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Antiferromagnetism in the Face-Centered Cubic Lattice. I. The Random-Phase Green's Function Approximation

M. E. LINES*
Bell Telephone Laboratories, Murray Hill, New Jersey

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The random-phase Green's function approximation is used to derive equations for zero-field magnetic susceptibility and two-spin correlation functions which are valid, at temperatures above the Curie or Néel point, for all ferromagnets and antiferromagnets which can be described by any isotropic Heisenberg Hamiltonian. At high temperatures, these expressions are also expanded as series in inverse powers of temperature. Detailed numerical calculations are carried out for the face-centered-cubic lattice with antiferromagnetic nearest- and next-nearest-neighbor exchange parameters J_1 and J_2. Susceptibility results are compared with molecular-field estimates at temperatures near the Néel point, and with the known terms of the exact power-series expansion at high temperatures. The spin correlations are computed for the first four shells of nearest neighbors. Finally, the sublattice-magnetization curves at temperatures below the Néel point are computed, in the random-phase Green's function approximation, for the type-2 antiferromagnetic order of the face-centered-cubic lattice. The curve shapes are found to be very insensitive to J_2/J_1 and approximate closely the shape of the molecular-field Brillouin-function curves. The significance of this result in connection with the biquadratic-exchange question in MnO is discussed in detail in the following paper by Lines and Jones.

1. INTRODUCTION

IN a recent publication,[1] the present author has employed the now familiar techniques of Green's function theory to develop a statistical treatment of antiferromagnetism. In that paper, the double-time temperature-dependent Green's functions are used with a simple random-phase decoupling approximation to present, for arbitrary spin S, a theory which is immediately applicable to any antiferromagnetic spin structure which can be separated into two translationally invariant ferromagnetic sublattices, and can be described by any isotropic Heisenberg Hamiltonian.

In the present paper, we point out that any results of this theory which are obtained for temperatures above the magnetic-transition temperature are valid for an even wider range of lattice structures, and we develop expressions for susceptibility and two-spin correlation functions which are valid (in the random-phase Green's function approximation) for all ferromagnets and antiferromagnets no matter how complex the spin arrangement which is preferred in the ordered state. These results have been used to compute in detail the susceptibility and near-neighbor correlations in the face-centered-cubic (fcc) lattice where we have given particular attention to that range of exchange interactions which favors the type-2 antiferromagnetic order[2] at temperatures below the Néel point.

Thus we consider, in general, an arbitrary lattice of interacting spins which may be described by the Hamiltonian

$$\mathcal{H}=\sum_{\langle i,j\rangle} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j\,, \tag{1.1}$$

where $\sum_{\langle i,j\rangle}$ runs over all pairs of spins $\mathbf{S}_i$ and $\mathbf{S}_j$. (Note that the exchange parameters J_{ij} as defined by the above Hamiltonian differ by a factor 2 from those in Ref. 1.) For the numerical computations we have considered the fcc lattice with nearest-neighbor exchange J_1, next-nearest-neighbor exchange J_2, and all other interactions equal to zero, investigating in particular the range $\frac{1}{2}<J_2/J_1<\infty$ for which the type-2 antiferromagnetic order (Fig. 1) is stable at low temperatures.

The reasons for this particular choice are as follows:

(i) The fcc antiferromagnetic structures require at least two exchange parameters (e.g., J_1 and J_2) if stable long range order is to set in at any nonzero temperature.[1] They are, therefore, among the more difficult structures to treat theoretically.

(ii) The molecular-field theory and many cluster theories tend to give more than usually poor results for these structures.[1,3]

(iii) Of the several different fcc antiferromagnetic spin structures which have been observed experimentally by neutron-diffraction techniques, the type-2 order has appeared most frequently. As a few examples we mention MnO, α-MnS, FeO, CoO, and NiO.[4]

(iv) The type-2 order covers a very wide range of antiferromagnetic situations; from the $J_2/J_1=\frac{1}{2}$ limit for which long-range order sets in only at the absolute zero of temperature, on the one hand, to the $J_1\rightarrow 0$ case for which the system goes over into the simplest of all three-dimensional antiferromagnets (the simple cubic structure with a single nearest-neighbor exchange parameter), on the other.

(v) An important question concerning the possible importance of biquadratic exchange in magnetic

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* Present address: Clarendon Laboratory, Oxford University, Oxford, England.

[1] M. E. Lines, Phys. Rev. **135**, A1336 (1964).

[2] P. W. Anderson, Phys. Rev. **79**, 705 (1950).

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[4] W. L. Roth, Phys. Rev. **110**, 1333 (1958).

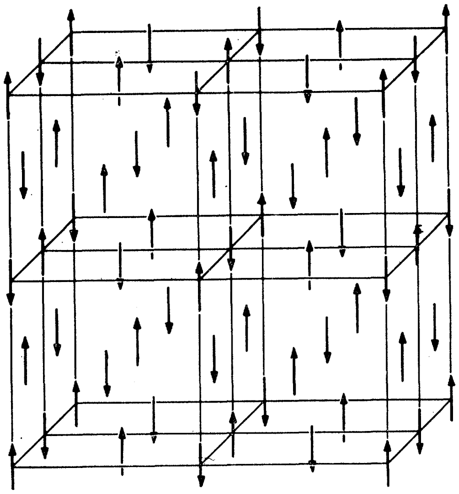

FIG. 1. The type-2 antiferromagnetic spin arrangement in the fcc lattice.

systems has grown up around certain of the properties of MnO and NiO, both examples of fcc type-2 antiferromagnets.[5,6]

In Sec. 2 we derive the random-phase Green's function expression for magnetic susceptibility at temperatures above the Néel point (T_N) and compute it specifically for the fcc type-2 order. We compare the curves with those obtained by molecular-field theory and note the marked difference between them for temperatures near T_N. In Sec. 3 we obtain the Green's function high-temperature expansion series for susceptibility and compare it with the exact series as calculated by Wojtowicz and Joseph.[7] We also compare the computed Green's function curve with estimates of susceptibility obtained by truncating the exact series. We find that the methods agree well at very high temperatures but that there is quite a large temperature range above T_N for which the number of known coefficients in the exact series is not sufficient for the latter to give estimates of susceptibility as accurate as those obtained by use of Green's function techniques.

