Specific heat of $(C_6H_{11}NH_3)CuBr_3$ and $(C_6H_{11}NH_3)CuCl_3$ within series analysis of finite-chain data

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The in-plane specific heat of the title compounds has been estimated by analysis of the finite-chain data in the framework of new polynomial extrapolations, displaying better convergence properties for $1/N \to 0$. Final results are consistent with those we found previously for the linear and parabolic extrapolations, as well as reveal an agreement with experiment and recent quantum transfer-matrix simulations.

There are physical systems which are built up from magnetic chains and display a magnetic order at very low temperatures. The following compounds are well-known examples: $(CD_3)_4NMnCl_3$ (Refs. 1 and 2) (denoted as TMMC), $CsNiF_3$ (Refs. 3 and 4), and $(C_6NH_3CuBr_3)$ and $(C_6NH_3CuCl_3$, referred to as CHAB and CHAC,[5] respectively.

Magnetic $S=\frac{1}{2}$ chains have been the subject of extensive theoretical investigations,[6] especially CHAB, which contains easy-plane anisotropy. Such a system can be mapped[7,8] onto a sine-Gordon (SG) model when an external field is applied in the easy plane provided that the spins are considered as classical vectors, their motion is confined to the easy plane, and the discreteness of the lattice is neglected. In view of the unknown effects of the various approximations underlying the SG model, quantum statistics have been recently applied in the framework of numerical simulations[9-14] and the renormalization-group (RG) approach.[14,15]

As to the simulations for CHAB, various approaches have been used. First, the thermodynamical properties of the macroscopic chains have been estimated from extrapolations of the numerical results for finite chains.[10-12,14,16] Second, with recourse to the Trotter formula,[17] the partition function of the quantum chain has been mapped onto a classical counterpart of the two-dimensional lattice of the Ising spins. The resulting classical system is then analyzed using Monte Carlo[9-12] or transfer-matrix techniques.[9,13,18] The simulations in question give a coherent description of CHAB in the framework of the anisotropic Heisenberg model

$$\mathcal{H}=-2\sum_i (J_x S_i^x S_{i+1}^x + J_y S_i^y S_{i+1}^y + J_z S_i^z S_{i+1}^z) - g\mu_B B \sum_i S_i^x , \quad (1)$$

where $J_x/k_B = J_y/k_B = 63\pm 3$ K, $J_z/k_B = 60.25$ K, and $g=2.01$. In particular, the recent quantum transfer-matrix method[18] (QTM) confirms the extrapolated finite-size results,[12,14,16] so that we want to reconsider our previous finite-chain ($N \le 12$) data,[14] constituting an extension of those[16] found for $N \le 11$, by recourse to a new extrapolation scheme.

The aim of this work is twofold: an improvement of our asymptotic analysis based previously[14] on polynomial extrapolations (linear and parabolic in $1/N$) for CHAB and CHAC as well as an evaluation of the low-field specific heat in order to resolve the discrepancy[10] in the peak positions of the excess specific heat ΔC for CHAB.

For a given value of B and T, our finite-size data form a series A_N, where $2 \le N \le 12$. In order to study the $N \to \infty$ limit A of the series A_N, different techniques can be used. In the ideal situation of optimal convergence of the series, one would expect all methods to lead to the same result. Unfortunately, our data belong to this category only in the high-temperature region. Since the analytic form of the N dependence of A_N is unknown, there is no *a priori* way to prefer one method to another. One has to compare the inherent quality criteria of the different methods in order to arrive at an acceptable guess for the value of A. Even then, the conclusion is not always very decisive.

