$$\Delta_s \to \Delta_s + (2\tau_{sd})^{-1} \quad \text{for } T \gtrsim 0, \tag{27}$$

upon introducing impurities into a two-band superconductor. It is the interband impurity scattering which causes the decrease of the s-band specific heat at low temperatures. The change in Δ_s due to impurity scattering in this temperature region is clearly indicated in Fig. 1. The tunneling experiments by Hafstrom and MacVicar[5] further support the conclusion that there is only one transition temperature associated with an impure two-band superconductor.

Finally, we remark that it is found experimentally that the transition temperature of niobium, T_c, is not sensitive to the amount of impurities present. This can be partly explained by the fact that the lowering of the transition temperature due to the presence of impurity scattering as shown by Eq. (21) is proportional to $(2\tau_{ds})^{-1}$, which is proportional to the small s-band density of states at the Fermi surface, $N_s(0)$. Thus, the illustration of the lowering of the transition temperature T_c from $T_{cd}^{(0)}$ due to the presence of impurities in Fig. 1 should be regarded as qualitative. Further, in the present investigation, we have not taken into account the possible contribution of phonon scattering which might be important for niobium with a transition temperature of the order of 10 °K.

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Heisenberg Ferromagnet with Biquadratic Exchange

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The usual Heisenberg Hamiltonian with bilinear exchange $-2J\,\vec{S}_1\cdot\vec{S}_2$ has been extended to include a biquadratic term $-2\alpha J(\vec{S}_1\cdot\vec{S}_2)^2$, with an adjustable parameter α. A method equivalent to constant coupling was employed to calculate the effect of the biquadratic exchange term on the Curie temperature, magnetization, susceptibility, specific heat, and entropy for lattices with spin-1 atoms. As α goes from 0 to 1, the Curie temperature falls by a factor 2 to 3, while the asymptotic Curie temperature is reduced by the factor 2. The magnetization rises much more rapidly below T_C, and the specific heat has a peak and discontinuity several times higher for $\alpha = 1$. The curvature of the inverse susceptibility increases with α, as does the entropy change taking place above T_C.

I. INTRODUCTION

We will consider the Hamiltonian

$$\mathcal{H} = -2J[\vec{S}_1\cdot\vec{S}_2 + \alpha(\vec{S}_1\cdot\vec{S}_2)^2] - \mu H(S_{1z} + S_{2z}) \,, \tag{1}$$

where J is the Heisenberg exchange integral between neighboring spins S_1 and S_2, with magnetic moments μS_z parallel to an effective (applied plus internal) field H.

For $\alpha = 0$, this is the same as the two-particle Hamiltonian of the form employed by Kasteleijn and van Kranendonk[1] in the constant-coupling approach. For $\alpha = 1$, it is the same as that used by Allan and Betts[2] to investigate the effect of biquadratic exchange on the Curie temperature by means of a high-temperature expansion in powers of reciprocal temperature.

For α small and negative, Joseph[3] also used this Hamiltonian for a high-temperature match of susceptibility data for $KMnF_3$. The need for a small negative biquadratic exchange term was first pointed out by Harris and Owen[4] and Rodbell *et al.*[5] to explain their data on paramagnetic resonance of Mn pairs in MgO. A theoretical basis for the existence of such a term was established by calculations by Anderson[6] and Huang and Orbach[7] of the superexchange interaction in the arrangement Mn-O-Mn.

Another possible origin of biquadratic exchange, mentioned by Allan and Betts, is the fact that the permutation operator for spin 1 is not $P_{ij}=2\vec{S}_i\cdot\vec{S}_j+\frac{1}{2}$ as for spin $\frac{1}{2}$, but instead

$$P_{ij}=\vec{S}_1\cdot\vec{S}_j+(\vec{S}_i\cdot\vec{S}_j)^2-1\ ,$$

a result found in a paper by Schrödinger.[8]

As pointed out by Birgeneau *et al.*,[9] various additions to the usual isotropic exchange interaction—among them, biquadratic and anisotropic terms—can be important for certain rare-earth compounds with incompletely quenched orbital angular momentum.

Finally, the procedure of taking the trace of the density matrix over all but a small number of spins, say, two, to get the two-particle density matrix and its associated Hamiltonian can give rise to a biquadratic term. For spin $\frac{1}{2}$, this imagined tracing process leads to the well-known equivalent Hamiltonian employed by Kasteleijn and van Kranendonk. However, for spin 1, there is no simple identity to reduce a biquadratic term to a bilinear one, and so $(\vec{S}_1\cdot\vec{S}_2)^2$, with an arbitrary coefficient, remains.

