Numerical Investigation of High Temperature Expansions of the Specific Heat of the Heisenberg Model*

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The ten-term high temperature expansion calculations by Baker et al. (1967) for the $d=3$, $S=1/2$, cubic lattice Heisenberg models have been investigated numerically. Critical values based on the ten-term series were unreliable, however graphical extrapolation yielded critical values with a consistent q dependence among the various results for the sc, fcc, bcc, FM, and AFM models. The short range order, as measured by $(S_\infty - S_c)/R$, is greater for the AFM models than for the FM model. The estimate of 0.35 ± 0.02 for $(S_\infty - S_c)/R$ of the sc-AFM model agrees with previous experimental work on $CoBr_2 \cdot 6\,H_2O$ and $CoCl_2 \cdot 6\,H_2O$. Results are presented on the slow convergence of the high temperature expansions. Extrapolation of the series is needed for $\varepsilon < 0.1$. Higher order corrections to the T^{-2} term are needed for $T/T_c < 5$. The critical values for the $I(1/2)$ and $H(1/2)$ models were interpolated to predict critical values for the sc and bcc $XY(1/2)$ models.

Introduction

The most complete nearest-neighbor high temperature expansion calculations on spin-1/2, three-dimensional Heisenberg-models for the cubic lattices reported to date are those given by Baker, Gilbert, Eve, and Rushbrooke [1]. Among other results they obtained ten terms for the specific heat of the simple cubic, body-centered cubic, and face-centered cubic lattices. Analysis of the susceptibility series gave excellent results for the critical points, the susceptibility critical index γ, and the gap parameter 2Δ. This was the first report to use scaling arguments to deduce a possible value $\alpha = -1/7$ for the specific heat critical exponent, a finding verified directly from renormalization group theory by Ahlers [2]. Baker, et al. studied the specific heat series for indication of the critical behavior using the Padé approximant technique. Specific heat series are notoriously slow to converge, and the Padé approximants were inconclusive, particularly in the case of the simple cubic lattice. The usual search for singular behavior yielded $\alpha = 0.4 \pm 0.1$, while interpretation of the gap parameter results suggested the possibility that $\alpha = -0.20$. Critical values for the entropy were obtained but not for the energy. They found $(S_\infty - S_c)/R = 0.264$ for the sc, 0.242 for the bcc, and 0.238 for the fcc lattice. Their only comment on the anti-ferromagnetic models referred to the critical point results of Rushbrooke and Wood [3]. Critical values for the energy were predicted in an earlier paper by Dalton and Wood [4].

This study was stimulated by a combination of theoretical and experimental interests in the critical values for antiferromagnets. The fact that the ground state energies [5], transition temperatures [3], and high temperature expansions [1] of $d=3$, $S=1/2$ Heisenberg-models for FM and AFM lattices with the same $|J_{nn}|$ are different suggests that the entropy and energy critical values are also different. This point has received little, if any, attention. The recent experimental paper by White and Bhatia [6] points out that the specific heat of $CoBr_2 \cdot 6\,H_2O$ and $CoCl_2 \cdot 6\,H_2O$ yield short range order results $(S_\infty - S_c)/R$ that exceed the predictions for the likely applicable models. The issue of the magnetic behavior of these salts is clouded by nonnegligible intrasublattice interactions and imprecise knowledge of crossovers from $d=2$ to $d=3$ and from Heisenberg to XY behavior [7]. Improved knowledge of the critical values of the $d=3$, $S=1/2$ sc-AFM Heisenberg-model would contribute to a better understanding of the experimental dilemma.

This paper presents a numerical investigation of the high temperature expansion calculations of Baker et al. [1]. Results concerning the series convergence, temperature dependence, and critical values are discussed. Interpolation for XY-model critical values is made, and a brief discussion of recent experimental results is given. Preliminary

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results of this work were presented at an American Physical Society meeting [8].

