High-Temperature Susceptibility of Heisenberg Ferrimagnets

PETER J. WOJTOWICZ
RCA Laboratories, Princeton, New Jersey
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This paper presents the results of the derivation of exact power-series expansions of the high-temperature susceptibility of Heisenberg ferrimagnets having a general two-sublattice structure with arbitrary values of the spins on the two sublattices. The calculations employ the extension of the general diagrammatic techniques developed by Rushbrooke and Wood. The calculations have been carried to terms including the fifth power of the intersublattice exchange divided by the temperature. The radii of convergence of a large number of examples of the series have been estimated.

EXACT power-series expansions of the high-temperature susceptibility and heat capacity of magnetic systems with Heisenberg exchange interactions have received the attention of numerous investigators.[1] In the case of nearest-neighbor ferromagnets and antiferromagnets having general structure and arbitrary values of the spin the most extensive calculations of the series expansions have been provided by Rushbrooke, Wood, and Morgan.[2–4] These results have been further generalized by Wojtowicz and Joseph[5–7] to include the contributions from second-neighbor interactions and from first-neighbor biquadratic interactions. Additional extensions of this work to include higher-order terms and more distant neighbor interactions (for spin $\frac{1}{2}$ only) have been given by Domb, Wood, and Dalton.[8–10] Higher-order coefficients for the general ferromagnet with first- and second-neighbor exchange have recently been provided by Pirnie and Wood.[11] The power series for the susceptibility of Heisenberg systems with nonequivalent lattice sites (we shall call such systems *ferrimagnets* independent of whether the dominant interactions are ferromagnetic or antiferromagnetic) have not been as widely studied, however. Preliminary reports on the susceptibility of certain garnet and spinel structures have been given by the present author.[12,13] Results pertaining to general structures have not yet appeared.

In this article we persent the results of the derivation of power-series expansions of the high-temperature susceptibility of Heisenberg ferrimagnets having a general two-sublattice structure with arbitrary values of the spins on the two non-equivalent sublattices. The theory presented here includes only inter-sublattice exchange interactions; the additional contributions which arise from intra-sublattice interactions are given elsewhere.[14] The calculations employ the extension of the general diagrammatic techniques developed by Rushbrooke and Wood[2]; the modifications required to account for the presence of nonequivalent lattice sites are described. The computations have been carried to terms including the fifth power of the exchange divided by the temperature. The radii of convergence of a large number of examples of the series have been estimated.

The physical system of interest is one formula weight of ferrimagnet, $A_aB_bC_cO_\delta$, containing Na A sites with atoms of spin S_A, Nb B sites with atoms of spin S_B, and Nc C sites with non-magnetic atoms. (N is Avagadro's number; A and B sites are defined so that $b \geqslant a$; c is very often zero; O_δ represents the anions.) Each B site has z nearest-neighbor A sites with which it interacts, while each A site interacts with rz nearest-neighbor B sites ($r=b/a \geqslant 1$). Interactions among the A sites and among the B sites are not considered here.[14] The spin Hamiltonian of this system in the presence of an external magnetic field H_z has the form

$$\mathcal{H} = -2J\mathbf{P} - g\mu H_z\mathbf{Q}\,,$$
$$\mathbf{P} = \sum_{ij}\mathbf{S}_i\cdot\mathbf{S}_j\,, \quad \mathbf{Q} = \Sigma_i\mathbf{S}_{iz} + \sum_j\mathbf{S}_{jz}\,, \tag{1}$$

where J is the strength of the A-B (inter-sublattice) exchange interaction, where $\mathbf{P}$ is the sum of Heisenberg exchange operators for all A-B pairs, and where $-g\mu H_z\mathbf{Q}$ is the Zeeman energy operator for the entire system. The index i is summed over A sites, while j is summed over B sites. The operators $\mathbf{P}$ and $\mathbf{Q}$ commute.

The Hamiltonian shown in Eq. (1) is formally identical (but different in detailed structure) to that considered by Rushbrooke and Wood[2] in their derivation of the susceptibility series for ferromagnets with all sites equivalent. The formal statistical mechanics of the present problem is therefore the same as that of the ferromagnetic problem and need not be reproduced here. The essential result is that the zero-field suscep-

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tibility can be formally expanded in a power series in the variable J/kT:

$$\chi=(C_M/T)\{1+\sum_{n=1} A_n(J/kT)^n\}, \tag{2}$$

where T is the temperature, k is Boltzmann's constant, and C_M is the molar Curie constant equal to $(a\tilde{A}+b\tilde{B})\times Ng^2\mu^2/3k$, where $\tilde{A}=S_A(S_A+1)$ and $\tilde{B}=S_B(S_B+1)$. The coefficients in the series are given by

$$A_n=\frac{3\cdot 2^n\Gamma_N\langle \mathbf{P}^n\mathbf{Q}^2\rangle}{Nn!(a\tilde{A}+b\tilde{B})}, \tag{3}$$

where $\langle \mathbf{P}^n\mathbf{Q}^2\rangle$ stands for the normalized trace of the direct-product matrix representation of the operator $\mathbf{P}^n\mathbf{Q}^2$, and where $\Gamma_N\langle \mathbf{P}^n\mathbf{Q}^2\rangle$ means "that part of $\langle \mathbf{P}^n\mathbf{Q}^2\rangle$ which is proportional to N". The first term in Eq. (2) is Curie's law for noninteracting spins, while succeeding terms represent increasing orders of the statistical mechanical perturbation of the exchange on the free-ion paramagnetism.

