero, ΔC_i as $C_{i_{\mathrm{OBS}}} - C(T_{i_{\mathrm{OBS}}})$ and, to compensate for the artifice of setting $\Delta T_i = 0$, letting W_{C_i} become $W_i = (\sigma_{C_i}^2 + \sigma_{P_i}^2)^{-1}$ where $\sigma_{P_i}^2 = (\partial C(T_i)/\partial T_i)^2 \sigma_{T_i}^2$ is the propagated variance in the measurement due to errors in the temperature. Thus we assume that for any fixed value of the independent variable T_i, repeated measurements of the dependent variable C_i are Gaussian distributed with standard deviation σ_{C_i}; that the errors at the point (C_i, T_i) are small and independent of the errors at any other point; and that the observed set of measurements of the parent distribution given by eq (1) is characterized by the maximum likelihood best estimates for α, T_c, A, B. Under these assumptions and those for the weighting given above, the probability for the observed set of measurements becomes [21]

$$P(\alpha, T_c, A, B) = \prod_{j=1}^{N} \sqrt{W_j/2\pi}$$

$$\exp\left\{-\frac{1}{2}\sum_{i=1}^{N} W_i\left[C_i - \frac{A}{\alpha}\left| T_i/T_c - 1\right|^{-\alpha} + \frac{A}{\alpha} - B\right]^2\right\}, \qquad (4a)$$

$$W_i = [\sigma_{C_i}^2 + (A\sigma_{T_i}/T_c)^2\, |\, T_i/T_c - 1\, |^{-2(\alpha+1)}]^{-1}. \qquad (4b)$$

This probability is maximum when $\chi_\nu^2(\alpha, T_c, A, B)$ of eq (2) is minimum.

The basic procedure was to start the fit using a small set of data points located a fixed amount from T_c. Within this set the data point furthest from T_c is denoted as ϵ_{MAX} and that nearest is called ϵ_{MIN}. Then while admitting into the fit additional data points nearer T_c (varying ϵ_{MIN}), the fit was continually repeated until the range of points included extended into the rounding region. In this manner we have obtained the dependence of α, T_c, A, B on the range of points included in the fit. The fiducial points for the analysis were fixed at $\epsilon_{MAX} = 0.1$ or less and were not varied. Our computer programs are efficient enough that we could obtain for each side of the transition twenty or so determinations of the parameters for increasingly larger numbers of data points. Our hope was that the parameters as functions of the range of points included in the fit would converge to final values before encountering the rounding region. This was realized in a few cases. Figure 3 shows a favorable situation for Ni. We also found it illuminating to computer-generate for each set of parameters determined from a given limited range of the data, deviation plots extending over the entire range of data. In this manner we could study how the parameters determined for any range fit the entire range. In most cases such a procedure revealed fairly well what were the best parameters for a given data set, since for too small or too large a range in ϵ the deviations would be systematic and clearly outside experimental error.

The actual search for the absolute minimum of the χ_ν^2 space for a given range of data proceeded in two steps. The first, executed by a program we call LINEAR, is patterned after the grid-type search method of van der Hoeven, et al. [24]. The method employs simple linear least-square techniques by incrementing over the nonlinear parameters. However, it does not automatically provide error estimates for α and T_c. We start with a given range of data, fix α' (α) of eq (1) at -1.5 and find the least-square adjusted values of A' (A) and B' (B) and the resulting value of $\chi_\nu^2(W_i=1)$ of eq (2) for a range of possible critical temperatures. The critical temperature range is over a 40 cell grid roughly centered on the peak of the specific heat curve. The cell size ranges from 0.00015 K to 0.15 K depending on the material being studied. The exponent α' (α) is then incremented in steps of 0.1 until it reaches a value of $+1.5$. At each step the above procedure is repeated. Figure 4 gives an example of the type of information stored at the end of the run for a given data range of a particular material. The algorithm locates the minimum $\chi_\nu^2(W_i=1)$ for each family member and of these locates the absolute minimum. For these particular values of α' (α) and T_c' (T_c), the least-square adjusted values of the linear parameters A' (A) and B' (B) are provided. These parameters are then taken to approximately locate the absolute minimum region in χ_ν^2 space and are used as initial starting parameters for an analytical search described below. The range of data is then increased and the process repeated until the range extends into the rounding region.

An analytical search (one employing an analytical description of the χ_ν^2 hypersurface) that involves inverting the curvature matrix of the hypersurface has the advantage of automatically providing uncertainties for the parameters. In our circumstances it is also 3 or 4 times as efficient as the brute-force mapping procedure described above, provided one has good starting parameters that characterize the absolute minimum and not a local minimum, maximum or a flat plateau. The latter conditions constantly plagued our earlier attempts to use various [25, 26] analytical search methods efficiently. For the purpose of discussing the

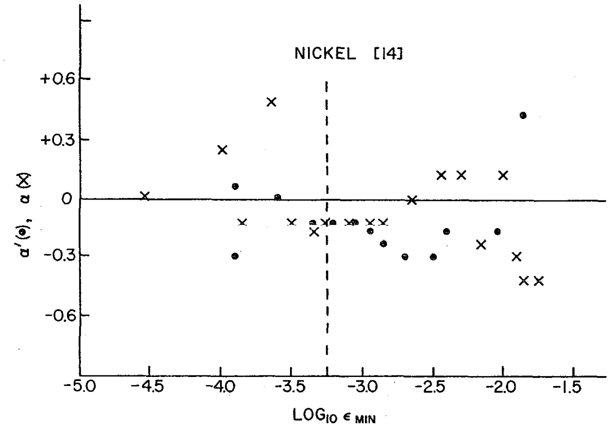


FIGURE 3. α' (●) and $\alpha(X)$ versus $\log_{10}\epsilon_{MIN}$ for Ni [14] (our analysis). The vertical dashed line is approximately where the rounding in the data begins. After some initial scatter both α' and α settle down to approximately -0.1 before the range of data extends into the rounding region. The exponents in the neighborhood of the dashed line have uncertainties of about ± 0.03.