Numerical Calculations

Baker, et al. started their high temperature expansion (HTE) calculations for the $d=3$, $S=1/2$ cubic Heisenberg-models with the Hamiltonian

$$\mathcal{H} = -\frac{J}{2}\sum_{\langle ij\rangle}\boldsymbol{\sigma}^{(i)}\cdot\boldsymbol{\sigma}^{(j)} - \mu H\sum_i \sigma_3{}^{(i)}, \quad (1)$$

where $\boldsymbol{\sigma}^{(i)}$ is the Pauli spin vector at site i of a given crystal lattice, σ_3 is the component of $\boldsymbol{\sigma}$ in the direction of the external magnetic field H, μ is the associated magnetic moment, and J is the nearest-neighbor exchange coupling constant. The free energy in zero magnetic field is defined by the HTE

$$F_0(x) = \sum_{n\geq 0} e_n x^n/2^n n!, \quad (2)$$

where $x = J/K_B T$ and the e_n are integer coefficients determined by the finite cluster method suggested originally by Domb [9]. The HTEs for the molar specific heat, entropy, and energy in zero field are expressed as

$$C/R = \sum_{n\geq 2} e_n n(n-1)x^n/2^n n!, \quad (3)$$

$$(S_\infty - S)/R = \sum_{n\geq 2} e_n (n-1)x^n/2^n n!, \quad (4)$$

and

$$(E_\infty - E)/RT_c = x_c \sum_{n\geq 2} e_n x^{n-1}/2^n (n-1)!, \quad (5)$$

respectively, where x_c refers to the critical point for the model and lattice determined from analysis of the susceptibility series. Baker et al. calculated values of e_n up to tenth order in x, which remain the longest HTEs to date for the $H(1/2)$ models [10].

A computer program was written to evaluate Eqs. (2) – (5) at various values of x/x_c, T/T_c, and $\varepsilon = (T-T_c)/T_c$ for six systems, namely, ferromagnetically (FM) and antiferromagnetically (AFM) coupled simple, body-centered, and face-centered cubic lattices. The values of x_c for the FM systems were 0.596, 0.397, and 0.249, respectively (Baker, et al. 1967). The values of x_N for the AFM systems were -0.528, -0.365, and -0.235, respectively, obtained from analysis of susceptibility series by Rushbrooke and Wood [3]. It is well-known that nearest-neighbor interactions cannot produce AFM order in the fcc lattice [11], however we thought there might be some mathematical interest in the behavior of this unstable model, assuming the extrapolated value of x_N.

Critical values were obtained from evaluations at $x = x_c$. C_c/R, $(S_\infty - S_c)/R$, and $(E_\infty - E_c)/RT_c$ follow directly from Equations (3) – (5). S_∞/R equals $Ln(2S+1)$, thus yielding S_c/R. E_∞/RT_c and thus E_c/RT_c are obtained from the relation

$$\frac{E_\infty}{RT_c} = qS^2\frac{|J|}{K_B T_c}\left(1+\frac{\gamma}{qS}\right) = qS^2|x_c|(1+\gamma/qS), \quad (6)$$

where $\gamma = 0.0$ for a FM and 0.6 for an AFM system [5]. The review by Domb and Miedema [12] discusses critical values at length.

Results and Discussion

The results of the computations detailed in the previous section are well represented by Figs. 1 – 5 and Tables 1 – 4 and need only a brief explanation. Figures 1 – 5 and Table 1 are direct results from the computer program and should be self-explanatory. The graphs have a consistent symbol code, i. e., circles, squares, and triangles for the sc, fcc, and bcc lattices, respectively, and open and closed symbols for FM and AFM coupling, respectively. Tables 2 and 3 were derived from further analysis of the results, and Table 4 gives some error calculations useful in estimating regions of applicability of the HTEs.

The most obvious observation from the plots is the poor behavior of the sc-series and the convergent behavior of the bcc- and fcc-series. This point was emphasized by Baker, et al. [1], however no graphical evidence was provided. Without the benefit of series plots, such as Figs. 2 and 3, the temperature plot for the sc-FM series in Fig. 1 would be deceiving due to the appearance near T_c of an asymptotic behavior similar to that of the bcc and fcc series. The only detectable defect of the sc-FM plot in Fig. 1 is a slight inflection point near $\varepsilon = 0.6$. The case of the sc-AFM series is more obvious even though it has better convergence properties than the sc-FM series. The ten-term sc-AFM series has the remarkable property of a maximum near $\varepsilon = 0.2$.

