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# Green Functions in the Theory of Antiferromagnetism

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A Green function method has been used to treat the statistics of a general antiferromagnetic structure with arbitrary spin value per site and with Heisenberg exchange interactions between any or all pairs of spins in the system. The only restrictions placed upon the type of order are that there shall be a single direction of spin alignment and that each of the two ferromagnetic sublattices shall be translationally invariant. Expressions are given for the sublattice magnetization and Néel temperature and, as a particular application of the results, the Néel temperatures for certain face-centered cubic orders are calculated explicitly. The behavior of a general antiferromagnetic structure in the presence of an external magnetic field is also examined. Expressions are derived for the parallel and perpendicular magnetic susceptibilities, and are discussed in detail at low and high temperatures and also at the Néel point.

## 1. INTRODUCTION

A FEW years ago, Bogolyubov and Tyablikov[1,2] first employed the double-time temperature-dependent Green functions in an approximate treatment of statistical problems in ferromagnetism. They demonstrated the manner in which it is possible to derive a formula for the magnetization of the Heisenberg ferromagnet which is a reasonable approximation over the entire temperature range. The exact treatment of the problem involves the solution of an infinite set of coupled equations in the Green functions (see, for example, Zubarev[3]) and approximate solutions are obtained by making the set of equations finite by using a decoupling approximation. In practice, almost all authors have, for simplicity, concentrated on finding a suitable decoupling which will isolate just one equation from the rest and hence allow for a comparatively simple solution.

The original Bogolyubov and Tyablikov theory was applied only to the case of spin-half and uses the so-called "random-phase" or "Tyablikov" decoupling approximation. The extension to higher spin values was accomplished by Tahir-Kheli and ter Haar[4] (to whom we may refer for reference to earlier efforts in this direction) using the same decoupling mechanism. More recently, progress has been made toward improving the calculation at low temperatures,[5,6] and Callen[7] has suggested a more satisfactory decoupling procedure. Recent papers by Tahir-Kheli[8] and by Hewson and ter Haar[9] have also shed light on the kind of deficiencies which the existing decoupling approximations possess.

In contrast with the wealth of literature on the Green function approach to the ferromagnetic problem, there has been comparatively little published concerning the analogous antiferromagnetic problem. Although the two problems are obviously closely related, and similar questions of decoupling procedure arise for both, the inequivalence of the sublattices in the presence of external magnetic fields and the almost limitless number of possible spin patterns add to the difficulties of presenting a comprehensive treatment of the antiferromagnetic problem. Of the papers which we know to have been published on the subject,[6,10,11] only Pu Fu-Cho[10] has included the effects of an external magnetic field or has tried to consider in any sense a general antiferromagnetic structure. His treatment, however, is restricted to spin-$\frac{1}{2}$ and to perpendicular susceptibility at low temperatures.

The aim of the present paper is to present a treatment, using the Green function techniques, of the statistics of a general antiferromagnetic structure with arbitrary spin $S$, with Heisenberg exchange interactions between any or all pairs of spins in the lattice, and in the presence of an external magnetic field. The only restrictions which are placed on the spin system are that there shall be a single preferred direction of antiferromagnetic alignment in the ordered state, and that each of the two ferromagnetic sublattices shall be translationally invariant. To show the way in which this latter restriction may be lifted, we also treat a special case of an ordering which does not conform in this respect. We use the simple "Tyablikov" decoupling throughout.

In Sec. 2 we treat the problem in the absence of an external magnetic field, and expressions are obtained for the sublattice magnetization and the Néel temperature $T_N$. As a special application of the results, we

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[1] N. N. Bogolyubov and S. V. Tyablikov, Dokl. Akad. Nauk SSSR **126**, 53 (1959) [English transl.: Soviet Phys.—Doklady **4**, 589 (1959)].

[2] S. V. Tyablikov, Ukrain. Mat. Zh. **11**, 287 (1959).

[3] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

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[5] K. Kawasaki and H. Mori, Progr. Theoret. Phys. (Kyoto) **28**, 690 (1962).

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[7] H. B. Callen, Phys. Rev. **130**, 890 (1963).

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[9] A. C. Hewson and D. ter Haar, Phys. Letters **6**, 136 (1963).

[10] Fu-Cho Pu, Dokl. Akad. Nauk SSSR **130**, 1244 (1960); **131**, 546 (1960) [English transl.: Soviet Phys.—Doklady **5**, 128 and 321 (1960)].

[11] M. E. Lines, Phys. Rev. **131**, 540 (1963).

obtain the Néel temperatures for the various face-centered cubic antiferromagnetic orders which are observed experimentally. In Sec. 3 we introduce a magnetic field parallel to the preferred direction of ordering and evaluate the parallel susceptibility. Finally, in Sec. 4, we discuss the perpendicular susceptibility. The results obtained for the susceptibilities are compared at low temperatures near $T_N$ and at high temperatures with the estimates of other methods.

## 2. THE FUNDAMENTAL GREEN FUNCTION EQUATIONS

The double-time temperature-dependent retarded Green function $\langle\langle A(t);B(t')\rangle\rangle$ involving the two Heisenberg operators $A(t)$ and $B(t')$ is defined by

$$\langle\langle A(t);B(t')\rangle\rangle=-i\theta(t-t')\langle[A(t),B(t')]_-\rangle\,, \tag{2.1}$$

where the square brackets denote a commutator; single-pointed brackets denote a thermal average over a canonical ensemble; and where $\theta(t-t')$ is a step function with the value unity when $t>t'$ and the value zero when $t<t'$. If the Hamiltonian is not explicitly time-dependent, the retarded Green function (2.1) is a function of $(t-t')$ and may therefore be Fourier transformed with respect to this quantity. The transform is a function of $E(=\hbar\omega)$ and may be denoted by $\langle\langle A;B\rangle\rangle_E$. It may be shown to satisfy the equation of motion (see Zubarev[3])

$$E\langle\langle A;B\rangle\rangle_E=(1/2\pi)\langle[A,B]_-\rangle+\langle\langle[A,\mathcal{H}]_-;B\rangle\rangle_E\,. \tag{2.2}$$

The only other equation which we shall require from Green function theory is that defining the relationship between $\langle\langle A;B\rangle\rangle_E$ and its related correlation function $\langle B(t')A(t)\rangle$. This may be written[3]

$$\langle B(t')A(t)\rangle=\lim_{\epsilon\to+0} i\int_{-\infty}^{\infty}\frac{\langle\langle A;B\rangle\rangle_{\omega+i\epsilon}-\langle\langle A;B\rangle\rangle_{\omega-i\epsilon}}{e^{\omega/kT}-1}\times e^{-i\omega(t-t')}d\omega\,, \tag{2.3}$$

where we work in a system of units for which $\hbar=1$.

In the present section we shall consider an infinite lattice of interacting spins for which we may write a Hamiltonian

$$\mathcal{H}=\sum_{\langle i,j\rangle}2J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j\,, \tag{2.4}$$

where $J_{ij}$ is the exchange constant for the interaction between the spins $\mathbf{S}_i$ and $\mathbf{S}_j$ (it is assumed to be a function only of the distance between the spins) and where $\sum_{\langle i,j\rangle}$ runs over all pairs of spins in the lattice. We shall not need to restrict the sign of $J_{ij}$ in any way and, in general, Eq. (2.4) will give rise to an antiferromagnetic ordering although the case of ferromagnetic spin alignment will be contained in the theory as a particular case.

Let us examine the motion of the function $\langle\langle S_g^+;f(S_h^z)S_h^-\rangle\rangle_E$—which we shall write, for brevity, in the form $\langle\langle S_g^+;B\rangle\rangle$—where $f(S_h^z)$ is an arbitrary function of $S^z$ at the site $h$, and where $S^\pm=S_x\pm iS_y$. Using the Hamiltonian (2.4), together with the well-known spin commutation relationships, we may write the equation of motion of this Green function in the form

$$E\langle\langle S_g^+;B\rangle\rangle=\frac{1}{2\pi}F\delta_{gh}+\sum_{j-g}2J_{jg}\langle\langle(S_g^zS_j^+-S_g^+S_j^z);B\rangle\rangle\,, \tag{2.5}$$

where

$$F=\langle[S_h^+;f(S_h^z)S_h^-]_-\rangle\,, \tag{2.6}$$

and where

$$J_{jj}=0\,.$$

Using the "Tyablikov" decoupling procedure we write

$$\left.\begin{aligned}\langle\langle S_g^zS_j^+;B\rangle\rangle&=\langle S_g^z\rangle\langle\langle S_j^+;B\rangle\rangle\,,\\ \langle\langle S_g^+S_j^z;B\rangle\rangle&=\langle S_j^z\rangle\langle\langle S_g^+;B\rangle\rangle\,,\end{aligned}\right\}\quad g\neq j \tag{2.7}$$

which gives, on substitution into (2.5),

$$E\langle\langle S_g^+;B\rangle\rangle=\frac{F\delta_{gh}}{2\pi}+\sum_{j-g}2J_{jg}[\langle S_g^z\rangle\langle\langle S_j^+;B\rangle\rangle-\langle S_j^z\rangle\langle\langle S_g^+;B\rangle\rangle]\,. \tag{2.8}$$

