Effect of Change of Spin on the Critical Properties of the Ising and Heisenberg Models

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High-temperature series expansions of the partition functions for the Ising and Heisenberg models are analyzed for various values of the spin s. The fcc lattice is used for which successive coefficients are sufficiently regular for estimates of critical behavior to be made with confidence. It is suggested that the magnetic susceptibility above the Curie temperature is of the form $A(1-T_c/T)^{-4/3}$ for the Heisenberg model for all s, instead of $A'(1-T_c/T)^{-5/4}$ for the Ising model. Critical estimates of energy and entropy show that the magnitude of the "tail" of the specific heat anomaly is insensitive to the value of s, and is about 2.5 times larger for the Heisenberg than for the Ising model. The sharpness of the anomaly at the Curie point increases as s increases, and on passing from the Heisenberg to the Ising model. A brief reference is made to experimental results.

1. INTRODUCTION

ALTHOUGH no exact solutions are available in three dimensions for the Ising model of spin $\frac{1}{2}$, many terms of series expansions for the initial susceptibility above the Curie point have been derived, and the critical behavior is now quite well established as $\chi_0 \simeq A(1-T_c/T)^{-5/4}$.[1–3] The coefficients in such series expansions increase in smoothness as the coordination number of the lattice increases; for the fcc lattice they are particularly smooth, and relatively few terms are needed to provide reliable information regarding the critical properties of the model.

It is of interest to examine how the critical susceptibility of the Ising model varies with change of spin. Although fewer terms of the expansion are available, the regularity of behavior still enables one to draw conclusions with confidence. When we pass to the Heisenberg model the coefficients in the series expansion are less regular for spin $\frac{1}{2}$, but we have found that they become smoother as s increases, and for $s=\infty$ it again seems possible to make reliable estimates near the critical point. From such susceptibility expansions, it is possible to estimate the position of the Curie point with considerable accuracy, and this is important for the assessment of the behavior of other thermodynamic quantities for which the series expansions are not so smooth.

The critical values of energy and entropy supply us with very useful information on the nature of the specific heat anomaly, and the relative proportions which lie above and below the critical point. Finally, the specific heat expansion at high temperatures tells us of the shape of this part of specific heat curve. Even if we are unable to deduce the precise form of singularity we can still determine how its shape is affected by change of spin or model, e.g., whether its steepness is increased or decreased by an increase in spin.

For the Ising model of spin $\frac{1}{2}$ it has been generally established that dimensionality is the primary factor in determining critical behavior, and lattice structure is of secondary importance.[1] All singularities seem to have the same character for lattices of the same dimension. We might reasonably expect a similar property to hold generally for different spins and for the Heisenberg model, and hence any results which we can establish for a particular lattice (the fcc for convenience) are likely to be characteristic of all three-dimensional lattices.

[1] C. Domb, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960), Vol 9, pp. 149, 245.
[2] C. Domb and M. F. Sykes, J. Math. Phys. 2, 63 (1961).
[3] G. A. Baker, Phys. Rev. 124, 768 (1961).

2. HIGH-TEMPERATURE EXPANSIONS

For the Ising model of spin s the Hamiltonian may be put in the form

$$\mathcal{H}^I = -\frac{J}{s^2}\sum_{i,j} s_{zi}s_{zj} - \frac{mH}{s}\sum_i s_{zi}. \tag{1}$$

Here s_{zi}, the z components of spin, can take integral values $-s$, $-(s-1)$, $\cdots$, $(s-1)$, s and $\pm J$ are the maximum and minimum energies of a pair of interacting spins; the maximum magnetic moment of a spin is m; the sum i, j is taken over all nearest neighbor pairs in the lattice, and the sum i is taken over all spins in the lattice. The atoms in the lattice are connected cyclically in the usual manner to avoid boundary effects. This choice of interaction parameters ensures that for given J and m the maximum internal energy and saturation magnetization remain constant as s varies, and, hence, a direct comparison is possible of the properties of the model for different values of s. For the Heisenberg model $s_{zi}s_{zj}$ must be replaced by $\mathbf{s}_i\mathbf{s}_j$ $(=s_{xi}s_{xj}+s_{yi}s_{yj}+s_{zi}s_{zj})$, where $\mathbf{s}$ denotes the vector spin operator.