The series A_N have been mainly analyzed in terms of polynomial expansions. These methods suppose that the A_N may be approximated by expressions of the form

$$A_N \simeq A_N(n) = \sum_{k=0}^{n} B_k y_N^k , \quad (2)$$

where the B_k are obtained by minimizing the mean-square deviation

$$\Delta^2 = \sum_{N=N_1}^{N_2} [A_N - A_N(n)]^2/M, \quad M = N_2 - N_1 + 1 , \quad (3)$$

and $y_N = f(1/N)$, with a function $f(x)$ fulfilling the property $f(0)=0$. The parameter B_0 is clearly the estimate for A in these methods. Apart from the magnitude of Δ^2, the quality of this analysis can be estimated from the rate of convergence obtained for the B_k when the lowest index N_1 is changed.

The polynomial extrapolations which have been performed so far[10-12,14,16,19,20] correspond to the choice

$y_N = 1/N$. Because of the limited number of A_N values ($N_2 = 12$), the results may not be improved by increasing the order n of the polynomial as the higher-order coefficients B_k do not always remain small. In practice, the series have been analyzed by linear ($n = 1$) and quadratic ($n = 2$) fits.

Obvious choices are also simple powers $f(x) = x^{\alpha} (\alpha > 0)$, or $f(x) = 1/\ln(x)$. One tries to obtain a better convergence by first transforming the variable $1/N$ into $y_N = f(1/N)$ and then by fitting the data A_N with a low-order polynomial of the form (2). In our case, however, the best results in terms of acceptable estimates with low Δ^2 were obtained with form

$$f(x) = (e^{\alpha x} - 1)/\alpha \ , \tag{4}$$

or $f(x) = x/(1 - \alpha x)$. In each case, α is a free parameter again determined by minimizing Δ^2. Although formally equivalent to the previous method (expansions in powers of $1/N$), it has the advantage of allowing the incorporation of higher-order terms in a low-order expansion.

Our finite-size data can also be analyzed in the framework of the Padé approximant method.[21,22] This method is based on the fact that our limit A can be obtained from

$$A = (1 - z)F(z)|_{z=1} \ , \tag{5}$$

where

$$F(z) = \sum_{N=0}^{\infty} A_N z^N \ , \tag{6}$$

or

$$(1 - z)F(z) = A_0 + \sum_{N=1}^{\infty} (A_N - A_{N-1}) z^N \ . \tag{7}$$

From the finite number of A_N coefficients, one can build (N,M) Padé approximants to $(1 - z)F(z)$, from which various estimates $A(N,M)$ for A are obtained. A straightforward quality criterion for this method is found in the consistency of the Padé table $A(N,M)$. Although consistent with the polynomial estimates, these numbers are usually too much scattered so that we do not present here explicitly the results found from this method.

The results presented below have been found from new polynomial extrapolations based on the formula (2).

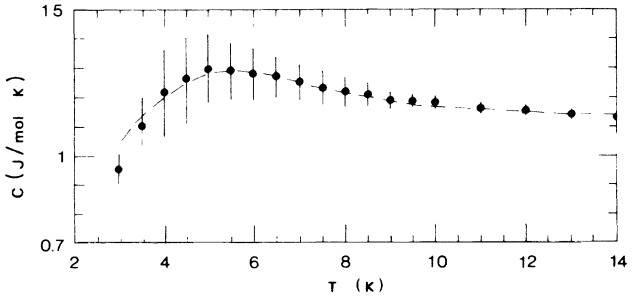

FIG. 1. Zero-field specific heat of CHAB. The dashed curve represents the experimental results. Present theoretical results are shown by solid circles with error bars.