We now restrict the order to one with a unique direction of spin alignment and split the lattice into two sublattices, the "up" and the "down," with average values of spin per site $\bar{S}$ and $-\bar{S}$, respectively. This presupposes that we know what the stable spin pattern will be. For many problems this will indeed be the case and for others, a simple molecular-field calculation will often supply the answer. In cases of doubt, any of the likely spin patterns can be assumed at this stage, the incorrect choices being easily recognized and eliminated later on when their instability can be detected by the imaginary values which will occur for some of the frequencies of the elementary excitations. If the two sublattices are translationally invariant, we may Fourier transform with respect to the reciprocal sublattices as follows. When $g$ and $h$ are on the same sublattice we define $G_{1\mathbf{K}}$ by

$$\begin{aligned}\langle\langle S_g^+;B\rangle\rangle&=(2/N)\sum_{\mathbf{K}}G_{1\mathbf{K}}\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})]\,,\\ G_{1\mathbf{K}}&=\sum_{g-h}\langle\langle S_g^+;B\rangle\rangle\exp[-i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})]\,,\end{aligned} \tag{2.9}$$

where $N$ is the total number of spins in the lattice, and where $\mathbf{K}$ is a reciprocal lattice vector which runs over $\frac{1}{2}N$ points in the first Brillouin zone of the reciprocal sublattice. In an exactly similar way we define $G_{2\mathbf{K}}$ for the case when $g$ and $h$ are on opposite sublattices. Choosing $h$ to be on the "up" sublattice, we may rewrite the equation of motion (2.8) in terms of $G_{1\mathbf{K}}$

and $G_{2\mathbf{K}}$. We obtain

$$(E-\mu\bar{S})G_{1\mathbf{K}}=(F/2\pi)+\lambda\bar{S}G_{2\mathbf{K}}\,, \qquad (2.10)$$

$$(E+\mu\bar{S})G_{2\mathbf{K}}=-\lambda\bar{S}G_{1\mathbf{K}}\,, \qquad (2.11)$$

where

$$\mu=\sum_{j-g}^{s} 2J_{jg}[\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]-1]+\sum_{j-g}^{d} 2J_{jg}\,, \qquad (2.12)$$

$$\lambda=\sum_{j-g}^{d} 2J_{jg}\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]\,, \qquad (2.13)$$

and where $\sum_{j-g}{}^{s}$ runs over all values for which $j$ and $g$ are on the same sublattice, and $\sum_{j-g}{}^{d}$ runs over all values for which $j$ and $g$ are on different sublattices.

Solving (2.10) and (2.11) for $G_{1\mathbf{K}}$ we find

$$4\pi G_{1\mathbf{K}}=\frac{(1-A)F}{E+E_0\bar{S}}+\frac{(1+A)F}{E-E_0\bar{S}}\,, \qquad (2.14)$$

where

$$A=\mu/(\mu^2-\lambda^2)^{1/2}\,, \qquad (2.15)$$

and

$$E_0=(\mu^2-\lambda^2)^{1/2}. \qquad (2.16)$$

Using Eqs. (2.3), (2.9), and (2.14), and employing the identity

$$\lim_{\epsilon\to+0}\left\{\frac{1}{\omega+i\epsilon-E_{\mathbf{K}}}-\frac{1}{\omega-i\epsilon-E_{\mathbf{K}}}\right\}=-2\pi i\delta(\omega-E_{\mathbf{K}})\,, \qquad (2.17)$$

we find, for the limit $t-t'\to 0$,

$$\langle BS_g{}^{+}\rangle=(F/N)\sum_{\mathbf{K}}[A\coth(E_0\bar{S}/2kT)-1]\times\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})]. \qquad (2.18)$$

For the case $g=h$, this becomes

$$\langle f(S_h{}^z)S_h{}^-S_h{}^+\rangle=\tfrac{1}{2}F\{\langle A\coth(E_0\bar{S}/2kT)\rangle_{\mathbf{K}}-1\}\,, \qquad (2.19)$$

where $\langle\cdots\rangle_{\mathbf{K}}$ indicates an average for $\mathbf{K}$ running over $\frac{1}{2}N$ values in the first Brillouin zone of the reciprocal sublattice.

Procedures for extracting an equation for $\bar{S}$ as a function of temperature from a relationship of the form (2.19) have been discussed by Tahir-Kheli and ter Haar[4] and by Callen.[7] The case for spin-$\frac{1}{2}$ is very simple. If we put $f(S^z)=1$, then we get from (2.19)

$$S(S+1)-\langle(S^z)^2\rangle=\bar{S}\langle A\coth(E_0\bar{S}/2kT)\rangle_{\mathbf{K}}. \qquad (2.20)$$

For the case $S=\frac{1}{2}$, we have $(S^z)^2=\frac{1}{4}$ and Eq. (2.20) reduces to

$$1/\bar{S}=2\langle A\coth(E_0\bar{S}/2kT)\rangle_{\mathbf{K}}. \qquad (2.21)$$

To obtain an equation for higher values of spin, we choose $f(S^z)$ to be different from unity. Thus, for example, for the case $S=1$ the simplest expression is probably $f(S^z)=S^z$. Using the result that $(S^z)^3=S^z$ in the spin-one case, Eqs. (2.19) and (2.20) may then be solved simultaneously to give $\langle(S^z)^2\rangle$ and $\bar{S}$ as functions of temperature. In general, by putting $f(S^z)=(S^z)^n$, where $n$ takes on values 0, 1, 2, $\cdots$, $2S-1$, consecutively, we obtain from (2.19) a set of $2S$ independent simultaneous equations in the $(2S+1)$ unknowns $\langle(S^z)^{n+1}\rangle$, $\langle(S^z)^{2S+1}\rangle$. The spin condition

$$\prod_{n=-S}^{+S}(S^z-n)=0 \qquad (2.22)$$

(where $n$ takes on integral or half-odd-integral values according to whether $S$ is integral or half-odd-integral), supplies the additional information which enables the equations to be solved for $\bar{S}$. This method is just that used by Tahir-Kheli and ter Haar[4] [except that these authors use a rather more complicated form for $f(S^z)$] who give explicit results up to $S=3$. The solution for general spin $S$ has been obtained by Callen[7] by writing $f(S^z)=\exp(aS^z)$ and exploiting the functional dependence of $F$ and $\langle f(S^z)S^-S^+\rangle$ on the parameter "$a$." His result [Eq. (52) of Ref. 7] is most conveniently expressed as

$$\frac{2\bar{S}+x}{2S+1}=\frac{(x+1)^{2S+1}+(x-1)^{2S+1}}{(x+1)^{2S+1}-(x-1)^{2S+1}}\,, \qquad (2.23)$$

where, for our case,

$$x=\langle A\coth(E_0\bar{S}/2kT)\rangle_{\mathbf{K}}. \qquad (2.24)$$

To obtain an expression for the Néel temperature (for general spin $S$), it is interesting to note that only the single $f(S^z)=1$, Eq. (2.20) is required. At and above $T_N$ we have $\langle S_x{}^2\rangle=\langle S_y{}^2\rangle=\langle S_z{}^2\rangle=S(S+1)/3$, and we obtain from (2.20)

$$2S(S+1)/3=\bar{S}\langle A\coth(E_0\bar{S}/2kT)\rangle_{\mathbf{K}}. \qquad (2.25)$$

As $T\to T_N$ from below, $\bar{S}\to 0$ and it follows that

$$S(S+1)/3kT_N=\langle A/E_0\rangle_{\mathbf{K}}=\langle\mu/(\mu^2-\lambda^2)\rangle_{\mathbf{K}}. \qquad (2.26)$$

At $T=0$, $x=\langle A\rangle_{\mathbf{K}}$ which for three-dimensional lattices will, in general, be a number a little larger than unity. If we put $\langle A\rangle_{\mathbf{K}}=1+\delta$, we obtain from (2.23)

$$\bar{S}_{T=0}=\bar{S}_0=S-\tfrac{1}{2}\delta+O(\delta^{2S+1})\,, \qquad (2.27)$$

which may be compared with the result $\bar{S}_0=S-\frac{1}{2}\delta$ which would result from a use of simple spin-wave theory.[12]

As an example of the use of Eq. (2.26) we may evaluate $T_N$ for the face-centered cubic (fcc) antiferromagnetic orders. The results for the simple cubic and body-centered cubic lattices with a single exchange between nearest neighbors are already well known, but the problem for the fcc orders has not yet been treated. Apart from molecular-field-type calculations[13] which

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[12] R. Kubo, Phys. Rev. **87**, 568 (1952).