The labor of calculating the coefficients, Eq. (3), is greatly reduced by the use of a diagram technique extensively developed by Rushbrooke and Wood.[2] Because of the formal similarity of the Hamiltonians in the ferromagnetic and ferrimagnetic problems the mechanics of the diagram method of Rushbrooke and Wood will be much the same here except for certain small differences.

The classification, enumeration and evaluation of the many different contributions contained in a given $\langle \mathbf{P}^n\mathbf{Q}^2\rangle$ are facilitated by the representation of these contributions in terms of diagrams (localized graphs) on the lattice. The pertinent diagrams consist of n lines and two crosses. A line connecting nearest-neighboring sites i and j represents the pair-exchange operator $\mathbf{S}_i\cdot\mathbf{S}_j$, while a cross on site k represents the spin operator $\mathbf{S}_{kz}(k=i$ or $j)$. Diagrams having isolated crosses, double crosses or points connected by only a single line are excluded since they all yield vanishing contributions.[2]

The use of the diagram method involves three separate stages: (a) the finding and cataloging of all the non-trivial diagrams or graphs constructed from n lines and two crosses, (b) counting the number of times that a diagram can occur on a lattice of $N(a+b)$ sites, and (c) evaluation of the traces of the products of the spin operators which correspond to the diagrams. All three stages of the computation are influenced by the fact that the diagrams of the present problem (unlike those of the ferromagnetic case) are characterized by having nonequivalent lattice sites connected by the interaction lines. The points in the various diagrams alternate A site, B site, A site, etc. This has the effect in (a) of essentially doubling the number of diagrams to be considered. For each diagram of a given topological type with lines connecting the points in the order $A, B, A, B, A, \cdots$ a similar figure with its points connected in the order $B, A, B, A, B, \cdots$ will most probably also exist as an independent diagram requiring separate treatments in (b) and (c). Some graphs will, of course, have sufficient symmetry so that no new diagrams are formed upon reversing the order of the lattice points. The alternation of nonequivalent sites in the diagrams does, on the other hand, serve to reduce the total number of graphs somewhat by making it impossible to construct figures containing closed polygons with an odd number of sides. Thus, in these calculations diagrams containing triangles and pentagons do not appear. Stages (b) and (c) proceed in the same manner as in the ferromagnetic problem[2] except that the occurrence factors are now functions of two nearest-neighbor numbers z and rz, while the traces become functions of the two spin values S_A and S_B. The number of nontrivial diagrams which required evaluation in the calculation of the first through fifth coefficients were 1, 3, 7, 12, and 67, respectively.

$A_4=\frac{2}{405}\frac{rz\tilde{A}\tilde{B}}{(\tilde{A}+r\tilde{B})}\cdot$

	$\tilde{A}^2\tilde{B}$	$\tilde{A}\tilde{B}^2$	$\tilde{A}\tilde{B}$	$\tilde{A}^2$	$\tilde{B}^2$	$\tilde{A}$	$\tilde{B}$	i
r^2z^3		40						
rz^3	40							
r^2z^2		-40			-20			
rz^2	-80	-80	-140					
z^2	-40			-20				
rz	40	32	116		36		93	
z	32	40	116	36		93		
q	-40	-40	-40					
1	8	8	-32	-16	-16	-48	-48	-45

FIG. 1. Tabular representation of the coefficient A_4.

The results obtained for the first three coefficients are as follows:

$$A_1=\frac{4rz\tilde{A}\tilde{B}}{3(\tilde{A}+r\tilde{B})}, \tag{4}$$

$$A_2=\frac{4rz\tilde{A}\tilde{B}}{9(\tilde{A}+r\tilde{B})}[(rz-1)\tilde{B}+(z-1)\tilde{A}-\tfrac{3}{2}], \tag{5}$$

$$A_3=\frac{4rz\tilde{A}\tilde{B}}{135(\tilde{A}+r\tilde{B})}\{4\tilde{A}\tilde{B}[5z(rz-r-1)+2]+12+\tilde{A}(9-15z)+\tilde{B}(9-15rz)\}. \tag{6}$$

The coefficients A_4 and A_5 are more complex and are presented in tabular form in Figs. 1 and 2, respectively. The meaning of the tables is straightforward: The numerical coefficients within the table are multiplied by the spin variables above and by the lattice parameters on the left. The sum of all these is then multiplied by the common factor preceding the dot. The quantity q is defined such that $\frac{1}{4}Nbzq$ is the total number of distinct squares which can be constructed on the lattice

$A_5 = \frac{4}{42525}\,\frac{rz\tilde{A}\tilde{B}}{(\tilde{A}+r\tilde{B})}$.