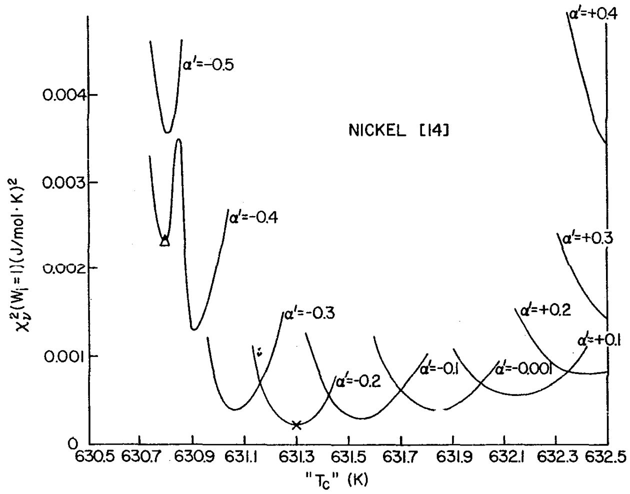


FIGURE 4. A family of locally minimized χ_ν^2 ($W_i=1$) vs. "T_c" curves for Ni [14] (our analysis) using data in the range $618.911 \leqslant T \leqslant 630.847$ K. The absolute minimum consistent with the incrementing interval is indicated by an X on the $\alpha' = -0.2$ curve. Note the local minimum at the point marked with a triangle on the $\alpha' = -0.4$ curve.

merits of analytical searching methods, we partition the hyperspace into two regions: a) the convex region of the absolute minimum and b) the rest of the surface outside of (a). By (a) we mean that region *around* the absolute minimum for which

$$\sum_{i,j} \left(\frac{\partial \chi_\nu^2}{\partial a_i \partial a_j}\right)_0 u_i u_j$$

remains positive definite. Here the sum is over the parameters $a_1 = \alpha$, $a_2 = T_c, \ldots$, and the partial derivatives are evaluated at the absolute minimum point of χ_ν^2. The position around this minimum is given by $u_1 = (\alpha - \alpha_0)$, $u_2 = (T_c - T_{c_0}), \ldots$, where $\alpha_0, T_{c_0}, \ldots$, specify the minimum point. No least square fitting method known to us claims to be able to analytically converge from region (b) to region (a) for any nonlinear function. Claims are usually made as to how rapidly a given method will converge to the absolute minimum point from some other point within the convex region (a). For example, starting from points "far away" but still in region (a), gradient search methods locate the immediate neighborhood of the absolute minimum quite rapidly but from there to the minimum point convergence can be painfully slow. On the other hand, Taylor series expansion methods converge rapidly to the minimum point from points in the immediate neighborhood but can not be relied on to converge for points "far away" [27a]. The method we used most extensively to determine the fit parameters was the gradient-expansion algorithm of Marquardt [27b]. Our error estimates of the parameters were obtained from the diagonal terms of Marquardt's inverse curvature matrix. The algorithm has the advantage of rapid approach to the minimum neighborhood from points far away (forte of pure gradient or steepest descent methods) and rapid convergence to the point of minimum χ_ν^2 from points nearby (forte of pure Taylor series expansion methods). For the present problem of fitting four parameters simultaneously, we found the initial starting parameters needed by the algorithm must *all* be indigenous to the region of the absolute minimum. Otherwise convergence would be erratic or incomplete, different initial starting values would give different final results, and convergence to local minima would occur. None of these problems arose when the initial starting values were obtained as described above.

One problem did occur with Marquardt's algorithm, however, even when the initial starting parameters were determined as described above. We compared the successive values of χ_ν^2 (via $\Delta\chi_\nu^2/\chi_\nu^2$) at each iteration to monitor the rate of convergence. On occasion, we noticed that even though the relative difference in χ_ν^2 converged to 10^{-12} and the parameters were successively equal to eight places, systematic deviations occurred in a data region where we expected eq (1) to fit the data. This prompted us to monitor not just $\Delta\chi_\nu^2/\chi_\nu^2$ and the parameters at each iteration but also the derivatives of χ_ν^2 with respect to the parameters ($\partial\chi_\nu^2/\partial a_j$) and Marquardt's λ parameter. The λ parameter determines if the algorithm behaves like a gradient search (λ large) or an expansion search (λ small). As the minimum point is approached λ tends to zero. We found that the above inconsistency was associated with large derivatives $\partial\chi_\nu^2/\partial a_j$ ($10^2 - 10^6$) and diverging values of λ ($> 10^5$). The occurrence of large λ values is referred to by Marquardt in a footnote (ref. [27b], page 438) as due to high (0.99) correlations among the parameters. However, we have seen the condition occur when the largest correlation is 0.97, and we have seen it not to occur with correlations as high as 0.9999. Monitoring the derivatives $\partial\chi_\nu^2/\partial a_j$ also indicated that they were significantly different from zero (say ~ 1) when the iterative process was stopped using a convergence criterion of $\Delta\chi_\nu^2/\chi_\nu^2 \sim 10^{-3}$. Indeed, many times the derivatives did not drop below 10^{-6} unless $\Delta\chi_\nu^2/\chi_\nu^2$ was around 10^{-8}. Thus we accepted for consideration only those parameter values leading to relative differences $\Delta\chi_\nu^2/\chi_\nu^2$, chi-square derivatives $\partial\chi_\nu^2/\partial a_j$, and λ values all predominantly in the range 10^{-7} to 10^{-12}. We further required the off-diagonal terms of the product of the curvative matrix and its inverse to be less than 10^{-10}. Of course the accuracy of the data can not demand such strong requirements, but they narrowed down sources of internal inconsistencies present in comparing experimental results.

4. Results

We found, in the literature, results of 49 experiments on the magnetic specific heat in the critical region. The magnets are listed in table 1 according to the publication date of the experimental results. The asterisks in column 1 of this table indicate those data sets we least square analyzed by the methods described above. For the remaining magnets, it was usually the case that the data were unavailable to us. Table 2 lists the results of our investigation (17 sets) together with all the parameters we found published (23 sets). For a given magnet, the first line gives the results of our analysis and the second line contains the parameter values reported in the references. The dagger indicates that the results of our analysis differ significantly from those reported in the references. We will discuss these differences first.

