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Sensitivity of Curie temperature to single-ion anisotropy

M. E. Lines
Bell Laboratories, Murray Hill, New Jersey 07974

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Existing numerical estimates of the sensitivity of Heisenberg Curie temperature T_C to crystal-field anisotropy have been obtained (primarily by Green's-function techniques) only for simple easy-axis anisotropy and low values of spin quantum number. In this paper we demonstrate the usefulness of the correlated-effective-field (CEF) theory in this context, showing that with modest computational effort numerical results for both easy-axis and easy-plane anisotropies can be obtained for any spin quantum number of physical relevance. Moreover, for cases where a comparison can be made with the existing literature, we show that the CEF results are more accurate than those obtainable from first-order equation-of-motion Green's-function techniques. Numerical calculations in the correlated-effective-field approximation are given for all three cubic lattices subject to the Hamiltonian $\mathcal{H}=\sum_i DS_{iz}^2-\sum_i\sum_j J\vec{S}_i\cdot\vec{S}_j$, where J is a nearest-neighbor exchange parameter. Results are given for the complete range $-\infty \le D/J \le \infty$ (where negative values refer to an easy-axis situation and positive values to a preferred easy plane) and for spin quantum numbers $S=1$ to 7/2 inclusive. For integer spin values and an easy-plane anisotropy we encounter the problem of singlet-ground-state ferromagnetism for which $T_C \to 0$ at a finite value of D/J.

I. INTRODUCTION

The influence of single-ion (i.e., crystal-field) anisotropy on the phase-transition temperatures in Heisenberg ferromagnets and antiferromagnets is an important theoretical problem for many magnetic materials. It has been studied extensively in recent years for the case where the single-ion anisotropy takes on perhaps its simplest form, viz., that of an easy-axis quadratic term DS_{iz}^2 with parameter D negative.[1–7] In spite of this considerable volume of literature there remain large gaps in our knowledge even for this simplest case. The problem centers around the fact that the existing approaches, which are almost all Green's-function schemes of one form or another, require such a computational effort that even at the simple random-phase level there are almost no numerical estimates valid for all D beyond the simplest nontrivial case with spin $S=1$, and absolutely none, as far as I can find, with $S>\frac{3}{2}$.

There are, however, other objections to the use of the Green's-function equation-of-motion methods in the present context. As first pointed out by Murao and Matsubara,[2] with this approach a physical quantity can usually be obtained from more than one set of Green's functions, which, in general, do not yield consistent results. This "redundancy" necessitates preference being given to one set over another on some subjective physical grounds, a most unsatisfactory situation. That used most frequently[3–5] amounts to choosing the set which, in the limit $D\to 0$, yields the familiar random-phase approximation (RPA) result for the isotropic Heisenberg Hamiltonian,[8,9] for which no such redundancy problem arises. Even this set of Green's functions, however, yields results which are not quantitatively very accurate in certain limits. For example, the method goes over to a simple molecular-field form in the limit of infinite (negative) D. For spin $S=1$ and a simple cubic (sc) lattice this represents an overestimate of Curie temperature by about 33%. Since the RPA Green's-function method as used in Refs. 3–7 is accurate to within a few percent in the opposite $D\to 0$ isotropic limit, the implication is that as a measure of the sensitivity of Curie temperature to easy-axis crystal-field anisotropy it may be suspect (yielding overestimates).

That this is indeed the case can be deduced from the very recent work of Yang and Wang.[10] Their use of a fully self-consistent Green's-function diagrammatic technique has shed much light on the redundancy problem of the equation-of-motion method and is accurate to within a few percent (as a measure of Curie temperature) in both limits $D\to 0$ and $D\to -\infty$, for which accurate series-expansion results are known. Here again, however, the complexity of the method appears to increase rapidly with increasing spin quantum number (and correspondingly with an increasing complexity of the crystal-field anisotropy), and the formalism has thus far been given only for $S=1$ and the easy-axis quadratic anisotropy form. High-temperature-series expansion techniques, which would doubtless give the most reliable estimates for the Curie temperature T_C, also require a great deal of computational labor and have thus far been attempted only for the corresponding Ising exchange problem,[11,12] for which counting procedures are much simpler.

In this paper we wish to suggest the correlated-effective-field (CEF) approximation[13] as an alternative to Green's-function methods for the study of the sensitivity of T_C to single-ion anisotropy. The CEF theory is constructed in such a manner that computations for any crystal-field form and any value of spin quantum number are readily performed with modest computer facilities. Most importantly, at least for the three cubic lattices, the method proves to be more accurate than the RPA Green's-function approach, particularly at high values of anisotropy, and compares quite well with the findings of Yang and Wang as a measure of the sensitivity of T_C to D for that single case (D negative, $S=1$) which has been computed by those authors. In this paper we shall consider a crystal-field anisotropy of the form DS_{iz}^2, but allow for both negative and positive D (the easy-axis and easy-plane situations, respectively, and give numerical results for all values of D, and for spin quantum number S from 1 to $\frac{7}{2}$ inclusive.

