Magnetic specific heat of linear chains with Heisenberg exchange and crystal-field anisotropy for $S = 1$

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(Received 18 July 1974)

Estimates of the specific heat C are presented for the infinite one-dimensional array of spins $S = 1$ with isotropic nearest-neighbor coupling J and an axial zero-field splitting Δ. The results are obtained from extrapolation of C for finite chains. For a number of ratio's Δ/J (including all sign combinations of J and Δ) curves are presented for all temperatures except for the region near $T = 0$. Attention is given to the justification of the extrapolation formula. In the case of ferromagnetic exchange a second maximum may appear in C for small Δ. Its position and amplitude are strongly dependent on Δ/J. For antiferromagnetic coupling, C is only slightly dependent on the sign and magnitude of Δ for small Δ.

I. INTRODUCTION

The calculation of thermodynamic properties of an infinite ensemble of magnetically interacting spins forms a problem which has been a challenge to many theoreticians over the last decades. Most of the progress has been made upon the introduction of model systems. In these systems the nature of the exchange interaction is restricted to a limited number of simplified forms (Ising, Heisenberg, XY). One further simplification can be found in restricting the dimensionality of the lattice as well as the spin quantum number. It is clear that due to their relative theoretical simplicity the one-dimensional model systems have attracted the most attention. However, even for these systems the exact solution of the Hamiltonian in terms of the thermodynamical potentials induces severe problems.

Until now closed-form expressions for the partition function could only be derived for the $S = \frac{1}{2}$ Ising model,[1] the $S = \frac{1}{2}$ XY model,[2] and for the classical limit $S \to \infty$ with arbitrary spin dimensionality.[3-6] In principle, the general spin Ising chain can also be solved with the use of the transfer-matrix technique.[7] For a number of other Hamiltonians, approximate solutions have been published. Among these we mention low-temperature approximations (spin-wave theory),[8] high-temperature-series expansions,[9,10] Green's-function approaches,[11] and limited-chain-length calculations.[12,13]

The approximate techniques were mostly applied to the case of isotropic interaction while in practice this may hardly be expected. Except for S-state ions such as Mn^{2+}, Fe^{3+}, and Gd^{3+} an anisotropy in the exchange or in the single-ion properties may be present. For $S = \frac{5}{2}$ (Mn^{2+}, Fe^{3+}) the Green's-function analysis of the specific heat[11] is therefore valuable, while for $S = \frac{1}{2}$ the general Hamiltonian with anisotropic exchange is reviewed by Bonner and Fisher.[12]

Except for $S = \frac{5}{2}, \frac{7}{2}$ all ions with $S > \frac{1}{2}$ will in practice exhibit a zero-field energy splitting due to interactions with the surrounding ligands. Among those the most experimental evidence is obtained on Ni^{2+} ($S = 1$) compounds. Since the magnitude of the zero-field splitting (Δ) is dependent on the actual surrounding, insight is obtained into the dependence of the thermal and magnetic behavior on one parameter in the Hamiltonian.

The theoretical prediction of a tricritical point in the related Blume-Emery-Griffiths model[14,15] make these Ni^{2+} compounds specialy interesting. Experimental observations also indicate a complicated magnetic behavior.[16-19] In some salts for instance it is observed that the specific heat displays two singularities, both of magnetic origin.[20,21] Except for some preliminary notes[22,23] no quantum-mechanical predictions are available for the thermal and magnetic behavior of $S = 1$ assemblies with Heisenberg exchange and $\Delta \neq 0$.

In view of this lack of theoretical predictions we have started an investigation of Hamiltonians for $S = 1$ with axial zero-field splitting and isotropic exchange. A logical start was found in the case of a one-dimensional arrangement of spins. In that case the lattice (a chain or ring) is so simple that other methods than the series expansion of a thermodynamic potential are possible. This paper deals with the specific heat of such linear systems and applies the methods of extrapolation from finite clusters of spins.

In an attempt to justify such extrapolation we derived a relation between the specific heat of clusters of different size and used this to obtain an estimate for the infinite chain. Like the earlier notes that deal with the same type of Hamiltonian we had to exclude the extreme-low-temperature limit. Attempts resembling those of

Bonner and Fisher to describe the low-temperature limit failed in the presence of Δ.