EuO: Figure 5 shows the dependence of α' and α on the range of data included in the fit. After initially varying widely, α' finally settles down to a distinctly negative value. On the high temperature side, α could be zero if we were content to include only a limited amount of data, but we interpret these results as indicating that α is positive and greater than 0.3.

$Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (MATS): Allowing T_c to be a free parameter in our analysis of MATS led to fairly inclusive results. Figure 6 shows α' varying widely right

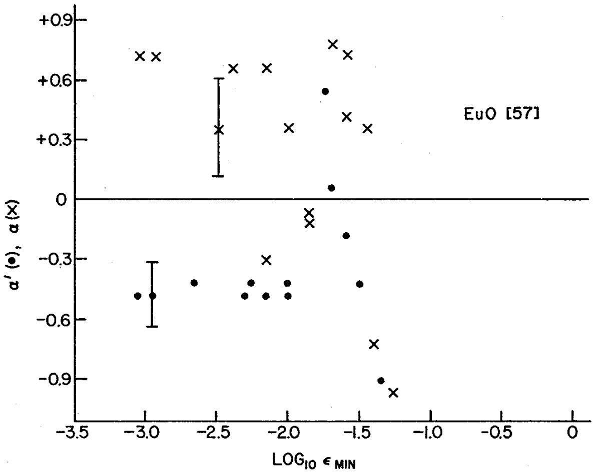


FIGURE 5. α' (●) and α (X) versus $\log_{10}\epsilon_{MIN}$ for EuO [57]. The reduced temperature axis is arbitrarily relative to 69.3 K. The exponents marked with their errorbars give the best overall fit to the data.

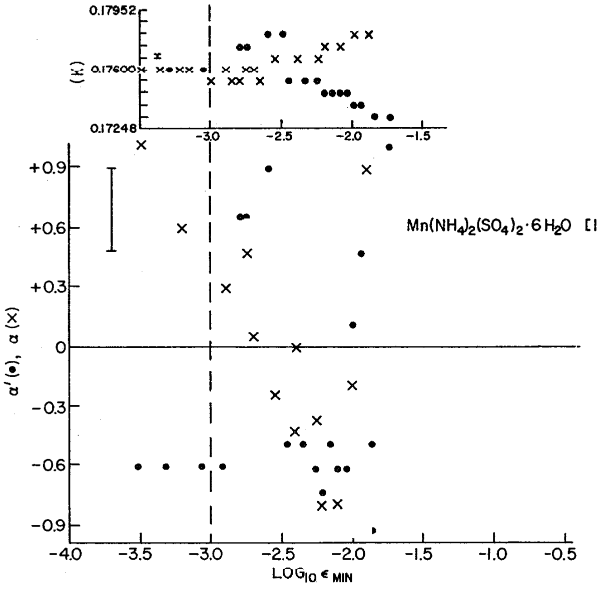


FIGURE 6. α' (●) and α (X) versus $\log_{10}\epsilon_{MIN}$ for $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ [17]. The reduced temperature axis is arbitrarily relative to 0.176 K. The approximate uncertainty in the exponents is indicated by the errorbar. The dashed line marks the beginning of the rounding region. The insert shows the predicted values of the "critical temperature" T_c' (●) and $T_c(X)$ over the same range.

up to the region of rounding. The insert in figure 6 suggests a value of 0.176 K for T_c, in agreement with the value taken by Rayl et al. in the analysis [17] of their data. When we fix T_c at 0.176 K the results of figure 7 occur as opposed to those of figure 6. This constraint removes the scatter in α', and we can say fairly conclusively that α' is not equal to α and neither appears to be equal to 1/8 [17]. The best fit is given by those exponents marked with their error bars. These are the values we entered in table 2, line 1 of MATS. A case for $\alpha' = \alpha = 1/8$ within the uncertainties of the exponents could be made for a special subset of the data, namely

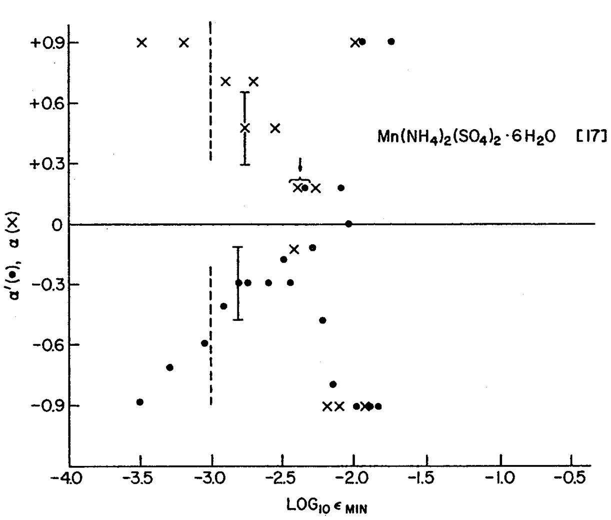


FIGURE 7. α' (●) and α (X) versus $\log_{10}\epsilon_{MIN}$ for $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ [17] with T_c fixed at 0.176 K. Compare with figure 6 in which T_c is a free parameter. The best fit to the data is given by those exponents marked with their errorbars. The exponents marked with an arrow could support the claim [17] that $\alpha' = \alpha = 1/8$.

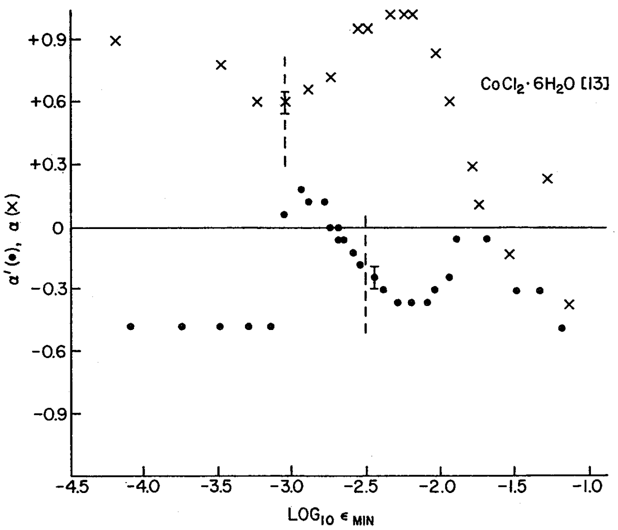


FIGURE 8. α'(●) and α (X) versus $\log_{10}\epsilon_{MIN}$ for $CoCl_2 \cdot 6H_2O$[13]. The reduced temperature axis is arbitarily relative to 2.2890 K. The dashed lines mark the beginning of the rounding region below and above the transition. The exponents marked with their errorbars give the best overall fit.

that represented by the exponents marked with an arrow in figure 7. Finally, we remark that due to scattering in the experimental data the differences that appear distinct using the kind of analysis embodied in figure 7 are hardly apparent in a deviation plot.