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

are more than usually poor for these orders, the only previous estimates[14,15] have been made by using spin-wave theory and attempting to extend it beyond its usual low-temperature region of validity. We shall consider the types 1, 2, and 3 order[13] (type 3 is sometimes called improved ordering of the first kind) including nearest and next-nearest-neighbor exchange interactions only, which we shall denote by $J_1$ and $J_2$, respectively.

For the types 1 and 2 order we may employ Eqs. (2.12) and (2.13) directly to obtain

$$\text{type 1:}\quad \mu=8J_1(1+c_1c_2)+8J_2(c_1^2+c_2^2+c_3^2-3)\,, \tag{2.28}$$

$$\lambda=8J_1(c_2c_3+c_3c_1)\,, \tag{2.29}$$

$$\text{type 2:}\quad \mu+\lambda=8J_1(c_1c_2+c_2c_3+c_3c_1)+8J_2(c_1^2+c_2^2+c_3^2)\,, \tag{2.30}$$

$$\mu-\lambda=8J_1(s_1s_2-s_2s_3-s_3s_1)+8J_2(s_1^2+s_2^2+s_3^2)\,, \tag{2.31}$$

where

$$c_1=\cos(K_xa)\,,\quad c_2=\cos(K_ya)\,,\quad c_3=\cos(K_za)\,, \tag{2.32}$$

$$s_1=\sin(K_xa)\,,\quad s_2=\sin(K_ya)\,,\quad s_3=\sin(K_za)\,, \tag{2.33}$$

and where we have taken "$a$" to be the distance between *next*-nearest neighbors. The Néel temperatures may now be computed directly from (2.26) and are shown in Figs. 1 and 2 together with the molecular-field values[13] and estimates obtained from spin-wave calculations.[14,15] The latter are plotted for a particular value of spin because the spin-wave estimates show $T_N\propto S(S+\frac{1}{2})$ and therefore cannot be represented for general spin $S$ by a single curve in Figs. 1 and 2.

Type 3 order (Fig. 3) is an example of a spin pattern for which the "up" and "down" sublattices are not translationally invariant. The results of the calculations of this section may therefore not be directly applied for this case. To treat this kind of ordering in the Green function approximation it is necessary to subdivide the lattice further. For type 3 order one can find four ferromagnetic sublattices which are each translationally invariant, and in this way four Green functions $G_{i\mathbf{K}}(i=1,2,3,4)$ may be introduced in place of the two which have so far been sufficient. The equation of motion (2.8) now gives rise to four equations in the $G_{i\mathbf{K}}$ which may readily be solved for these functions. Estimates for $\bar{S}$ and for $T_N$ now follow from $G_{i\mathbf{K}}$ in the same way as before. The detailed solution of the problem is given in the Appendix and the results for the Néel temperature are shown in Fig. 2.

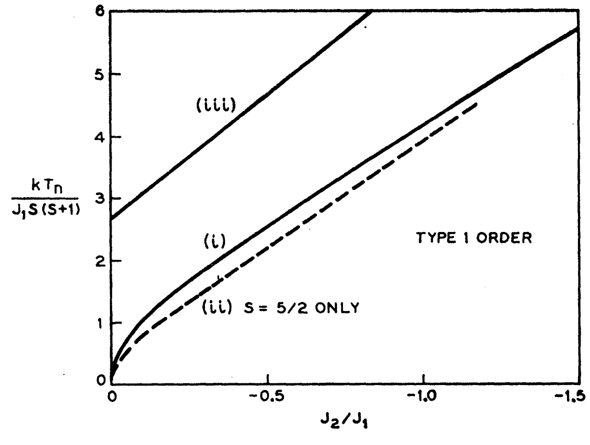

FIG. 1. The Néel temperature for the fcc type 1 order as a function of the ratio of next-nearest to nearest-neighbor exchange: (i) as calculated from the present work, (ii) from Ref. 15, and (iii) from molecular-field theory.

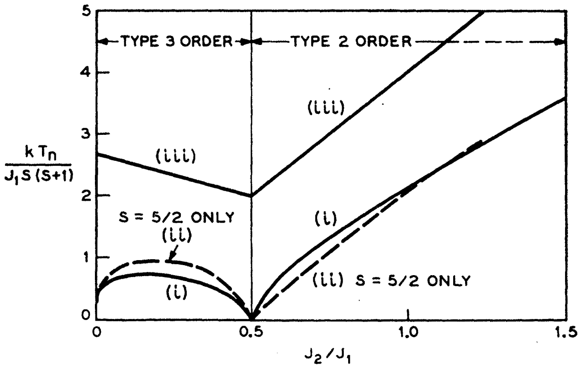

FIG. 2. The Néel temperature for the fcc types 2 and 3 order as a function of the ratio of next-nearest to nearest-neighbor exchange (i) as calculated from the present work, (ii) from Ref. 15, and (iii) from molecular-field theory.

### 3. THE PARALLEL SUSCEPTIBILITY

In this section we shall consider an antiferromagnet in the presence of an external magnetic field $H$ which is applied parallel to the direction ($z$) of antiferromagnetic spin alignment. We write for the Hamiltonian of the system

$$\mathcal{H}=\sum_{\langle ij\rangle}2J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j-g\mu_BH\sum_i S_i^z\,, \tag{3.1}$$

where $\mu_B$ is the Bohr magneton. Introducing again the Green function transform

$$\langle\langle S_g^+;B\rangle\rangle=\langle\langle S_g^+;f(S_h^z)S_h^-\rangle\rangle_E$$

and decoupling it in the "Tyablikov" approximation, its equation of motion is

$$(E-g\mu_BH)\langle\langle S_g^+;B\rangle\rangle=\frac{F\delta_{gh}}{2\pi}+\sum_{j-g}2J_{jg}[\langle S_g^z\rangle\langle\langle S_j^+;B\rangle\rangle-\langle S_j^z\rangle\langle\langle S_g^+;B\rangle\rangle]\,. \tag{3.2}$$

If we assume that the ordering is one that can be divided into two translationally invariant ferromagnetic

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[14] J. M. Ziman, Proc. Phys. Soc. (London) **A66**, 89 (1953).
[15] M. E. Lines, Proc. Roy. Soc. (London) **A271**, 105 (1963).

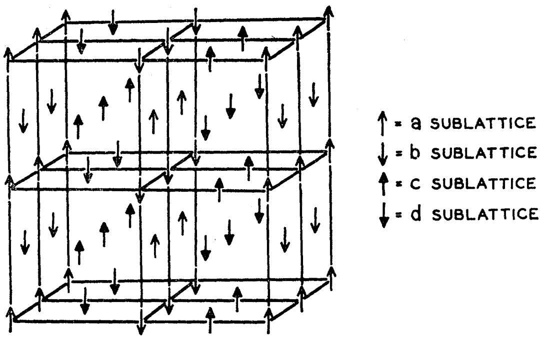

FIG. 3. The type 3 order of the fcc lattice showing the four translationally invariant ferromagnetic sublattices *a*, *b*, *c*, and *d*.

sublattices, then we may Fourier transform the Green functions with respect to the reciprocal sublattices and introduce functions $G_{1\mathrm{K}}$ and $G_{2\mathrm{K}}$ exactly as in Sec. 2 [Eq. (2.9)]. These are defined for the case when spin $h$ is on the "up" sublattice. In the case where an external field is present the average spin per site on the "up" sublattice (which we shall now symbolize as $\bar{S}_u$) is no longer equal and opposite to the average "down" spin ($\bar{S}_d$) and the equations of motion will therefore contain these two averages in place of the single $\bar{S}$ of the previous section. Using (3.2), the equations of motion for $G_{1\mathrm{K}}$ and $G_{2\mathrm{K}}$ are

$$(E-g\mu_BH-\mu_1\bar{S}_u-\mu_2\bar{S}_d)G_{1\mathrm{K}}=(F_u/2\pi)+\lambda\bar{S}_uG_{2\mathrm{K}}, \tag{3.3}$$

$$(E-g\mu_BH-\mu_1\bar{S}_d-\mu_2\bar{S}_u)G_{2\mathrm{K}}=\lambda\bar{S}_dG_{1\mathrm{K}}, \tag{3.4}$$

where

$$F_u=\langle[S_h^+,f(S_h^z)S_h^-]_-\rangle, \tag{3.5}$$

for the case when $h$ is on the "up" sublattice, and where [compare (2.12) and (2.13)]

$$\mu_1=\sum_{j-g}^{s}2J_{jg}[\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]-1], \tag{3.6}$$

$$\mu_2=-\sum_{j-g}^{d}2J_{jg}, \tag{3.7}$$

$$\lambda=\sum_{j-g}^{d}2J_{jg}\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]. \tag{3.8}$$

