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Sensitivity of Curie Temperature to Crystal-Field Anisotropy. I. Theory

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This paper discusses the statistical mechanics of ferromagnetic and antiferromagnetic systems in the presence of uniaxial anisotropy, which is included both as anisotropic exchange $D_{ij}S_i^zS_j^z$ and in the form of single-ion crystal-field terms $D_0(S_i^z)^2$. Emphasis is given to the calculation of magnetic transition temperatures T_N and particularly to a discussion of the sensitivity of T_N to crystal-field anisotropy. Earlier efforts in this direction have produced widely varying results, some Green's-function calculations predicting a sensitivity fully ten times the equivalent molecular-field result. A Green's-function theory is developed for which the decoupling of anisotropy terms is carried out in a manner which is essentially consistent with the random-phase decoupling of exchange terms, at least in the limit of small anisotropy. As such, the theory is an improvement on earlier decoupling schemes and allows, in particular, for a value of $\langle(S^z)^2\rangle$ at T_N, which differs from the isotropic result $\frac{1}{3}S(S+1)$. It indicates a sensitivity of T_N to D_0 which is smaller than suggested by earlier Green's-function theories but still considerably larger than given by molecular-field theory. Quantitative calculations are carried out for simple cubic and body-centered cubic lattices and the detailed results for the different theories are compared. In Paper II the theory is applied to the salt FeF$_2$ for which the spin Hamiltonian contains a sizeable crystal-field anisotropy of the form $D_0(S_i^z)^2$.

1. INTRODUCTION

In this paper we discuss the statistical mechanics of simple ferromagnets and antiferromagnets in the presence of uniaxial anisotropy, with special emphasis on the sensitivity of magnetic transition temperatures T_N to crystal-field anisotropy. The uniaxial anisotropy is included both as anisotropic exchange $D_{ij}S_i^zS_j^z$ and in the form of crystal-field single-spin terms $D_0(S_i^z)^2$. The former terms can be accommodated in most of the well-tried statistical theories of magnetism without difficulty, and the extension of these theories to include such terms is readily accomplished. Crystal-field terms, on the other hand, are generally much more difficult to treat, except in the limit of very high or very low temperatures for which cases high-temperature expansion methods[1] and simple spin-wave approximations[2] can be used, respectively.

The present paper is concerned primarily with finding a statistical approximation which is able to describe the magnetic properties of ordered ferromagnets and antiferromagnets in the presence of crystal-field anisotropy for temperatures right up to T_N. Earlier efforts in this direction have been made using molecular-field theory,[3,4] cluster approximations,[5] and Green's-function methods[6,7] and with very widely varying results. For example, we shall show that the Green's-function method used by Narath[6] predicts a sensitivity of T_N to crystal-field anisotropy which is about ten times greater than that which is obtained from a molecular-field calculation.

In this paper we have used a Green's-function approach which decouples the exchange terms according to the random-phase approximation (RPA) and which allows us to formulate the theory in a manner sufficiently general to allow for a wide range of possible spin patterns. The entire problem centers around the manner in which the crystal-field anisotropy terms enter the theory and this, in turn, reduces to the problem of adequately decoupling the associated "anisotropy Green's function." We have devised a procedure which is essentially consistent with the random-phase decoupling of the exchange terms, at least for the limit of small anisotropy. This decoupling scheme reduces to that used by Anderson and Callen[7] in the low-temperature limit but it differs quite basically from the latter at higher temperatures. It removes, in particular, a deficiency of the Anderson-Callen decoupling approximation which results in the estimate for the ensemble average $\langle(S^z)^2\rangle$ at the transition temperature being always equal to the isotropic result $S(S+1)/3$.

In general, however, our numerical calculations for the sensitivity of transition temperature to crystal-field anisotropy do not differ widely from those which follow from the decoupling scheme proposed by Anderson and Callen.[7] They do differ very markedly though from molecular-field estimates and also from results obtained using the Green's-function decoupling scheme employed by Narath.[6] It would seem likely that molecular-field theory underestimates this sensitivity whereas the Narath approach seriously overestimates it. The claim in Ref. 6 that the decoupling approximation of that paper is adequate for $D_0 \ll kT_N$ is not correct. The Narath decoupling also fails by predicting spurious anisotropy effects for spin $\frac{1}{2}$ for which case $(S^z)^2=\frac{1}{4}$ and the pertinent crystal-field anisotropy vanishes.

In Sec. 2 we generate relevant molecular-field results which are used at a later stage for comparison with the estimates from the various Green's-function theories. Section 3 constructs the basic Green's-function equa-

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tions and Sec. 4 develops the decoupling scheme to be used for the crystal-field anisotropy terms. In Sec. 5 we derive an expression for the transition temperature T_N and compute the sensitivity of T_N to D_0 for simple cubic and body-centered cubic ferromagnets and antiferromagnets for values of spin $S=1$ and $S=\infty$. These results are compared with estimates from molecular-field theory and from the Green's-function approximations of Refs. 6 and 7.

Finally, in Sec. 6, we discuss the difficulties which are encountered by all the Green's-function approximations when an attempt is made to extend the results into the region for which anisotropy is large.

2. MOLECULAR-FIELD THEORY

Consider a Hamiltonian of the form

$$\mathcal{H}=\sum_{\langle i,j\rangle}[J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j+D_{ij}S_i^zS_j^z]-\sum_i D_0(S_i^z)^2, \tag{2.1}$$

where $\sum_{\langle i,j\rangle}$ runs over all pairs of spin S_i and S_j, and where $\sum_i$ runs over all spins in the lattice. In this Hamiltonian we include anisotropy with axial symmetry, and allow both for single-spin crystal-field terms and for two-spin exchange anisotropy terms. The isotropic exchange parameters J_{ij} need not be restricted as to range or sign, but we shall assume that the anisotropy is such that it gives rise to an ordered state with a single preferred axis z of spin alignment. The ordered state will be taken to be antiferromagnetic although the results for a ferromagnetic lattice are included as a particular case.

We obtain the molecular-field Hamiltonian for a spin S_i by replacing the various functions of all spins $S_j\neq S_i$ by their average values, thus neglecting all correlations between the spins. That part of the Hamiltonian containing S_i then becomes

$$\mathcal{H}_i=\sum_j (J_{ij}+D_{ij})S_i^z\langle S_j^z\rangle-D_0(S_i^z)^2, \tag{2.2}$$

where the z axis has been singled out as the direction of spin alignment in the ordered state, and where we have replaced spins S_j by their average values $\langle S_j^z\rangle$. The Hamiltonian (2.2) is already in diagonal form with eigenvalues

$$E_i=\sum_j (J_{ij}+D_{ij})m\langle S_j^z\rangle-D_0m^2, \tag{2.3}$$

where m and m^2 are, respectively, the eigenvalues of S_i^z and $(S_i^z)^2$.