$CoCl_2 \cdot 6H_2O$: The dependence of α' and α on the range of data included in the fit for $CoCl_2 \cdot 6H_2O$ is shown in figure 8. It is unlikely that α is zero, and to accommodate $\alpha' = 0$, points somewhat in the rounded region must be included in the fit. However, these results are inconclusive since the data below and above the transition led to significantly different values of T_N. We obtained

$T_N'=2.2885\pm0.0010$ K and $T_N=2.2828\pm0.0006$ K. The weighted average is 2.2844 ± 0.005 K, which is right at the peak in the data. Since the critical temperature is usually found above the peak for an asymmetric transition, we feel that $T_N=2.2885$ is a better choice for the critical temperature. Holding T_N fixed at this value gives the results of figure 9. This constraint resulted in lowering the best α somewhat while α' changed little; however, the range of data giving the best overall fit has shifted away from the transition, and the deviation of the fit from the data is more systematic. Finally, it now appears that even α' is most likely not zero.

$CoCs_3Cl_5$: In the original analysis of this data [28], Wielinga, et al. took $T_N=0.523$ K corresponding to the peak in the data. They obtained $\alpha'=0.0$ and $\alpha=0.75$. Later [18], as a result of convoluting the ideal temperature dependence with a Gaussian distribution in transition temperatures, they concluded $T_N=0.527$ K, which gives $\alpha'=0.19+0.04$ and $\alpha=0.50+0.05$. Allowing T_N to a free parameter, we find $T_N'=0.5229+0.0050$ and $T_N=0.5247+0.0023$. Unlike the case for $CoCl_2 \cdot 6H_2O$, the errors in these determinations of T_N overlap. In addition they encompass the previously obtained values of 0.523 K and 0.527 K. Thus, the scatter in the data does not permit choosing any of these four determinations as the most likely value of T_N. This scatter is reflected in the results for α' and α versus ϵ_{MIN} (fig. 10). Below T_N, α' does not appear to be converging, while above T_N, α varies widely before abruptly leveling off at rather large values.

We now wish to discuss those materials appearing more than once in table 2. These are Gd, Ni and $MnCl_2 \cdot 4H_2O$. Their exponents are summarized in table 3 (at the end of section 5).

Gd: Below T_c our analysis of Lewis' [15] data agrees both with his results and with our analysis of the much earlier data of Griffel, et al. [29], at least within experimental error. Above T_c our analysis of Lewis' data agrees quite well with his result for α, but not with the value of α we obtained for Griffel's data. Except for $\epsilon>10^{-2}$ our analysis of α versus ϵ_{MIN} shows that a negative exponent above T_c is not consistent with Griffel's data. The data of Griffel et al., was not intended to be high resolution work at the critical point, and we did not subtract out nonmagnetic contributions from this data, as Lewis did for his data, though these contributions probably have little influence on the exponents [15]. What is perhaps more important is that Griffel's data were obtained using adiabatic calorimetry and Lewis' data were obtained by the ac method. We will return to this point when discussing Ni.

Ni: The first published results for the exponents of Ni appear to be those of Kraftmakher [30], who concludes that the specific heat is logarithmic on both sides of the transition. Since then Ni has been extensively studied [31, 32, 14, 33], and this conclusion has been significantly modified. Assuming a value of 630 K for T_c of Kraftmakher's data, his figure 2 suggests that his data extend to about $\epsilon=2\times10^{-3}$. Our figure 3 suggests that this range of data might admit $\alpha=0$ but not $\alpha'=0$. A continuing series of measurements by Handler, Mapother, and Rayl [31], Maher and McCormick [32], and Connelly, Loomis, and Mapother [14, 33] has gone almost to $\epsilon=10^{-5}$. These measurements have established the result that α' for Ni is negative. The results of Connelly, Loomis, and Mapother obtained in 1969 [14] and 1971 [33] replace as more accurate the 1967 results of Handler, Mapother, and Rayl [31]. Of these, the results of Connelly, et al., reported

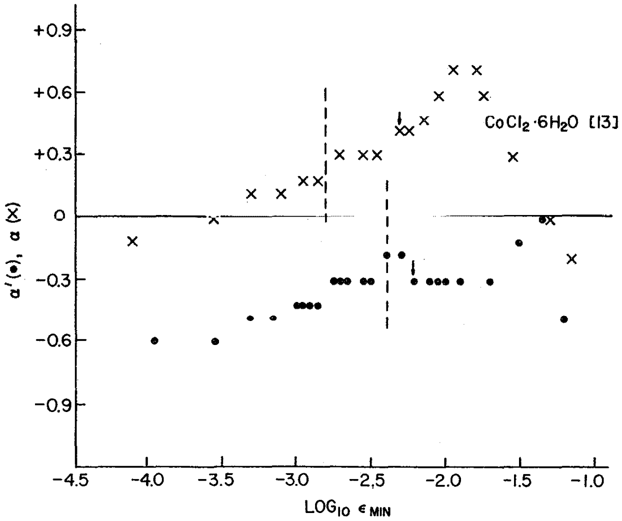


FIGURE 9. α' (●) and α (X) versus $\log_{10}\epsilon_{MIN}$ for $CoCl_2 \cdot 6H_2O$ [13] with T_N fixed at 2.2885 K. Compare with figure 8 in which T_N is a free parameter. The dashed lines indicate the beginning of the rounding region. The arrows mark exponents giving the best overall fit. Their position on the temperature axis has been shifted further away from the transition as compared with figure 8.