The partition function is given by

$$Z_N(\beta,H) = \langle\exp(\beta\mathcal{H})\rangle = 1+\beta\langle\mathcal{H}\rangle + \beta^2\langle\mathcal{H}^2\rangle/2! + \cdots \beta^r\langle\mathcal{H}^r\rangle/r!, \tag{2}$$

where $\langle\ \rangle$ denotes traces, $\beta=1/kT$, and the rth term in the expansion will be a polynomial of order r in N. This is the analog of a moment expansion in statistics. We should expect on physical grounds that for sufficiently large N,

$$Z_N(\beta,H)\sim[Z(\beta,H)]^N, \tag{3}$$

where $Z(\beta,H)$ does not depend on N. If formally we take the logarithm of (3) we obtain the analog of a cumulant expansion

$$\ln\langle\exp(\beta\mathcal{H})\rangle=\beta\langle\mathcal{H}\rangle+(\beta^2/2!)[\langle\mathcal{H}^2\rangle-\langle\mathcal{H}\rangle^2] \\ +(\beta^3/3!)[\langle\mathcal{H}^3\rangle-3\langle\mathcal{H}^2\rangle\langle\mathcal{H}\rangle+2\langle\mathcal{H}\rangle^3]+\cdots, \tag{4}$$

and each term is now of order N. Thus, by comparison with (3), we are furnished with an expansion in powers of β of $\ln Z(\beta,H)$; an alternative formal method of obtaining the rth term in (4) is to pick out the coefficient of N in the corresponding term in (2).

The contributions to $\langle\mathcal{H}^r\rangle$ can be divided into various groups corresponding to different types of linear graph. Two basic calculations are then required: (a) The number of independent graphs of a particular type which can exist on a given lattice, and (b) the mean value of the spin operators in (1) for the particular graph.

These calculations are the limiting factor in the evaluation of higher-order terms in the expansions (2) and (4) and precise details have been described elsewhere. For the Ising model, (b) is a straightforward calculation for any graph, and (a) limits the extent of the expansions. When $s=\frac{1}{2}$, the product $(s_{z1}s_{z2})$ can take only two values, and by a suitable transformation all graphs with multiple bonds can be eliminated. For this reason, several more terms can be calculated than for general spin, s. For the Heisenberg model, (b) involves the calculation of averages of noncommuting operators and is probably a greater limitation than (a).

2. MAGNETIC SUSCEPTIBILITY ABOVE THE CURIE POINT

For the Ising model of spin $\frac{1}{2}$, nine terms are available of the reduced susceptibility expansion for the fcc lattice, and their detailed analysis has been undertaken elsewhere.[2] For general spin s, six terms have been calculated,[4] but since they have not been available in a particularly convenient form, we have retabulated coefficients $h_r(s)$ $(r=1$ to $6)$ in Appendix I, where

$$\frac{3skT\chi_0}{N(s+1)m^2}=\sum_{r=0}^{\infty}h_r(s)K^r/s^{2r}, \tag{5}$$

where $K=J/kT$ and $\chi_0=$ magnetic susceptibility. It will be noted that with the form of normalization adopted in (1) the coefficient of K^r remains finite as $s\to\infty$.