We now introduce two sublattices; an "up" sublattice which includes the spin S_i, and a "down" sublattice. Writing the average value of spin equal to $+\bar{S}$ on the "up" sublattice and equal to $-\bar{S}$ on the "down" sublattice, we may calculate the ensemble average $\langle S_i^z\rangle$ in the form

$$\langle S_i^z\rangle=\bar{S}=\frac{\sum m\exp[Xm+D_0m^2]/kT}{\sum\exp[Xm+D_0m^2]/kT}, \tag{2.4}$$

where the summations run over all allowed values of m between $-S$ and $+S$, and where

$$X=\sum_j^d (J_{ij}+D_{ij})\bar{S}-\sum_j^s (J_{ij}+D_{ij})\bar{S}, \tag{2.5}$$

where $\sum_j{}^d$ runs only over those values j for which S_i and S_j are on different sublattices, and where $\sum_j{}^s$ runs only over values j for which S_i and S_j are on the same sublattice. Equation (2.4) is now an implicit relationship for $\bar{S}$ which can be solved numerically for any specific case of interest.

The transition temperature T_N is derived from (2.4) by considering the limit $\bar{S}\to 0$. Expanding the exponentials $e^{Xm/kT}$ and retaining only the lowest-order nonzero terms, we find

$$kT_N=\Big[\sum_j^d (J_{ij}+D_{ij})-\sum_j^s (J_{ij}+D_{ij})\Big]F(kT_N), \tag{2.6}$$

where

$$F(kT_N)=\frac{\sum_m m^2\exp[D_0m^2/kT_N]}{\sum_m \exp[D_0m^2/kT_N]}. \tag{2.7}$$

We see that in this approximation the exchange anisotropy terms behave simply as extra contributions to the isotropic exchange. Thus, for example, the shape of sublattice magnetization curves as functions of temperature will be unaffected in the molecular-field approximation by the presence of such terms. The crystal-field D_0 terms are more interesting. They do affect the magnetization curve shapes (see, for example, Honma[8]) although it is likely that the molecular-field theory does not give a very quantitative estimate of the magnitude of the effect.

In the present discussion we shall concentrate primarily on the transition temperature and its dependence upon the single spin anisotropy. Using Eqs. (2.6) and (2.7) we may write

$$T_N(D_0)=\frac{3F(kT_N)}{S(S+1)}T_N(0), \tag{2.8}$$

where $T_N(D_0)$ is the transition temperature in the presence of crystal-field terms, $\sum_i D_0(S_i^z)^2$, and where $T_N(0)$ refers to the situation with $D_0=0$. The result (2.8) remains valid for nonzero values of D_{ij}. It is also interesting to note that $F(kT_N)$ is just the average value of $(S^z)^2$ at the transition temperature so that (2.8) can also be written in the form

$$T_N(D_0)/T_N(0)=3\langle(S^z)^2\rangle_{T_N}/S(S+1). \tag{2.9}$$

In the limit of very large single spin anisotropy, S^z is effectively restricted to take only the values $\pm S$ so that $(S^z)^2\to S^2$ for all except extremes of high temperature. In particular, $\langle(S^z)^2\rangle_{T_N}\to S^2$ and

$$T_N(D_0)/T_N(0)\to 3S/(S+1),\quad D_0\to\infty. \tag{2.10}$$

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[8] A. Honma, J. Phys. Soc. Japan **15**, 456 (1960).

We verify throughout that the case for spin-$\frac{1}{2}$ is indeed trivial so that the simplest case of interest is that for spin $S=1$. We shall calculate the variation of transition temperature with crystal-field anisotropy in detail below for the case $S=1$ and $S=\infty$.

Let us consider simple cubic (sc) and body-centered cubic (bcc) lattices for which the anisotropic exchange D_{ij} is zero, and for which we have only a single isotropic exchange parameter J (for nearest-neighbor interactions). The Hamiltonian of interest is then

$$\mathcal{H}=\sum_{nn} J\mathbf{S}_i\cdot\mathbf{S}_j-\sum_i D_0(S_i^z)^2, \tag{2.11}$$

where $\sum_{nn}$ is a sum over all nearest-neighbor pairs. The results throughout this paper are valid both for ferromagnetism and for antiferromagnetism so that we can take J to be of either sign. Using Eqs. (2.7) and (2.8) we may calculate the ratio $T_N(D_0)/T_N(0)$ as a function of D_0/J for the sc and the bcc cases. The molecular-field results for spin-one and spin-infinity are included in the figures of Sec. 5 and 6 (Figs. 3 to 8), where they may be compared with the results of the Green's-function calculations below.

3. GREEN'S-FUNCTION EQUATIONS

Green's-function techniques were initially applied to statistical problems in ferromagnetism by Bogolyubov and Tyablikov.[9,10] The method has since been developed by a large number of authors for use in ferromagnetism (see, for example, Tahir-Kheli and ter Haar,[11] Callen,[12] and Tahir-Kheli[13]), antiferromagnetism,[7,14] and ferrimagnetism.[15]

We define a temperature-dependent Green's function by the equation

$$\langle\langle A(t);B\rangle\rangle=-i\theta(t)\langle[A(t),B]\rangle, \tag{3.1}$$

where the square brackets denote a commutator, the single pointed brackets denote an average with respect to the canonical density operator $\exp[-\mathcal{H}/kT]$, and where $\theta(t)$ is the unit step function (zero for negative argument and unity for positive argument). If we denote the Fourier transform of the Green's function with respect to time by $\langle\langle A;B\rangle\rangle$, then the equation of motion satisfied by this function is

$$E\langle\langle A;B\rangle\rangle=(1/2\pi)\langle[A,B]\rangle+\langle\langle[A,\mathcal{H}];B\rangle\rangle. \tag{3.2}$$

Knowledge of $\langle\langle A;B\rangle\rangle$ is sufficient to determine the correlation function $\langle BA(t)\rangle$ through the equation (see, Zubarev[16] for details)

$$\langle BA(t)\rangle=\lim_{\epsilon\to+0} i\int_{-\infty}^{\infty}\frac{\langle\langle A;B\rangle\rangle_{E=\omega+i\epsilon}-\langle\langle A;B\rangle\rangle_{E=\omega-i\epsilon}}{e^{\omega/kT}-1}\times e^{-i\omega t}d\omega. \tag{3.3}$$