Figures 2, 4, and 5 give series plots for the $H(1/2)$ specific heat, entropy, and energy for $T = T_c$. If the series were well converged at T_c after ten terms, the results given in Table 1 would be the critical values for the $H(1/2)$ models. The critical values in Table 1 are quite irregular in their q de-

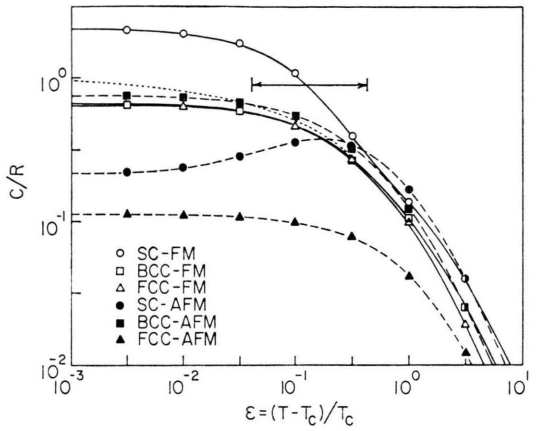

Fig. 1. Temperature dependence ($T>T_c$) of the specific heat of $H(1/2)$ models near T_c for the first ten terms of the high temperature expansions. The dotted curve corresponds to a fit to a Padé approximant to the fcc-FM series, assuming $\alpha=-0.20$. The interval marked indicates the region of the fit [1].

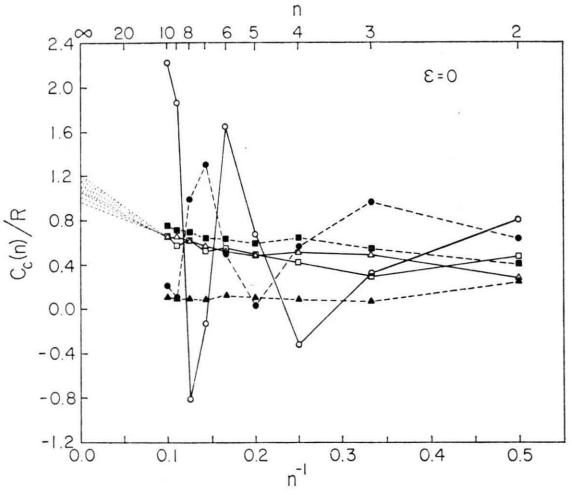

Fig. 2. Series plots of the specific heat of $H(1/2)$ models at $T=T_c$ ($\varepsilon=0$) for the first ten terms of the high temperature expansions. The dotted curves indicate predictions of $C_c(\infty)$ using fits of Padé approximants to the bcc-FM and fcc-FM series, assuming $\alpha=-0.20$ and -0.25 [1]. Refer to Fig. 1 for an explanation of the symbols.

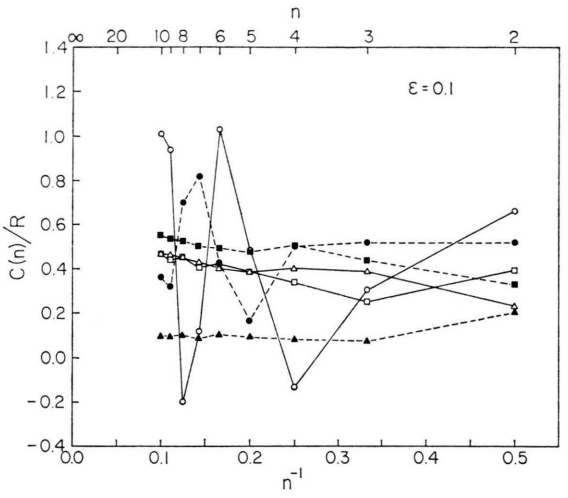

Fig. 3. Series plots of the specific heat of $H(1/2)$ models at $T=1.1\,T_c$ ($\varepsilon=0.1$) for the first ten terms of the high temperature expansions. Refer to Fig. 1 for an explanation of the symbols.

pendence, as judged by the $I(1/2)$ critical values given by Domb [13] and reproduced in the top half of Table 3. Figure 3 indicates that the convergence problem persists even at $\varepsilon=0.1$.

The traditional solution to the convergence problem is to extrapolate the series by a number of powerful methods, particularly the use of Padé approximants [1, 10]. The virtual certainty that α is negative for the Heisenberg models [2, 10, 13] makes the Padé approximant technique of questionable value, that is, the specific heat series do not have a singularity at $T=T_c$. The asymptotic form

$$C/R = A - B\,\varepsilon^{-\alpha} + \ldots, \qquad (7)$$

has the value A at the critical point and the remaining terms presumably give a confluent zero. The temperature derivative of Eq. (7) may have a simple singularity at the critical point in the case of the $H(1/2)$ models. The author is currently study-

Table 1. Critical values for three-dimensional Heisenberg-models after ten terms ($S=1/2$) [a].