Having established with some confidence the behavior of the terms of the expansion for $s=\frac{1}{2}$, it seemed convenient to compare the behavior of the coefficients for general s with those for $s=\frac{1}{2}$, and, hence, determine the form of the susceptibility for general s. If only two terms of the expansion are taken into account, the Curie temperature is given by

$$kT_c=qJ(s+1)/3s, \tag{6}$$

where $q=$ coordination number of lattice. This naturally suggests examining the quantity,

$$u_n(s)=\frac{3s}{s+1}\frac{h_n(s)}{s^2h_{n-1}(s)}=\frac{3h_n}{Xh_{n-1}},\quad X=s(s+1), \tag{7}$$

for a given s, and finding its limiting value for large n. In a previous paper[4] we analyzed the behavior of

$$R_n(s)=u_n(s)/u_n(\tfrac{1}{2}), \tag{8}$$

and showed that for $s=1$ and $s=\infty$ successive increments are approximately in geometric progression, tending rapidly to limiting values 1.0424 and 1.0709, respectively. We may thus write, for example,

$$R_n(1)\simeq1.0424+\delta^n,\quad(\delta<1) \tag{9}$$

and since we have established the behavior,

$$u_n(\tfrac{1}{2})\sim u_c(1+\tfrac{1}{4}n), \tag{10}$$

we readily find that

$$u_n(1)\sim1.0424u_c(1+\tfrac{1}{4}n). \tag{11}$$

Hence, we may deduce that change in s does not affect the critical behavior of the high-temperature susceptibility, which remains of the form $A(1-T_c/T)^{-5/4}$. The actual change in the susceptibility curve arising from change of s is quite small and is comparable with the change due to difference in crystal structure (in three dimensions).

For the Heisenberg model of spin $\frac{1}{2}$ the terms are less regular, and our previous analysis[4] was less conclusive. Calculations were subsequently made by Rushbrooke and Wood[5] for general s; these can again be cast into the form (5), and the coefficients $h_r(s)$ $(r=1$ to $6)$ are tabulated in Appendix II for the fcc lattice. We have recently examined the behavior of the coefficients of K^r as s increases, and we find that they increase steadily in smoothness. When $s\to\infty$ we feel that these coefficients are sufficiently regular for a refined analysis to be undertaken, with which we now proceed.

In the limit $s\to\infty$ Eq. (5) becomes

$$3kT\chi_0/Nm^2=1+4K+14.666667K^2 \\ +51.733333K^3+178.459259K^4 \\ +606.745397K^5+20\,942.10041K^6+\cdots. \tag{10'}$$

Following the method used previously,[2] we attempt to fit the nth coefficient, a_n, in the series (10′) to an asymptotic formula

$$a_n\sim An^gK_c^{-n}, \tag{11'}$$

for which the formula

$$\delta_n=a_n/a_{n-1}\simeq(1/K_c)(1+g/n) \tag{12}$$

[4] C. Domb and M. F. Sykes, Proc. Roy. Soc. (London) **A240**, 214 (1957).

[5] G. S. Rushbrooke and P. J. Wood, Mol. Phys. **1**, 257 (1958).

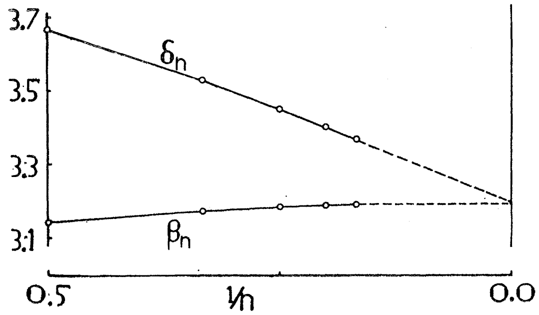

FIG. 1. Heisenberg model $s=\infty$, susceptibility expansion for the fcc lattice. δ_n the ratio of successive coefficients, a_n/a_{n-1}, becomes linear as a function of $1/n$ with slope $\simeq 1/3$. $\beta_n = n\delta_n/(n+1/3)$ approaches the axis horizontally.

is valid. In Fig. 1 we have plotted δ_n against $1/n$; it will be seen that the relationship is very nearly linear, showing that (12) rapidly becomes a reasonable approximation. Each pair of successive values of δ_n yields estimates of $1/K_c$ and g, and these are reproduced in Table I. Successive estimates of both quantities are monotonic, and those of g seem to be approaching a value approximately equal to $\frac{1}{3}$.