We shall consider the Hamiltonian (2.1) for which the anisotropy is such that it gives rise to a single axis spin pattern in the ordered state. Let us examine the motion of the function $\langle\langle S_g^+;f(S_h^z)S_h^-\rangle\rangle$—which we write for economy of notation in the form $\langle\langle S_g^+;B_h\rangle\rangle$—where $f(S_h^z)$ is, for the moment, an arbitrary function of S^z at the site h. The resulting equation of motion is

$$\begin{aligned}E\langle\langle S_g^+;B_h\rangle\rangle=(F/2\pi)\delta_{gh}+D_0\langle\langle S_g^+S_g^z+S_g^zS_g^+;B_h\rangle\rangle\\+\sum_{j-g}[J_{jg}\langle\langle S_j^+S_g^z-S_g^+S_j^z;B_h\rangle\rangle\\-D_{jg}\langle\langle S_j^zS_g^+;B_h\rangle\rangle],\end{aligned} \tag{3.4}$$

where

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

and where $J_{jj}=D_{jj}=0$. This equation is exact, and the various approximations used for Green's-function calculations occur in the relationships assumed to exist between the more complex Green's functions on the right-hand side of (3.4) and our basic function of interest $\langle\langle S_g^+;B_h\rangle\rangle$. Algebraically the simplest decoupling scheme is the random-phase approximation (RPA), see for example Tyablikov,[10] Tahir-Kheli and ter Haar,[11] and Lines[14] which, although possessing certain well-known limitations, does give a generally acceptable description of Heisenberg ferromagnetic and antiferromagnetic systems over the entire temperature range. It has the further advantage, over most more sophisticated decoupling procedures, of remaining a tractable formalism in the presence of exchange interactions between more than one type of near neighbor.

The RPA approximation proceeds by making the decoupling

$$\begin{aligned}\langle\langle S_g^zS_j^+;B_h\rangle\rangle=\langle S_g^z\rangle\langle\langle S_j^+;B_h\rangle\rangle,\\\langle\langle S_g^+S_j^z;B_h\rangle\rangle=\langle S_j^z\rangle\langle\langle S_g^+;B_h\rangle\rangle,\end{aligned} \tag{3.6}$$

which, by use of (3.3) for $t=0$, implies relationships of the form

$$\langle f(S_h^z)S_h^-S_g^zS_j^+\rangle=\langle S_g^z\rangle\langle f(S_h^z)S_h^-S_j^+\rangle. \tag{3.7}$$

In general, this approximation represents the neglect of certain correlations between S_g^z and the rest of the lattice. There is one important exception, however, which is for $h=g=j$. In this case, the approximation (3.7) is a statement concerning the spin averages on a single site.

For the Heisenberg Hamiltonian, the coefficient of terms with $g=j$ is zero so that the RPA approximation

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for this case cannot include terms with $h=g=j$, and the total approximation concerns the neglect of certain inter-spin correlations. Inclusion of single-ion crystal-field anisotropy terms, however, changes the situation and raises the problem of decoupling terms for which $g=j$.

In principle, the best procedure is probably to write down the equation of motion for the function $\langle\langle S_g^+S_g^z+S_g^zS_g^+;B_h\rangle\rangle$ of Eq. (3.4) and to decouple in the spirit of the RPA approximation at a later stage. In practice, this approach introduces severe complications and one is tempted to look for an acceptable decoupling of the form

$$\langle\langle S_g^+S_g^z+S_g^zS_g^+;B_h\rangle\rangle=\Phi_g\langle\langle S_g^+;B_h\rangle\rangle, \qquad (3.8)$$

where Φ_g is independent of E (but not necessarily independent of B or of $g-h$).

We shall reserve the term "random-phase approximation" for the decoupling (3.6) when it excludes the case $j=g$. With such a restriction, we shall show that a function Φ_g can be derived which is consistent with the RPA approximation for the limit of small anisotropy. This function Φ_g is not equal to $2\langle S_g^z\rangle$, which is the result obtained by applying Eq. (3.6) for the case $j=g$ (and is the decoupling formula used by Narath[6]), nor is it equal to the function proposed by Anderson and Callen[7] except in the limit of very low temperature.

Setting aside for the moment the discussion concerning the most acceptable form for Φ_g, and using the decoupling approximations of (3.6) and (3.8), the equation of motion (3.4) becomes

$$\begin{aligned}(E-D_0\Phi_g)\langle\langle S_g^+;B_h\rangle\rangle=(F\delta_{gh}/2\pi)&\\ +\sum_{j-g}\{J_{jg}\langle S_g^z\rangle\langle\langle S_j^+;B_h\rangle\rangle&\\ -(J_{jg}+D_{jg})\langle S_j^z\rangle\langle\langle S_g^+;B_h\rangle\rangle\}.&\qquad (3.9)\end{aligned}$$

We now restrict the possible order to one with a unique axis of spin alignment z and split the lattice into two sublattices, the "up" and the "down" sublattices, with average values of spin per site $+\bar{S}$ and $-\bar{S}$, respectively. If the two sublattices are translationally invariant we may Fourier transform with respect to the recpirocal sublattices as follows. When g and h are on the same sublattice we define $G_{1\mathbf{K}}$ by

$$\langle\langle S_g^+;B_h\rangle\rangle=(2/N)\sum_{\mathbf{K}}G_{1\mathbf{K}}\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})], \qquad (3.10)$$

where N is the 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 the same way we define $G_{2\mathbf{K}}$ for the case when g and h are on opposite sublattices. We now write $\Phi_g=2\langle S_g^z\rangle\Gamma$, where Γ is an as yet undetermined function of temperature and of B, but which is independent of $g-h$ (justification for this step is developed in the following section). Choosing h to be on the "up" sublattice, we now find equations of motion of the form

$$\begin{aligned}(E-\mu\bar{S})G_{1\mathbf{K}}&=(F/2\pi)+\lambda\bar{S}G_{2\mathbf{K}},\\ (E+\mu\bar{S})G_{2\mathbf{K}}&=-\lambda\bar{S}G_{1\mathbf{K}},\end{aligned} \qquad (3.11)$$

where

$$\begin{aligned}\mu=\sum_{j-g}^{s}\{J_{jg}[\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})]-1]-D_{jg}\}&\\ +\sum_{j-g}^{d}[J_{jg}+D_{jg}]+2\Gamma D_0,&\qquad (3.12)\end{aligned}$$

$$\lambda=\sum_{j-g}^{d}J_{jg}\exp[i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})], \qquad (3.13)$$

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 the Green's-function equations of motion for $G_{1\mathbf{K}}$ and using (3.3) and (3.10) we find, for the limit $t\rightarrow 0$

$$\begin{aligned}\langle B_hS_g^+\rangle=(F/N)\sum_{\mathbf{K}}[A\coth(E_0\bar{S}/2kT)-1]&\\ \times\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})],&\qquad (3.14)\end{aligned}$$

where

$$A=\mu/(\mu^2-\lambda^2)^{1/2}, \qquad (3.15)$$

$$E_0=(\mu^2-\lambda^2)^{1/2}, \qquad (3.16)$$

and where $B_h=f(S_h^z)S_h^-$. Later it will be convenient for us to choose $f(S_h^z)=(S_h^z)^n$ with n a non-negative integer.