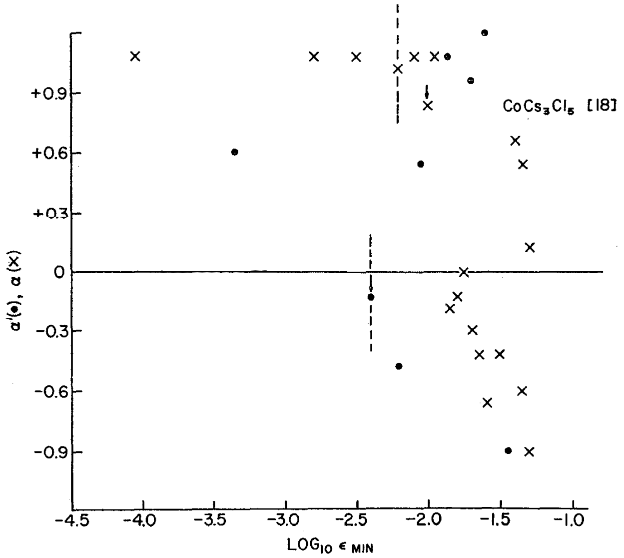


FIGURE 10. α' (●) and α (X) versus $\log_{10}\epsilon_{MIN}$ for $CoCs_3Cl_5$ [18]. The reduced temperature axis is arbitrarily relative to 0.523 K. The dashed lines mark the beginning of the rounding region below and above the transition. The arrows indicate the exponents giving the best overall fit.

in ref. [33] are considered by them their most detailed measurements. Our analysis of their 1969 [14] data agrees quite well with their results (table 3). Two entirely different measurement techniques have been applied to Ni. Conventional adiabatic calorimetry was used by Maher and McCormick [32] to obtain specific heat point accuracy of 1.5 percent, and the ac method was used by Connelly, et al. [14, 33], to obtain continuously recorded specific heat accuracy of 0.5 percent. Thus, the observation that for Ni, α' is negative is to this date the most firmly established result of any magnetic crystal specific heat exponent, even though a factor of 2.5 separates the known observations (table 3). The situation above T_c is not as clear. Above T_c, the measurements of Maher and McCormick differ in an essential way from those of Connelly, et al. The former find a divergence given by $\alpha=+0.10\pm0.05$ and the latter find a cusp given by $\alpha=-0.10\pm0.03$. After considering various aspects of experimental methods, sample configuration, chemical purity, experimental accuracy and normalization procedures, Connelly, et al., conclude that the source of the differences in the two determinations of α is obscure. We see a parallel between these results and those for Gd, which has comparable magnetic anisotropy. Namely, the adiabatic calorimetric method and the ac method agree with respect to the sign of alpha below T_c but not above (table 3). Above the transition the calorimetric method yields positive and almost equal exponents for Gd and Ni, while the ac method gives negative and practically equal exponents for these materials.

$MnCl_2\cdot4H_2O$: The data of Dixon and Rivers [34] are the more reliable here since those of Friedberg and Wasscher [35] were not intended to be high resolution work at the critical point. The large uncertainty we found for α' from the data of Friedberg and Wasscher could admit the possibility that $\alpha'=0$ for their data. As a matter of fact we obtained $\alpha'=0.001\pm0.2$ when all the data down to $\epsilon=10^{-3}$ were included in the fit, but a value of $\alpha'=-0.27\pm0.20$ was more consistent with the behavior of α' versus ϵ_{MIN} and predicted a more random deviation plot. Above T_{N}, the value of $\alpha=0.63+0.10$ we obtained for the data of Friedberg and Wasscher is not very reliable; it provided the best overall fit but the scatter in the α versus ϵ_{MIN} plot could easily accommodate Dixon and Rives value of $\alpha=0.35$.

5. Discussion

We now discuss some general features of the results given in table 2. Our analysis has not revealed any outstanding difference in the range of α' and α between ferromagnets and antiferromagnets. We also find little in the way of significant differences in the ranges of α' and α when the materials are grouped according to representative system Hamiltonians. The ranges are:

	α' range	α range
Heisenberg FM	0 to − 0.5	[a] 0.0 to 0.4 [b] − 0.2 to 0.4
Ising AFM (Exchange)	0 to − 0.4	0 to 0.6
Heisenberg AFM	0 to < 0	0 to 0.1
Ising AFM (Dipolar)	0 to − 0.3	0 to 0.3

[a] Calorimetric method only.

[b] Calorimetric and ac method inclusive.

Model calculations reveal that the nature of the transition depends less on the details of the interaction than on the symmetry of the ordered spin state. But our results, especially for the ordered state, indicate that even the spin symmetry (Ising vs. Heisenberg anisotropy) assumed to be present in these materials is not being reflected in the measured magnetic specific heat singularity. A feature most apparent in these results is the preponderant number of negative exponents for the ordered state. The first to report a negative α' were Handler, Mapother, and Rayl for Ni [31], though our analysis shows previously published data [29, 36, 37, 38, 57] predict negative α' exponents. Below the transition 16 out of 24 materials have negative exponents, while only 6 out of 24 (including Gd and Ni) have negative exponents above the transition. Most Heisenberg model calculations predict a negative exponent above the critical temperature, whereas we find mostly positive α's. The fact that the data do not distinguish between model Hamiltonians suggests this effect may be due to an intrinsic property of the material not accounted for in the Hamiltonian.

The scaling hypothesis referred to in the Introduction also implies a scaled equation of state that has been applied to a wide variety of substances [67]. Thus, we should make a comparison between the α exponents obtained here and those provided by fits of scaled equations of state to magnetic field (H)–magnetization (M)–temperature (T) data. (See ref. [67] for such fits and references to *HMT* data.) Only for Gd and Ni do we find such a comparison possible. *HMT* data, together with the scaling relation $\beta(\delta+1)=2-\alpha$ and the scaling result that α must be equal to α', have been used in ref. [67] to obtain $\alpha=0.01\pm0.09$ for Gd and $\alpha=-0.03\pm0.15$ for Ni. The exponents β and δ describe, respectively, the asymptotic power law for the coexistence curve: $M\propto|T-T_c|^{\beta}$, and the critical isotherm: $H\propto M^{\delta}$. For Gd our results (see table 3) do not support the assumption that α equals α', and even allowing for the large uncertainty in the *HMT* value of α, we do not find agreement between α obtained from the specific heat data of Lewis [15] and α obtained from the *HMT* data. The situation for Ni is somewhat different (table 3). The results of Connelly, Loomis, and Mapother (CLM) [14, 33] support the equality of α and α' while those of Maher and McCormick (MM) [32] do not. Also the large uncertainty of the

HMT value of α for Ni allows for agreement within this error with the specific heat exponents of CLM but not with the α' of MM.