We will calculate the Curie temperature as a function of α for all lattices. Also, for $\alpha=0$ and 1, we will calculate the magnetization, susceptibility, energy, specific heat, and entropy change. Only the spin-1 case is thoroughly treated, although spin $\frac{1}{2}$ is briefly considered. Graphical results are given for the bcc lattice.

The procedure to evaluate the internal field in (1) is equivalent to the constant-coupling approximation. As is well known this can be done in several ways.[10] The particular method employed here is to take the partial trace over one spin of a two-particle density matrix and require that this reduce to the one-particle density matrix, i.e., the molecular field theory (MFT). This, it turns out, is equivalent to computing the average magnetizations from these two density matrices and equating them. This will be called the consistency condition.

II. CURIE TEMPERATURE

If the spin quantum number is S_0, the eigenvalues (ev) of the Hamiltonian (1) are given exactly by

$$\text{ev of }(-\beta\mathcal{H})=\tfrac{1}{2}p\bar{S}^2[\alpha\bar{S}^2-(4\alpha\bar{S}_0^2-2)]+\lambda M+\text{const}\ ,\tag{2}$$

where

$$\bar{S}^2=S(S+1),\quad \vec{S}=\vec{S}_1+\vec{S}_2,\quad M=S_{1z}+S_{2z}\ ,$$

$$p=\beta J,\quad \lambda=\beta\mu H\ ,\quad \beta=1/kT\ .$$

The partition function and density matrix are

$$Z=\sum_{S,M}e^{-\beta\mathcal{H}},\quad \rho=e^{-\beta\mathcal{H}}/Z\ ,\tag{3}$$

where M is summed from $-S$ to S and S from 0 to $2S_0$. On the other hand, the MFT Hamiltonian is

$$-\beta\mathcal{H}=\lambda' S_z\ .\tag{4}$$

To find the Curie temperature, let the applied field be zero and the internal field small. If we then require that, for a lattice with coordination number n,

$$\lambda=(n-1)a,\quad \lambda'=na\ ,\tag{5}$$

where a is an internal field due to one neighboring spin, the consistency condition gives the Curie temperatures as the roots of

$$2n\bar{S}_0^2\sum_S(2S+1)e^{p_c f_\alpha(S)/2}=(n-1)\sum_S\bar{S}^2(2S+1)\,e^{p_c f_\alpha(S)/2}\ ,\tag{6}$$

where

$$p_c=J/kT_C\ ,\quad f_\alpha(S)=\bar{S}^2[\alpha\bar{S}^2-(4\alpha\bar{S}_0^2-2)]\ .\tag{7}$$

For $S_0=\frac{1}{2}$, the solution is

$$p_c=\frac{1}{2-\alpha}\ln\left(\frac{n}{n-4}\right)\ .\tag{8}$$

Thus, T_C appears to vary linearly with α, decreasing to one-half its $\alpha=0$ value when $\alpha=1$. Since α is not an experimentally variable parameter, this is not a verifiable conclusion.

For $S_0=1$, the Curie temperature equation becomes

$$10(n-3)e^{(6-6\alpha)p_c}-6(n+1)\,e^{(2-6\alpha)p_c}-4n=0\ .\tag{9}$$

For $\alpha=1$, this has a simple solution:

$$p_c=\frac{1}{4}\ln\left(\frac{n+1}{n-5}\right)\ ,\tag{10}$$

but otherwise must be solved numerically. Graphs of T_C vs α are shown in Fig. 1. Again, there is no possible comparison with experiment, but there are some theoretical data. The point obtained by Allan and Betts[2] for $\alpha=1$ and $n=12$ is $kT_C/J=3.07$[11] and the earlier result[1] for $\alpha=0$ is $kT_C/J=12.0$ for this fcc case. It is seen that there is considerable difference in the results of the two methods (the high-temperature approximation and the constant coupling) although both indicate the same general trend: T_C decreases as α goes from 0 to 1.