4. THE DECOUPLING SCHEME

From the decoupling equation (3.8) we find, using (3.3), the equation

$$\langle B_h(S_g^+S_g^z+S_g^zS_g^+)\rangle=\Phi_g\langle B_hS_h^+\rangle, \qquad (4.1)$$

which relates Φ_g to ensemble averages, and allows the crystal-field decoupling parameter to be chosen (at least in principle) in a manner consistent with the exchange decoupling. Consider, in particular, the case $B_h=S_h^-$[i.e., $f(S_h)=1,\ \ n=0$]. For this case the left-hand side of (4.1) can be written $\langle S_h^-S_g^+(2S_g^z+1)\rangle$ and is readily evaluated in the limit $D_0\rightarrow 0$ by considering the Green's function $\langle\langle S_h^-;B_g\rangle\rangle$, where $B_g=S_g^+(2S_g^z+1)$, and by decoupling the exchange terms using the RPA approximation. We find

$$\begin{aligned}\langle S_h^-B_g\rangle=(1/N)\langle[S_g^-,B_g]\rangle\sum_{\mathbf{K}}[1-A\coth(E_0\bar{S}/2kT)]&\\ \times\exp[i\mathbf{K}\cdot(\mathbf{g}-\mathbf{h})],&\qquad (4.2)\end{aligned}$$

where A and E_0 are defined in (3.15) and (3.16). Putting B_g in turn equal to $S_g^+(2S_g^z+1)$ and to S_g^+, and eliminating the summation over $\mathbf{K}$ between the resulting two equations, we have

$$\begin{aligned}\langle S_h^-S_g^+(2S_g^z+1)\rangle\langle[S_g^-,S_g^+]\rangle&\\ =\langle S_h^-S_g^+\rangle\langle[S_g^-,S_g^+(2S_g^z+1)]\rangle.&\qquad (4.3)\end{aligned}$$

It follows immediately that

$$\Phi_g = \langle [S_g^-, S_g^+(2S_g^z+1)] \rangle / \langle [S_g^-, S_g^+] \rangle , \qquad (4.4)$$

from which, using the familiar commutation relationships for spin components, we have

$$\Phi_g = \langle S_g^z \rangle \frac{\langle 3(S_g^z)^2 - S(S+1) \rangle}{(\bar{S})^2} , \qquad (4.5)$$

and

$$\Gamma = \langle 3(S^z)^2 - S(S+1) \rangle / 2(\bar{S})^2 , \qquad (4.6)$$

which is independent of lattice site (i.e., of $g-h$).

This result applies strictly only to the decoupling for the case $B_h = S_h^-$, for which the corresponding equation (3.14) relates $\langle S^{(z)2} \rangle$ to $\bar{S}$. It enables us to express the transition temperature in terms of the value of $\langle (S^z)^2 \rangle$ at T_N [see Eq. (5.5)], but it completely determines the problem only for the case of spin $\frac{1}{2}$. For this case, moreover, the anisotropy problem is trivial since $(S^z)^2 = \frac{1}{4}$. This fact is reflected in (4.6) for which we find $\Gamma = 0$ for $S = \frac{1}{2}$.

In principle, no doubt, a similar argument could be used to derive the decoupling factors for more complicated forms of B_h. In practice, this procedure is prohibitively difficult and we choose a simpler method of approach. Putting $f(S_h^z) = (S_h^z)^n$, where $n = 0, 1, 2, \cdots$, we write

$$\begin{aligned} \langle\langle S_g^+ S_g^z + S_g^z S_g^+ ; (S_h^z)^n S_h^- \rangle\rangle &= \langle (S_h^z)^{n-\sigma} \rangle \\ &\quad \times \langle\langle S_g^+ S_g^z + S_g^z S_g^+ ; (S_h^z)^\sigma S_h^- \rangle\rangle , \qquad (4.7) \\ \langle\langle S_g^+ ; (S_h^z)^n S_h^- \rangle\rangle &= \langle (S_h^z)^{n-\sigma} \rangle \\ &\quad \times \langle\langle S_g^+ ; (S_h^z)^\sigma S_h^- \rangle\rangle , \end{aligned}$$

where $\sigma = 0$ for even n and where $\sigma = 1$ for odd n. This, decoupling implies approximations of the form $\langle (S^z)^{2n+2} \rangle = \langle (S^z)^{2n} \rangle \langle (S^z)^2 \rangle$ and $\langle (S^z)^{2n+1} \rangle = \langle (S^z)^{2n} \rangle \langle (S^z) \rangle$, and is always qualitatively sound. We avoid, in particular, approximations of the form $\langle (S^z)^{2n+2} \rangle = \langle (S^z)^{2n+1} \rangle \langle (S^z) \rangle$ which break down completely as $T \to T_N$ and which spell disaster for simple decoupling schemes such as that used for crystal-field terms in Ref. 6.

From (4.7) it follows that the decoupling parameter Γ of Eq. (4.6) is good for all even values of n [where $B_h = (S_h^z)^n S_h^-$]. It also follows that all the "odd-n" equations of the form (4.1) decouple in the same way but that the "odd-n" decoupling will probably differ from the "even-n" decoupling. It remains to find the "odd-n" decoupling parameter $\Phi_g = \Phi_g'$ for which

$$\langle\langle S_g^+ S_g^z + S_g^z S_g^+ ; S_h^z S_h^- \rangle\rangle = \Phi_g' \langle\langle S_g^+ ; S_h^z S_h^- \rangle\rangle . \qquad (4.8)$$

In order to evaluate T_N it is only necessary to use the equations for $n = 0, 1$, so that, for this task, the above approximations are not necessary. However, higher-order equations are required for any detailed description of $\bar{S}$ as a function of temperature for all $S \geq \frac{3}{2}$ and a decoupling recipe is therefore necessary for the more general problem.

Calculation of Φ_g' by a method analogous to that used for Φ_g is not readily accomplished since it requires the examination of a more complex class of Green's function, viz., $\langle\langle S_h^z S_h^- ; B_g \rangle\rangle$, for which adequate decoupling schemes have not yet been obtained. However, the theory of Sec. 3 requires only that Φ_g' can be written in the form $2\langle S_g^z \rangle \Gamma'$, where Γ' is independent of $g-h$. We may verify that this is certainly true for low temperatures since, for all spins except $S = 1$, $S^z S^+ \to S S^+$ and $S^+ S^z \to (S-1) S^+$ for an "up" site, and $S^z S^+ \to -(S-1) S^+$ and $S^+ S^z \to -S S^+$ for a "down" site as $T \to 0$. It follows that $S^+ S^z + S^z S^+$ goes as $(2S-1) S^+$ for an "up" site and as $-(2S-1) S^+$ for a "down" site, giving $\Gamma' = \Gamma = 1 - 1/2S$ in the low-temperature limit in agreement with spin-wave theory and with Anderson-Callen decoupling,[7] but again in disagreement with the decoupling of Ref. 6.