Again following our previous procedure, we tentatively assume the limit $\frac{1}{3}$, and calculate

$$\beta_n = n\delta_n/(n+g). \tag{13}$$

If g is equal to $\frac{1}{3}$, β_n as a function of $1/n$ will approach the limit $1/K_c$ horizontally. The β_n are given in Table II, and plotted against $1/n$ in Fig. 1. We feel that the conjecture $g=\frac{1}{3}$ is reasonably substantiated, so that the critical behavior of the susceptibility for this model is, therefore,

$$\chi_0 \simeq B(1-T_c/T)^{-4/3}. \tag{14}$$

Our estimate for the critical value, $1/K_c$, is 3.1902, and we feel, on referring to Tables I and II, that the error should not exceed a few units in the final place.

We now investigate the Heisenberg model for general s by a method similar to the Ising model, but using $s=\infty$ as our reference standard. Defining, by analogy with (8),

$$T_n(s) = u_n(\infty)/u_n(s), \tag{15}$$

we find a somewhat larger deviation from unity as s varies from ∞ to $\frac{1}{2}$; but again successive increments seem to be approximately in geometrical progression, so that the asymptotic behavior (14) should be valid for general spin s. There is thus only a small difference

TABLE I. Approximations to $1/K_c$ and g.

Values of n	Estimates of $1/K_c$	Estimates of g
2, 3	3.2485	0.2575
3, 4	3.2166	0.2898
4, 5	3.2012	0.3104
5, 6	3.1944	0.3216

TABLE II. Approximation to $1/K_c$ by β_n.

n	β_n
2	3.1429
3	3.1745
4	3.1842
5	3.1874
6	3.1885

between the critical behavior of the high-temperature susceptibility for the Ising and Heisenberg models.

Our estimates of the limiting value of $T_n(s)$ as $n\rightarrow\infty$ are 1.175 for $s=\frac{1}{2}$, and 1.068 for $s=1$. Hence, our final estimates of Curie temperatures for Ising and Heisenberg models are given as follows

$$\begin{aligned}(kT_c/qJ)3s/(s+1) &= 0.816,\quad 0.851,\quad 0.874,\quad \text{(Ising)};\\ &= 0.679,\quad 0.747,\quad 0.798,\quad \text{(Heisenberg)}; \end{aligned}\tag{16}$$

for $s=\frac{1}{2}$, 1, ∞, respectively, in each case. The Heisenberg estimate for $s=\frac{1}{2}$ is a few percent lower than the value given by us previously,[4] and our present estimates are consistently lower than those of Rushbrooke and Wood[5]; but we think that the present derivation is more reliable than those undertaken previously and is sufficiently accurate to permit a detailed analysis and extrapolation of the series for energy and free energy.

4. ENERGY AND ENTROPY

The zero-field partition function for both Ising and Heisenberg models can conveniently be written in the form

$$\ln Z_N = N\ln(2s+1) + \frac{Nq}{2}\sum_{r=2}^{\infty} c_r(s)K^r/s^{2r}r!. \tag{17}$$

The internal energy is then given by

$$E_N = -\frac{NqJ}{2}\sum_{r=2}^{\infty} c_r(s)K^{r-1}/s^{2r}(r-1)!. \tag{18}$$

For the Ising model $c_r(s)$ have been calculated for values up to $r=8$, and are tabulated for the fcc lattice in Appendix I (these have not been published previously). For the Heisenberg model the calculations of Rushbrooke and Wood enable $c_r(s)$ to be determined for values up to $r=7$, and these are tabulated in Appendix II. From $\ln Z_N$ and E_N the entropy can readily be found.