Lattice	q	LT Phase	$\frac{J_{nn}}{K_B T_c}$	$\frac{C_c}{R}$	$\frac{S_c}{R}$	$\frac{S_\infty - S_c}{R}$	$\frac{S_\infty}{R}$	$\frac{E_c}{RT_c}$	$\frac{E_\infty - E_c}{RT_c}$	$\frac{E_\infty}{RT_c}$
sc	6	FM ($\gamma=0.0$)	0.596	2.217	0.259	0.435	0.693	0.124	0.770	0.894
bcc	8	FM ($\gamma=0.0$)	0.397	0.664	0.450	0.244	0.693	0.328	0.467	0.795
fcc	12	FM ($\gamma=0.0$)	0.249	0.654	0.461	0.232	0.693	0.337	0.411	0.748
sc	6	AFM ($\gamma=0.6$) [c]	−0.528 [b]	0.211	0.410	0.284	0.693	0.340	0.610	0.950
bcc	8	AFM ($\gamma=0.6$) [c]	−0.365 [b]	0.754	0.411	0.283	0.693	0.324	0.515	0.838
fcc (unstable)	12	AFM ($\gamma=0.6$) [d]	−0.235 [d]	0.113	0.619	0.074	0.693	0.604	0.172	0.776

[a] Based on calculations by Baker et al. [1] [b] Rushbrooke and Wood [3]. [c] Keffer [5]. [d] Assumptions for this work.

Table 2. Critical values for three-dimensional Heisenberg-models with graphical extrapolation ($S=1/2$).

Lattice	q	LT Phase	$\frac{J_{nn}}{K_B T_c}$	$\frac{C_c}{R}$	$\frac{S_c}{R}$	$\frac{S_\infty - S_c}{R}$	$\frac{S_\infty}{R}$	$\frac{E_c}{RT_c}$	$\frac{E_\infty - E_c}{RT_c}$	$\frac{E_\infty}{RT_c}$
sc	6	FM ($\gamma=0.0$)	0.596 (0.588) [a]	1.10 ± 0.50	0.393	0.300 ± 0.040 (0.265) [a] (0.264) [b]	0.693	0.279	0.615 ± 0.040 (0.595) [a]	0.894
bcc	8	FM ($\gamma=0.0$)	0.397 (0.393) [a]	0.82 ± 0.10 (0.97) [c]	0.443	0.250 ± 0.010 (0.235) [a] (0.242) [b]	0.693	0.320	0.475 ± 0.010 (0.460) [a]	0.795
fcc	12	FM ($\gamma=0.0$)	0.249 (0.246) [a]	0.80 ± 0.10 (1.21) [c]	0.453	0.240 ± 0.005 (0.220) [a] (0.238) [b]	0.693	0.333	0.415 ± 0.005 (0.430) [a]	0.748
sc	6	AFM ($\gamma=0.6$) [e]	−0.528 [d]	1.30 ± 0.30	0.343	0.350 ± 0.020	0.693	0.260	0.690 ± 0.020	0.950
bcc	8	AFM ($\gamma=0.6$) [e]	−0.365 [d]	1.02 ± 0.15	0.388	0.305 ± 0.015	0.693	0.288	0.550 ± 0.015	0.838
fcc (unstable)	12	AFM ($\gamma=0.6$) [f]	−0.235 [f]	0.12 ± 0.02	0.618	0.075 ± 0.005	0.693	0.606	0.170 ± 0.005	0.776

[a] Dalton and Wood [4]; [b] Baker et al.[1]; [c] Baker et al.[1] assuming $\alpha=-0.20$; [d] Rushbrooke and Wood [3]; [e] Keffer [5]; [f] Assumptions for this work.

ing Eq. (3) with this idea in mind and will report the results in a later publication.

In order to obtain critical value estimates for the $H(1/2)$ models that are superior to those of Table 1, we have employed a graphical extrapolation technique. This approach has proven to be successful in extrapolating series plots [14]. The difficulty with specific heat series is that ten terms are often insufficient to estimate the central tendency of a series. For this reason our estimates for the specific heat maxima and for all of the sc lattice properties are tentative. Each of the critical values was obtained independently by establishing the mean of the graphically estimated upper and lower bounds for the series. The results of this procedure are given in Table 2 with error estimates expressing a measure of the spread between the upper and lower bounds. Earlier estimates by others are also given.

Several important points emerge from the study of Table 2 and Figs. 2, 4, and 5. Most significantly is the consistency of the q dependence among the various results. The values of $(E_\infty - E_c)/RT_c$ for the FM series agree quite well with those of Dalton and Wood (1965), who made their estimates for a five term series. The values of $(S_\infty - S_c)/R$ for the FM series agree with previous estimates for the bcc and fcc series but not the sc series. Our larger estimate of 0.30 is quite reasonable after intercomparison with the $I(1/2)$ critical values given in Table 3.