We shall assume Γ' to be independent of $g-h$ at all temperatures although we have not been able to prove it as was done for Γ. A similar assumption is common to both the other anisotropy decoupling schemes,[6,7] but these require also that $\Gamma = \Gamma'$ at all temperatures, a condition which results in the erroneous prediction of zero anisotropy at the transition temperature, i.e., $\langle (S^z)^2 \rangle \to S(S+1)/3$ as $T \to T_N$. The calculation for $\langle (S^z)^2 \rangle$ at T_N depends directly on the assumptions made concerning Φ_g', and since the results obtained in the present paper for the former are essentially in agreement with molecular-field theory, we feel that the assumption made concerning Γ' is to some extent justified a posteriori.

If Γ' is independent of $g-h$, then it follows from (4.8) and (3.3) that

$$\Phi_g' = 2\langle S_g^z \rangle \Gamma' = \langle S_g^z S_g^- (S_g^+ S_g^z + S_g^z S_g^+) \rangle / \langle S_g^z S_g^- S_g^+ \rangle , \qquad (4.9)$$

which is readily expressed as the quotient of two polynomials in $\langle (S_g^z)^n \rangle$, and agrees with the result $\Gamma' \to 1 - 1/2S$ for low temperatures and for all spins except $S = 1$.

In the limit of small anisotropy, we may write the decoupling parameters Γ and Γ' as functions of $\bar{S}$ alone by making use of a theorem due to Callen and Strickman[17] which states that the higher moments $\langle (S^z)^n \rangle$ are related to $\langle S^z \rangle$ in exactly the same way for all theories which use a one-particle density operator of the form $\rho = \exp(xS^z)/\mathrm{Tr}[\exp(xS^z)]$. Our theory is such in the limit of small anisotropy. As pointed out in Ref. 17, this means that we can use simple molecular-field theory to calculate these relationships and, for the case $D_0 \to 0$, will obtain results which are valid for all renormalized collective oscillation theories as well.

We have obtained, therefore, a decoupling recipe which enables us to treat single-ion anisotropy terms at least for the cases when these are small compared with

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[17] H. B. Callen and S. Strickman, Solid State Commun. 3, 5 (1965).

the exchange energy of the system. We shall be interested in particular in calculating the sensitivity of the transition temperature to single-ion anisotropy and this problem will be considered in detail in the following section.

Meanwhile, it is interesting to compare the decoupling obtained in the present work with that proposed by Narath[6] and by Anderson and Callen.[7] The latter authors suggest a decoupling

$$\Gamma=\Gamma'=1-(\alpha/2S^2)[S(S+1)-\langle(S^z)^2\rangle], \qquad (4.10)$$

where $\alpha=1$. The decoupling used by Narath[6] is given by (4.10) with $\alpha=0$. If we relate $\langle(S^z)^2\rangle$ to $\bar{S}$, using the Callen-Strickmann theorem, we may equate the results (4.6) and (4.10) for Γ and calculate α as a function of $\bar{S}$. The result is shown in Fig. 1 where we see that $\alpha=1$ is quite a good approximation, particularly so for smaller values of spin quantum number. In Fig. 2 we show the function Γ [from Eq. (4.6)] as a function of $\bar{S}$.

The situation is very different when we consider Γ'. From (4.9) we calculate

$$\Phi_g'=\frac{\langle 2(S_g^z)^4+3(S_g^z)^3-(2S^2+2S-1)(S_g^z)^2-S(S+1)S_g^z\rangle}{\langle(S_g^z)^3+(S_g^z)^2-S(S+1)S_g^z\rangle}. \qquad (4.11)$$

We find, in particular, that for spin-$\frac{1}{2}$ $\Phi_g'=0$ (as it should), and that for spin-1 $\Phi_g'=-1$. For other values of spin, Φ_g' is temperature-dependent and approaches the value $2S-1$ as $T\to 0$ and remains finite as $\bar{S}\to 0 (T\to T_N)$. The latter feature we find essential if the theory is to predict any anisotropy at T_N. It means that α (and Γ') diverge as $\bar{S}\to 0$. The Anderson-Callen decoupling ($\alpha=1$) is thus unsatisfactory for the "odd-n" equations except for very low temperatures.

The final solution of our problem may now be set out formally as the solution of the set of equations (3.14) for which $B_h=(S_h^z)^n S_h^-$ and for which the parameter Γ of (3.12) is given by Eq. (4.6) [Fig. 2] for the case when n is even, and is put equal to Γ' of Eq. (4.9) for n odd. If we put $h=g$, then the set of equations with $n=0, 1, 2, \cdots, 2S-1$, are independent and may be solved for $\bar{S}$ as a function of temperature in the usual way.[11]

5. THE TRANSITION TEMPERATURE

To calculate the transition temperature T_N requires a knowledge of the decoupling parameters Γ and Γ' as $\bar{S}\to 0$. Let us consider the parameter Γ of Eq. (4.6). For small anisotropy, we may readily evaluate it at T_N by using a one-particle density operator of the form $\rho=\exp(xS^z)/\mathrm{Tr}[\exp(xS^z)]$. Calculating $\bar{S}$ as $\mathrm{Tr}(\rho S^z)$ and $\langle(S^z)^2\rangle$ as $\mathrm{Tr}[\rho(S^z)^2]$ in the limit $x\to 0$, we find

$$\Gamma(T_N)=(3/20)(4S^2+4S-3)/S(S+1). \qquad (5.1)$$

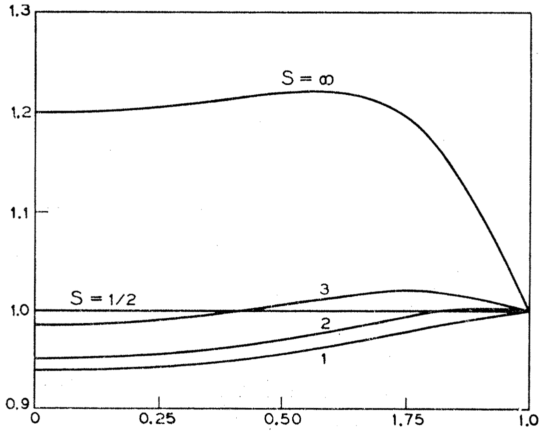

FIG. 1. The parameter α from Eq. (4.10) plotted as a function of $\bar{S}/S$, for different values of spin quantum number S.