In Sec. 4 we derive the Green's function estimate for near-neighbor spin-correlation functions and calculate them numerically for the first, second, third, and fourth nearest neighbors in the fcc lattice for temperatures $T > T_N$. We also write the Green's function result as a high-temperature series expansion in powers of inverse temperature. Finally, in Sec. 5, we calculate the sublattice magnetization as a function of temperature in the ordered state. We find, for the fcc type-2 order, that the curve *shapes* are very insensitive to the value of J_2/J_1 and follow closely the molecular-field Brillouin curve,[8] in disagreement with results obtained by use of the Monte Carlo method.[9] This last result is very important in connection with the biquadratic exchange question,[6] and indicates that the anomalous sublattice magnetization curves observed for MnO and NiO are probably due to terms which have been omitted from the Hamiltonian (1.1). We shall develop this question in detail in Part II where we consider the magnetic properties of MnO.

2. SUSCEPTIBILITY ABOVE THE NÉEL TEMPERATURE

Reference 1 uses Green's function techniques to discuss those antiferromagnets with spin patterns capable of separation into two translationally invariant ferromagnetic sublattices. At temperatures greater than or equal to the Néel temperature T_N, and in the presence of an external magnetic field H, the average spin value per site $\delta\bar{S}$ is given by Eq. (3.34) of Ref. 1 as

$$\frac{2S(S+1)}{3\delta\bar{S}} = \left\langle \frac{\sinh\alpha}{\cosh\alpha - \cosh\beta} \right\rangle_{\mathbf{K}}, \qquad (2.1)$$

where

$$\alpha = [g\mu_B H + \delta\bar{S}(\mu_1 + \mu_2)]/kT, \qquad (2.2)$$

$$\beta = \lambda\delta\bar{S}/kT, \qquad (2.3)$$

$$\mu_1 = \sum_{j-g}^{s} J_{jg}[\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})] - 1], \qquad (2.4)$$

$$\mu_2 = -\sum_{j-g}^{d} J_{jg}, \qquad (2.5)$$

$$\lambda = \sum_{j-g}^{d} J_{jg} \exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})], \qquad (2.6)$$

where $\sum_{j-g}{}^{s}$ ($\sum_{j-g}{}^{d}$) runs only over values for which j and g are on the same (different) sublattice, and where $\langle\cdots\rangle_{\mathbf{K}}$ is an average value for the wave vector $\mathbf{K}$ running over the values allowed by periodic boundary conditions in the first Brillouin zone of the reciprocal sublattice.

In the limit of very small fields, Eq. (2.1) reduces to

$$2S(S+1)/3\delta\bar{S} = \langle(\alpha+\beta)^{-1} + (\alpha-\beta)^{-1}\rangle_{\mathbf{K}}. \qquad (2.7)$$

If the allowed values of $\mathbf{K}$ are now taken to run over more than one reciprocal *sublattice* Brillouin zone and, in particular, if they are taken to run throughout the first Brillouin zone of the reciprocal *lattice*, then Eq. (2.7) is naturally still valid, but it may now be simplified further to read

$$S(S+1)/3\delta\bar{S} = \langle 1/(\alpha+\beta)\rangle_{\mathbf{K}}, \qquad (2.8)$$

where $\langle\cdots\rangle_{\mathbf{K}}$ is now an average for $\mathbf{K}$ running over the

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[6] D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, Phys. Rev. Letters 11, 10 (1963).

[7] P. J. Wojtowicz and R. I. Joseph, Phys. Rev. 135, A1314 (1964).

[8] A. B. Lidiard, Rept. Progr. Phys. 17, 201 (1954).

[9] E. A. Harris, Phys. Rev. Letters 13, 158 (1964).

values allowed by periodic boundary conditions in the first Brillouin zone of the reciprocal *lattice*. The right-hand side of this equation involves exchange interactions only in the form

$$\rho=\mu_1+\mu_2+\lambda=\sum_{j-g} J_{jg}[\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]-1], \tag{2.9}$$

where $\sum_{j-g}$ runs over *all* pairs of spins in the lattice. Thus, this equation and the resulting susceptibility of Eq. (2.11) are completely independent of any sublattice structure which may become evident when the temperature falls below T_N. They can, of course, be obtained in a rather simpler manner by using a single Green's function transform $G_{\mathbf{K}}$ (Fourier transformed with respect to the whole reciprocal lattice) throughout the calculation in place of the two functions $G_{1\mathbf{K}}$ and $G_{2\mathbf{K}}$ defined in Ref. 1. This simply recognizes the equivalence of all spins in the lattice for temperatures above T_N, and shows that the equations are not subject to the two sublattice restriction of Ref. 1.

Writing the zero-field magnetic susceptibility χ equal to $Ng^2\mu_B{}^2\chi_0$, where N is the number of spins in the lattice, and where

$$\chi_0=(\delta\bar{S}/g\mu_BH)_{H\to 0}, \tag{2.10}$$

we obtain, from (2.8), the equation

$$1/\chi_0\tau=\langle 1/(1+\chi_0\rho)\rangle_{\mathbf{K}}, \tag{2.11}$$

where

$$\tau=3kT/S(S+1), \tag{2.12}$$

and where ρ is given by Eq. (2.9). This equation for susceptibility is valid for *all* ferromagnetic and antiferromagnetic structures which can be described by a Hamiltonian of the form (1.1). For comparison, the molecular-field result, in a similar notation, reads