Writing $\bar{S}_u=\bar{S}+\delta\bar{S}$ and $\bar{S}_d=-\bar{S}+\delta\bar{S}$, we may solve Eqs. (3.3) and (3.4) for $G_{1\mathrm{K}}$ and, using the identity (2.17) together with (2.3) and (2.9), obtain an expression for the correlation function $\langle f(S_h^z)S_h^-S_h^+\rangle$ in the form

$$\langle f(S_h^z)S_h^-S_h^+\rangle$$

$$=\tfrac{1}{2}F_u\left\langle\frac{\sinh(\alpha)-A'\sinh(\beta)}{\cosh(\alpha)-\cosh(\beta)}-1\right\rangle_{\mathrm{K}}, \tag{3.9}$$

where

$$\alpha=(1/kT)[g\mu_BH+\delta\bar{S}(\mu_1+\mu_2)], \tag{3.10}$$

$$\beta=(1/kT)[(\mu_1-\mu_2)^2(\bar{S})^2-\lambda^2(\bar{S})^2+\lambda^2(\delta\bar{S})^2]^{1/2}, \tag{3.11}$$

$$A'=(\mu_1-\mu_2)\bar{S}/kT\beta. \tag{3.12}$$

For the case when spin $h$ is on the down sublattice, we may perform a completely analogous calculation to obtain

$$\langle f(S_h^z)S_h^-S_h^+\rangle$$

$$=\tfrac{1}{2}F_d\left\langle\frac{\sinh(\alpha)+A'\sinh(\beta)}{\cosh(\alpha)-\cosh(\beta)}-1\right\rangle_{\mathrm{K}}, \tag{3.13}$$

where $\alpha$, $\beta$, and $A'$ are as above, and where $F_d$ is given by (3.5) but where $h$ is now on the "down" sublattice. Note that for $\delta\bar{S}\rightarrow0$, we have $A'\rightarrow A$ and $\beta\rightarrow E_0\bar{S}/kT$ with $A$ and $E_0$ given by (2.15) and (2.16).

### A. Temperatures Below the Néel Point

For treatment of susceptibility in the ordered state we shall first consider the simplest case of $S=\frac{1}{2}$. For this case, if we put $f(S^z)=1$, we obtain from (3.9)

$$\bar{S}+\delta\bar{S}=\left[2\left\langle\frac{\sinh(\alpha)-A'\sinh(\beta)}{\cosh(\alpha)-\cosh(\beta)}\right\rangle_{\mathrm{K}}\right]^{-1}, \tag{3.14}$$

and from (3.13)

$$-\bar{S}+\delta\bar{S}=\left[2\left\langle\frac{\sinh(\alpha)+A'\sinh(\beta)}{\cosh(\alpha)-\cosh(\beta)}\right\rangle_{\mathrm{K}}\right]^{-1}. \tag{3.15}$$

We shall consider the case where $g\mu_BH/kT\rightarrow0$ and discuss the zero-field parallel susceptibility. In this limit, Eqs. (3.14) and (3.15) may be combined to give

$$\delta\bar{S}=C/2(C^2-B^2), \tag{3.16}$$

where

$$B=\langle A\coth(\tfrac{1}{2}\beta_0)\rangle_{\mathrm{K}}, \tag{3.17}$$

$$C=\langle-\tfrac{1}{2}\alpha\operatorname{csch}^2(\tfrac{1}{2}\beta_0)\rangle_{\mathrm{K}}, \tag{3.18}$$

and where

$$\beta_0=(\bar{S}/kT)[(\mu_1-\mu_2)^2-\lambda^2]^{1/2}=E_0\bar{S}/kT. \tag{3.19}$$

Neglecting $C^2$ with respect to $B^2$ (an approximation which is valid in the zero-field limit right up to the Néel point) and noting that, for spin-$\frac{1}{2}$, we have the relationship $\bar{S}=1/2B$; we obtain

$$\delta\bar{S}=(\bar{S})^2\langle\alpha\operatorname{csch}^2(E_0\bar{S}/2kT)\rangle_{\mathrm{K}}. \tag{3.20}$$

Using (3.10), it follows that

$$\chi_{\parallel}=\frac{Ng\mu_B\delta\bar{S}}{H}$$

$$=\frac{Ng^2\mu_B^2(\bar{S})^2\langle\operatorname{csch}^2(E_0\bar{S}/2kT)\rangle_{\mathrm{K}}}{kT-(\bar{S})^2\langle(\mu_1+\mu_2)\operatorname{csch}^2(E_0\bar{S}/2kT)\rangle_{\mathrm{K}}}. \tag{3.21}$$

For systems where there is no interaction between spins on the same sublattice, we have $\mu_1=0$. Since $\mu_2$ is not dependent on $\mathbf{K}$, the result simplifies for these cases to

$$\chi_{\parallel}=Ng^2\mu_B{}^2(\bar{S})^2R/(kT-\mu_2(\bar{S})^2R)\,, \qquad (3.22)$$

where

$$R=\langle\operatorname{csch}^2(E_0\bar{S}/2kT)\rangle_{\mathrm{K}}\,, \qquad (3.23)$$

which is a result obtained previously (for the case $S=\frac{1}{2}$) by Ginzburg and Fain.[16] For very low temperatures, both (3.21) and (3.22) reduce to

$$\chi_{\parallel}=Ng^2\mu_B{}^2(\bar{S})^2R/kT\,. \qquad (3.24)$$

For the case of general spin $S$, we have to resort to the Callen solution (2.23) but where, for Eq. (3.9)

$$x=x_u=\frac{\sinh(\alpha)-A'\sinh(\beta)}{\cosh(\alpha)-\cosh(\beta)}\,,\quad \bar{S}=\bar{S}_u\,, \qquad (3.25)$$

and for Eq. (3.13)

$$x=x_d=\frac{\sinh(\alpha)+A'\sinh(\beta)}{\cosh(\alpha)-\cosh(\beta)}\,,\quad \bar{S}=\bar{S}_d\,. \qquad (3.26)$$

From these two equations for $\bar{S}_u$ and $\bar{S}_d$ we obtain, after a little algebra, an expression for $\delta\bar{S}$. It is, in the limit $g\mu_BH/kT\ll1$,

$$\delta\bar{S}=\tfrac{1}{4}F(B)\langle\alpha\operatorname{csch}^2(E_0\bar{S}/2kT)\rangle_{\mathrm{K}}\,, \qquad (3.27)$$

where

$$1-F(B)=\frac{4(2S+1)^2(B^2-1)^{2S}}{[(B+1)^{2S+1}-(B-1)^{2S+1}]^2}\,, \qquad (3.28)$$

and where $B$ is given by Eq. (3.17). For the case of $S=\frac{1}{2}$ we regenerate Eq. (3.20) as a particular case.

From (3.27), using (3.10), it follows that (for general spin $S$)

$$\chi_{\parallel}=\frac{Ng^2\mu_B{}^2F(B)\langle\operatorname{csch}^2(E_0\bar{S}/2kT)\rangle_{\mathrm{K}}}{4kT-F(B)\langle(\mu_1+\mu_2)\operatorname{csch}^2(E_0\bar{S}/2kT)\rangle_{\mathrm{K}}}\,, \qquad (3.29)$$

and for very low temperatures this simplifies to

$$\chi_{\parallel}=Ng^2\mu_B{}^2F(B)R/4kT\,. \qquad (3.30)$$

The simple spin-wave result for this very low-temperature region has been given by Ziman[17] as

$$\chi_{\parallel\mathrm{Sp.w.}}=Ng^2\mu_B{}^2R'/4kT\,, \qquad (3.31)$$

where $R'$ is obtained from $R$ [Eq. (3.23)] by replacing $\bar{S}$ by $S$. For $T\rightarrow0$, $B\rightarrow\langle A\rangle_{\mathrm{K}}=1+\delta$ where $\delta$, for most three-dimensional lattices, is a number small compared with unity. From (3.28) we find, to the lowest order in $\delta$,

$$F(B)=1+[(2S+1)^2\delta^{2S}/2^{2S}]\,. \qquad (3.32)$$

Thus, at very low temperatures, $F(B)$ is a number which rapidly approaches unity (even for comparatively large $\delta$) as spin $S$ increases. The Green function result, therefore, differs slightly from the spin-wave estimate for small values of spin, but the difference very rapidly decreases as we move to higher spin values.