Section II defines the Hamiltonian and describes the general theory. The basic formula that justifies the extrapolation procedure is derived on the basis of a series expansion. In Sec. III the results for varying Δ and J (in magnitude as well as in sign) will be presented and discussed.

II. THEORY

A one-dimensional assembly of N spins $S=1$ with axial zero-field splitting Δ and nearest-neighbor isotropic exchange J may be represented by the Hamiltonian

$$\mathcal{H} = -2J \sum_{i=1}^{N-1} (\vec{S}_i \cdot \vec{S}_{i+1}) - \Delta \sum_{i=1}^{N} (S_{iz}^2 - \tfrac{2}{3}) . \tag{1}$$

In this form $\mathcal{H}$ represents an open chain. For the description of a ring an additional coupling between S_1 and S_N can be assumed. For small N the eigenvalues and associated eigenstates of $\mathcal{H}$ can be calculated by exact diagonalization of the corresponding matrix. No solution is known for the eigenvalues or for the partitionfunction in the case $N \to \infty$.

The maximum N for which calculations can be performed is determined by the dimension of the eigenvalue problem. Therefore, good quantum numbers are of great help since by their application the matrix is divided in blocks, which can be diagonalized separately.

The z component of total spin $T_z = \sum S_{iz}$ commutes with $\mathcal{H}$ and basis functions can be chosen that are eigenfunctions of T_z. The translational invariance of $\mathcal{H}$ in the case of rings make the irreducible representations (IR) of the group D_N (for N spins in the ring) good quantum numbers. Application of projection operators creates the appropriate basis functions belonging to a certain IR. For $N>3$ some of the IR are two dimensional, resulting in a twofold degeneracy of the eigenvalues. This further reduces the eigenvalue problem. For a chain the only symmetry element is an inversion center and therefore $\mathcal{H}$ transforms according to D_2. Calculations were performed on a Burroughs B6700 computer and this set a maximum allowable dimension of 300 for the matrix equations. The application of good quantum numbers then enables ring calculation up to $N=8$. Due to the lower symmetry the largest chain for which $\mathcal{H}$ can be solved has seven spins.

Once the eigenvalues E_i are known, the specific heat per spin may be calculated as

$$C_N = \frac{kT}{N} \frac{\partial^2}{\partial T^2} \left[T \ln \left(\sum_i e^{-E_i/kT} \right) \right] . \tag{2}$$

The results of such a calculation for chains with various N are shown in Fig. 1 for a case with ferromagnetic exchange. In order to obtain an estimate for the specific heat of an infinite chain, a correlation must be found between the results of the finite clusters of different size. Sometimes a sufficiently reliable result is obtained from an interpolation between C_N and C_{N+1} for various N, if C_∞ is approached alternatingly. This behavior is displayed by antiferromagnetic rings.[12] In case of ferromagnetic coupling however, C_∞ is approached monotonically for rings as well as for chains as is shown in Fig. 1. In this case an *extrapolation* of the data is required, introducing severe problems in the estimation of error bounds. In order to avoid these uncertainties a relation of the form $C_N = f(N, C_\infty)$ is desirable to establish a rigid base for the extrapolation formula. Such a relation may be obtained, at least for the high-temperature tail, through an expansion of C_N in powers of β $(=J/kT)$,

$$C_N = \sum_{i=2}^{\infty} a_i^N \beta^i \tag{3}$$

and then deriving a relation of the form $a_i^N = g(N, a_i^\infty)$. To do this, a_i^N is expressed in traces of the Hamiltonian for a chain of N spins. The traces are correlated with the occurrence of certain graphs on the lattice,[9] through which the dependence of a_i^N on the chain length N is determined. This procedure will be outlined in more detail for a_4^N. Thereafter, general arguments will be sufficient to derive the relation for all coefficients. In the example of a_4^N we will restrict ourselfs to the case $\Delta=0$. However, the results are valid for the more general Hamiltonian as well.