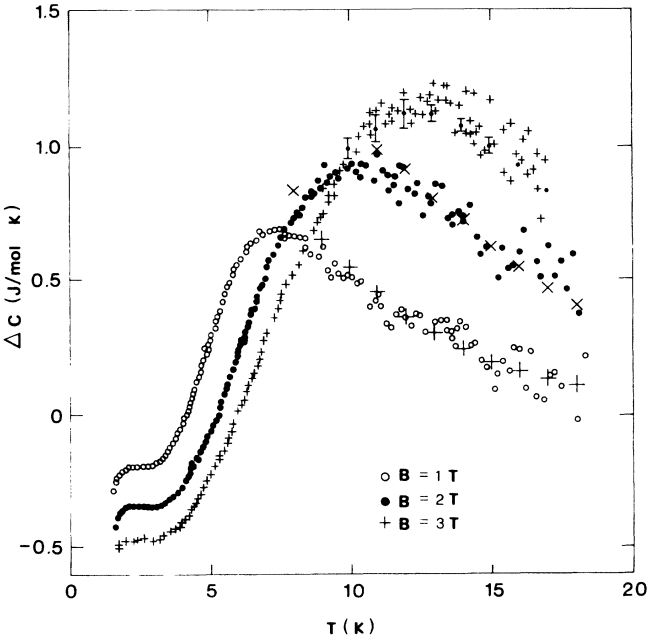

FIG. 2. Excess specific heat $\Delta C(T,B) = C(T,B) - C(T,0)$ of CHAB for $B = 1$, 2, and 3 T. Open circles, solid circles, and small crosses represent the experimental data. Bigger crosses and points with error bars show present estimates.

Then the inherent quality criteria are well fulfilled in the experimental region of temperatures and the variation of the estimates is considerably diminished with respect to those found from the Padé approximant method and simple linear or parabolic extrapolations in $1/N$.

First, we calculate the zero-field specific heat for CHAB. The value $J/k_B = 63 \pm 3$ K was found[16] by fitting the finite-size data extracted from the linear extrapolations for the chains $N \leq 11$ to the experimental data and was then confirmed by the QTM simulations.[18] In Fig. 1 the dashed curve represents the experimental zero-field specific-heat data, whereas our present estimates are re-

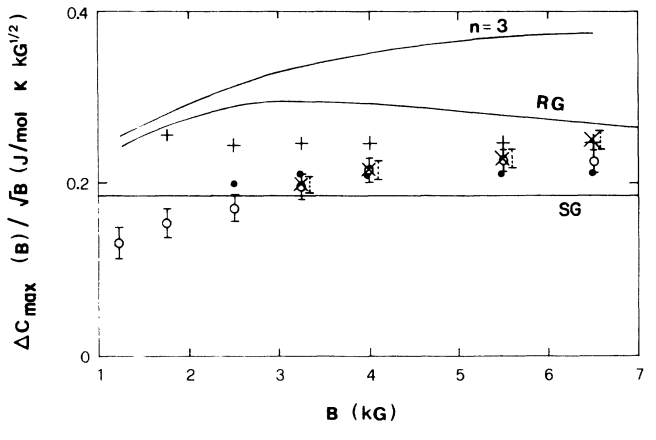

FIG. 3. Field dependence of the reduced maximum excess specific heat $\Delta C_{max}(B)/\sqrt{B}$ for CHAB. Present results are shown by rotated crosses. The other symbols are explained in the text.

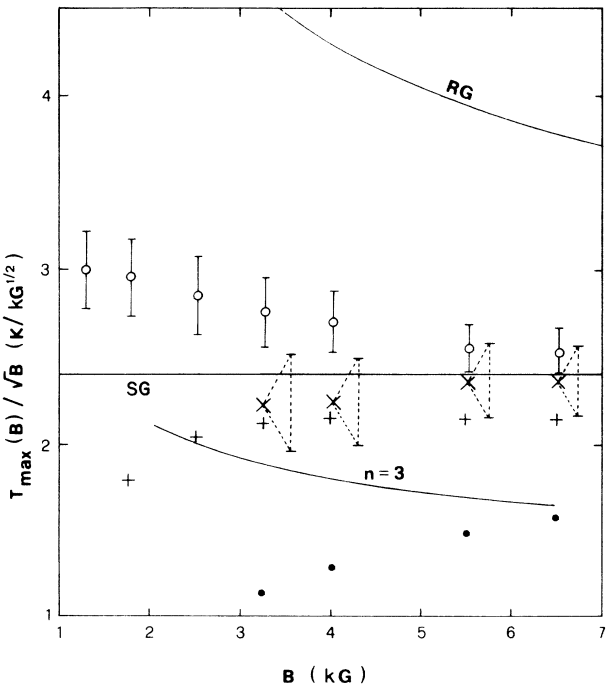

FIG. 4. Reduced peak positions $T_{max}(B)/\sqrt{B}$ vs the magnetic field B for CHAB. The notations are the same as Fig. 3.

ported by solid circles. The vertical intercepts show the corresponding error bars. Our estimates are consistent with the choice $J/k_B = 63$ K.