These results, by themselves, do not lend convincing support to scaling. This situation for magnets most likely occurs because the experimental results are still ambiguous, and we lack a firm theoretical understanding of the data rounding. One would expect the experimental precision represented by the high resolution work on Ni [32, 14, 33] to have afforded a more definitive comparison with theory, but the diverse though precise results obtained from different Ni samples indicate that the fundamental problem of obtaining uniform single crystals has still not been solved.

Acknowledgements

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TABLE 1. A chronological listing of experiments on the magnetic specific heat in the critical region[a]

Material		Ref.		State below T_c (K)		Parameters given
$FeCl_2$		[39]	1935	AFM	23.55	None
Cr_2O_3		[40]	1937	AFM	306.5	None
β-UH_3		[41]	1942	FM	172.0	None
$NiCl_2$		[42]	1952	AFM	52.39	None
$MnCl_2 \cdot 4H_2O$	*	[35]	1953	AFM	1.622	None
Gd	*	[29]	1954	FM	291.76	None
CoF_2		[43]	1955	AFM	37.5	None
NiF_2		[44]	1955	AFM	73.33	None
UI_3	*	[45]	1955	AFM	2.61	None
FeF_2		[46]	1955	AFM	78.11	None
Dy		[47]	1956	AFM	175.3	None
Tb	*	[36]	1957	FM	227.67	None
Sm		[65]	1957	AFM	13.6	None
Sm	*	[37]	1959	FM	105.8	None
$NiCl_2 \cdot 6H_2O$		[48]	1960	AFM	5.2	None
$CoCl_2$	*	[49]	1962	AFM	24.71	None
$CrCl_2$	*	[50]	1962	AFM	16.06	None
$CuCl_2$	*	[51]	1962	AFM	23.91	None
$CoCl_2 \cdot 2H_2O$		[52]	1964	AFM	17.2	None
$KMnF_3$		[53]	1964	AFM	88.0	None
$CoCl_2 \cdot 6H_2O$	*	[13]	1964	AFM	2.2890	$\alpha', \alpha, T_N, A', A, B', B$
Gd		[54]	1965	FM	290.45	None
MnF_2		[55]	1965	AFM	67.33	$\alpha', \alpha, A', A, B', B$
$CrBr_3$		[56]	1965	FM	32.55	None
EuO	*	[57]	1965	FM	69.3	α, A
$CuK_2Cl_4 \cdot 2H_2O$	*	[38]	1965	FM	0.89	$\alpha', \alpha, T_c, A', A, B', B$
Fe		[59]	1965	FM	1042	$\alpha', \alpha, A'/A$
Ni		[30]	1966	FM	630	$\alpha', \alpha, A', A, B', B$
$RbMnF_3$		[58]	1966	AFM	83	α', α, A
$Dy_3Al_5O_{12}$		[60]	1967	AFM	2.54	$\alpha', \alpha, T_N', T_N, A, B', B$
Ni	*	[31]	1967	FM	625	α', α
$CoCs_3Cl_5$	*	[28]	1967	AFM	0.527	$\alpha', \alpha, T_N, A, B$
$CoCs_3Br_5$		[28]	1967	AFM	0.282	$\alpha', \alpha, A', A, B', B$
EuS	*	[24]	1968	FM	16.426	$\alpha', \alpha, T_c', T_c, A', A, B', B$
$Mn(CH_3COO)_2 \cdot 4H_2O$	*	[61]	1968	FIM	3.180	None
$Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$	*	[17]	1968	FM	0.176	α', α, A', A
$DyAlO_3$		[66]	1968	AFM	3.52	None
$TbAlO_3$		[66]	1968	AFM	3.95	None
$GdAlO_3$		[66]	1968	AFM	3.69	None

TABLE 1. A chronological listing of experiments on the magnetic specific heat in the critical region.[a] — Continued

Material	Ref.	State below T_c (K)	Parameters given
Ni	[32] 1969	FM 629.635	$\alpha', \alpha, T_c, A', A, B', B$
Ni *	[14] 1969	FM 631.55	$\alpha', \alpha, T_c, A', A, B', B$
Cr	[62] 1969	AFM 310.7	α', A'
$MnCl_2 \cdot 4H_2O$	[34] 1969	AFM 1.62	$\alpha', \alpha, A', A, B', B$
Pd-Mn(0.54 at % Mn)	[19] 1970	FM 1.98	$\alpha', \alpha, T_c, A', A, B', B$
Pd-Mn(1.35 at % Mn)	[63] 1970	FM 4.477	$\alpha', \alpha, T_c, A', A, B', B$
Pd-Mn(2.54 at % Mn)	[19] 1970	FM 5.783	$\alpha', \alpha, T_c, A', A, B', B$
$ErCl_3 \cdot 6H_2O$	[64] 1970	AFM 0.356	$\alpha', \alpha, T_N, A', A, B', B$
Gd *	[15] 1970	FM 291.35	α', α, T_c
Ni	[33] 1971	FM 631.58	$\alpha', \alpha, T_c, A', A, B', B$

[a] Column 1. The asterisks indicate data sets we have least square analyzed by methods described in the text.

Column 2. The left hand member is the reference number and on the right is the date of publication.

Column 3. FM = ferromagnet, AFM = antiferromagnet, FIM = ferrimagnet indicate the state immediately below the given transition temperature. The transition temperature listed is that reported by the investigators in the references. When more than one transition temperature is found, a representative value is entered here.

Column 4. The parameters are defined by eq (1) in the text. An entry in this column means that either the parameter as defined by eq (1) is given in the reference or that it can be derived from whatever parameters are given. For this tabulation, the transition temperature is not considered a parameter unless it was explicitly treated as such in the data analysis reported by the investigator.