The relation between a_4^N and the traces of $\mathcal{H}_N$ is given by

$$a_4^N = \mathrm{tr}(\mathcal{H}_N^4) - 3[\mathrm{tr}(\mathcal{H}_N^2)]^2 , \tag{4}$$

where $\mathrm{tr}(\mathcal{H}_N)$ denotes the normalized trace $\mathrm{Tr}(\mathcal{H}_N)/(2S+1)^N$. The only graph that contributes to $\mathrm{tr}(\mathcal{H}_N)^2$ is $(\vec{S}_1 \cdot \vec{S}_2)^2$, denoted by d_2. In $\mathcal{H}^4$ the nonvanishing graphs are

$$\begin{aligned} d_4^1 &= (\vec{S}_1 \cdot \vec{S}_2)^4 , \\ d_4^2 &= 4(\vec{S}_1 \cdot \vec{S}_2)^2 (\vec{S}_3 \cdot \vec{S}_4)^2 \\ &\quad + 2(\vec{S}_1 \cdot \vec{S}_2)(\vec{S}_3 \cdot \vec{S}_4)(\vec{S}_1 \cdot \vec{S}_2)(\vec{S}_3 \cdot \vec{S}_4) , \\ d_4^3 &= 6(d_2)^2 . \end{aligned} \tag{5}$$

The traces can now be expressed in the graphs by counting their frequency of occurrence on the lattice. For finite as well as for infinite chains the occurrence numbers are given in Table I. Using these numbers we arrive at

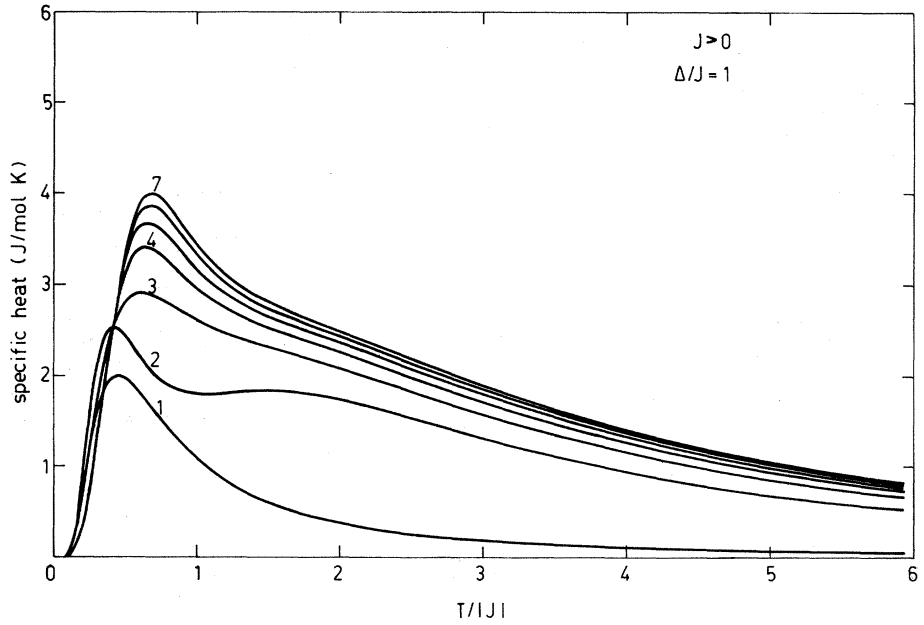

FIG. 1. C_N vs T/J for finite chains for ferromagnetic exchange and $\Delta < 0$.

$$a_4^N \propto \frac{1}{N}\{15(d_2)^2 - 2d_4^2 - d_4^1 + N[d_4^1 + d_4^2 - \tfrac{5}{2}d_4^3 + 6(d_2)^2] + N^2[\tfrac{1}{2}d_4^3 - 3(d_2)^2]\} \tag{6a}$$

and

$$a_4^\infty \propto d_4^1 + d_4^2 - \tfrac{5}{2}d_4^3 + 6(d_2)^2 . \tag{6b}$$

Now a_4^N may be expressed in a_4^∞:

$$a_4^N = a_4^\infty - [d_4^1 + 2d_4^2 - 15(d_2)^2]/N . \tag{7}$$

To obtain expressions like Eq. (7) for all a_i^N it is observed that in analogy with Eq. (6a), a_i^N can be expressed in a polynomial in N,