$$1/\chi_0\tau=1+\sum_{j-g} J_{jg}/\tau. \tag{2.13}$$

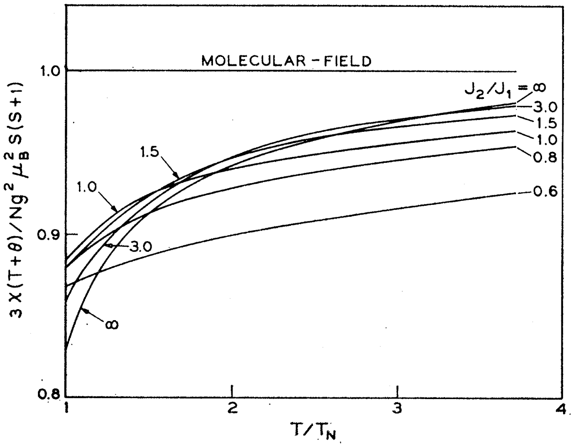

FIG. 2. Curves of magnetic susceptibility as a function of temperature, calculated in the random-phase Green's function approximation, for the fcc lattice with antiferromagnetic nearest- and next-nearest-neighbor exchange parameters J_1 and J_2. [θ is the Curie-Weiss constant of Eq. (2.16).]

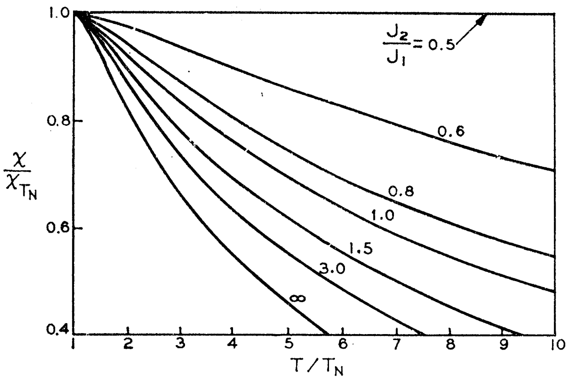

FIG. 3. The same as Fig. 2, but with the curves now plotted on a "reduced" scale, making them independent of the absolute magnitude of exchange.

We shall now compute the susceptibility from (2.11) for our particular case of interest, which is the type-2 antiferromagnetic order in the fcc lattice (see Fig. 1). We define a nearest-neighbor exchange J_1, a next-nearest-neighbor exchange J_2 (putting all other exchange parameters equal to zero), and consider the range $J_2/J_1=\frac{1}{2}\to\infty$ over which the type-2 spin arrangement is the stable ordered state. For this case we may write

$$\rho=4J_1(c_1c_2+c_2c_3+c_3c_1-3)+4J_2(c_1{}^2+c_2{}^2+c_3{}^2-3), \tag{2.14}$$

where

$$c_1=\cos(K_xa), \quad c_2=\cos(K_ya), \quad c_3=\cos(K_za), \tag{2.15}$$

where x, y, z, label the cubic axes, and where "a" is half the distance between *next* nearest neighbors. The average $\langle\cdots\rangle_{\mathbf{K}}$ is to be taken for K_x, K_y, K_z, running independently between $-\pi/a$ and π/a. Thus, we have treated the fcc lattice not in terms of its primitive translations, i.e., as a monatomic lattice, but as a cubic lattice with four spins per cell. Such a procedure lessens the burden of machine computation.

The results of this computation are shown graphically in Figs. 2 and 3. In Fig. 2 we plot $3\chi_0(T+\theta)/S(S+1)$, where θ is the Curie-Weiss constant given by

$$\theta=(12J_1+6J_2)S(S+1)/3k, \tag{2.16}$$

as a function of T/T_N, where T_N has (also) been calculated by the simple random-phase Green's function theory (using the results of Ref. 1 which are reproduced graphically in Fig. 4). The ordinate of Fig. 2 is, therefore, a quantity which is equal to unity on molecular-field theory for all values of $T>T_N$. The Green's function curves are seen to approach unity for very large values of T/T_N but they do so rather slowly if J_1 is larger than

J_2. Near the Néel point, the departure from a Curie-Weiss behavior is seen to be greatest for the simple cubic ($J_1=0$) limit. In Fig. 3, we plot a reduced susceptibility against T/T_N to give a set of curves which depend only on the ratio J_2/J_1, i.e., are completely independent of the magnitude of exchange. Such curves are useful in giving very direct information about the ratio of exchange interactions, as will be seen in Part II. In Fig. 5, for comparison, we show the same curves calculated by molecular-field theory.

3. COMPARISON WITH EXACT SERIES EXPANSIONS

The theory of high-temperature magnetic susceptibility of Heisenberg ferromagnets and antiferromagnets, using the exact power-series expansion method of Opechowski,[10] has, over the years, been extensively developed by several authors.[11,12] The susceptibility is expanded as a Taylor series in reciprocal temperature and, for systems with only a single exchange parameter, the coefficients are now known up to the sixth-power term.[12] Only recently, however, has the problem been developed for Hamiltonians in which two exchange parameters are present.[7] The latter susceptibility expansions are extended as far as the fourth-power term in inverse temperature and are directly applicable to the present problem. The series-expansion formulas, like the equivalent Green's function ones, are applicable to both ferromagnets and antiferromagnets, i.e., for exchange interactions of either sign.

In the present section, the Green's function Eq. (2.11) will be expanded as a series in inverse powers of temperature and compared with the exact expansion results of Wojtowicz and Joseph.[7] In this way we can obtain some indication of the accuracy of the random-phase Green's function approximation in this high-temperature region. We shall also compare the various truncated exact power-series expansions with the computed Green's function curves to estimate for what range of temperatures the latter results are likely to be the more useful.