TABLE 2. Some critical parameters for 24 different magnetic crystals [1]

Ferromagnets

Material	Ref.	α'	α	A'	A	B'	B	A'/A
Gd	[29] 1954	−0.24 ± 0.07	0.11 ± 0.01	12.33 ± 2.12	2.02 ± 0.09	22.46 ± 2.38	27.25 ± 0.19	6.10
Tb	[36] 1957	−0.70 ± 0.08	0.55 ± 0.04	202.8 ± 8.3	1.12 ± 0.15	−213.5 ± 8.5	26.28 ± 0.47	181.07
Sm	[37] 1959	−0.27 ± 0.10	0.60 ± 0.09	4.35 ± 0.90	0.10 ± 0.03	29.0 ± 1.0	26.05 ± 0.15	43.50
EuO†	[57] 1965	−0.50 ± 0.15	0.34 ± 0.24	12.46 ± 0.80	1.61 ± 1.11	1.40 ± 1.60	0.076 ± 2.46	7.74
		< 0	0		3.61		−7.25 ^{a}	
$CuK_2Cl_4 \cdot 2H_2O$	[38] 1965	−0.02 ± 0.13	0.03 ± 0.14	1.89 ± 0.77	1.53 ± 0.70	3.00 ± 1.23	−0.12 ± 1.27	1.24
		0.0	0.0	1.69	1.69	3.58	−0.42	1.00
Ni	[30] 1966							
		0.0	0.0	1.65	1.65	28.65 ^{b}	25.94 ^{b}	1.00
Fe	[59] 1966							
		0.0	0.0					1.
Ni	[31] 1967							
		−0.3 ± 0.1	0.0 ± 0.1					
EuS	[24] 1968	−0.25 ± 0.03	0.00 ± 0.02	7.63 ± 0.79	3.99 ± 0.31	4.19 ± 1.07	−2.01 ± 0.61	1.91
		−0.25 ± 0.03	0.00 ± 0.03	7.59	4.21	4.33	−2.50	1.80
$Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$†	[17] 1968	−0.30 ± 0.20	0.50 ± 0.20	19.74	0.10	−10.03	9.46	197.4
		0.125	0.125	2.34 ^{c}	0.78 ^{c}	22.45 ^{c}	6.65 ^{c}	3.00
		0.125	0.125	2.21 ^{d}	0.76 ^{d}	25.23 ^{d}	6.56 ^{d}	2.91
Ni	[32] 1969							
		−0.26 ± 0.06	0.10 ± 0.05	4.60	0.67	24.34	29.24	6.87
Ni	[14] 1969	−0.09 ± 0.03	−0.14 ± 0.02	1.60 ± 0.20	2.21 ± 0.07	2.09 ± 0.41	−3.36 ± 0.14	0.72
		−0.11 ± 0.03	−0.11 ± 0.03	1.73	1.99	1.86	−3.00	0.87
Pd-Mn(0.54 at % Mn)	[19] 1970							
		−1.78	−0.14 ^{e}	0.1227	0.0110	−0.0217	0.0091	11.15

TABLE 2. Some critical parameters for 24 different magnetic crystals [1]—Continued

Ferromagnets

Material	Ref.	α'	α	A'	A	B'	B	A'/A
Pd-Mn(1.35 at % Mn)	[63] 1970	-1.36 ± 0.12	-0.20 ± 0.06 [e]	0.1467	0.0234	-0.0009	0.0215	6.27
Pd-Mn(2.45 at % Mn)	[19] 1970	-1.18	-0.41 [e]	0.1622	0.0584	0.0289	0.0461	2.78
Gd	[15] 1970	-0.31 ± 0.06 -0.29 ± 0.05	-0.17 ± 0.02 -0.17 ± 0.05	1.75 ± 0.33 [f]	0.84 ± 0.07 [f]	9.54 ± 0.39 [f]	8.60 ± 0.12 [f]	2.08
Ni	[33] 1971	-0.10 ± 0.03	-0.10 ± 0.03	1.416 ± 0.005	1.609 ± 0.005	1.51	-2.60	0.88

Antiferromagnets

Material	Ref.	α'	α	A'	A	B'	B	A'/A
$MnCl_2 \cdot 4H_2O$	[35] 1953	-0.27 ± 0.20	0.63 ± 0.10	13.1 ± 9.2	0.31 ± 0.12	-3.8 ± 12.0	2.44 ± 0.53	42.26
UI_3	[45] 1955	0.8 ± 1.0	-0.4 ± 1.0	0.41 ± 1.3	8.10 ± 3.0	0.28 ± 1.0	-8.60 ± 3.0	0.051
$CoCl_2$	[49] 1962	-0.39 ± 0.05	0.57 ± 0.06	9.58 ± 1.5	0.19 ± 0.04	-4.04 ± 1.6	8.66 ± 0.14	50.42
$CuCl_2$	[51] 1962	-0.70 ± 0.26	0.05 ± 0.20	12.68	0.34	-6.81	8.54	37.29
$CrCl_2$	[50] 1962	-0.75 ± 0.50	-0.50 ± 0.30	21.95	10.42	-14.34	-5.73	2.11
$CoCl_2 \cdot 6H_2O$†	[13] 1964	-0.25 ± 0.04 0.0	0.59 ± 0.04 0.0	6.38 ± 0.84 2.25	0.22 ± 0.02 2.25	-4.12 ± 1.06 2.78	3.83 ± 0.11 -1.99	29.00 1.00
MnF_2	[55] 1965	0.0	0.0 to 0.1	4.15	2.17	6.82	1.16	1.91
$RbMnF_3$	[58] 1966	<0	0.0 to 0.05	…………	1.34			
$Dy_3Al_5O_{12}$	[60] 1967	0.0	0.31 ± 0.02	3.96	0.35 [g]	-3.68 [g]	1.13 [g]	11.31
$CoCs_3Cl_5$†	[28] 1967	-0.11 0.19 ± 0.04	0.87 0.50 ± 0.05 [i, l]	3.47 1.50 ± 0.32 [k]	0.13 0.29 ± 0.20 [l, k]	4.59 7.90 ± 0.42 [j]	1.40 0.58 ± 0.42 [l]	26.69 5.17
$CoCs_3Br_5$	[28] 1967	0.0	0.0	3.66 ± 0.17	4.57 ± 0.17	-1.58 ± 0.83	-6.90 ± 0.83	0.80
Cr	[62] 1969	0.34 ± 0.02	…………	0.031 ± 0.002	…………			
$MnCl_2 \cdot 4H_2O$	[34] 1969	0.0	0.35 ± 0.02	6.07 ± 0.07	0.49 ± 0.04	4.82 ± 0.58	3.88 ± 0.09	12.39
$ErCl_3 \cdot 6H_2O$	[64] 1970	-0.26 ± 0.06	-0.07 ± 0.05 [m]	17.11	1.00	-18.39	0.338	17.11