$$a_i^N = \frac{1}{N}\sum_{k\geq 0} b_k^i N^k , \tag{8}$$

where the coefficients b_k^i are combinations of graphs d_i. Since for large N the result should be finite, all b_k^i vanish for $k>1$ (as was shown for a_4^N). For a_i^N we may thus write

$$a_i^N = b_1^i + b_0^i/N . \tag{9}$$

In the limit $N \to \infty$ this should equal a_i^∞, and combining this result with Eq. (3), we obtain the required general expression between C_N, C_∞, and N,

$$C_N = C_\infty[1 - \alpha(T)/N] , \tag{10}$$

with $\alpha(T)$ independent of N. Expression (10) explains the fact that $C_N(T)$ is a monotonic function of N for ferromagnetic as well as for antiferromagnetic chains.

A plot of C_N vs $1/N$ should result in a straight line from which C_∞ may be obtained. This actually turns out to be the case for $kT \gg |J|$ but for lower temperatures discrepancies from the linear relation appear. This can be understood when the conditions mentioned in Table I are taken into account, since they affect the validity of Eq. (9). In general it can be stated that Eq. (9) is subject to the condition that N should be large enough so that the chain contains all graphs in $\mathrm{tr}(\mathcal{H}^i)$ at least once. For high temperatures the series expansion (3) is limited to one term of appreciable importance. Therefore Eq. (10) can be applied to all chains that contain the graph of $\mathrm{tr}(\mathcal{H}^2)$, and thus for $N \geq 2$. For decreasing temperature more and more terms in (3) are of importance and consequently a longer chain is required to contain the largest diagram.

The discrepancies of the linear relation (10) turn out to be alternating in sign for even and odd N and therefore it is possible to use the plot of C_N vs $1/N$ even for fairly low temperatures.

TABLE I. Occurrence of diagrams in $\mathcal{H}^2$ and in $\mathcal{H}^4$ on an infinite lattice and on finite chains of length N. For this last case the formulas are subject to the conditions in the right-most column.

Diagram	Occurrence for $N \to \infty$	Occurrence for finite N	Conditions
d_2	N	$N-1$	$N>1$
d_4^1	N	$N-1$	$N>1$
d_4^2	N	$N-2$	$N>2$
d_4^3	$\frac{1}{2}N(N-3)$	$\frac{1}{2}(N-2)\,(N-3)$	$N>3$

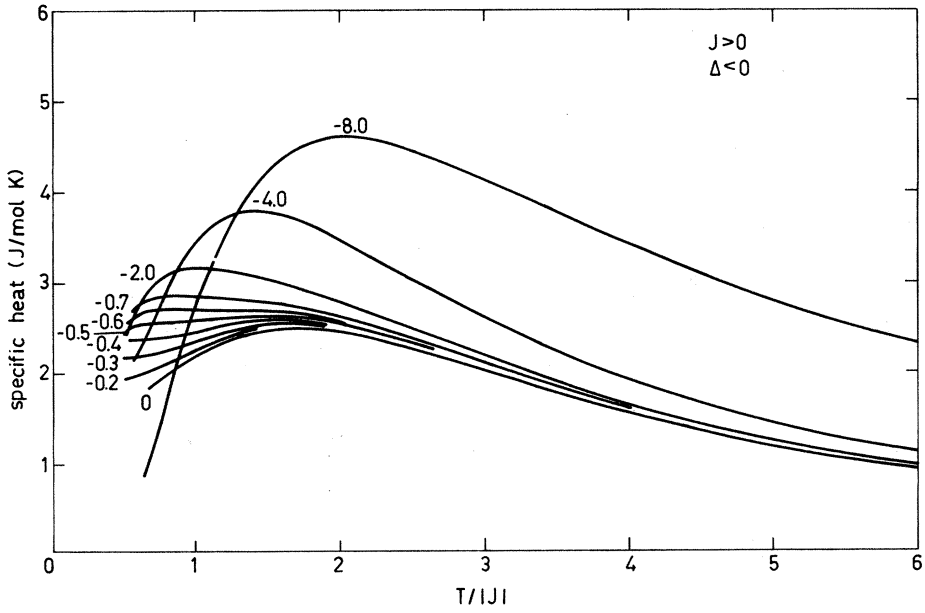

FIG. 2. Estimated specific heat of an infinite chain with ferromagnetic interaction and $\Delta < 0$. The ratio $\Delta/|J|$ is indicated. The curves are drawn only for temperatures where the estimated error is less then 4%. C_∞ is expressed in the experimental units J/mol K.