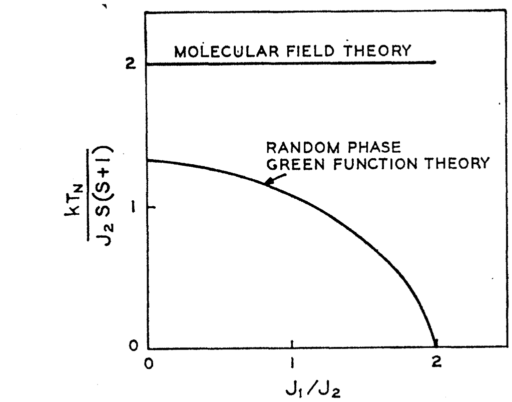

FIG. 4. The Néel temperature T_N for the fcc antiferromagnetic type-2 order, as calculated by the molecular-field theory and the random-phase Green's function theory.

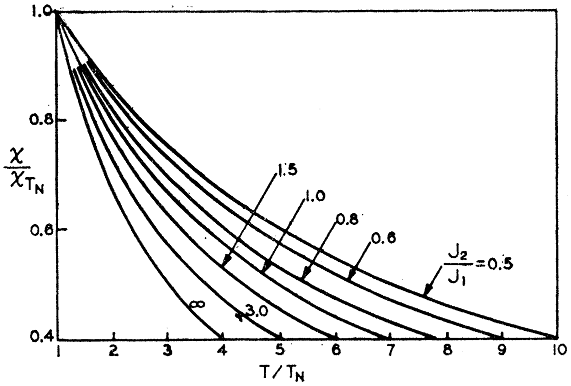

FIG. 5. Curves of magnetic susceptibility against temperature, as calculated for the fcc lattice (with antiferromagnetic nearest- and next-nearest-neighbor exchange parameters J_1 and J_2) by molecular-field theory. These curves are to be compared with the equivalent Green's function estimates of Fig. 3.

From Eq. (2.11) it is possible to obtain high-temperature series expansions for susceptibility or its inverse. We shall concentrate on the series expansion for inverse susceptibility because the pertinent coefficients are much simpler for this case, and the molecular-field approximation also takes on a particularly simple form. Expanding χ_0^{-1} as a power series in $1/\tau$, using Eq. (2.11), we obtain

$$\chi_0^{-1}=\tau\Big[1+\sum_{i=1}^{\infty} C_i/\tau^i\Big], \tag{3.1}$$

where

$$C_1=-\langle\rho\rangle_{\mathbf{K}}, \tag{3.2}$$

$$C_2=\langle\rho^2\rangle_{\mathbf{K}}-\langle\rho\rangle_{\mathbf{K}}^2, \tag{3.3}$$

$$C_3=-\langle\rho^3\rangle_{\mathbf{K}}+3\langle\rho\rangle_{\mathbf{K}}\langle\rho^2\rangle_{\mathbf{K}}-2\langle\rho\rangle_{\mathbf{K}}^3, \tag{3.4}$$

where ρ is given by Eq. (2.9). For the particular case of the fcc lattice with exchange parameters J_1 and J_2, these coefficients work out to be

$$C_1=12J_1+6J_2, \tag{3.5}$$

$$C_2=12J_1^2+6J_2^2, \tag{3.6}$$

$$C_3=-24J_1^2(2J_1+3J_2). \tag{3.7}$$

In molecular-field approximation we should find C_1 as in Eqs. (3.2) and (3.5) and all other coefficients equal to zero.

If we write the high-temperature expansion for inverse susceptibility in the form

$$(\chi_0\tau)^{-1}=\sum_{m,n=0}^{\infty} C_{nm}(J_1/\tau)^n(J_2/\tau)^m, \tag{3.8}$$

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[10] W. Opechowski, Physica 4, 181 (1937); 6, 1112 (1939).

[11] H. A. Brown and J. M. Luttinger, Phys. Rev. **100**, 685 (1955).

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

TABLE I. Numerical values of the coefficients C_{nm} of Eq. (3.8) as calculated for the fcc lattice with exchange parameters J_1 and J_2 and spin quantum number S.

	$X=S(S+1)$ Exact[a]	Random-phase Green's function approx.	Molecular-field approx.
C_{00}	1	1	1
C_{10}	12	12	12
C_{01}	6	6	6
C_{20}	$12+9/X$	12	0
C_{11}	0	0	0
C_{02}	$6+9/2X$	6	0
C_{30}	$(-6/5)(36+11/X-6/X^2)$	-48	0
C_{21}	$-72-36/X$	-72	0
C_{12}	0	0	0
C_{03}	$(3/5)(4+9/X+6/X^2)$	0	0

[a] Reference 7.

then the coefficients of the Green's function expansion may readily be compared with the exact expansion coefficients as obtained by Wojtowicz and Joseph.[7] Such a comparison is made for the fcc lattice in Table I, where the molecular-field results are also included. We note firstly that the Green's function coefficients C_{nm} are not spin-dependent whereas the exact coefficients, with a few exceptions, are.

If we call $n+m$ the order of the coefficient C_{nm}, then all three sets of coefficients coincide exactly only for the zeroth- and first-order terms. In the second order, the Green's function coefficients are correct in the limit of infinite spin but become progressively worse for smaller spin values. Only in the case of spin $\frac{1}{2}$ (and possibly spin 1), however, are they badly astray. In the third order, some of the Green's function terms are incorrect even in the infinite spin limit, but again the major terms are rather well approximated, particularly so for high spin values.

In Part II, we shall be concerned with the properties of MnO for which $S=\frac{5}{2}$ and $J_1\approx J_2$. It is of interest, therefore, to consider this particular case in more detail, and to compare the inverse susceptibility as computed from Eqs. (2.11) and (2.14) with the estimates obtained by use of the exact series expansion. Such a comparison is shown in Fig. 6 where we plot the computed Green's function curve together with a set of four exact series-expansion curves obtained by terminating the series, in turn, at the first-, second-, third-, and fourth-order terms. Since the exact coefficients of fifth- and higher-order terms have not yet been published for Hamiltonians containing more than one exchange parameter, we are not able, at the present time, to plot any curves of higher order.