III. SPIN-$\frac{1}{2}$ CASE

If the consistency condition is solved for arbitrary values of λ instead of only $\lambda\ll 1$ as in finding T_C, we find the following result for the internal field as a function of temperature:

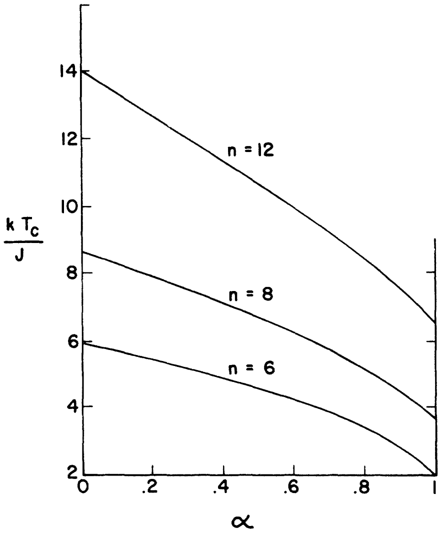

FIG. 1. Dependence of the transition temperature T_C on the strength of the biquadratic exchange α, for the fcc ($n = 12$), bcc ($n = 8$), and simple cubic ($n = 6$) lattices for spin 1.

$$\frac{1 + e^{(\alpha-2)p}}{2} = \frac{\sinh(\frac{1}{2}n - 1)a}{\sinh\frac{1}{2}na} . \tag{11}$$

From the behavior of p_c in (8), we see that the internal field and, hence, all thermodynamic properties will be independent of α if they are plotted as functions of the reduced temperature, $t = T/T_C$. That this must result is seen from the use of the identity for $\vec{\sigma} = 2\vec{S}$:

$$(\vec{\sigma}_1 \cdot \vec{\sigma}_2)^2 = 3 - 2\vec{\sigma}_1 \cdot \vec{\sigma}_2 ,$$

to get

$$2[\vec{S}_1 \cdot \vec{S}_2 + \alpha(\vec{S}_1 \cdot \vec{S}_2)^2] = 2(1 - \tfrac{1}{2}\alpha)(\vec{S}_1 \cdot \vec{S}_2) + \text{const} .$$

Thus, the presence of the biquadratic term serves only to modify the magnitude of the exchange integral. The spin-$\frac{1}{2}$ results for all α will be the same as those of Kasteleijn and van Kranendonk.[1]

IV. SPIN-1 CASE

For the case $S_0 = 1$, detailed examination of the thermodynamic properties has been carried out only for $\alpha = 0$ and $\alpha = 1$. Other values of α present no problem.

$\alpha = 0$

For $\alpha = 0$, the partition function is (including the constant in the eigenvalues of $\mathcal{H}$)

$$Z = [1 + e^{2p}(1 + 2\cosh\lambda) + e^{6p}(1 + 2\cosh\lambda + 2\cosh 2\lambda)]e^{-4p} . \tag{12}$$

The "magnetization" (actually the average value of S_{iz}) is

$$\bar{m} = \frac{1}{2}\,\frac{\partial \ln Z}{\partial \lambda} . \tag{13}$$

The consistency condition, using the MFT result

$$\bar{m} = \frac{2\sinh\lambda'}{1 + 2\cosh\lambda'} , \tag{14}$$

and Eq. (5) give an implicit equation for the reduced effective field a:

$$1 + Ae^{2p} + Be^{6p} = 0 , \tag{15}$$

where

$$A = 1 + 2\cosh(n-1)a - \frac{\sinh(n-1)a(1 + 2\cosh na)}{2\sinh na} ,$$
$$B = A + C , \tag{16}$$
$$C = 2\cosh 2(n-1)a - \frac{\sinh 2(n-1)a(1 + 2\cosh na)}{\sinh na} .$$

The numerical solutions of this equation are then put into the expression for $\bar{m}$ to give the spontaneous magnetization. Since the magnetization per atom is $\mu\bar{m}$, the susceptibility is

$$\chi = \mu\frac{\bar{m}}{H_0} = \frac{(\mu)^2}{kT}\,\frac{\bar{m}}{c} = \frac{(\mu)^2}{2kT}\left(\frac{\partial^2 \ln Z}{\partial\lambda^2}\right)_0\left(\frac{d\lambda}{dc}\right)_0 , \tag{17}$$

where

$$c = \mu H_0/kT , \quad H_0 = \text{applied field}$$

and the derivatives are to be evaluated for zero field. The derivative $d\lambda/dc$ can be found by replacing (5) by

$$\lambda = (n-1)a + c, \quad \lambda' = na + c \tag{5'}$$

and applying the consistency condition, keeping only linear terms in a and c. The result obtained is