In Fig. 2 the CHAB high-field specific-heat data are reported. The small symbols denoted by crosses and open and solid circles show the experimental[16] excess specific heat $\Delta C(T,B)$. The bigger crosses and solid circles with the error bars represent our estimates found from the polynomial fitting (2). The convergence of the present extrapolations is better than before,[14,16] and the agreement with experiment is improved. We encounter a good convergence of the extrapolations for temperatures $T \geq 10$ K, which contains the position of the peak for $B = 3$ T, as well as find agreement with recent QTM predictions.[18]

An interesting comparison with experiment can be also made in the low-field region as far as the heights (Fig. 3) and the positions (Fig. 4) of the peaks in the excess specific heat are concerned. In Figs. 3 and 4 the experimental excess specific heat measurements on CHAB (Ref. 8) are shown by open circles with error bars. The solid lines described as $n = 3$, RG, and SG refer to the classical $n = 3$ component model,[8] the renormalization-group approach,[14] and SG approach,[23] respectively. The crosses represent the quantum transfer-matrix[19] estimates, the

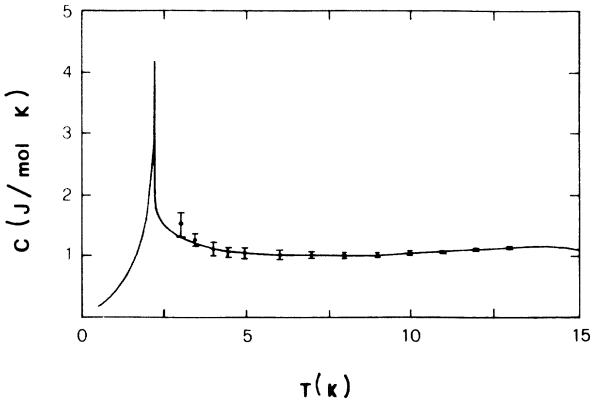

FIG. 5. Zero-field specific heat of CHAC. The continuous line shows the experimental data, and the symbols display our estimates.

solid circles, the previous finite-size results[10] obtained from the chains with $N \leq 10$, whereas our results are reported by rotated crosses with error bars. The latter show a substantial improvement for the peak positions with respect to the former. Moreover, the present estimates are somewhat superior to those found from the QTM technique[13] (assuming, however, the value $J/k_B = 55$ K).

Finally, the zero-field specific heat is calculated for $S = \frac{1}{2}$ compound CHAC.[5] From the ferromagnetic resonance experiment it has been established[24] that CHAC can be described by the anisotropic Hamiltonian (1), where $J_x/k_B = 45.52$ K, $J_y/k_B = 44.99$ K, and $J_z/k_B = 44.49$ K. In Fig. 5 the experimental curve is drawn in the solid line with the sharp peak demonstrating the phase transition point to the three-dimensional (3D) ordering. Our results are reported by the circles and are consistent with the experimental findings (apart from the vicinity of the transition temperature) as well as with our previous[14] linear or parabolic predictions in $1/N$.

In conclusion, we have performed an asymptotic analysis of finite-size data series by recourse to the polynomial and Padé approximant extrapolations. We have found that the former better fulfills the inherent quality criteria, so that we have compared here the polynomial estimates with the experimental results for CHAB and CHAC. The series in question have been evaluated in our preceding paper,[14] except for those describing the low-field behavior of CHAB (Figs. 3 and 4). The agreement between our numerical calculations and both experimental measurements and the QTM simulations has been revealed.

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