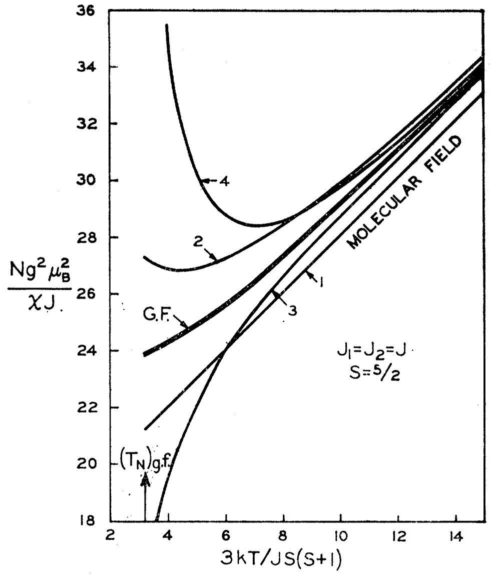

FIG. 6. Estimates of high-temperature magnetic susceptibility for the fcc lattice in the case $S=\frac{5}{2}$, $J_1=J_2$. The Green's function curve (G.F.) is compared with successive approximations (1,2,3,4,) obtained by use of the exact high-temperature series expansion (Ref. 7).

For the higher values of temperature, we see that the successive exact series-expansion curves converge rapidly and enable a good quantitative estimate of susceptibility to be made. For temperatures below $\sim 3T_N$, however, the series-expansion curves converge very slowly or not at all indicating that, for this temperature region, far more terms in the series are required before any reasonable susceptibility estimates can be made using this approach. Thus, for temperatures below $\sim 3T_N$, the Green's function method, at least for this particular problem, is the more direct approach. We are, therefore, encouraged by the fact that the Green's function curve (Fig. 6) appears to be in very close agreement with the best series estimates in the temperature region where the series-expansion approximations converge rapidly.

4. NEAR-NEIGHBOR SPIN CORRELATIONS FOR $T>T_N$

In an external magnetic field H parallel to an axis z we may write a Hamiltonian for a magnetic system, in standard notation, as

$$\mathcal{H}=\mathcal{H}_0-g\mu_B H\sum_{i=1}^{N} S_i^z, \tag{4.1}$$

where $\mathcal{H}_0$ is the Hamiltonian for the system in the absence of the field. The thermodynamic and magnetic properties of the system are derived from the partition function

$$Z=\mathrm{Tr}\{\exp(-\mathcal{H}/kT)\}, \tag{4.2}$$

and it follows, therefore, that the magnetic susceptibility in the limit of zero field is given by

$$\chi(T)=\frac{Ng^2\mu_B^2}{kT}\sum_{g-h}\langle S_h^z S_g^z\rangle, \tag{4.3}$$

where $\langle S_h^z S_g^z\rangle$ is the thermodynamic mean correlation between the z components of the spins at sites h and g in zero field. This longitudinal correlation is also of direct physical interest in other connections such as the thermodynamic energy, specific heat and the diffuse magnetic scattering of neutrons.

For temperatures $T>T_N$ the longitudinal and transverse correlations resulting from the Hamiltonian (1.1) are equal and are thus very easily calculated in the random-phase Green's function approximation from the theory of Ref. 1. The calculation of longitudinal correlations for $T<T_N$ (which will not be considered in the present paper) is somewhat more difficult to carry out in the Green's function formalism, but a method has recently been demonstrated for ferromagnetism by Tahir-Kheli and Callen.[13]

Solving Eqs. (3.3) and (3.4) of Ref. 1 for $G_{1\mathbf{K}}$ and $G_{2\mathbf{K}}$, we readily establish equations for the correlation $\langle S_h^- S_g^+\rangle$. Writing the average spin per site equal to $\delta\bar{S}$ for both sublattices, we find: (i) for g and h on the same sublattice

$$\langle S_h^- S_g^+\rangle=\delta\bar{S}\left\langle\left(\frac{\sinh\alpha}{\cosh\alpha-\cosh\beta}-1\right)e^{i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})}\right\rangle_{\mathbf{K}} \qquad (4.4)$$

and (ii) where g and h are on different sublattices

$$\langle S_h^- S_g^+\rangle=\delta\bar{S}\left\langle\frac{-\sinh\beta}{\cosh\alpha-\cosh\beta}e^{i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})}\right\rangle_{\mathbf{K}}, \qquad (4.5)$$

where α and β are as defined in Sec. 2, and where $\mathbf{K}$ runs over its allowed values in the first Brillouin zone of the reciprocal *sub*lattic.

In the limit of zero magnetic field, these equations reduce to

$$\text{(i)}\ \langle \mathbf{S}_h\cdot\mathbf{S}_g\rangle=\lim_{H\to0}\,(3\delta\bar{S}/2)\langle[(\alpha+\beta)^{-1}+(\alpha-\beta)^{-1}]\times e^{i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})}\rangle_{\mathbf{K}}, \qquad (4.6)$$

$$\text{(ii)}\ \langle \mathbf{S}_h\cdot\mathbf{S}_g\rangle=\lim_{H\to0}\,(3\delta\bar{S}/2)\langle[(\alpha+\beta)^{-1}-(\alpha-\beta)^{-1}]\times e^{i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})}\rangle_{\mathbf{K}}, \qquad (4.7)$$

for all cases $g\neq h$. Using the same argument as in Sec. 2 concerning the extension of $\langle\cdots\rangle_{\mathbf{K}}$ to run over all allowed values in the first Brillouin zone of the reciprocal *lattice* (rather than sublattice), we find that, with this new definition of $\langle\cdots\rangle_{\mathbf{K}}$, Eqs. (4.6) and (4.7) take the identical form

$$\langle \mathbf{S}_h\cdot\mathbf{S}_g\rangle=\lim_{H\to0}3\delta\bar{S}\left\langle\frac{\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})]}{\alpha+\beta}\right\rangle_{\mathbf{K}}, \qquad (4.8)$$

indicating again that the sublattice description of the system is not necessary for discussing properties above the transition temperature. Using Eqs. (2.2), (2.3), and (2.10), we obtain the final form

$$\langle \mathbf{S}_h\cdot\mathbf{S}_g\rangle=3kT\left\langle\frac{\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})]}{\chi_0^{-1}+\rho}\right\rangle_{\mathbf{K}}, \qquad (4.9)$$

giving a relationship between the spin-correlation function and the inverse magnetic susceptibility which is valid for all $g\neq h$ and for all temperatures $T>T_N$.