Apart from C_∞, a least-squares-fitting procedure to the points gives a measure of the linearity and consequently results in an estimate of the uncertainty in C_∞. Independently, we calculated the high-temperature series up to the thirteenth coefficient. The details of this calculation will be presented in a subsequent paper dealing with the general spin Heisenberg chain. The use of Padé approximants make these series useful for $kT > 2J$. Comparison of the results obtained from the outlined extrapolation method with those of the series expansions show no differences.

For rings a relation between C_N and C_∞ may also be derived. In that case however, the number of spins equals the number of bonds and it can be proved that the first term in Eq. (8) vanishes. Consequently, Eq. (10) reduces to $C_N = C_\infty$ for all N. Here too the formula is subject to the condition that all graphs contributing appreciably to the series (3) be present in the ring. Moreover the ring graphs of order $k \geq N$ that occur in $\mathrm{tr}(\mathcal{H}^k)$ for a ring of N spins should *not* contribute. This last condition probably explains the observed fact that extrapolation from rings is useful only for

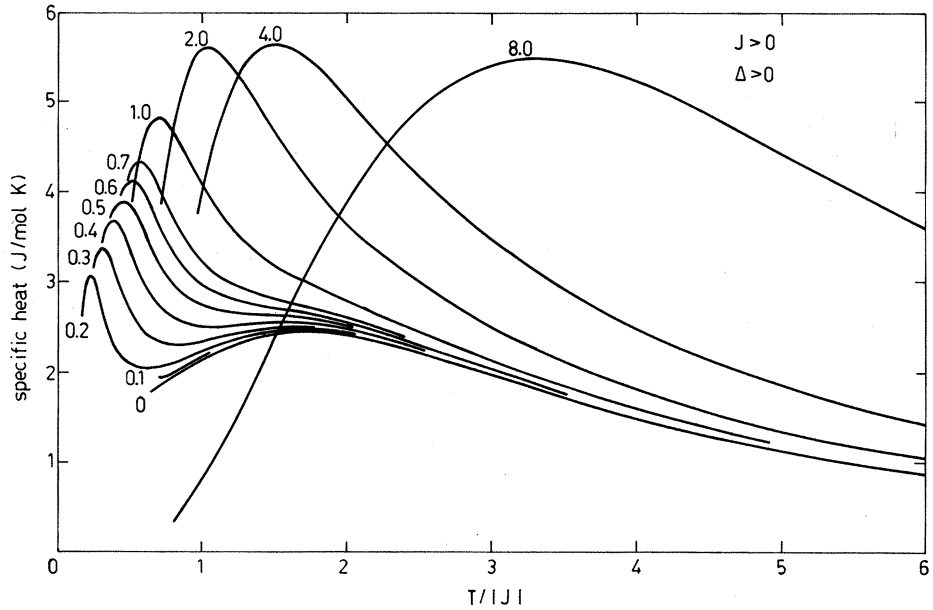

FIG. 3. C_∞ when $J > 0$ and $\Delta > 0$. Otherwise the comment of Fig. 2 applies.