$$\left(\frac{d\lambda}{dc}\right)_0 = 1 + (n-1)\left(\frac{da}{dc}\right)_0 = \frac{2 + 6x^2 + 10x^6}{2n + 3(n+1)x^2 - 5(n-3)x^6} ,$$

where $x = e^p$. Finally, the susceptibility (for small fields) is

$$\chi = \frac{C}{T}\,\frac{3(x^2 + 3x^4 + 5x^6 + 20x^8 + 25x^{12})}{(1 + 3x^2 + 5x^6)[2n + 3(n+1)x^2 - 5(n-3)x^6]} , \tag{18}$$

with

$$C = \frac{2\mu^2}{3k} \quad \left(\text{or } \frac{g^2\beta^2 S_0(S_0+1)}{3k} \text{ in usual notation}\right) \cdot \tag{19}$$

For high temperatures, $T \gg T_C$, the susceptibility takes on the Curie-Weiss form

$$\chi = C/(T-\theta)\ , \tag{20}$$

with

$$k\theta/J = \tfrac{4}{3}n = \tfrac{2}{3}nS_0(S_0+1) \tag{21}$$

and

$$\theta/T_C = \tfrac{4}{3}np_c = 1.79,\ 1.36,\ 1.23,\ 1.14\ , \tag{22}$$

respectively, for $n=4$, 6, 8, 12.

The exchange energy per atom is

$$E_{\mathrm{ex}} = -\frac{n}{2}\,\frac{\partial \ln Z}{\partial \beta}\ , \tag{23}$$

or, in units of J,

$$\epsilon = \frac{E_{\mathrm{ex}}}{J} = -\frac{n}{2}\,\frac{\partial \ln Z}{\partial p}\ . \tag{24}$$

Above the Curie temperature, this is

$$\epsilon = -\frac{n(3x^2+15x^6)}{1+3x^2+5x^6} + 2n\ , \tag{25}$$

and below,

$$\epsilon = -\frac{n(\alpha x^2+3\beta x^6)}{1+\alpha x^2+\beta x^6} + 2n\ , \tag{26}$$

where, in this equation only, we have

$$\alpha = 1+2\cosh\lambda\ ,\quad \beta = \alpha + 2\cosh 2\lambda\ , \tag{27}$$

which must be evaluated numerically from the consistency condition. The exchange contribution to the specific heat per atom dE_{ex}/dT can be written as

$$\frac{C}{k} = -p^2\frac{d\epsilon}{dp} = -p^2\left(\frac{\partial\epsilon}{\partial p} + \frac{\partial\epsilon}{\partial\lambda}\,\frac{d\lambda}{dp}\right)\ . \tag{28}$$

Above T_C, the second term is zero and the result can be found directly from (25). Below T_C, the λ-p relationship is known only implicitly from (15). Instead of using this to find $d\lambda/dp$ we have evaluated the specific heat numerically from (26) by the relation

$$\frac{C}{k} = \frac{\Delta\epsilon}{\Delta(1/p)}\ . \tag{29}$$

The result given by (28) can be used to find the discontinuity in the specific heat at T_C. It is found to be

$$\frac{\Delta C}{k} = -p_c^2\left(\frac{\partial\epsilon}{\partial\lambda^2}\right)_0\left(\frac{d\lambda^2}{dp}\right)_0 \tag{30}$$

by expanding ϵ and p in powers of λ^2. For $S_0=1$, $\alpha=0$, and $n=8$, we have $\Delta C/k = 1.76$ per atom.

By numerical integration, we can find the entropy change above T_C from

$$\frac{\Delta S}{k} = \int_1^\infty \frac{C}{k}\,\frac{dt}{t} \simeq 0.1316 \quad \text{for } n=8. \tag{31}$$

$\alpha = 1$

The partition function for $\alpha=1$, $S_0=1$ is

$$Z = \left[1+e^{-4p}(1+2\cosh\lambda) + (1+2\cosh\lambda+2\cosh 2\lambda)\right]e^{4p}\ , \tag{32}$$

from which we find

$$\bar{m} = \frac{1}{2}\,\frac{\partial \ln Z}{\partial\lambda} = \frac{(1+e^{-4p})\sinh\lambda + 2\sinh 2\lambda}{2(1+\cosh\lambda+\cosh 2\lambda)+e^{-4p}(1+2\cosh\lambda)}\ . \tag{33}$$