Using this equation, together with the results of Sec. 2 for inverse susceptibility, we may compute these correlations for any particular case of interest [Eq. (4.9) being, like Eq. (2.11), valid for all ferromagnetic and antiferromagnetic structures which can be described by Hamiltonian (1.1)]. As in the earlier sections, we have singled out the fcc lattice for detailed consideration. The fcc lattice is particularly interesting in this respect for the following reason. In the simpler types of antiferromagnetic structure, e.g., the simple cubic or body-centered-cubic lattices (with a single-exchange parameter), the signs of the near-neighbor correlations are immediately evident from simple physical considerations, and reflect the long-range ordering which sets in below the Néel point. Thus, for the above examples, the nearest-neighbor correlation is negative, the next-nearest one positive, and so on, with the magnitude of the correlation (for a particular temperature) falling off monotonically with increasing distance. For the fcc antiferromagnets the situation is not always so immediately evident. Consider the type-2 order of Fig. 1 for example. As drawn, it appears to have six positive and six negative nearest-neighbor correlations. Such a single axis spin arrangement is, however, not a unique solution for the isotropic Hamiltonian (1.1), even when the exchange parameters have values favoring the type-2 spin structure. More specifically,[2,14] the type-2 order requires only that all *next* nearest neighbors are oppositely oriented in the ordered state. The only restriction on nearest-neighbor spins is therefore that their vectorial sum shall be zero. (In actual salts which exhibit the fcc type-2 spin arrangement, e.g., MnO, α MnS, NiO, FeO, etc., the single axis order *is* found to exist and is stabilized by anisotropy and/or slight distortion of the lattice from its cubic form.[15–17]) It is not likely, therefore, that the correlation for $T>T_N$ will reflect the spin pattern of Fig. 1 when we calculate for the fcc type-2 order and Hamiltonian (1.1). Nor, we shall see, do the correlations necessarily fall off monotonically with distance.

Using Eqs. (4.9) and (2.14), together with the results of Sec. 2 [Eq. (2.11)] for susceptibility, we have computed the near-neighbor correlation functions for $T>T_N$ and for values of J_2/J_1 which favor the type-2 spin pattern in the ordered state. The results are shown

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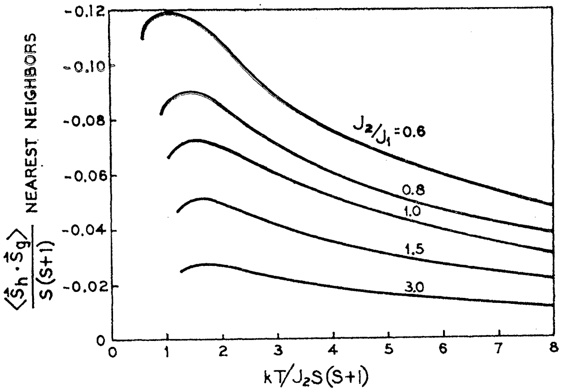

FIG. 7. Temperature dependence of nearest-neighbor spin correlations, as calculated for the fcc lattice with antiferromagnetic nearest- and next-nearest-neighbor exchange interactions J_1 and J_2, for temperatures above the Néel point.

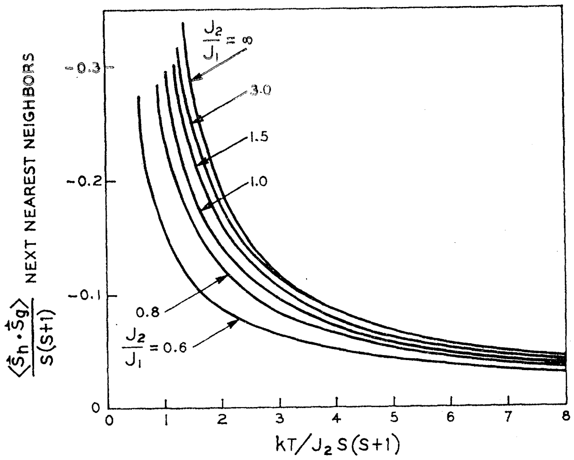

FIG. 8. The same as Fig. 7 but for next-nearest neighbors.

in Figs. 7 to 10, in which we plot $\langle \mathbf{S}_h \cdot \mathbf{S}_g \rangle / S(S+1)$ against temperature for first, second, third, and fourth nearest neighbors, respectively. We find, in particular, that the nearest-neighbor correlations are negative, are the same for all nearest-neighbor pairs and, in the temperature range close to the Néel point, are generally very much smaller in magnitude than the next-nearest-neighbor correlations. These results are in qualitative agreement with those of Harris[9] who studied the fcc Ising lattice by a Monte Carlo method.

At extremes of high temperature, we may expand the Green's function equation (4.9) as a power series in inverse powers of temperature. Using the previously evaluated power series for χ_0^{-1} we may readily calculate the first few terms in the high-temperature expansion series for the correlation functions. We find

$$\langle \mathbf{S}_h \cdot \mathbf{S}_g \rangle / S(S+1) = \langle \exp[i\mathbf{K} \cdot (\mathbf{g}-\mathbf{h})] \sum_{i=1}^{\infty} A_i/\tau^i \rangle_{\mathbf{K}}, \quad (4.10)$$

where

$$A_1 = -\rho, \quad (4.11)$$

$$A_2 = (\rho - \langle \rho \rangle_{\mathbf{K}})^2, \quad (4.12)$$

$$A_3 = 2\rho(\langle \rho^2 \rangle_{\mathbf{K}} - \langle \rho \rangle_{\mathbf{K}}^2) - (\rho - \langle \rho \rangle_{\mathbf{K}})^3, \quad (4.13)$$

and where $\mathbf{K}$ runs over the first Brillouin zone of the reciprocal lattice.