The energy and entropy represent integrals of c_v, the specific heat, and c_v/T, respectively. Hence, they provide information about the area under the specific heat curve, and, in particular, by studying their critical values, we can learn of the magnitude of the "tail" of the specific heat anomaly above the Curie temperature. For more detailed knowledge of the shape of the specific heat curve near the Curie point we must study the mathematical behavior of the specific heat itself.

In order to compare the specific heat curves for the various models, it is convenient to take T_c as unit of temperature, and consider c_v as a function of $t\ (=T/T_c)$. Then

$$S_c=\int_0^1 \frac{c_v}{t}dt,\qquad S_\infty-S_c=\int_1^\infty \frac{c_v}{t}dt, \tag{19}$$

so that the values of S_c and $S_\infty-S_c$ enable us to compare the magnitude of the specific heat curves below and above the Curie temperature. The sum of the two terms, S_∞, is known for any model and tells us the total magnitude of the specific heat anomaly. Critical values of the entropy are particularly useful for comparison with experiment since they are independent of the interaction energy.

Similarly, for the internal energy it is useful to study

$$(E_c-E_0)/kT_c=\frac{1}{k}\int_0^1 C_v dt,\qquad (E_\infty-E_c)/kT_c=\frac{1}{k}\int_1^\infty C_v dt \tag{20}$$

These values represent directly the areas under the specific heat curve below and above the Curie temperature, and are also independent of the interaction energy.

The total entropy change from $T=0$ to $T=\infty$ for a model of given s is $\ln(2s+1)$. Hence, the area under the curve $c_v(t)/t$ increases steadily but slowly as s increases; as $s\rightarrow\infty$ this area becomes logarithmically infinite. The corresponding area under the $c_v(t)$ curve is given by $-E_0/kT_c$, and from (16) this increases approximaely as $3s/(s+1)$, i.e., by a factor of 3 as s goes from $\frac{1}{2}$ to ∞. We may thus expect that for large s the major change in c_v occurs near $t=0$.

To compare the critical values of E_c/kT_c for different s for the Ising model, we evaluate the coefficients c_v from Appendix I, and use the kT_c estimates of (16) to derive the following series for the high-temperature expansion of $-E/kT_c$:

$$\begin{aligned}-E/kT_c&=0.06257t'(1+0.4085t'+0.2260t'^2\\&\quad+0.1420t'^3+0.09639t'^4+0.06985t'^5\\&\quad+0.05324t'^6+0.04207t'^7+\cdots),\quad s=\tfrac{1}{2};\\&=0.05756t'(1+0.3919t'+0.2627t'^2\\&\quad+0.1763t'^3+0.1254t'^4+0.09375t'^5\\&\quad+0.07272t'^6+\cdots),\quad s=1;\\&=0.05456t'(1+0.3815t'+0.2805t'^2\\&\quad+0.1915t'^3+0.1411t'^4+0.1081t'^5\\&\quad+0.08550t'^6+\cdots),\quad s=\infty,\quad t'=1/t=T_c/T.\end{aligned} \tag{21}$$

The term outside the bracket, which dominates at high temperatures, decreases slowly as s increases; however, when t' approaches unity, the series within the brackets increases as s increases, the net result being a slight increase in $-E_c/kT_c$ as s increases from $\frac{1}{2}$ to ∞. The series can readily be extrapolated at $t'=1$ by methods described previously,[6] and similar treatment can be given to the corresponding series for $\ln Z_N$.

Final estimates for critical values are as follows:

$$\begin{aligned}(E_\infty-E_c)/kT_c&=0.150,\quad 0.160,\quad 0.175;\\(S_\infty-S_c)/k&=0.102,\quad 0.116,\quad 0.131;\end{aligned} \tag{22}$$

for $s=\frac{1}{2}$, 1, ∞, respectively, in each case. Although these are not as accurate as the estimates of the Curie temperature, the errors should not exceed a few percent. Hence, we see that the "tail" of the specific heat curve remains small for all s; as s increases only a small fraction of the increase in area under the specific heat curve occurs in the region above the Curie temperature, and most of it must be in the region below the Curie temperature.