The MFT result is given by (14). Using (5), the consistency condition gives an explicit expression for $p(\alpha)$:

$$\frac{1+e^{-4p}}{2}$$

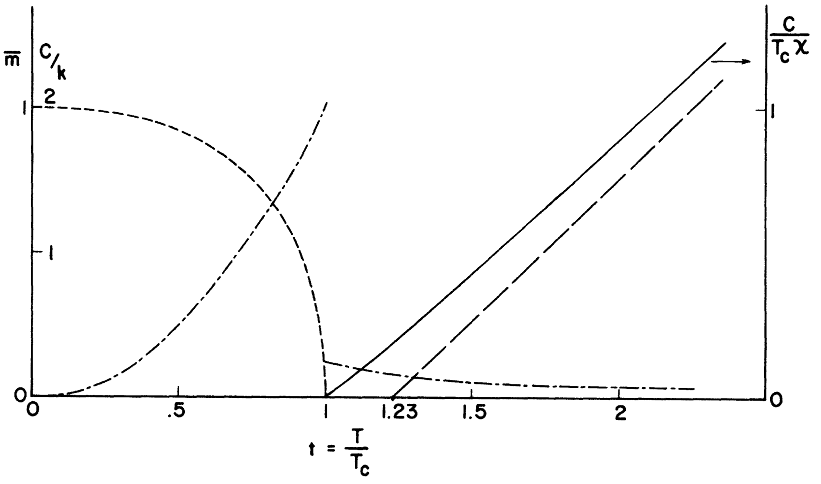

FIG. 2. Thermodynamic properties of the bcc lattice with spin 1 and $\alpha = 0$. $\bar{m}$ (dashed curve) is the average value of S_z or the reduced magnetization, C (dash-dot curve) is the magnetic contribution to the heat capacity per atom and χ (solid line) is the susceptibility (the C there is the Curie constant). The dashed straight line is the Curie-Weiss limit of χ^{-1}.

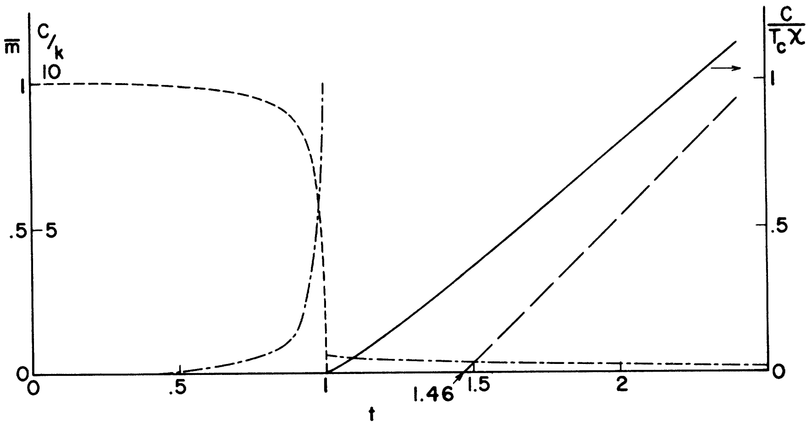

FIG. 3. Same as Fig. 2, but for $\alpha = 1$. Note the change in scale for the heat capacity.

$$= \frac{2\sinh(n-2)a + \sinh 2(n-1)a - \sinh na}{\sinh(2n-1)a + 3\sinh a + 2\sinh na - \sinh(n-1)a}, \tag{34}$$

with which we evaluate $\overline{m}$ numerically.

The susceptibility is considerably simpler than for $\alpha = 0$:

$$\chi = \frac{C}{T}\ \frac{e^{-4p} + 5}{(n+1)e^{-4p} - (n-5)}, \tag{35}$$

with C given by (19). The limiting Curie-Weiss form (20) gives

$$\frac{k\theta}{J} = \frac{2n}{3} = \frac{nS_0(S_0+1)}{3} \tag{36}$$

or one-half the value in (21), whereas the ratios

$$\frac{\theta}{T_C} = \frac{2}{3}np_c = 1.95,\ 1.46,\ 1.24, \tag{37}$$

respectively, for $n = 6$, 8, 12, are considerably larger than for $\alpha = 0$ because of the decrease in T_C.