Ferrimagnets

Material	Ref.	α'	α	A'	A	B'	B	A'/A
$Mn(CH_3COO)_2 \cdot 4H_2O$	[61] 1968	0.14 ± 0.02	-0.19 ± 0.04	0.99 ± 0.06	1.52 ± 0.21	2.74 ± 0.13	2.53 ± 0.31	0.65

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[1] The values of A', A, B', and B are in J/mol K unless indicated otherwise. The parameters are defined by $C=(A/\alpha)(\epsilon^{-\alpha}-1)+B$ or for $\alpha=0$ by $C=-A\ln\epsilon+B$ where $\epsilon=|T/T_c-1|$. Primed quantities refer to below the transition and unprimed quantities refer to above. The dagger in column 1 indicates that a significant difference occurs between the results of our analysis and those reported in the references. For a given magnet, the first line gives the results of our analysis and the second line contains the parameter values reported in the references.

[a] Estimated from figure 3, page 53 of ref. [57].

[b] In converting Kraftmakher's equation for C (ref. [30]) to our eq (1), we assume $T_c=630$ K.

[c] The coefficients of eq (3) in ref. [17] should be interchanged. Also the values of $B_\pm$ are not given in eq (3), although their presence is assumed in eq (1) of this reference. Using their eq (3) and the solid lines of their figure 4, we obtain $B_-=0.15$ and $B_+=0.05$ giving $B'=22.45$ J/mol K and $B=6.65$ J/mol K. These latter values are entered in table 2.

[d] When we fix α' (α) at 1/8 and T_c at 0.176 K we get for eq (3) ref. [17]: $C_+/R=0.733\epsilon^{-1/8}+0.0556$ $(1.73\times10^{-3}\leq\epsilon\leq1.76\times10^{-2})$ and $C_-/R=2.13|\epsilon|^{-1/8}+0.908$ $(1.57\times10^{-3}\leq|\epsilon|\leq1.88\times10^{-2})$. These parameters imply those entered in table 2.

[e] The temperature dependence used in ref. [19 and 63] is $C_\pm=(P_\pm/\alpha_\pm)\,(1-\epsilon_\pm^{-\alpha_\pm})+Q_\pm$ where $\epsilon_\pm=1-(T_c/T)^{\pm1}$. Below T_c this differs from our eq (1) only by the sign of P_-, but above T_c we can write $C_+=(-P_+/\alpha_+)[(\epsilon-\epsilon^2+\epsilon^3-\ldots)^{-\alpha_+}-1]+Q_+$ where $\epsilon=|T/T_c-1|$ (not ϵ_+). Thus to the extent that the higher order term in ϵ can be

neglected we make the association $\alpha=\alpha_+$, $A=-P_+$, $B=Q_+$. For Pd–Mn (1.35 at % Mn), using this association in our eq (1) gives a 0.006 percent error at $\epsilon=10^{-3}$, 0.1 percent error at $\epsilon=10^{-2}$ and 1.4 percent error at $\epsilon=10^{-1}$. The experimental error in C is about 0.2 percent, so below $\epsilon=10^{-2}$ this association leads to an undetectable error.

[f] These values are in the arbitrary units of ref. [15].

[g] Deduced from figure 2 and figure 3 of ref. [60] and using T_N=2.537 K. Also the sign of A_- in figure 2, ref. [60] is incorrect.

[h] The data for $CoCs_3Cl_5$ included about 4 points with quite large deviations from the calculated curve; thus, we did not obtain reliable estimates of the uncertainties in the parameters. If these points are not included in the data analysis, we estimate the uncertainty in α' and α to be about 20 percent.

[i] Remarks similar to footnote e apply here.

[j] In ref. [28], figure 6, the signs of the coefficients 8.5 and 1.6 in the expression for $C(T<T_N)$ should be reversed. They are given correctly in the text. In ref. [18], page 61, figure 7, the sign of the coefficient 0.193 in the expression for $C(T<T_N)$ should also be reversed. It is given correctly in the text.

[k] The errors for A' and A were determined ignoring the covariances between these coefficients and the critical exponents α' and α, respectively.

[l] These parameters for $T>T_N$ derived from those of ref. [28 and 18] predict a curve that differs systematically from that given in the above references. The difference can not be accounted for by differences in the choice of the temperature axis (see footnote e).

[m] Remarks similar to footnote e apply here.

TABLE 3. The exponents for those materials appearing more than once in table 2[a]

Material	Ref.	α'	α
Gd	[29] 1954*	−0.24 ± 0.07	0.11 ± 0.01
	[15] 1970†	−0.31 ± 0.06	−0.17 ± 0.02
		−0.29 ± 0.05	−0.17 ± 0.05
Ni	[30] 1966		
		0.0	0.0
	[31] 1967		
		−0.3 ± 0.1	0.0 ± 0.1
	[32] 1969*		
		−0.26 ± 0.06	0.10 ± 0.05
	[14] 1969†	−0.09 ± 0.03	−0.14 ± 0.02
		−0.11 ± 0.03	−0.11 ± 0.03
	[33] 1971†		
		−0.10 ± 0.03	−0.10 ± 0.03
$MnCl_2 \cdot 4H_2O$	[35] 1953	−0.27 ± 0.20	0.63 ± 0.10
	[34] 1969		
		0.0	0.35 ± 0.02

* Adiabatic calorimetry.

† ac method.

[a] The top line for each reference entry gives the results our analysis and the bottom line contains the exponent values reported in the references.

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