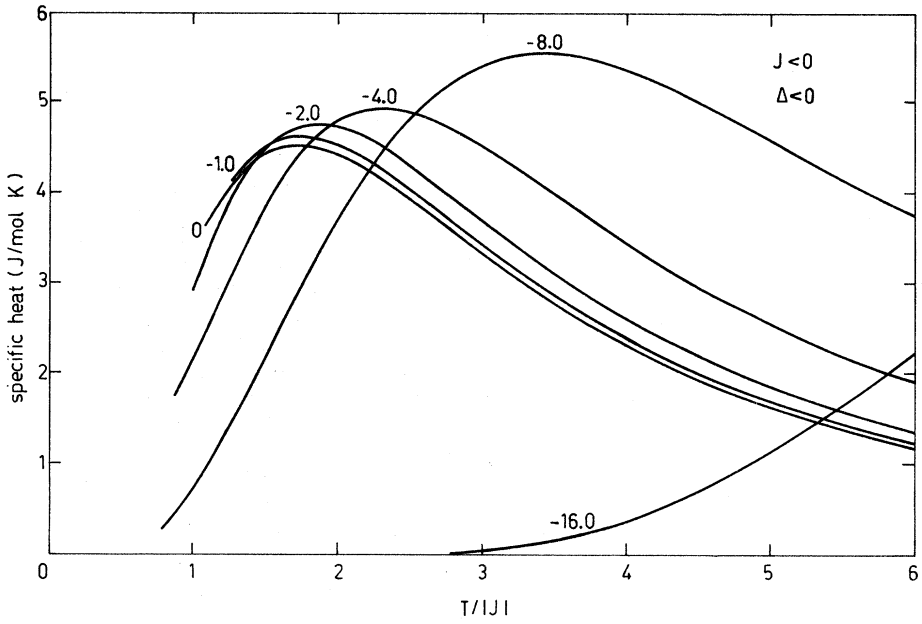

FIG. 4. C_∞ when $J<0$ and $\Delta<0$. The number of different ratios Δ/J is limited for typographical reasons. Otherwise as Fig. 2.

$kT \gg J$.

III. RESULTS

Calculations were performed for all four possible sign combinations of J and Δ, with a variety of values for Δ/J. Estimates of the magnetic specific heat for an infinite chain (C_∞), resulting from the extrapolation procedure sketched in Sec. II, are shown in Fig. 2–5.[24] As we mentioned before, the uncertainty in the extrapolation increases with decreasing temperature. The results displayed in the figures are restricted to the temperature region where the estimated uncertainty is less than 4%. At $kT/J=1$ a typical value for the possible error is 0.5%.

Discussing the results we will distinguish two cases: the ferromagnetic ($J>0$) and the antiferromagnetic chain ($J<0$). The most interesting behavior is observed in the case of ferromagnetic exchange (Figs. 2 and 3). For small positive Δ the curves show a pronounced peak at the low-temperature side. For small negative Δ the peak is less pronounced and reduces to a "shoulder." For moderate values of Δ ($|\Delta/J| \simeq 1$) the tempera-

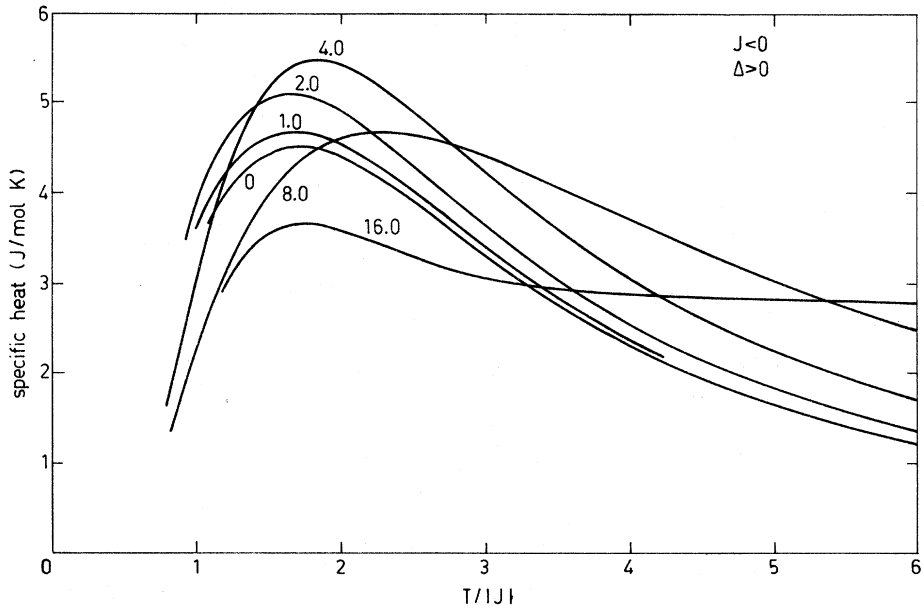

FIG. 5. C_∞ when $J<0$ and $\Delta>0$. For comments see Fig. 4.