The critical values given in Table 2 for the AFM $H(1/2)$ systems are entirely new to the best of our knowledge. The predicted absence of AFM ordering in the fcc lattice [11] is evidenced by peculiar behavior, observable in Figures 2 – 5. These plots show clearly that C_c/R, $(S_\infty - S_c)/R$, and

Table 3. Critical values for three-dimensionalising- and XY-models ($S=1/2$).

Lattice	q	Model	$\frac{J_{nn}}{K_B T_c}$	$\frac{S_c}{R}$	$\frac{S_\infty - S_c}{R}$	$\frac{S_\infty}{R}$	$\frac{E_c}{RT_c}$	$\frac{E_\infty - E_c}{RT_c}$	$\frac{E_\infty}{RT_c}$
sc [a]	6	Ising	0.443	0.558	0.135	0.693	0.445	0.220	0.665
bcc [a]	8	Ising	0.315	0.582	0.111	0.693	0.458	0.172	0.630
fcc [a]	12	Ising	0.204	0.590	0.103	0.693	0.461	0.152	0.613
sc [b]	6	XY	0.495 [c]	0.472	0.221	0.693	0.331	0.412	0.743
bcc [b]	8	XY	0.344 [c]	0.511 (0.52)	0.182 (0.17) [c]	0.693	0.368 (0.44)	0.320 (0.25) [c]	0.688
fcc [c]	12	XY	0.221	0.518	0.172	0.693	0.380	0.283	0.663

[a] Domb [13]; [b] This work; [c] Betts [15].

$(E_\infty - E_c)/RT_c$ are greater for the sc-AFM and bcc-AFM systems than their FM counterparts. Once again the q dependence in Table 2 between the FM and AFM critical values appears satisfactory.

This analysis for critical values was extended one step further for the convenience of experimentalists wishing to relate specific heat data to model predictions. The bottom half of Table 3 gives new predictions for the critical values of $d=3$, $S=1/2$ XY-models, assuming the fcc calculations for $XY(1/2)$ by Betts [15] are exact. Critical values for the sc and bcc XY $(1/2)$ systems were obtained by means of interpolation ratios from q^{-1} dependence plots of our $H(1/2)$ results from Table 2 and the $I(1/2)$ values in Table 3. The sc critical values for $XY(1/2)$ are entirely new. The value of $(S_\infty - S_c)/R$ for the bcc lattice agrees with an estimate by Betts [15], however the finding for $(E_\infty - E_c)/RT_c$ disagrees by 28%.

In the introduction we indicated that this investigation was partially motivated by a recent experimental study by White and Bhatia [6]. $CoBr_2 \cdot 6\,H_2O$ and $CoCl_2 \cdot 6\,H_2O$ are $q=6$, $S'=1/2$, AFM systems with lattice and spin-space anisotropy. As a result these crystals may order as $D=2$, $d=2$ or $D=2$, $d=3$ or $D=3$, $d=3$ systems (D-spin dimension; d-lattice dimension). We are inclined to think that a $d=2$ to $d=3$ crossover occurs well above T_N. The deviation from $D=3$ is not too great, thus yielding critical values substantially in agreement with the sc-AFM $H(1/2)$ results in Table 2. Somewhere in the critical region $(\varepsilon<0.1)$ a second crossover from $D=3$ to $D=2$ behavior is expected. The alternative choice of extensive $D=2$, $d=2$ behavior into the critical region depends critically on a sufficiently small interlayer coupling that can overcome the influence of the deviation from $D=2$. The recent discussions by Ikeda [7], Stanley [13], and Singh and Jasnow [16] on crossover phenomena are particularly useful in this regard. The point resolved by this investigation was our concern for the large values of $(S_\infty - S_c)/R$ obtained for $CoBr_2 \cdot 6\,H_2O$ (0.30) and $CoCl_2 \cdot 6\,H_2O$ (0.36) as compared with the estimate of 0.264 by Baker, et al. [1] for the sc-FM $H(1/2)$ system. The new results of this investigation show that the ordering of these substances is not anomalous, however complicated an accurate model Hamiltonian may be.