We can proceed in an exactly analogous manner with the Heisenberg model, the series corresponding to (21) being now

$$\begin{aligned}-E/kT_c&=0.2712t'(1+0.3682t'\\&\quad+0.02511t'^2-0.02157t'^3+0.01702t'^4\\&\quad+0.03131t'^5+\cdots),\quad (s=\tfrac{1}{2})\\&=0.2240t'(1+0.4044t'\\&\quad+0.1711t'^2+0.09041t'^3+0.05619'^4\\&\quad+0.03875t'^5+\cdots),\quad (s=1)\\&=0.1964t'(1+0.4178t'\\&\quad+0.2335t'^2+0.1459t'^3+0.09733t'^4\\&\quad+0.06883t'^5+\cdots),\quad (s=\infty).\end{aligned} \tag{23}$$

The terms are irregular for $s=\frac{1}{2}$ and have not settled down to steady behavior. However the regularity improves rapidly with increasing s, and it seems that the one negative term in the $s=\frac{1}{2}$ series may represent an isolated small number effect. It will be seen by comparison with (21) that the term outside the bracket is three or four times as large for the Heisenberg model. Estimates of critical values based on (23) are not quite as accurate as those for the Ising model, but should still be adequate to delineate the major difference in critical behavior between the two models. We find that

$$\begin{aligned}(E_\infty-E_c)/kT_c&=0.439,\quad 0.449,\quad 0.474;\\(S_\infty-S_c)/k&=0.265,\quad 0.289,\quad 0.322;\end{aligned} \tag{24}$$

for $s=\frac{1}{2}$, 1, ∞, respectively, in each case. Hence, for the Heisenberg model the "tail" of the specific heat curve is appreciably larger.

[6] C. Domb and M. F. Sykes, Proc. Roy. Soc. (London) **A235**, 247 (1956).

5. SPECIFIC HEAT

If we wish to analyze the detailed behavior of the high-temperature specific heat curve and its variation with change of lattice structure, spin, or model, it is useful to examine and compare reduced high temperature expansions for this quantity. We have already investigated the effect of change of dimension on the Ising model of spin $\frac{1}{2}$ by comparing the triangular and fcc lattices.[7] We found that the "tail" was much smaller but steeper for the three dimensional lattice, and there were indications that the asymptotic behavior was approximately represented by

$$c_v/k \sim A(1-T_c/T)^{-1/5}. \tag{25}$$

To demonstrate the effect of change of spin, we now compare corresponding series expansions for the fcc lattice as follows:

$$\begin{aligned} c_v/k &= 0.06257t'^2(1+0.8170t'+0.6779t'^2 \\ &\quad +0.5680t'^3+0.4819t'^4+0.4191t'^5 \\ &\quad +0.3727t'^6+0.3365t'^7+\cdots), \quad (s=\tfrac{1}{2}) \\ &= 0.05756t'^2(1+0.7838t'+0.7882t'^2 \\ &\quad +0.7052t'^3+0.6268t'^4+0.5625t'^5 \\ &\quad +0.5091t'^6+\cdots), \quad (s=1) \\ &= 0.05456t'^2(1+0.7629t'+0.8414t'^2 \\ &\quad +0.7660t'^3+0.7055t'^4+0.6487t'^5 \\ &\quad +0.5985t'^6+\cdots), \quad (s=\infty). \end{aligned} \tag{26}$$

It will be seen that there is an appreciable increase in sharpness as s increases from $\frac{1}{2}$ to ∞ which will increase the index in (25) perhaps to $\frac{1}{4}$ for $s=1$ and $\frac{1}{3}$ for $s=\infty$.