	$\tilde{A}^2\tilde{B}^2$	$\tilde{A}^2\tilde{B}$	$\tilde{A}\tilde{B}^2$	$\tilde{A}\tilde{B}$	$\tilde{A}^2$	$\tilde{B}^2$	$\tilde{A}$	$\tilde{B}$	1
r^2z^4	2800								
r^2z^3	-5600		-3200						
rz^3	-5600	-3200							
r^2z^2	2800		3200			2100			
rz^2	6160	7280	7280	8715					
z^2	2800	3200			2100				
rz	-560	-3080	-3080	-5565		-3150		-4725	
z	-560	-3080	-3080	-5565	-3150		-4725		
1	-800	-40	-40	1272	1320	1320	2376	2376	1728
rzq	-2800		-1400						
zq	-2800	-1400							
q	3360	3080	3080	2940					

FIG. 2. Tabular representation of the coefficient A_5.

with nearest-neighbor A-B bonds; the other quantities have been defined above. The numerical values of the lattice parameters for several structures are presented in Table I.

Considerable care was taken to ensure the reliability of the computed coefficients. At several stages in the calculations the results were checked against those of Rushbrooke and Wood[2] by removing the restriction that the spins and sublattices be nonequivalent. Upon making the reductions, $a=b=\frac{1}{2}$, $r=1$, $S_A=S_B$, the present results go over into those of Ref. 2 exactly (except for the lack of triangle and pentagon terms as described above.)

The reciprocal susceptibility can also be expanded as a power series:

$$\chi^{-1}=(T/C_M)\{1+\sum B_n(J/kT)^n\}, \qquad (7)$$

where the coefficients may be computed from the formula

$$B_n=-\sum_{r=1}^{n} A_r B_{n-r}, \quad B_0=1. \qquad (8)$$

Explicit formulas for the B_n will not be given; they are much more complex in form than the corresponding A_n. When numerical values of the B_n are desired, the most efficient procedure is to compute the values of the A_n first and then use Eq. (8) to obtain the B_n. For the convenience of potential users simplified forms of the coefficients have been computed for several common structures. These formulas are presented in the Appendix.

TABLE I. Numerical values of the lattice parameters for several structures of ferrimagnetic interest.

Structure	Formula[a]	a	b	r	z	q
Spinel	$(A)[B_2]O_4$	1	2	2	6	12
ad Garnet	$\{C_3\}[A_2](B_3)O_{12}$	2	3	1.5	4	2
cd Garnet	$\{A_3\}[C_2](B_3)O_{12}$	3	3	1	6	4
ac Garnet	$\{B_3\}[A_2](C_3)O_{12}$	2	3	1.5	4	2

[a] ( ) = tetrahedral site, [ ] = octhedral site, { } = dodecahedral site; C is nonmagnetic.

TABLE II. Numerical values of constants appearing in Eq. (10) for several ferrimagnetic structures.

Structure	α	β	γ	ϵ
Spinel	0.06	0.22	4.45	0.599
ad, *ac* Garnets	0.01	0.30	2.08	0.537
cd Garnet	0.18	0.18	2.88	0.572

It is well known that the zero-field susceptibility of a ferromagnet tends to infinity as the Curie temperature is approached from above. Utilizing this property, Rushbrooke and Wood[2] illustrated the procedure by which accurate Curie points may be obtained from estimates of the radii of convergence of the appropriate susceptibility series expansions. Such estimates of the Curie points of the three cubic lattices (simple, body-centered and face-centered) with various values of the spin ($S=\frac{1}{2}$ to 3) were then found to fit the following very remarkable formula:

$$(kT_c/J)=0.579(z-1)[S(S+1)-0.12]. \qquad (9)$$

Following this example we have also investigated the radii of convergence of the susceptibility series in the case of the spinels and several garnets for 25 different spin pairs ($S_A=\frac{1}{2}$ to $\frac{5}{2}$ and $S_B=\frac{1}{2}$ to $\frac{5}{2}$). Estimates of the radii of convergence were obtained by plotting $(A_n/A_{n-2})^{1/2}$ against $1/n$ and then extrapolating to $1/n=0$. This particular sequence of terms was found to behave quite regularly and the extrapolations were very smooth, particularly for large spins. In a number of cases additional information obtained from the extrapolation of the sequence of $A_n^{1/n}$ proved helpful. The accuracy of individual radii of convergence is judged to be about 2%. This body of numerical data was then analyzed for its dependence on the spin values. The following formula for the Curie temperature was found to summarize these results to within about 2%.