The reduced exchange energy per atom is found to be

$$\epsilon = -2n(1 + \tfrac{1}{2}e^{-4p})^{-1} \tag{38}$$

above T_C and

$$\epsilon = -2n\left(1 + e^{-4p}\frac{1 + 2\cosh\lambda}{2(1 + \cosh\lambda + \cosh 2\lambda)}\right)^{-1} \tag{39}$$

below. The specific heat above T_C is then

$$C/k = 4np^2 e^{-4p}(1 + \tfrac{1}{2}e^{-4p})^{-2}, \tag{40}$$

and just above T_C this becomes

$$\left(\frac{C}{k}\right)_{T_C^+} = \frac{n}{9}\ \frac{(n-5)(n+1)}{(n-1)^2}\left(\ln\frac{n+1}{n-5}\right)^2. \tag{41}$$

Below T_C, the specific heat per atom is found numerically from (39). The discontinuity at T_C can be found explicitly by using (30):

$$\frac{\Delta C}{k} = \frac{1}{18}\ \frac{n(n+1)^2(n-5)^2}{(n-1)(n-2)}\left(\ln\frac{n+1}{n-5}\right)^2, \tag{42}$$

which, for $n = 8$, has the value 9.31.

The total entropy change above T_C can be found

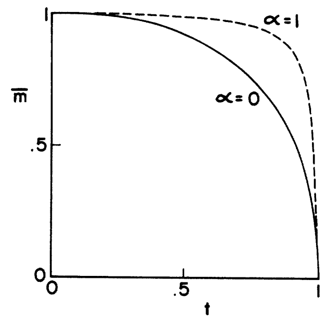

FIG. 4. Results for the reduced magnetization, $\overline{m}$ vs reduced temperature t compared for $\alpha = 0$ and $\alpha = 1$.

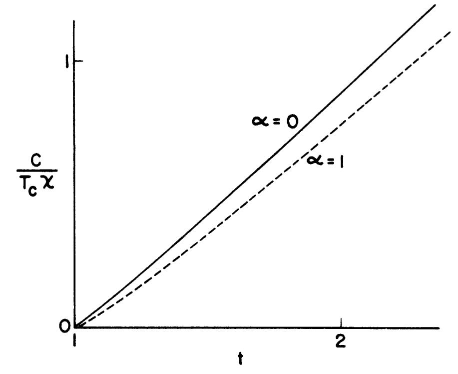

FIG. 5. Comparison of reciprocal susceptibilities for $\alpha = 0$ and 1.

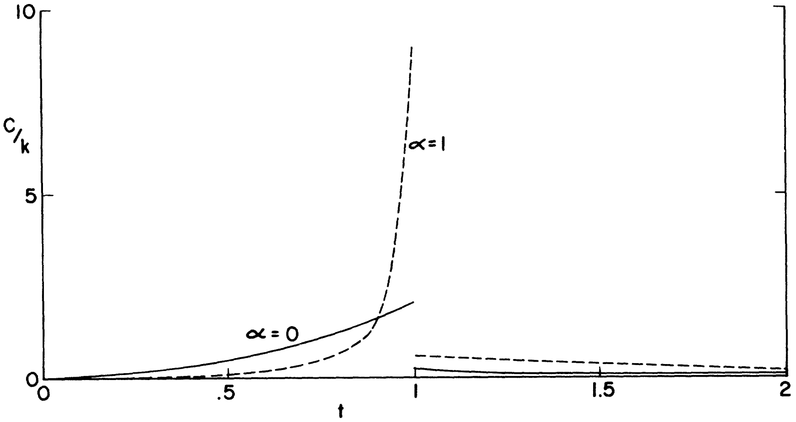

FIG. 6. Comparison of the specific heat per atom for $\alpha = 0$ and 1 on the same scale.

from (40):

$$\frac{\Delta S}{k} = \int_1^\infty \left(\frac{C}{k}\right)\frac{dt}{t} = n\int_1^{u_c} \frac{\ln u \, du}{(1+2u)^2} , \qquad (43)$$

where $u = e^{4p}$. For $n = 8$ the result is

$\Delta S/k = 0.3775$ per atom,

considerably higher than for $\alpha = 0$. For the whole temperature range, $T = 0$ to ∞, the result is