The corresponding series expansions for the Heisenberg model are

$$\begin{aligned} -c_v/k &= 0.2712t'^2(1+0.7364t'+0.07533t'^2-0.08629t'^3 \\ &\quad +0.08511t'^4+0.18792t'^5+\cdots), \quad (s=\tfrac{1}{2}) \\ &= 0.2240t'^2(1+0.8088t'+0.5133t'^2+0.3616t'^3 \\ &\quad +0.2810t'^4+0.2325t'^5+\cdots), \quad (s=1) \\ &= 0.1964t'^2(1+0.8357t'+0.7006t'^2+0.5836t'^3 \\ &\quad +0.4866t'^4+0.4130t'^5+\cdots), \quad (s=\infty). \end{aligned} \tag{27}$$

The tail is much larger than for the Ising model, but the sharpness is decreased. The series in parenthesis for $s=\infty$ is comparable with the corresponding Ising series, (26), for $s=\frac{1}{2}$. For the Heisenberg model of spin $\frac{1}{2}$ the terms are not yet smooth enough for analysis, but from the general trend established, the specific heat will be less steep than (25) and may be logarithmically infinite.

6. CONCLUSIONS

We have thus suggested that the magnetic susceptibility above the Curie temperature is only slightly dependent on the magnitude of the spin or on the type of model. The entropy change above the Curie temperature is little dependent on spin magnitude, but significantly dependent on the model, a variation of a factor of about 2.5 occurring in the change from Ising to Heisenberg interaction. The detailed shape of the specific heat curve is more sensitive to the magnitude of spin. We consider that the errors in our estimates of critical values of energy and entropy may be a few percent, but they should not seriously affect our conclusions.

Previous theoretical work[4,6] has shown that dimensionality rather than lattice structure is the major factor in the determination of cooperative behavior. Thus, although our calculations have been made only for the fcc lattice, we think that the conclusions apply to all three dimensional structures.

The entropy at the critical point is a particularly useful quantity for comparison with experiment, since it does not depend on the magnitude of the interaction. In experiments on the antiferromagnetic salts $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$, Robinson and Friedberg[8] found that the values of $(S_\infty - S_c)/k$ were about 0.44 and 0.36, respectively, the former corresponding to $s=1$ and the latter to $s=\frac{1}{2}$. These figures are comparable with the two-dimensional Ising model and Robinson and Friedberg, following a previous analysis by one of us,[9] suggested that the effective coordination number might be rather small for these salts. This would certainly give a contribution in the right direction, but we feel on the basis of our present work that the change from Ising to Heisenberg model is of greater significance. Our results in (24) are still low compared with those observed experimentally, but they apply only to a ferromagnet, since the Heisenberg model is not symmetric in the sign of the interaction for any lattice. A calculation for the Heisenberg model of an antiferromagnet might well yield results in better agreement with experiment.

The experimental measurements by Stout and Catalano[10] of the specific heats of MnF_2, FeF_2, NiF_2, and CoF_2 are also of considerable significance for a comparison between theory and experiment. In analyzing their results these authors were particularly careful to devise a suitable method of subtracting off contributions to the specific heat arising from lattice vibrations. The resulting estimates of the electronic entropy (Tables IV and V of reference 10) can thus be compared directly with theory, and are as follows:

Substance	MnF_2	FeF_2	NiF_2	CoF_2
Spin value	5/2	2	1	1/2
$(S_\infty - S_c)/k$	0.262	0.208	0.321	0.14

It will be seen by comparison with (22) and (24) that the experimental values are intermediate between those predicted for the Ising and Heisenberg models (with the

[7] C. Domb and M. F. Sykes, Phys. Rev. **108**, 1415 (1957).

[8] W. K. Robinson and S. A. Friedberg, Phys. Rev. **117**, 402 (1960).

[9] C. Domb, *Changements de Phases* (Paris, 1952), p. 192.