As mentioned in the previous section, Γ' diverges as $\bar{S}\to 0$ and we therefore concentrate on evaluating Φ'. From Eq. (4.11) we have

$$\Phi'(T_N)=\langle 2(S^z)^4-(2S^2+2S-1)(S^z)^2\rangle/\langle(S^z)^2\rangle, \qquad (5.2)$$

from which, by use of the density operator ρ in the limit $x\to 0$, we calculate

$$\Phi'(T_N)=-\tfrac{1}{5}(4S^2+4S-3). \qquad (5.3)$$

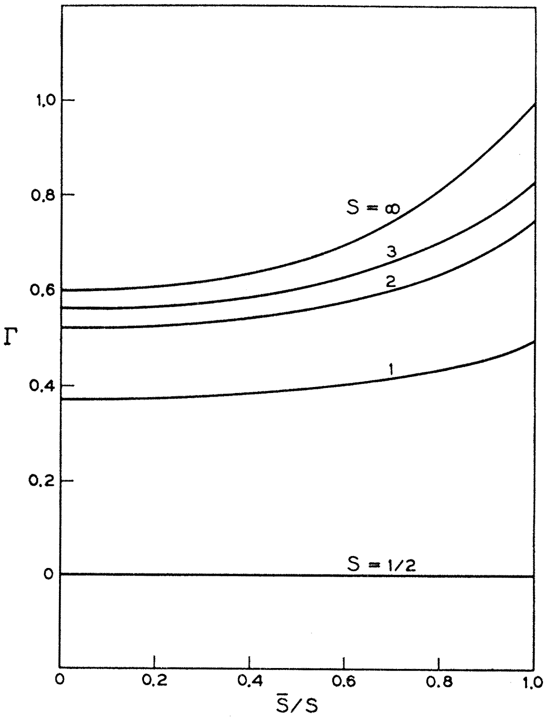

FIG. 2. The decoupling parameter Γ of Eq. (4.6) plotted as a function of $\bar{S}/S$, for different values of spin quantum number S.

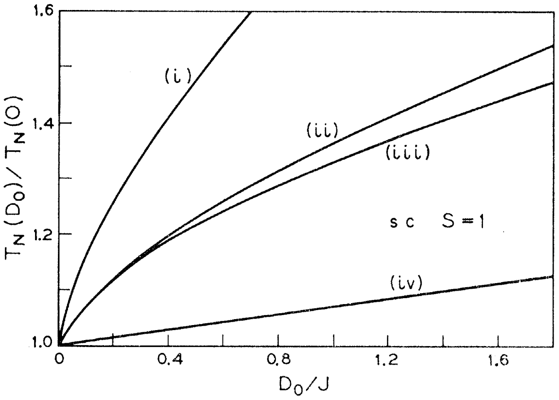

FIG. 3. The ratio $T_N(D_0)/T_N(0)$, where $T_N(D_0)$ is the Néel temperature in the presence of an axial crystal-field anisotropy D_0[Eq. (2.1)], is plotted as a function of D_0/J, for a simple cubic system with isotropic nearest-neighbor exchange J and for spin $S=1$. The curves (i), (ii), and (iii) are calculated from random-phase Green's-function theories where the anisotropy terms are decoupled, respectively, according to Narath (Ref. 6), Anderson and Callen (Ref. 7), and the theory of the present paper. Curve (iv) shows the results of a molecular-field calculation.

Consider Eq. (3.14) for the case $h=g$, $n=0$. It takes the form

$$S(S+1)-\langle(S^z)^2\rangle=\bar{S}\langle A\coth(E_0\bar{S}/2kT)\rangle_{\mathbf{K}}, \quad (5.4)$$

where $\langle\cdots\rangle_{\mathbf{K}}$ is an average for the wave vector $\mathbf{K}$ running over $\frac{1}{2}N$ values in the first Brillouin zone of the reciprocal sublattice. For $\bar{S}\to 0$, E_0 remains finite and (5.4) reduces to

$$2kT_N=\frac{S(S+1)-\langle(S^z)^2\rangle}{\langle\mu/(\mu^2-\lambda^2)\rangle_{\mathbf{K}}}, \quad (5.5)$$

where

$$\mu=\sum_{j-g}^{s}\{J_{jg}[e^{i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})}-1]-D_{jg}\}+\sum_{j-g}^{d}[J_{jg}+D_{jg}]+2D_0\Gamma(T_N), \quad (5.6)$$

$$\lambda=\sum_{j-g}^{d}J_{jg}e^{i\mathbf{K}\cdot(\mathbf{j}-\mathbf{g})}, \quad (5.7)$$

and where $\langle(S^z)^2\rangle$ in (5.5) refers to its value for $T=T_N$.

Consider now Eq. (3.14) for $g=h$, $n=1$. As $\bar{S}\to 0$, $\Gamma'\to\infty$ and hence E_0 diverges in such a way that $E_0\bar{S}\to\mu\bar{S}\to D_0\Phi'(T_N)=-(D_0/5)(4S^2+4S-3)$, and A of Eq. (3.15) takes the value unity. For this case, Eq. (3.14) reduces to

$$\langle(S^z)^2\rangle(1+3\coth\xi)=S(S+1)(1+\coth\xi), \quad (5.8)$$

where

$$\xi=D_0(4S^2+4S-3)/10kT_N. \quad (5.9)$$

Substituting $\langle(S^z)^2\rangle$ from (5.8) into (5.5), we obtain the final expression for the transition temperature as

$$kT_N\langle\mu/(\mu^2-\lambda^2)\rangle_{\mathbf{K}}=S(S+1)(\coth\xi)/(1+3\coth\xi), \quad (5.10)$$

where μ and λ are given by (5.6) and (5.7).

We see immediately from (5.8) that any theory for which $\xi\to 0$ as $\bar{S}\to 0$ will give the result that $\langle(S^z)^2\rangle$ at T_N is $S(S+1)/3$. Both the Narath and the Anderson and Callen decoupling schemes show this property and hence allow for no anisotropy at the transition temperature. They therefore give transition temperatures in the form

$$kT_N\langle\mu/(\mu^2-\lambda^2)\rangle_{\mathbf{K}}=S(S+1)/3. \quad (5.11)$$

They differ only in the value to be taken for $\Gamma(T_N)$ which is unity for Narath decoupling and $(2S-1)/3S$ for Anderson-Callen decoupling.

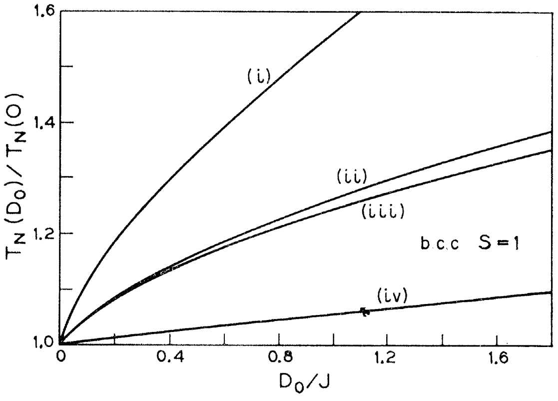

FIG. 4. As Fig. 3 but for a body-centered cubic lattice.