Our final comments concern the results given in Table 4. A direct application for HTEs involves fitting experimental data to verify models and predict exchange couplings. Figures 1 – 5 provide the user of the $H(1/2)$ specific heat series with a suitable caveat. Figure 3 suggests that only the fcc-FM series can be trusted down to $\varepsilon=0.1$. Using truncation of the tenth term as a criterion, Table 4 indicates that all six series are reliable down to $\varepsilon=1$. Detailed analysis is required for usage in the $0.1<\varepsilon<1.0$ region, and a choice of some sort of

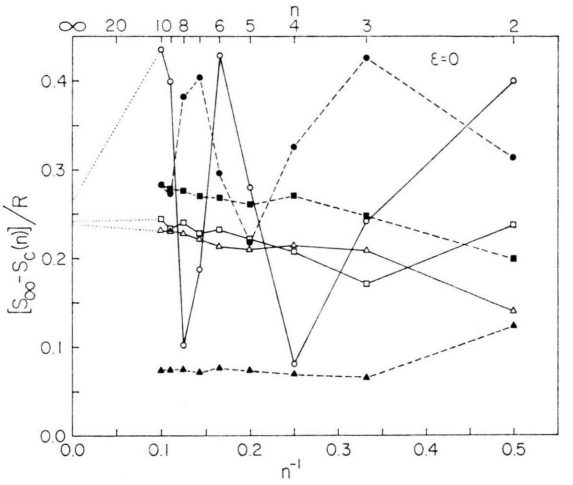

Fig. 4. Series plots of the entropy $[S_\infty - S_c(n)]/R$ of $H(1/2)$ models at $T=T_c$ $(\varepsilon=0)$ for the first ten terms of the high temperature expansions. The dotted curves indicate predictions of the extrapolated critical values [1]. Refer to Fig. 1 for an explanation of the symbols.

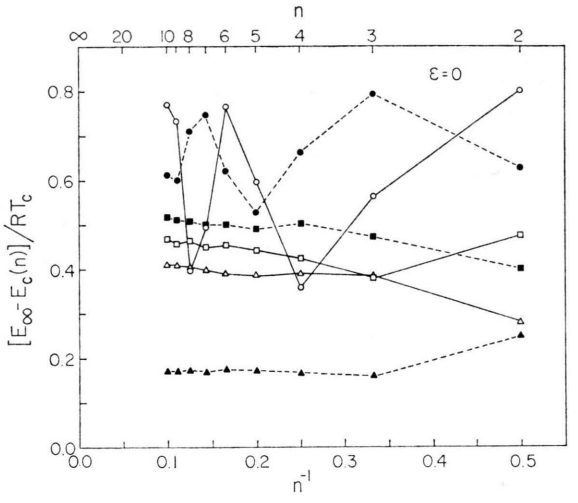

Fig. 5. Series plots of the energy $[E_\infty - E_c(n)]/RT_c$ of $H(1/2)$ models at $T=T_c$ $(\varepsilon=0)$ for the first ten terms of the high temperature expansions. Refer to Fig. 1 for an explanation of the symbols.

Table 4. Per cent error in the specific heat of three-dimensional Heisenberg-models due to the truncation of terms from the ten-term high temperature expansion calculations ($S=1/2$) [a].

Lattice	q	LT Phase	Truncation of Term 10			Truncation of Terms 3−10					
			$\varepsilon=0$	$\varepsilon=0.1$	$\varepsilon=1$	$\varepsilon=0$	$\varepsilon=0.1$	$\varepsilon=1$	$\varepsilon=10$	$\varepsilon=19$	$\varepsilon=99$
sc	6	FM	16.10	12.85	0.26	63.93	38.26	−47.59	−6.36	−3.27	−0.61
bcc	8	FM	14.71	8.09	0.09	28.68	15.90	−11.19	−3.49	−1.95	−0.40
fcc	12	FM	2.57	1.38	0.02	57.28	50.73	28.44	6.42	3.62	0.74
sc	6	AFM	49.77	11.25	0.06	−196.6	−43.64	6.33	4.05	2.41	0.52
bcc	8	AFM	5.47	2.90	0.03	47.16	40.05	19.04	3.38	1.85	0.37
fcc (unstable)	12	AFM	8.34	3.67	0.02	−121.1	−108.6	−48.08	−6.78	−3.64	−0.71

[a] Based on calculations by Baker et al. [1]

Padé approximant is recommended. Truncation of terms 3 − 10 indicates that the usual fit of high temperature magnetic specific heat data with a T^{-2} term is not well advised because most of the available data is in the $1<\varepsilon<10$ range. Extension of the T^{-2} fit to still higher temperatures is impractical for numerous reasons.

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