[10] J. W. Stout and Edward Catalano, J. Chem. Phys. **23**, 2013 (1955).

exception of NiF_2). FeF_2 and CoF_2 are closer to the Ising value, and MnF_2 is closer to the Heisenberg value; NiF_2 is somewhat larger than the Heisenberg value for a ferromagnet, and calculations for an antiferromagnet would again be useful for comparison. The ordering is antiferromagnetic for all of these compounds; it seems that a model using a suitable coupling intermediate between Ising and Heisenberg should be able to predict the detailed character of the specific heat anomaly.

More experimental data of this kind would seem to be very desirable, to provide a searching test of the calculations and the assumptions underlying them.

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APPENDIX I

Zero-Field Energy and Susceptibility Coefficients for the Ising Model (fcc Lattice)

$$c_2(s)=X^2/9,$$
$$c_3(s)=8X^3/27,$$
$$c_4(s)=(X^2/225)(514X^2-116X+1),$$
$$c_5(s)=(2X^3/405)(184X^2-56X+1),$$
$$c_6(s)=(X^2/297\,675)(83\,599\,648X^4-36\,144\,288X^3+4\,664\,376X^2-118\,584X+675),$$
$$c_7(s)=(8X^3/14\,175)(7\,996\,592X^4-4\,275\,072X^3+817\,524X^2-35\,076X+435),$$
$$c_8(s)=(X^2/212\,625)(18\,568\,249\,616X^6-11\,735\,319\,488X^5+3\,100\,557\,664X^4-343\,347\,552X^3+14\,868\,306X^2-246\,780X+945).$$

$$h_0(s)=1,$$
$$h_1(s)=4X,$$
$$h_2(s)=(2X/5)(38X-1),$$
$$h_3(s)=(2X/75)(2124X^2-136X+1),$$
$$h_4(s)=(X/3150)(656\,648X^3-70\,772X^2+2331X-15),$$
$$h_5(s)=(X/330\,750)+(251\,682\,608X^4-39\,096\,208X^3+2\,440\,236X^2-49\,104X+225),$$
$$h_6(s)=(X/1\,984\,500)(5\,480\,403\,392X^5-1\,125\,263\,472X^4+105\,206\,144X^3-4\,607\,196X^2+79\,290X-315).$$

$$\ln Z(\beta,0)=\ln(2s+1)+6\sum_{r=2} c_r(s)K^r/s^{2r}r!,$$
$$E(\beta,0)=-6J\sum_{r=2} c_r(s)K^{r-1}/s^{2r}(r-1)!,\quad (K=J/kT),$$
$$\frac{c_v}{k}=6\sum_{r=2} c_r(s)K^r/s^{2r}(r-2)!.$$

APPENDIX II

Zero-Field Energy and Susceptibility Coefficients for the Heisenberg Model (fcc Lattice)

$$c_2(s)=X^2/3,$$
$$c_3(s)=(X^2/18)(16X-3),$$
$$c_4(s)=(2X^2/45)(107X^2-78X+3),$$
$$c_5(s)=(X^2/54)(2048X^3-2220X^2+420X-9),$$
$$c_6(s)=(X^2/5670)(2\,288\,704X^4-3\,209\,664X^3+1\,383\,465X^2-111\,420X+1728),$$
$$c_7(s)=(X^2/1620)(8\,854\,016X^5-14\,814\,272X^4+9\,484\,000X^3-1\,886\,331X^2+98\,928X-1242).$$

$$h_0(s)=1,$$
$$h_1(s)=4X,$$
$$h_2(s)=(X/3)(44X-3),$$
$$h_3(s)=(X/45)(2328X^2-382X+12),$$
$$h_4(s)=(X/540)(96\,368X^3-26\,432X^2+2352X-45),$$
$$h_5(s)=(X/14\,175)(8\,600\,616X^4-3\,377\,996X^3+526\,440X^2-30\,060X+432),$$
$$h_6(s)=(X/340\,200)(694\,722\,560X^5-358\,715\,504X^4+81\,267\,018X^3-8\,691\,207X^2+367\,290X-4347).$$

(Thermodynamic formulas as for Ising model.)