$\Delta S/k = \ln(2S_0 + 1) = 1.099.$

V. RESULTS

The behavior of T_C vs α, shown in Fig. 1, has already been discussed. Figure 2 shows the results of our calculations for $\alpha = 0$, $S_0 = 1$, and $n = 8$. Included are the values of $\bar{m}$ below T_C ($\bar{m}$ is also the reduced spontaneous magnetization, $M/M_{\max}$), the reduced reciprocal paramagnetic susceptibility, $C/T_C\chi$, where C is the Curie constant (19) along with its high-temperature asymptote (20), and the exchange specific heat per atom in units of Boltzmann's constant, C/k, above and below T_C, all as functions of the reduced temperature, $t = T/T_C$. Figure 3 shows the same quantities as in Fig. 2, calculated for $\alpha = 1$. The rather considerable differences brought about by this change in α are made more obvious by plotting the corresponding curves together, as in Fig. 4 for $\bar{m}$, Fig. 5 for $1/\chi$, and Fig. 6 for C.

The magnetization in Fig. 4 is seen to rise much more rapidly just below T_C for $\alpha = 1$ and to approach absolute zero along a more nearly horizontal line. The net effect is that the $\alpha = 0$ curve is the usual almost circular arc while the $\alpha = 1$ curve is closer to the two sides of a square formed by the horizontal and vertical lines for $\bar{m} = 1$ and $t = 1$, although not so extremely as for an Ising model.

The susceptibility curves show an increased curvature (for $1/\chi$) for the $\alpha = 1$ case and a higher intercept on the t axis for the asymptotes (see Figs. 2 and 3). While the asymptotic Curie temperature is lowered by one-half in this case, the Curie temperature falls faster as α goes from 0 to 1, hence the higher intercept on the t axis.

The specific heat is considerably lower well below T_C for $\alpha = 1$ and considerably higher as T_C is approached and has a discontinuity at T_C some five times greater than for $\alpha = 0$ (9.31 to 1.76). This behavior is related to that of $\bar{m}$ through the $(d\lambda/dp)$ factor in the specific heat [Eq. (28)].

The entropy change of the spin system is therefore brought about more slowly for $\alpha = 1$ as temperature is raised from absolute zero than for $\alpha = 0$, but shows a more rapid rise as T_C is approached. The qualitative behavior is shown in Fig. 7. The entropy changes from 0 to T_C are approximately 88% and 66% of the total for $\alpha = 0$ and 1, respectively, for the bcc. Allan and Betts[2] found the corresponding fractions for the fcc to 73% and 67%.

The results show that by including a positive biquadratic exchange interaction we are able to obtain a considerably steeper magnetization curve, as is experimentally observed, and that the curvature of the inverse susceptibility curve can be adjusted as can the intercept by adjusting the strength of the biquadratic term. The theory allows values

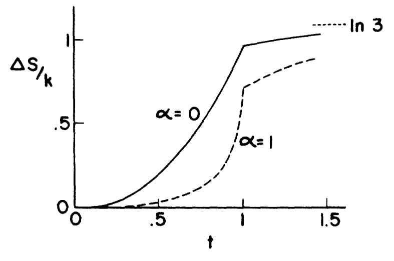

FIG. 7. Net change in the entropies, $\Delta S = S(t) - S(0)$, for $\alpha = 0$ and 1.

of θ/T_C between 1.23 and 1.46 for α going from 0 to 1. The ferromagnetic elements have values in the range 1.03–1.06 but many ferromagnetic compounds ($CrCl_3$, $CrBr_3$, MnP, FeP, Fe_2P, Fe_3P, and CoS_2) have ratios from 1.06 to 1.84.[12]

Additional freedom is also given to the value of the specific-heat discontinuity as α is varied. Experimental values of ΔC for the ferromagnetic elements go from about 2 to 7 cal/deg mole. Our derived values for the spin-1 bcc lattice for $\alpha = 0$ and 1 are given by Eqs. (30) and (42) and have the approximate values 0.9 and 4.7 cal/deg mole (k erg atom $\approx$ 2 cal/mole). Again, the presence of this extra parameter α allows the possibility of approximate agreement with experiment. Finally, the persistence of spin ordering as temperature is raised is considerably greater for $\alpha = 1$ than for $\alpha = 0$, as is seen from the specific-heat and entropy curves.

We are not interested in exact numerical comparisons since the theory presented here should be applicable only to spin-1 isotropic nonconducting ferromagnets. Rather, we are interested in determining what quantities will vary, roughly by how much, and in which direction when biquadratic exchange is included.

ACKNOWLEDGMENTS

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[11] A factor of 2 difference in their definition of J makes the comparable number 6.14 against the value 6.46 from (10).

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