If we consider again the case of the fcc lattice, then we may use Eq. (2.14) and calculate the expansions specifically. We find

$$\langle \mathbf{S}_h \cdot \mathbf{S}_g \rangle / S(S+1) = \sum_{i=1}^{\infty} B_i/\tau^i, \quad (4.14)$$

where, if $\mathbf{S}_h$ and $\mathbf{S}_g$ are nearest neighbors, the coefficients B_i^{nn} for the first few terms are

$$B_1^{nn} = -J_1, \quad (4.15)$$

$$B_2^{nn} = 4J_1(J_1+J_2), \quad (4.16)$$

$$B_3^{nn} = -J_1(21J_1^2+36J_1J_2+12J_2^2), \quad (4.17)$$

and, if $\mathbf{S}_h$ and $\mathbf{S}_g$ are next nearest neighbors, the coefficients B_i^{nnn} are

$$B_1^{nnn} = -J_2, \quad (4.18)$$

$$B_2^{nnn} = 4J_1^2, \quad (4.19)$$

$$B_3^{nnn} = -24J_1^2(J_1+J_2) - 3J_2^3. \quad (4.20)$$

In the limit $J_1 \rightarrow 0$, coefficients B_i^{nnn} give the result for simple cubic lattice nearest neighbors with exchange parameter J_2.

We may easily extend this calculation to more distant neighbors when we find that $B_1 = 0$ for all neighbors beyond the second, i.e., only those neighbors with a nonzero exchange between them have a term in $1/\tau$. Those correlations which have a leading term in $1/\tau^2$ are as follows,

third neighbors, $B_2 = 2J_1(J_1+J_2)$; (4.21)

fourth neighbors, $B_2 = J_1^2 + 2J_2^2$; (4.22)

fifth neighbors, $B_2 = 2J_1J_2$; (4.23)

and eighth neighbors, $B_2 = J_2^2$. (4.24)

We may now carry out a check on these results by employing Eq. (4.3) which, for temperatures above the Néel point, may be written

$$\chi_0 = (1/\tau) \sum_{g-h} \langle \mathbf{S}_h \cdot \mathbf{S}_g \rangle / S(S+1). \quad (4.25)$$

Using the fact that $\langle \mathbf{S}_h \cdot \mathbf{S}_h \rangle = S(S+1)$, and noting that the numbers of first, second, third, fourth, fifth, and eighth nearest neighbors in the fcc lattice are, respectively, 12, 6, 24, 12, 24, and 6, we calculate from (4.25) and the above coefficients B the result

$$\chi_0 = \frac{1}{\tau} - \frac{12J_1+6J_2}{\tau^2} + \frac{6(22J_1^2+24J_1J_2+5J_2^2)}{\tau^3} + \cdots, \quad (4.26)$$

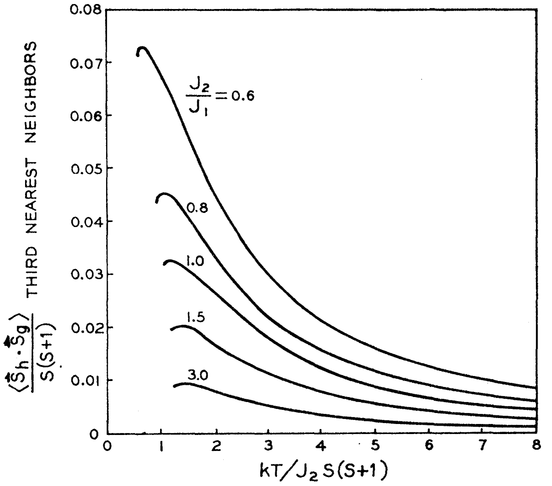

FIG. 9. The same as Fig. 7 but for third-nearest neighbors.

which agrees with the susceptibility calculations of Sec. 3 [Eqs. (3.1), (3.5), (3.6)].

5. SUBLATTICE MAGNETIZATION FOR $T<T_N$

In this final section, we shall investigate the zero-field sublattice magnetization as a function of temperature in the ordered state. This is of particular interest for the fcc type-2 antiferromagnetic order because a number of salts possessing this spin arrangement have been found to have sublattice magnetizations which deviate very significantly as functions of T/T_N from the results of molecular field theory.[14,18,19] One possible cause of this deviation has been suggested by Rodbell *et al.*[6] to be the inadequacy of Hamiltonian (1.1) to describe the substances in question. They point out that the inclusion of biquadratic exchange terms helps to bring the molecular-field theory into accord with experiment. On the other hand, Harris[9] concludes, from an analysis of an fcc Ising lattice using a Monte Carlo method, that the effect may possibly be due almost entirely to the crudeness of molecular-field theory. His work suggests that a more accurate treatment of Hamiltonian (1.1) would lead to results for sublattice magnetization as a function of T/T_N which differ markedly from the molecular field Brillouin curves.