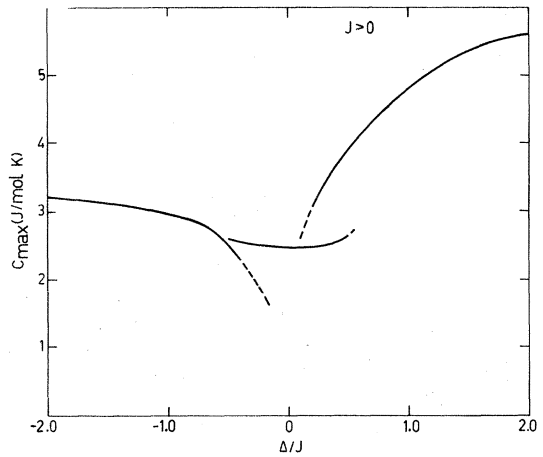

FIG. 6. Maxima and shoulder in C_∞ for ferromagnetic exchange as a function of Δ/J. The behavior of the shoulder near $\Delta=0$ is uncertain and the dashed part of the curve is not reliable.

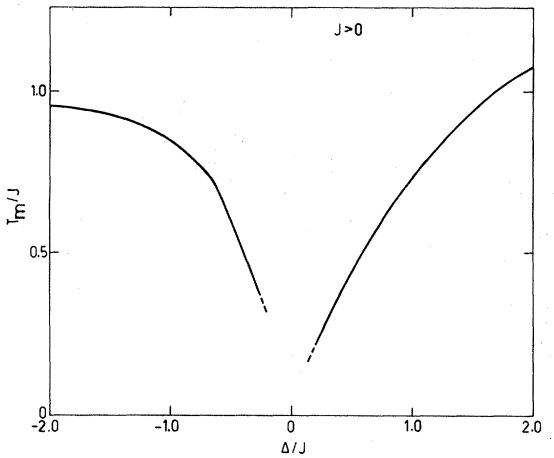

FIG. 7. Temperature for which C_∞ reaches a maximum or displays a shoulder as a function of Δ/J for $J>0$. The region near $\Delta=0$ is an extrapolation.

ture dependence of C_∞ is smooth and for large Δ ($|\Delta/J|>4$) a Schottky-type anomaly appears in the high-temperature tail. For convenience in the use of these results the maxima and "shoulder" in C_∞ are shown in Figs. 6 and 7 as a function of Δ/J. The position of the shoulder is determined by the extreme of $\partial^2 C/\partial T^2$. Figure 6 shows the amplitude of the maxima, while Fig. 7 shows their temperature dependence.

The influence of Δ in the case of an antiferromagnetic exchange is far less specific (Figs. 4 and 5). The specific-heat curves remain smooth and the maximum gradually shifts to higher temperatures with increasing Δ/J. For $|\Delta|<|J|$ the calculated curve hardly depends on Δ. In a comparison with experimental data it will probably be very difficult to determine even the sign of Δ in this case. For large Δ ($|\Delta/J|>4$) a Schottky-type anomaly is also observed.

As could be expected, the contribution of the exchange disappears for large negative Δ, since the ground state is then a singlet.

The rather different effect of increasing Δ on the low-temperature specific heat of a ferromagnetic and an antiferromagnetic chain seems, at first glance, somewhat surprising. A possible physical interpretation of this effect may be found in the different behavior near $T=0$ of a ferromagnet and an antiferromagnet. For $\Delta=0$, the specific heat near $T=0$ can be written as $C \propto T^\alpha$ with $\alpha=\frac{1}{2}$ for $J>0$ and $\alpha=1$ for $J<0$,[12] while for increasing Δ a gradual change to an exponential behavior should be observed, irrespective to the sign of J. From this low-temperature behavior it can be concluded that the entropy gain near $T=0$ is relatively large for a ferromagnet compared with an antiferromagnet when $\Delta=0$, while it vanishes in the case of large $|\Delta|$.

As the total entropy gain between $T=0$ and $T\to\infty$ is fixed one may expect an increase in C at higher temperatures for increasing Δ. In view of the above-mentioned argument this increase will be more significant in the case $J>0$.

ACKNOWLEDGMENTS

The authors would like to thank Professor Dr. P. van der Leeden and Dr. C. H. W. Swüste for their encouraging interest and stimulating discussions.

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