### B. Temperatures Above the Néel Point

In the region above the Néel temperature $\bar{S}_u=\bar{S}_d=\delta\bar{S}$ ($\bar{S}=0$) and the Eqs. (3.9) and (3.13) become identical. If we put $f(S^z)=1$ in (3.9), we obtain

$$S(S+1)-\langle(S_u{}^z)^2\rangle=\bar{S}_u\left\langle\frac{\sinh(\alpha)-A'\sinh(\beta)}{\cosh(\alpha)-\cosh(\beta)}\right\rangle_{\mathrm{K}}\,. \qquad (3.33)$$

However, for the temperatures where we have no long-range order, we may write $\langle(S_u{}^z)^2\rangle=S(S+1)/3$ and (3.33) therefore gives us an equation for $\bar{S}_u$ ($=\delta\bar{S}$) for the case of general spin S. It is

$$\frac{2S(S+1)}{3\delta\bar{S}}=\left\langle\frac{\sinh(\alpha)}{\cosh(\alpha)-\cosh(\beta)}\right\rangle_{\mathrm{K}}\,, \qquad (3.34)$$

where we have used the fact that $A'=0$ when $\bar{S}=0$, and where $\beta$ now assumes the simple form [compare (3.11)]

$$\beta=\lambda\delta\bar{S}/kT\,. \qquad (3.35)$$

For the infinitesimal field limit, (3.34) reduces to

$$S(S+1)/3\delta\bar{S}=\langle\alpha/(\alpha^2-\beta^2)\rangle_{\mathrm{K}}\,. \qquad (3.36)$$

We may use this implicit equation for $\delta\bar{S}$ to derive a series expansion for $\chi_{\parallel}$ in inverse powers of the temperature.

Let us write $\alpha=\alpha_0+\alpha_1$, where

$$\alpha_0=g\mu_BH/kT\,, \qquad (3.37)$$

$$\alpha_1=(\mu_1+\mu_2)\delta\bar{S}/kT\,. \qquad (3.38)$$

Expanding (3.36) as a power series in $\alpha_1/\alpha_0$ and $\beta/\alpha_0$ we find

$$\frac{S(S+1)}{3\delta\bar{S}}=\frac{1}{\alpha_0}\left\langle\left[1-\frac{\alpha_1}{\alpha_0}+\frac{\alpha_1{}^2+\beta^2}{\alpha_0{}^2}-\frac{\alpha_1{}^3+3\alpha_1\beta^2}{\alpha_0{}^3}+\cdots\right]\right\rangle_{\mathrm{K}}\,, \qquad (3.39)$$

from which it follows that

$$\chi_{\parallel}=(Ng^2\mu_B{}^2/\tau)[1+(C_1/\tau)+(C_2/\tau^2)+\cdots]\,, \qquad (3.40)$$

where

$$\tau=3kT/S(S+1)\,, \qquad (3.41)$$

$$C_1=\langle(\mu_1+\mu_2)\rangle_{\mathrm{K}}\,, \qquad (3.42)$$

$$C_2=2\langle(\mu_1+\mu_2)\rangle_{\mathrm{K}}{}^2-\langle(\mu_1+\mu_2)^2+\lambda^2\rangle_{\mathrm{K}}\,. \qquad (3.43)$$

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[16] V. L. Ginzburg and V. M. Fain, Zh. Eksperim. i Teor. Fiz. 39, 1323 (1960) [English transl.: Soviet Phys.—JETP 12, 923 (1961)].

[17] J. M. Ziman, Proc. Phys. Soc. (London) A65, 540 and 548 (1952).

The molecular-field result differs from the above by having $C_2=C_1^2$. The coefficients $C_i$ should, for a given lattice, be independent of the type of antiferromagnetic spin arrangement which occurs below the Néel temperature since the exact high-temperature expansions for $\chi_{\parallel}$ have this property.[18] That $C_1$ and $C_2$, as given above, do have this property is readily demonstrated by noting that $\langle\lambda\rangle_{\mathrm{K}}=0$ [see Eq. (3.8)], and therefore (3.42) and (3.43) may be written

$$C_1=\langle\rho\rangle_{\mathrm{K}}\,, \tag{3.44}$$

$$C_2=2\langle\rho\rangle_{\mathrm{K}}^2-\langle\rho^2\rangle_{\mathrm{K}}\,, \tag{3.45}$$

where

$$\rho=\mu_1+\mu_2+\lambda=\sum_{j-g}2J_{jg}\{\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]-1\}\,, \tag{3.46}$$

and where $\sum_{j-g}$ runs over *all* pairs of spins in the lattice.

As an example we may consider the face-centered cubic lattice where we limit the exchange interactions to nearest and next-nearest neighbors ($J_1$ and $J_2$, respectively) which is the case considered in the previous section. Direct application of Eqs. (3.44) and (3.45) yields

$$(C_1)_{\mathrm{fcc}}=-(24J_1+12J_2)\,, \tag{3.47}$$

$$(C_2)_{\mathrm{fcc}}=528J_1^2+576J_1J_2+120J_2^2\,. \tag{3.48}$$

### C. At the Transition Temperature

To evaluate $\chi_{\parallel}$ at the Néel temperature we shall use the result (3.29) which has been calculated for the ordered state. Consider the limit as the temperature approaches $T_N$ from below. We may write

$$\operatorname{csch}(E_0\bar{S}/2kT)\rightarrow 2kT_N/E_0\bar{S}\,, \tag{3.49}$$

$$F(B)\rightarrow 4S(S+1)/3B^2\,, \tag{3.50}$$

$$\bar{S}\rightarrow 2S(S+1)/3B\,. \tag{3.51}$$

The last result follows from (2.23) by noticing that $x=B$ in the zero-field limit.

Inserting these relationships into (3.29) gives

$$(\chi_{\parallel})_{T_N}=\frac{Ng^2\mu_B^2\langle 1/E_0^2\rangle_{\mathrm{K}}}{S(S+1)/3kT_N-\langle(\mu_1+\mu_2)/E_0^2\rangle_{\mathrm{K}}}\,. \tag{3.52}$$

Since, in the present notation, $T_N$ is given by

$$S(S+1)/3kT_N=\langle(\mu_1-\mu_2)/E_0^2\rangle_{\mathrm{K}}\,, \tag{3.53}$$

we may (noticing that $\mu_2$ is independent of $\mathbf{K}$) write (3.52) as

$$(\chi_{\parallel})_{T_N}=Ng^2\mu_B^2/-2\mu_2=Ng^2\mu_B^2\Big/\sum_{j-g}^{d}4J_{jg}\,. \tag{3.54}$$

This is just the molecular-field result[19] and it indicates that the susceptibility at the Néel point depends only upon those interactions which are between spins on opposite sublattices. This same result may also be obtained by using (3.34) and examining the limit as the temperature approaches $T_N$ from the high-temperature side, indicating that $\chi_{\parallel}$ is continuous in this region.

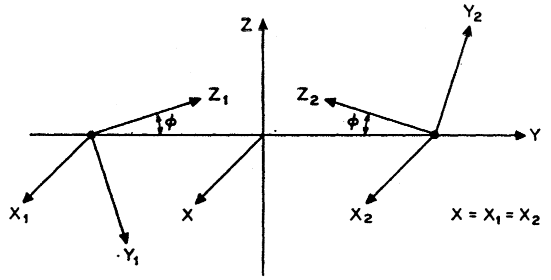

FIG. 4. The orthogonal coordinate systems $x_1$, $y_1$, $z_1$ and $x_2$, $y_2$, $z_2$ as used in Sec. 4.

### 4. THE PERPENDICULAR SUSCEPTIBILITY

In this section we introduce an external field $H$ in a direction $z$ which we choose to be perpendicular to the preferred direction $y$ of antiferromagnetic spin alignment. When the field is applied, each sublattice rotates through an angle $\varphi$ towards the $z$ direction. Let us introduce two new sets of orthogonal coordinates, one for each sublattice, which are defined with respect to the equilibrium positions $\varphi$ of the sublattices. The new coordinates $x_1$, $y_1$, $z_1$ for sublattice 1, and $x_2$, $y_2$, $z_2$ for sublattice 2, are shown in Fig. 4 and are obtained from $x$, $y$, $z$ by the transformations

$$\begin{pmatrix}x_1\\y_1\\z_1\end{pmatrix}=\begin{pmatrix}1&0&0\\0&\sin\varphi&-\cos\varphi\\0&\cos\varphi&\sin\varphi\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix}\,, \tag{4.1}$$

$$\begin{pmatrix}x_2\\y_2\\z_2\end{pmatrix}=\begin{pmatrix}1&0&0\\0&\sin\varphi&\cos\varphi\\0&-\cos\varphi&\sin\varphi\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix}\,. \tag{4.2}$$

In the new coordinates, the Hamiltonian (3.1) may be written

$$\begin{aligned}\mathcal{H}=&\sum_{\langle i,i'\rangle}2J_{ii'}\mathbf{S}_i\cdot\mathbf{S}_{i'}+\sum_{\langle j,j'\rangle}2J_{jj'}\mathbf{S}_j\cdot\mathbf{S}_{j'}\\&+\sum_{\langle i,j\rangle}2J_{ij}\{S_i^{x_1}S_j^{x_2}+\sin(2\varphi)[S_i^{z_1}S_j^{y_2}-S_i^{y_1}S_j^{z_2}]\\&-\cos(2\varphi)[S_i^{y_1}S_j^{y_2}+S_i^{z_1}S_j^{z_2}]\}-g\mu_BH\\&\times\sum_i(-\cos\varphi S_i^{y_1}+\sin\varphi S_i^{z_1})-g\mu_BH\\&\times\sum_j(\cos\varphi S_j^{y_2}+\sin\varphi S_j^{z_2})\,,\end{aligned} \tag{4.3}$$

where, for this equation, the suffix $i$ refers to spins on sublattice 1, and the suffix $j$ to spins on sublattice 2.