We shall again use the Green's function expressions from Ref. 1 and compute them for the particular case of the fcc type-2 order. Sublattice magnetization $\bar{S}$, in the absence of an external magnetic field, is given, in the random-phase Green's function approximation, by Eqs. (2.23) and (2.24) of Ref. 1. They are

$$\bar{S}/S = B_s(2S\coth^{-1}x)\,, \tag{5.1}$$

and

$$x=\left\langle \frac{\mu}{[\mu^2-\lambda^2]^{1/2}}\coth\left[\frac{\bar{S}(\mu^2-\lambda^2)^{1/2}}{2kT}\right]\right\rangle_{\mathbf{K}}, \tag{5.2}$$

where B_s signifies the Brillouin function for spin S, where $\mu=\mu_1-\mu_2$ with μ_1, μ_2, λ, as defined in Sec. 2, and where $\langle\cdots\rangle_{\mathbf{K}}$ can be taken over the reciprocal lattice or sublattice. For type-2 order (Fig. 1) we may write

$$\mu+\lambda=4J_1(c_1c_2+c_2c_3+c_3c_1)+4J_2(c_1^2+c_2^2+c_3^2)\,, \tag{5.3}$$

$$\mu-\lambda=4J_1(s_1s_2+s_2s_3+s_3s_1)+4J_2(s_1^2+s_2^2+s_3^2)\,, \tag{5.4}$$

where c_1, c_2, c_3, are defined in (2.15), and where

$$s_1=\sin(K_xa)\,,\quad s_2=\sin(K_ya)\,,\quad s_3=\sin(K_za)\,. \tag{5.5}$$

The averages are taken for each component of wave vector running independently between $-\pi/a$ and π/a, and we have computed $\bar{S}$ for the case $S=\frac{5}{2}$. This value is the one applicable to MnO, which is the simplest and most widely discussed of the salts with the fcc type-2 spin arrangement, and is also the value considered by Harris.

The results of the computation are shown in Fig. 11, where we plot $\bar{S}$ as a function of kT/J_2 for temperatures between absolute zero and the Néel point. We observe that the Néel temperature T_N and the value of $\bar{S}$ at $T=0$ are both dependent on the parameter J_2/J_1 and, thus, differ very markedly from the molecular-field results which are

$$\bar{S}_{T\to 0}=S=\tfrac{5}{2}\,,\quad kT_N/J_2=2S(S+1)=17.5\,. \tag{5.6}$$

The *shape* of the curves, however, when plotted in the reduced form $\bar{S}/\bar{S}_{T\to 0}$ against T/T_N, is found to be

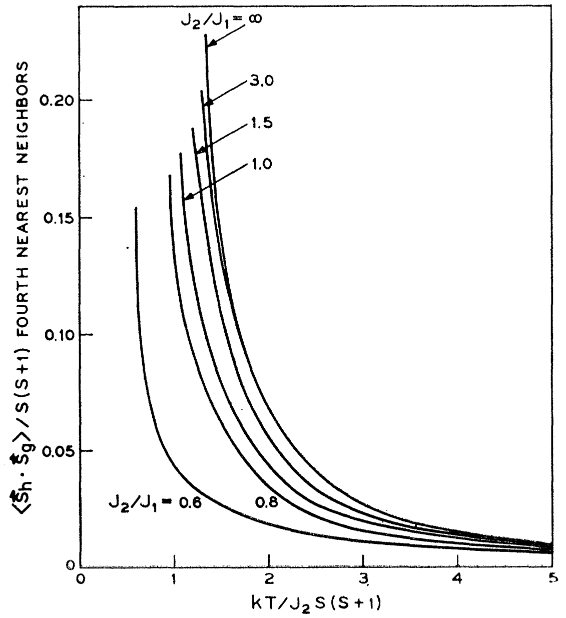

FIG. 10. The same as Fig. 7 but for fourth-nearest neighbors.

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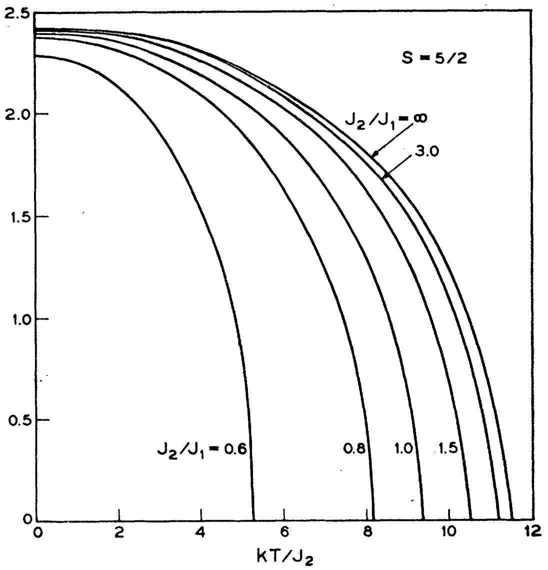

FIG. 11. Average spin per site as a function of temperature (between absolute zero and Néel point) for the type-2 antiferromagnetic order in the fcc lattice and the case $S=\frac{5}{2}$.

almost completely insensitive to J_2/J_1 and, moreover, is described very well indeed by the molecular-field Brillouin function for $S=\frac{5}{2}$. It is precisely this latter property, viz., shape of the reduced curves, which is found to be anomalous in MnO, the measured sublattice magnetization having a much slower "roll-off" than the associated Brillouin curve. We are therefore in disagreement with Harris and find that the observed sublattice magnetization curve cannot be explained by a Hamiltonian of form (1.1). The fault with the Monte Carlo method as described by Harris[9] is that it calculates a quantity $(1/N)\sum_i|S_i^z|$, where the summation is over all lattice sites. This quantity is **not** the sublattice spin per site $\bar{S}$. It does not, as Harris notes, go to zero at T_N, and it will take values which are larger than the true sublattice magnetization at all temperatures. This lack of sensitivity of reduced magnetization curves to the ratio of exchange parameters in simple Heisenberg exchange problems has also been noted recently by Callen and Callen[20] for the case of fcc ferromagnets by using a two-particle cluster approximation.

A satisfactory solution of the MnO problem seems likely, therefore, to depend on the modification of Hamiltonian (1.1). In Part II, the magnetic properties of MnO will be discussed in detail, and we shall show that the anomalous temperature dependence of sublattice magnetization is due almost entirely to effects produced by the small distortion of the lattice from cubic form, which occurs at temperatures below the Néel point. The importance of this distortion in affecting the magnetic properties of MnO was first pointed out by Kanamori,[21] and was later discussed in more detail by Rodbell and Owen[22] using a molecular-field theory. To obtain a quantitative agreement between theory and experiment, however, we shall find that it is necessary to use theories which are more accurate than the molecular field.

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