$$(kT_c/J)=\gamma[S_A(S_A+1)-\alpha]^{1/2}[S_B(S_B+1)-\beta]^{1/2}, \qquad (10)$$

where the numerical values of the factors α, β, and γ are given in Table II for the several structures examined. The values of α, β, and γ listed for the spinel lattice differ somewhat from those reported in Ref. 12 and represent Curie temperatures which are about 2–3% lower than those reported earlier. The current values are to be considered the more reliable; not only was greater care taken in making the extrapolations, but the additional data from the $A_n^{1/n}$ was utilized.

Pursuing the similarity to Eq. (9) further, the factor ϵ defined as $\gamma(z-1)^{-1/2}(rz-1)^{-1/2}$ was also computed for the three structures, and the numerical values obtained are displayed in Table II. We note that ϵ is almost a constant independent of structure, and further than it is very close to the value of the corresponding constant (0.579) in the Rushbrooke-Wood formula Eq. (9).

The dependence of the Curie temperature in nonequivalent-sublattice structures on spin and nearest-neighbor numbers is thus found to be essentially analogous to that of the less complex cubic lattices. The appearance of the square roots, moreover, is not unexpected in as much as the simple molecular field approximation to the Curie point of a ferrimagnetic structure is known to contain the factor $[rz^2S_A(S_A+1)S_B(S_B+1)]^{1/2}$.

APPENDIX

The coefficients for the spinel are

$$A_1=G_s=16\tilde{A}\tilde{B}/(\tilde{A}+2\tilde{B}),$$

$$A_2=G_s(5\tilde{A}+11\tilde{B}-1.5)/3,$$

$$A_3=G_s(1088\tilde{A}\tilde{B}-81\tilde{A}-171\tilde{B}+12)/45,$$

$$A_4=G_s(10280\tilde{A}^2\tilde{B}+23192\tilde{A}\tilde{B}^2-8504\tilde{A}\tilde{B}-520\tilde{A}^2 -2464\tilde{B}^2+510\tilde{A}+1068\tilde{B}-45)/270,$$

$$A_5=G_s(7629760\tilde{A}^2\tilde{B}^2-1258360\tilde{A}^2\tilde{B}-2719960\tilde{A}\tilde{B}^2 +563862\tilde{A}\tilde{B}+58020\tilde{A}^2+265920\tilde{B}^2 -25974\tilde{A}-54324\tilde{B}+1728)/14175.$$

The above forms for A_4 and A_5 correct certain small errors which appeared in these quantities in Ref. 12.

The coefficients for the *cd* garnet are

$$A_1=G_{cd}=8\tilde{A}\tilde{B}/(\tilde{A}+\tilde{B}),$$

$$A_2=G_{cd}[5(\tilde{A}+\tilde{B})-1.5]/3,$$

$$A_3=G_{cd}[128\tilde{A}\tilde{B}-8(\tilde{A}+\tilde{B})+12]/145,$$

$$A_4=G_{cd}[4700(\tilde{A}^2\tilde{B}+\tilde{A}\tilde{B}^2)-3840\tilde{A}\tilde{B} -520(\tilde{A}^2+\tilde{B}^2)+510(\tilde{A}+\tilde{B})-45]/270,$$

$$A_5=G_{cd}[1504480\tilde{A}^2\tilde{B}^2-552200(\tilde{A}^2\tilde{B}+\tilde{A}\tilde{B}^2) +259992\tilde{A}\tilde{B}+58020(\tilde{A}^2+\tilde{B}^2) -25974(\tilde{A}+\tilde{B})+1728]/14175.$$

The coefficients for the *ac* and *ad* garnets are

$$A_1=G_a=8\tilde{A}\tilde{B}/(\tilde{A}+1.5\tilde{B}),$$

$$A_2=G_a(3\tilde{A}+5\tilde{B}-1.5)/3,$$

$$A_3=G_a(288\tilde{A}\tilde{B}-51\tilde{A}-81\tilde{B}+12)/45,$$

$$A_4=G_a(1576\tilde{A}^2\tilde{B}+2680\tilde{A}\tilde{B}^2-2312\tilde{A}\tilde{B}-192\tilde{A}^2 -520\tilde{B}^2+324\tilde{A}+510\tilde{B}-45)/270,$$

$$A_5=G_a(506560\tilde{A}^2\tilde{B}^2-197160\tilde{A}^2\tilde{B}-320360\tilde{A}\tilde{B}^2 +160662\tilde{A}\tilde{B}+22320\tilde{A}^2+58020\tilde{B}^2-16524\tilde{A} -25974\tilde{B}+1728)/14175.$$