Since we shall be concerned only with time-averaged

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

[19] J. H. Van Vleck, J. Chem. Phys. **9**, 85 (1941).

properties of the system, we shall assume that, in the equations of motion for the Green functions, we may neglect from the Hamiltonian all terms which either exactly or to a good approximation average to zero with time. In this approximation, the Hamiltonian reduces to

$$\mathcal{H}=\sum_{\langle i,i'\rangle} 2J_{ii'}\mathbf{S}_i\cdot\mathbf{S}_{i'}+\sum_{\langle j,j'\rangle} 2J_{jj'}\mathbf{S}_j\cdot\mathbf{S}_{j'}$$
$$+\sum_{\langle i,j\rangle} 2J_{ij}\{S_i^{x1}S_j^{x2}-\cos(2\varphi)[S_i^{y1}S_j^{y2}+S_i^{z1}S_j^{z2}]\}$$
$$-g\mu_BH\sin\varphi[\sum_i S_i^{z1}+\sum_j S_j^{z2}]. \quad (4.4)$$

We shall consider the Green function transforms $\langle\langle S_g^{x1};B\rangle\rangle$, $\langle\langle S_g^{y1};B\rangle\rangle$, $\langle\langle S_g^{x2};B\rangle\rangle$, $\langle\langle S_g^{y2};B\rangle\rangle$, where $B$ may be $S_h^{x1}$ or $S_h^{y1}$. That is to say, we consider the case for which $h$ refers to a site on sublattice 1. Equations of motion for these functions may be written down using Eq. (2.2) and decoupled by simple random-phase approximations of the form [compare (2.7)]

$$\langle\langle S_g^{z1}S_j^{y2};B\rangle\rangle=\langle S_g^{z1}\rangle\langle\langle S_j^{y2};B\rangle\rangle, \quad (4.5)$$

$$\langle\langle S_g^{y1}S_j^{z2};B\rangle\rangle=\langle S_j^{z2}\rangle\langle\langle S_g^{y1};B\rangle\rangle. \quad (4.6)$$

The decoupled equations are most conveniently expressed in terms of the Fourier transforms $G_{i\mathbf{K}}(i=1,2,3,4)$ with respect to the reciprocal sublattices. Defining $G_{i\mathbf{K}}$ as follows [compare (2.9)]

$$\langle\langle S_g^{x1};B\rangle\rangle=(2/N)\sum_{\mathbf{K}} G_{1\mathbf{K}}\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})], \quad (4.7)$$

$$G_{1\mathbf{K}}=\sum_{g-h}\langle\langle S_g^{x1};B\rangle\rangle\exp[-i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})], \quad (4.8)$$

together with exactly similar equations for

$$\langle\langle S_g^{y1};B\rangle\rangle(G_{2\mathbf{K}}),\quad \langle\langle S_g^{x2};B\rangle\rangle(G_{3\mathbf{K}}),$$

and

$$\langle\langle S_g^{y2};B\rangle\rangle(G_{4\mathbf{K}});$$

the equations of motion for the $G_{i\mathbf{K}}$ are

$$\begin{bmatrix} E & -i\mu'\bar{S} & 0 & i\lambda_1\bar{S} \\ i\mu'\bar{S} & E & i\lambda_2\bar{S} & 0 \\ 0 & i\lambda_1\bar{S} & E & -i\mu'\bar{S} \\ i\lambda_2\bar{S} & 0 & i\mu'\bar{S} & E \end{bmatrix}\begin{bmatrix} G_{1\mathbf{K}} \\ G_{2\mathbf{K}} \\ G_{3\mathbf{K}} \\ G_{4\mathbf{K}} \end{bmatrix}=\frac{1}{2\pi}\begin{bmatrix} F_x \\ F_y \\ 0 \\ 0 \end{bmatrix}, \quad (4.9)$$

where we have written $\langle S^{z1}\rangle=\langle S^{z2}\rangle=\bar{S}$, and where

$$\mu'=\sum_{j-g}^{s} 2J_{jg}\{\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]-1\}$$
$$+\sum_{j-g}^{d} 2J_{jg}\cos(2\varphi)+\frac{g\mu_BH\sin\varphi}{\bar{S}}, \quad (4.10)$$

$$\lambda_1=\sum_{j-g}^{d} 2J_{jg}\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]\cos(2\varphi), \quad (4.11)$$

$$\lambda_2=\sum_{j-g}^{d} 2J_{jg}\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})], \quad (4.12)$$

$$F_x=\langle[S_h^{x1},B]_-\rangle, \quad (4.13)$$

$$F_y=\langle[S_h^{y1},B]_-\rangle. \quad (4.14)$$

Equations (4.9) may be solved for $G_{i\mathbf{K}}$ and the associated correlation functions then follow using (2.3), (2.17), and (4.8) in a manner exactly analogous to that used in the previous sections. We omit the tedious but straightforward algebra and simply give the results as follows:

$$\langle S_h^{x1}S_g^{x1}\rangle=\tfrac{1}{4}\bar{S}\langle[A_1\coth(\psi_1)+A_2\coth(\psi_2)]\times\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})]\rangle_{\mathbf{K}}, \quad (4.15)$$

$$\langle S_h^{y1}S_g^{y1}\rangle=\tfrac{1}{4}\bar{S}\langle[(1/A_1)\coth(\psi_1)+(1/A_2)\coth(\psi_2)]\times\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})]\rangle_{\mathbf{K}}, \quad (4.16)$$

$$\langle S_h^{x1}S_g^{x2}\rangle=\tfrac{1}{4}\bar{S}\langle[A_1\coth(\psi_1)-A_2\coth(\psi_2)]\times\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})]\rangle_{\mathbf{K}}, \quad (4.17)$$

$$\langle S_h^{y1}S_g^{y2}\rangle=\tfrac{1}{4}\bar{S}\langle[(1/A_1)\coth(\psi_1)-(1/A_2)\coth(\psi_2)]\times\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})]\rangle_{\mathbf{K}}, \quad (4.18)$$

where

$$A_1=[(\mu'-\lambda_1)/(\mu'+\lambda_2)]^{1/2},$$
$$A_2=[(\mu'+\lambda_1)/(\mu'-\lambda_2)]^{1/2}, \quad (4.19)$$

$$\psi_1=[(\mu'+\lambda_2)(\mu'-\lambda_1)]^{1/2}\bar{S}/2kT, \quad (4.20)$$

$$\psi_2=[(\mu'+\lambda_1)(\mu'-\lambda_2)]^{1/2}\bar{S}/2kT. \quad (4.21)$$

With a given value of external field $H$, the equilibrium value of $\varphi$ is that value which minimizes the free energy of the system. The condition is

$$\partial/\partial\phi\{kT\log[\mathrm{tr}\exp(-\mathcal{H}/kT)]\}=0, \quad (4.22)$$

and reduces to

$$\langle\partial\mathcal{H}/\partial\phi\rangle=0. \quad (4.23)$$

From (4.3) we see that this condition requires a knowledge of the $\varphi$ dependence of the correlation functions containing the $z$ components of the spins, which cannot be evaluated by using the simple decoupling procedure of this paper.[5] These difficulties prevent us from extracting from the theory a general functional dependence of $\chi_\perp$ on temperature. We may, however, obtain some results for certain restricted ranges of temperature.