Let us now compare the result (5.8) for $\langle(S^z)^2\rangle$ at the transition temperature with the result of molecular-field theory for the same quantity. The molecular-field value is

$$\langle(S^z)^2\rangle=\sum_{m=-S}^{S}m^2\exp(D_0m^2/kT_N)\Big/\sum_{m=-S}^{S}\exp(D_0m^2/kT_N), \quad (5.12)$$

and is readily shown to be identical with (5.8) for spin $\frac{1}{2}$ and for spin 1. For higher values of spin, the results agree to first order in an expansion in powers of D_0/kT_N.

We may now compute T_N for simple cases of interest. We shall consider the results for simple cubic (sc) and body-centered cubic (bcc) lattices for which the anisotropic exchange contribution D_{jg} is zero, and for which we have only a single nearest-neighbor isotropic exchange parameter J. We include a crystal-field anisotropy term D_0 and investigate the sensitivity of the transition temperature to the ratio D_0/J. For each of the theories discussed, the results obtained apply both to ferromagnets and to antiferromagnets, i.e., for either sign of J.

Our basic Hamiltonian is

$$\mathcal{H}=\sum_{nn} J\mathbf{S}_i\cdot\mathbf{S}_j-\sum_{i} D_0(S_i^z)^2\,, \tag{5.13}$$

where $\sum_{nn}$ runs over all pairs of nearest neighbors and $\sum_i$ runs over all sites in the lattice. The general result for T_N, as calculated by the Green's-function theories, is

$$kT_N\langle[1+\gamma_{\mathrm{K}}+2D_0\Gamma(T_N)/zJ]^{-1}\rangle_{\mathrm{K}} =zJS(S+1)(\coth\xi)/(1+3\coth\xi)\,, \tag{5.14}$$

where z is the number of nearest neighbors, where

$$\gamma_{\mathrm{K}}=\tfrac{1}{3}(\cos K_xa+\cos K_ya+\cos K_za)\ (\mathrm{sc})\,, \tag{5.15}$$

$$\gamma_{\mathrm{K}}=\cos(\tfrac{1}{2}K_xa)\cos(\tfrac{1}{2}K_ya)\cos(\tfrac{1}{2}K_za)\ (\mathrm{bcc})\,, \tag{5.16}$$

a being the lattice constant, and where (i) for Narath decoupling $\Gamma(T_N)=1$, and $\xi\to 0$; (ii) for Anderson-Callen decoupling $\Gamma(T_N)=(2S-1)/3S$, $\xi\to 0$; (iii) for the work of the present paper $\Gamma(T_N)$ is given by (5.1) and ξ by Eq. (5.9). Results have been computed for $T_N(D_0)/T_N(0)$ as a function of D_0/J for the cases $S=1$ and $S=\infty$. They are displayed in Figs. 3–6, where we have also included the molecular-field results for completeness.

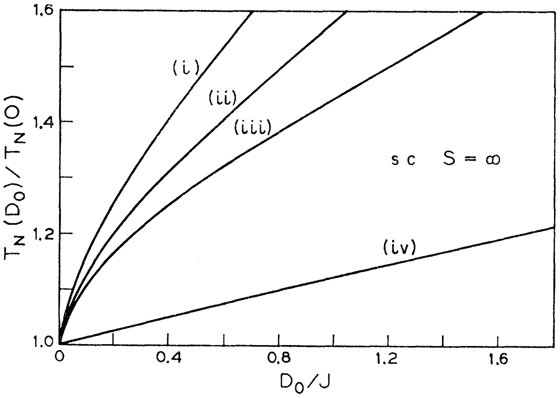

FIG. 5. As Fig. 3 but for spin quantum number $S=\infty$.

The results are remarkable for the lack of agreement between the different approximations. The Narath decoupling scheme predicts a sensitivity of T_N to single-spin anisotropy about ten times larger than the estimate from molecular-field theory. There would seem to be little doubt that the molecular-field approximation underestimates this sensitivity whilst the Narath result is probably too large by a factor of 2. The results of the present paper for T_N differ from those of Anderson-Callen in two ways; the values to be used for ξ and for $\Gamma(T_N)$. These two differences tend to cancel for smaller values of spin, but produce effects of the same sign for larger spin values. Thus, the two approximations are in better agreement for the spin-one case of Figs. 3 and 4 than for the case of infinite spin (Figs. 5 and 6).

6. RESULTS FOR LARGE ANISOTROPY

The decoupling scheme for the single-spin anisotropy terms as used in the present paper has been constructed in such a way that it is basically valid in the limit of small anisotropy. The question arises as to how good the approximation is likely to be for larger values of anisotropy. It is easily seen that the decoupling breaks down completely for the limit $D_0\to\infty$, when (5.5) shows $kT_N\to\infty$, (the same is also true for the Narath and Anderson-Callen decoupling schemes) whereas the true result for this case is quite finite and may be evaluated approximately by use of Ising theory.[18]

The reason for this unsatisfactory behavior in the limit of extreme anisotropy can be traced to the expression $\bar{S}(\mu^2-\lambda^2)^{1/2}$ for the energy of the collective oscillations in the system, which also diverges in the limit $D_0\to\infty$. These excitations are simply spin waves with energy renormalized according to the sublattice magnetization, and it will be recalled that simple noninteracting spin-wave energies result from a careful consideration of the matrix elements of spin between the ground and first excited single spin states $|S\rangle$ and $|S-1\rangle$ (or $|-S\rangle$ and $|-S+1\rangle$). Thus, the underlying assumption in all these theories is that the important single-spin excitations in the system are those between the ground state $|S\rangle$ and nearby states $|S-1\rangle$, $|S-2\rangle$, etc. This ceases to be true for systems with large single-spin anisotropy for which excitations $|S\rangle\to|-S\rangle$ take over as the more important. In particular, the latter do not diverge in energy in the limit $D_0\to\infty$ as do the excitations $|S\rangle\to|S-1\rangle$. For the simple (single exchange parameter) ferromagnetic and antiferromagnetic structures discussed in detail in Sec. 5, we may readily calculate the condition that the two types of excitation have comparable magnitudes, by use of molecular-field theory; it is

$$D_0\sim zJ\bar{S}\,. \tag{6.1}$$

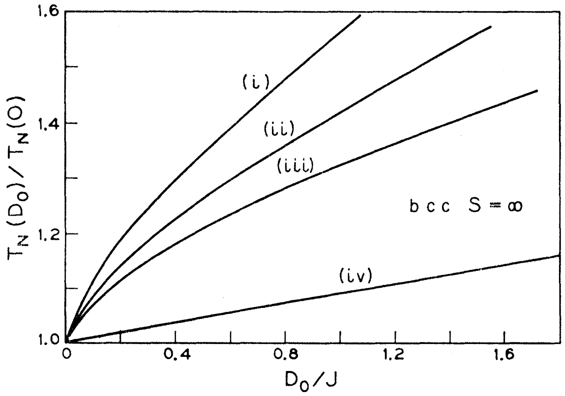

FIG. 6. As Fig. 3 but for a body-centered cubic lattice and spin $S=\infty$.