### A. Temperatures Well Below the Néel Point

For temperatures approaching absolute zero, the hyperbolic cotangent terms in (4.15) to (4.18) approach unity for all values of $\mathbf{K}$. The correlation functions in this region are thus determined by $\bar{S}$ together with terms like

$$\langle A_1\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})]\rangle_{\mathbf{K}}$$

and

$$\langle A_2 \exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})]\rangle_{\mathbf{K}}.$$

A careful analysis of these terms shows that for structures which exhibit long-range order they are, to a good approximation, independent of $\varphi$. This result is just a mathematical demonstration of the usual physical assumption which is made for the ordered state at low temperatures—that the effect of a perpendicular field is to change the angle between the average sublattice magnetizations without appreciably modifying the motion of the spins about their equilibrium directions. For higher temperatures the approximation will become less good especially for large values of $\varphi$ where there will be a considerable increase in $\bar{S}$ due to the component of field parallel to the sublattice magnetization. Using this approximation, we replace $\langle S_i^z S_j^y\rangle$ type terms in (4.23) by the values which they take in the absence of a field—namely zero.

Eq. (4.23) now has solutions

$$\cos\varphi=0, \tag{4.24}$$

and

$$\sin\varphi=g\mu_B H\bar{S}\Big/\sum_{j-g}^{d} 4J_{jg}\langle S_g^{y_1}S_j^{y_2}+S_g^{z_1}S_j^{z_2}\rangle. \tag{4.25}$$

The solution (4.24) represents the ferromagnetic state, and is stable for values of $H\geq H_c$ where

$$g\mu_B H_c\bar{S}=\sum_{j-g}^{d} 4J_{jg}\langle S_g^{y_1}S_j^{y_2}+S_g^{z_1}S_j^{z_2}\rangle. \tag{4.26}$$

In molecular-field theory, we should approximate $\langle S_g^{y_1}S_j^{y_2}\rangle$ by zero, and $\langle S_g^{z_1}S_j^{z_2}\rangle$ by $(\bar{S})^2$, to give the result

$$g\mu_B H_c=\sum_{j-g}^{d} 4J_{jg}\bar{S}. \tag{4.27}$$

For values of $H<H_c$ the total magnetization $M=Ng\mu_B\bar{S}\sin\varphi$ is proportional to $H$ and we may write

$$\chi_\perp=\frac{M}{H}=Ng^2\mu_B^2(\bar{S})^2\Big/\sum_{j-g}^{d} 4J_{jg}\langle S_g^{y_1}S_j^{y_2}+S_g^{z_1}S_j^{z_2}\rangle, \tag{4.28}$$

which is a result recently obtained by Kanamori and Tachiki.[20]

In the very low-temperature range for which this result is valid [note the obvious breakdown for the limit $T\to T_N$ when (4.28) shows the zero-field susceptibility tending to zero] we shall assume that we may replace $\langle S_g^{z_1}S_j^{z_2}\rangle$ by $(\bar{S})^2$ for all values of $j-g$, when we obtain

$$\chi_\perp=Ng^2\mu_B^2\Big/\sum_{j-g} 4J_{jg}(1+\Delta), \tag{4.29}$$

where

$$\Delta(\bar{S})^2=\langle S_g^{y_1}S_j^{y_2}\rangle. \tag{4.30}$$

This differs from the molecular-field result simply by the term $\Delta$ in the denominator.

At the absolute zero of temperature the value of $\Delta$ is given by

$$\Delta=(1/4\bar{S})\langle[(1/A_1)-(1/A_2)] \times\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]\rangle_{\mathbf{K}}, \tag{4.31}$$

and, as a simple application of these formulas, we may estimate $\chi_\perp$ (in the zero-field limit) at $T=0$ for the simplest case of the simple-cubic lattice with antiferromagnetic nearest-neighbor exchange only. For this case we find, using (4.19), (4.10) to (4.12) and putting $\varphi=0$,

$$\langle S_g^{y_1}S_j^{y_2}\rangle=(\bar{S}/6)\left\langle\frac{\gamma_{\mathbf{K}}\cos(K_x a)}{[1-(\gamma_{\mathbf{K}}/3)^2]^{1/2}}\right\rangle_{\mathbf{K}}, \tag{4.32}$$

where

$$\gamma_{\mathbf{K}}=\cos(K_x a)+\cos(K_y a)+\cos(K_z a), \tag{4.33}$$

where $j-g=a$, and where the components of $\mathbf{K}$ each run over values between $-\pi/a$ and $\pi/a$. Computing the average over $\mathbf{K}$ gives the numerical result as

$$\langle S_g^{y_1}S_j^{y_2}\rangle=0.13\bar{S}, \tag{4.34}$$

from which it follows that

$$(\chi_\perp)_{T=0}=Ng^2\mu_B^2/24J[1+(0.13/\bar{S})], \tag{4.35}$$

which, to the first order in $1/S$, is the result obtained by Kubo[12] in his "second approximation" of the spin-wave theory.

Some further results, which are of considerable interest and comparatively simple to calculate, are the values of the correlation functions (4.15) to (4.18) at the Néel temperature. Since there is no long-range order at $T_N$, the $x$, $y$, and $z$ correlation functions must be equal, and an estimate of any one of them will give a general measure of the short-range order which exists at the Néel point.

First let us consider the case where spins $S_g$ and $S_j$ are on opposite sublattices. As $T\to T_N$ from below, $\bar{S}\to 0$ and, from (4.18)

$$\langle S_g^{y_1}S_j^{y_2}\rangle\to kT_N\left\langle\frac{\lambda_1\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]}{(\mu')^2-\lambda_1^2}\right\rangle_{\mathbf{K}}. \tag{4.36}$$

For the case when no external field is present $\mu'$ and $\lambda_1$ go over to $\mu$ and $\lambda$, as given in Sec. 2, and $T_N$ is given by (2.26). We may, therefore, write

$$\langle S_g^{y_1}S_j^{y_2}\rangle_{T_N}\left\langle\frac{\mu}{\mu^2-\lambda^2}\right\rangle_{\mathbf{K}} =\frac{S(S+1)}{3}\left\langle\frac{\lambda\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]}{\mu^2-\lambda^2}\right\rangle_{\mathbf{K}}. \tag{4.37}$$

In an exactly similar way [but using (4.16) in place of (4.18)] we find, for the case where $j$ and $g$ are on the

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[20] J. Kanamori and M. Tachiki, J. Phys. Soc. Japan **17**, 1384 (1962).

same sublattice

$$\langle S_g^{y_1} S_j^{y_1}\rangle_{T_N}\left\langle\frac{\mu}{\mu^2-\lambda^2}\right\rangle_{\mathrm{K}}$$

$$=\frac{S(S+1)}{3}\left\langle\frac{\mu\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]}{\mu^2-\lambda^2}\right\rangle_{\mathrm{K}}. \quad (4.38)$$

In particular, putting $j-g=0$ gives the well-known result

$$\langle (S^y)^2\rangle_{T_N}=S(S+1)/3. \quad (4.39)$$

Applying (4.37) to the (single-exchange parameter) simple cubic lattice, for the case where $j$ and $g$ are nearest neighbors, we have

$$\langle S_g^{y_1} S_j^{y_2}\rangle_{T_N}=\frac{S(S+1)}{27}\frac{\langle\gamma_{\mathrm{K}}^2/(1-\gamma_{\mathrm{K}}^2/9)\rangle_{\mathrm{K}}}{\langle 1/(1-\gamma_{\mathrm{K}}^2/9)\rangle_{\mathrm{K}}}, \quad (4.40)$$

which computes to $0.113S(S+1)$.

### B. Temperatures Above the Néel Point

For temperatures $T\geq T_N$ there is no long-range order and we must, therefore, have $\chi_\perp=\chi_{\shortparallel}$ for these cases. That we do regenerate exactly the results of Sec. 3B by using the equations of the present section is easily demonstrated.

Above the Néel temperature we have $\varphi=\frac{1}{2}\pi$, and the Eqs. (4.10) to (4.12) and (4.19) to (4.21) reduce to $A_1=A_2=1$, and $\psi_i=E_i\bar{S}/2kT$ $(i=1,2)$, where

$$E_1=\mu_1+\mu_2+\lambda+g\mu_BH/\bar{S}, \quad (4.40)$$

$$E_2=\mu_1+\mu_2-\lambda+g\mu_BH/\bar{S}, \quad (4.41)$$

with $\mu_1$, $\mu_2$, and $\lambda$ defined as in Sec. 3.

Let us rewrite $\bar{S}$ as $\delta\bar{S}$ (for $T>T_N$) to conform with the notation of Sec. 3. From (4.15) and (4.16) we have

$$\langle (S^{x_1})^2\rangle=\langle (S^{y_1})^2\rangle$$
$$=\tfrac{1}{4}\bar{S}\langle\coth(E_1\delta\bar{S}/2kT)+\coth(E_2\delta\bar{S}/2kT)\rangle_{\mathrm{K}}. \quad (4.42)$$

Since, for $T>T_N$, $\langle (S^{x_1})^2\rangle=\langle (S^{y_1})^2\rangle=S(S+1)/3$, we have

$$4S(S+1)/3\delta\bar{S}=\langle\coth(E_1\delta\bar{S}/2kT)$$
$$+\coth(E_2\delta\bar{S}/2kT)\rangle_{\mathrm{K}}, \quad (4.43)$$

which may be rewritten in the form

$$2S(S+1)/3\delta\bar{S}=\left\langle\frac{\sinh(\alpha)}{\cosh(\alpha)-\cosh(\beta)}\right\rangle_{\mathrm{K}}, \quad (4.44)$$

where

$$\alpha=(1/kT)[g\mu_BH+\delta\bar{S}(\mu_1+\mu_2)], \quad (4.45)$$

$$\beta=(1/kT)\lambda\delta\bar{S}, \quad (4.46)$$

which is Eq. (3.34) of Sec. 3B.