Thus, the Green's-function theories will certainly break

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[18] C. Domb, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. 2A.

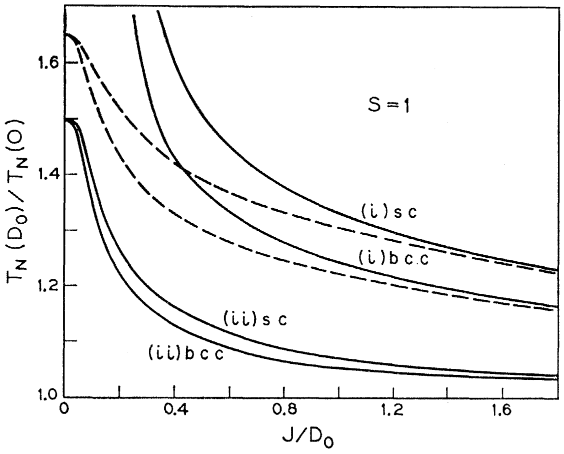

FIG. 7. The ratio $T_N(D_0)/T_N(0)$ plotted as a function of J/D_0 for highly anisotropic systems and for spin $S=1$. Curves are calculated for both simple cubic (sc) and for body-centered cubic (bcc) lattices with isotropic nearest-neighbor exchange J. Curves (i) and (ii) show, respectively, the results as calculated from the Green's-function theory of the present paper and from the molecular-field theory. Also shown (dashed) are curves which extrapolate the small anisotropy Green's-function curves so that they go over smoothly to the correct extreme anisotropy (Ising) limit.

down when $D_0 \gtrsim zJ\bar{S}$. This we observe is a considerably stronger condition that merely having $D_0 \gg J$. It implies a breakdown as $\bar{S} \rightarrow 0$ even for small anisotropy. Thus, we do not expect the theories in their present form to be adequate for the paramagnetic state. The predicted transition temperatures, however, are probably quite good provided that the theory is adequate up to temperatures for which $\bar{S} \sim S/4$ or $S/5$ (by which time the temperature is within a few percent of T_N) since the present theory indicates no anomalous behavior of sublattice magnetization as $\bar{S} \rightarrow 0$. The associated restriction is estimated below.

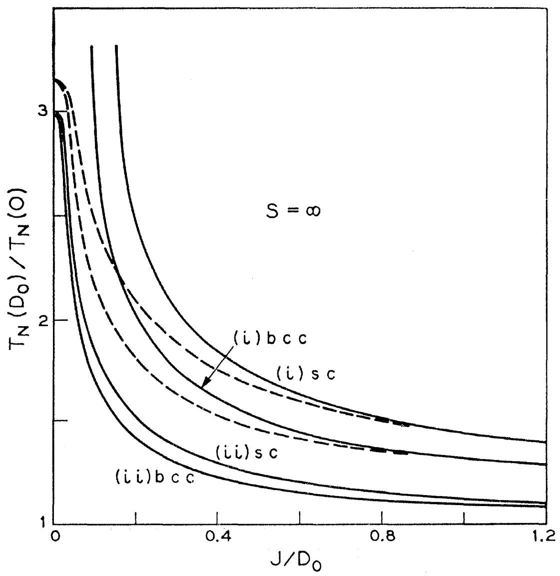

FIG. 8. As Fig. 7 but for spin quantum number $S=\infty$.

In Figs. 7 and 8 we have extended the calculations of T_N for the sc and bcc lattices to higher values of anisotropy D_0. These results are obtained by use of Eq. (5.14) with the decoupling parameters $\Gamma(T_N)$ and ξ given by Eqs. (5.1) and (5.9), respectively. Also indicated on these figures are the results obtained from Ising theory for the extreme anisotropy limit. For spin S and for $D_0 \rightarrow \infty$ we have from Domb[18]

$$kT_N/zJ = 0.752S^2 \text{ (sc)}, \quad kT_N/zJ = 0.794S^2 \text{ (bcc)}. \tag{6.2}$$

In the absence of anisotropy, the best estimates for transition temperatures are probably those obtained from high-temperature series expansions. For spin S, Rushbrooke and Wood[19] give

$$kT_N/J = 5(z-1)[11S(S+1)-1]/192. \tag{6.3}$$

The Ising results apply to both ferromagnets and antiferromagnets. The Rushbrooke and Wood results were calculated for ferromagnetic structures but should also be valid to a good approximation for antiferromagnets. Indeed, perhaps the best understood antiferromagnetic compound of all (viz., MnF_2) has a Néel temperature which is related quite accurately to its dominant exchange interaction J by Eq. (6.3). We shall assume the result (6.3) to be valid to a good approximation for both signs of exchange.

Combining Eqs. (6.2) and (6.3) we find

$$\frac{T_N(D_0 \rightarrow \infty)}{T_N(D_0 = 0)} = \frac{192zS^2p}{5(z-1)[11S(S+1)-1]}, \tag{6.4}$$

where $p=0.752$ for the sc lattice and $p=0.794$ for the bcc lattice. For spin unity we find a value $T_N(\infty)/T_N(0)=1.65$ for both lattices, and for infinite spin we calculate a value 3.15 again for both lattices. These values compare quite favorably with the results 1.5 and 3.0 given by molecular-field theory [Eq. (2.10)].

In Fig. 7 we show the molecular-field curves and the Green's-function results of the present paper as calculated for $S=1$ and for highly anisotropic systems. We have also extrapolated the Green's-function curves so that they go over smoothly to the correct extreme anisotropy limit. For the spin-1 case, the latter curves differ significantly from the large anisotropy Green's-function estimates for $J/D_0 \lesssim 0.5$ (bcc) and for $J/D_0 \lesssim 0.7$ (sc). The corresponding numbers for the classical spin limit are seen from Fig. 8 to be 0.3 (sc) and 0.2 (bcc). In general it would seem that the Green's-function theory of this paper is able to give at least semiquantitative estimates for $T_N(D_0)$ up to values $D_0 \sim \frac{1}{4}zJ$ (for $S=1$) and to values $D_0 \sim \frac{1}{2}zJ$ for large values of spin.

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