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### APPENDIX

In this appendix we consider the fcc antiferromagnetic type 3 order for the case of nearest-neighbor ($J_1$) and next-nearest-neighbor ($J_2$) exchange only. This type of order may be divided into four ferromagnetic translationally invariant sublattices ($a,b,c,d$) as shown in Fig. 3.

Consider the Green function transform

$$\langle\langle S_g^+;\, f(S_h^z)S_h^-\rangle\rangle_E$$

which is discussed in Sec. 2. We shall choose $S_h$ to be on the "$a$" sublattice. We define Fourier transforms $G_{i\mathrm{K}}(i=1,2,3,4)$ with respect to the reciprocal sublattices in the form

$$\langle\langle S_g^+;\, f(S_h^z)S_h^-\rangle\rangle_E=(4/N)\sum_{\mathrm{K}} G_{1\mathrm{K}}\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})], \quad \text{(A1)}$$

$$G_{1\mathrm{K}}=\sum_{g-h}\langle\langle S_g^+;\, f(S_h^z)S_h^-\rangle\rangle_E\exp[-i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})],$$

for the case where $S_g$ is on the "$a$" sublattice, together with exactly equivalent equations for $G_{2\mathrm{K}}$, $G_{3\mathrm{K}}$, $G_{4\mathrm{K}}$ for the cases where $S_g$ is on the "$b$," "$c$," and "$d$" sublattices, respectively ($\sum_{\mathrm{K}}$ runs over $\frac{1}{4}N$ values in the first Brillouin zone of a reciprocal sublattice). The decoupled equation of motion (2.8) for the Green function may be expressed in terms of $G_{i\mathrm{K}}$, when we obtain

$$\begin{bmatrix} E-\alpha' & -\beta' & -\gamma' & -\delta' \\ \beta' & E+\alpha' & \delta' & \gamma' \\ -\delta' & -\gamma' & E-\alpha' & -\beta' \\ \gamma' & \delta' & \beta' & E+\alpha' \end{bmatrix}\begin{bmatrix} G_{1\mathrm{K}} \\ G_{2\mathrm{K}} \\ G_{3\mathrm{K}} \\ G_{4\mathrm{K}} \end{bmatrix}=\begin{bmatrix} F/2\pi \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad \text{(A2)}$$

where $F$ is as defined in (2.6), where

$$\alpha'=\alpha\bar{S}=[8J_1-12J_2+8J_2(c_1^2+c_3^2)]\bar{S}, \quad \text{(A3)}$$

$$\beta'=\beta\bar{S}=[8J_1c_1c_3-4J_2+8J_2c_2^2]\bar{S}, \quad \text{(A4)}$$

$$\gamma'=\gamma\bar{S}=4J_1[c_1e^{-iK_ya}+c_3e^{iK_ya}]\bar{S}, \quad \text{(A5)}$$

$$\delta'=\delta\bar{S}=4J_1[c_1e^{iK_ya}+c_3e^{-iK_ya}]\bar{S}, \quad \text{(A6)}$$

with $c_i$ defined by (2.32), and where we have written the average spins on the "$a$" and "$c$" lattices equal to $\bar{S}$ and those on the "$b$" and "$d$" lattices equal to $-\bar{S}$.

Solving (A2) for $G_{1\mathrm{K}}$ we extract the correlation function $\langle f(S_h^z)S_h^-S_h^+\rangle$ by use of (2.3), (2.17), and (A1) when we find

$$\langle f(S_h^z)S_h^-S_h^+\rangle=\frac{F}{4}\left\langle\frac{\alpha-A}{E_1}\coth\left(\frac{E_1\bar{S}}{2kT}\right)\right.$$
$$\left.+\frac{\alpha+A}{E_2}\coth\left(\frac{E_2\bar{S}}{2kT}\right)-2\right\rangle_{\mathrm{K}}, \quad \text{(A7)}$$

where

$$A=[2\alpha\gamma\delta-\beta(\gamma^2+\delta^2)]/\Delta^{1/2}, \tag{A8}$$

$$E_1{}^2=\alpha^2-\beta^2-\Delta^{1/2}, \tag{A9}$$

$$E_2{}^2=\alpha^2-\beta^2+\Delta^{1/2}, \tag{A10}$$

$$\Delta=(\gamma^2-\delta^2)^2-4\alpha\beta(\gamma^2+\delta^2)+4\gamma\delta(\alpha^2+\beta^2). \tag{A11}$$

Putting $f(S_h{}^z)=1$, Eq. (A7) yields

$$S(S+1)-\langle(S^z)^2\rangle=\tfrac{1}{2}\bar{S}\left\langle\frac{\alpha-A}{E_1}\coth\left(\frac{E_1\bar{S}}{2kT}\right)+\frac{\alpha+A}{E_2}\coth\left(\frac{E_2\bar{S}}{2kT}\right)\right\rangle_{\mathrm{K}}. \tag{A12}$$

Near $T_N$, $\langle(S^z)^2\rangle=S(S+1)/3$, and $\bar{S}\rightarrow 0$. We write, therefore,

$$2S(S+1)/3=kT_N\langle(\alpha-A)/E_1{}^2+(\alpha+A)/E_2{}^2\rangle_{\mathrm{K}}, \tag{A13}$$

which in terms of $\alpha$, $\beta$, $\gamma$, $\delta$ is

$$\frac{S(S+1)}{3kT_N}=\left\langle\frac{\alpha(\alpha^2-\beta^2)+\beta(\gamma^2+\delta^2)-2\alpha\gamma\delta}{[(\alpha+\beta)^2-(\gamma+\delta)^2][(\alpha-\beta)^2+(\gamma-\delta)^2]}\right\rangle_{\mathrm{K}}. \tag{A14}$$

Using Eqs. (A3) to (A6), we have evaluated $T_N$ by computer and the results are shown in Fig. 2.

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# Paramagnetic Resonance of *S*-State Ions in Metals of High Paramagnetic Susceptibility

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The paramagnetic resonance of $Gd^{3+}$ in metals shows $g$ shifts with respect to the free ionic $g$ value which are due to the valence-electron polarization in metallic hosts, and the effective exchange interaction of $Gd^{3+}$ with these valence electrons. These shifts have been studied in metals and intermetallic compounds with high paramagnetic susceptibility such as Pd, $Ni_5Y$, and $Pd_3U$ and in many alloys involving these metals and compounds. The effective exchange interaction is found to be generally much smaller than expected from the atomic spectra. It is negative for valence bands of $d$ character and positive in valence bands of $5f$ and $s$ character, and is therefore not the result of simple atomic exchange only. The shape of the Gd resonance lines gives information on the spatial variations in the valence-electron polarization of the host metals. Thus, it was found that Pd alloyed with La or H segregates into two phases. The valence-electron polarization can be altered by admixture of other magnetic ions, and it was therefore possible to measure the exchange interaction for many rare earths and Fe, Co, Ni in Pd, and some rare earths in $Ni_5Y$. The Gd line shape in these experiments allowed a study of the nonlocal character of the valence-electron susceptibility, and it appears that in Pd and in $Ni_5Y$ this susceptibility has a larger range than predicted by the free-electron calculation of Ruderman-Kittel-Yosida.

## I. INTRODUCTION

In a previous article, we have described the electron paramagnetic resonance (EPR) of $GdAl_2$ and of dilute alloys of Gd in the Pd series.[1] The present paper is a continuation of this work. The technique previously described is exploited and expanded to study the coupling between valence electrons and magnetic ions in several classes of alloys. At the same time we studied the variation of the induced valence-electron polarization, from the macroscopic down to the atomic scale. It is found that the explanation of the valence-electron polarization as due to direct ion-valence-electron exchange processes only[2] has to be abandoned. Also, it appears that the spatial variation of the valence-electron polarization is, in several cases, of a different nature than the one predicted by the theory of the susceptibility of a free-electron gas.[3,4]

The EPR spectra observed were due to ions in the $S$ state ($Gd^{3+}$, and Mn in a not quite understood valence state) and consisted of a single resonance line, of about 500 G half-half-width. The $g$ value of this

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