We do not wish to imply that the CEF method can compete with series-expansion techniques in accuracy or that the method is necessarily superior to equation-of-motion Green's-function techniques at lower temperatures (it is basically a high-temperature approximation, although its low-temperature limitations have not yet been explored). We *do* wish to suggest that the method will provide estimates of T_C usually accurate to within a few percent for three-dimensional lattices (the largest discrepancy which we have found with known series-expansion results occurs for the simple cubic lattice with $S=1$ and $D\rightarrow-\infty$, for which the CEF value of T_C is low by about 12%) without ambiguity and with modest computational effort even for relatively complicated local anisotropy forms and higher spin quantum numbers. We shall also discuss in passing the case of the corresponding Ising problem as discussed in Refs. 11 and 12, and establish that the sensitivities of Ising and Heisenberg Curie temperatures to easy-axis crystal-field anisotropy are not the same, the Heisenberg system being more sensitive.

II. CEF FORMALISM

The static form of the correlated-effective-field approximation for $T \geq T_C$, which is all that will be required in the present paper, has been given in an earlier publication.[13] The approximation is essentially an extension of the local field concept to include that measure of static interspin correlations which brings the theory into accord with that requirement of the fluctuation dissipation theorem which relates static correlations and static response (and which is violated by the molecular-field theory itself). We shall consider first the general formalism for a lattice of spins $\vec{S}_i$ interacting via a Heisenberg exchange $-\sum_i\sum_j J_{ij}\vec{S}_i\cdot\vec{S}_j$, where J_{ij} measures exchange between general spins $\vec{S}_i$ and $\vec{S}_j$, and each subject to a local crystal field V_{ci}. Within the CEF approximation[13] a local Hamiltonian is written for the ith spin in the form

$$\mathcal{H}_i = V_{ci} - \sum_\lambda \sum_j J_{ij}\,\alpha^\lambda (S_i^\lambda)^2, \tag{2.1}$$

in which j runs over neighbor spins (not necessarily nearest neighbor only), λ runs over the three Cartesian coordinates x, y, z, and α^λ are correlation parameters which are completely determined from the fluctuation theorem in the form

$$\alpha^\lambda = \frac{\sum_{\vec{q}} J(\vec{q})\{kT - 2[J(\vec{q}) - \alpha^\lambda J(0)]\langle S^\lambda : S^\lambda\rangle\}^{-1}}{\sum_{\vec{q}} J(0)\{kT - 2[J(\vec{q}) - \alpha^\lambda J(0)]\langle S^\lambda : S^\lambda\rangle\}^{-1}}, \tag{2.2}$$

where $\vec{q}$ is a reciprocal-lattice vector, $J(\vec{q})$ is the Fourier transform with respect to the lattice of J_{ij}, and the colon product ensemble average is defined by

$$\langle S^\lambda : S^\lambda\rangle = \sum_n \rho_n \left(S_{nn}^\lambda S_{nn}^\lambda + 2kT \sum_{m\neq n} \frac{S_{nm}^\lambda S_{mn}^\lambda}{E_m - E_n} \right), \tag{2.3}$$

where S_{nm}^λ are the matrix elements of the λth component of spin between the nth and mth eigenstates of Eq. (2.1), E_n and E_m are the respective eigenenergies of these levels, and ρ_n is the density matrix

$$\exp\left(\frac{-E_n}{kT}\right) \Big/ \sum_n \exp\left(\frac{-E_n}{kT}\right).$$

In the most general case α^x, α^y, and α^z can all be different, in which case (2.2) defines three different equations for these three quantities as functions of temperature. The equations are not in general independent, but they are not difficult to solve numerically to an acceptable accuracy without great effort. In many cases the problem may simplify by symmetry with two, or even all three, of the correlation parameters being equal. In such cases the numerical problem is correspondingly simpler.

One further result of formal static CEF theory will be required, namely that for uniform static susceptibility in the direction λ. It is[13]

$$\chi^\lambda = \frac{g_\lambda^2 \mu_B^2 \langle S^\lambda : S^\lambda\rangle}{kT - 2J(0)(1-\alpha^\lambda)\langle S^\lambda : S^\lambda\rangle}, \tag{2.4}$$

and it diverges when

$$kT = kT_C^\lambda = 2J(0)\,(1-\alpha^\lambda)\,\langle S^\lambda : S^\lambda\rangle. \tag{2.5}$$

The actual Curie temperature will be the largest of the T_C^λ ($\lambda = x, y, z$) and represents an onset of long-range order in the corresponding direction. Although the formalism above is valid without restriction of sign or signs of exchange J_{ij} to Eq. (2.4), the relationship (2.5) for transition temperature has been calculated as a divergence of uniform response and is therefore restricted to systems undergoing a transition to a ferromagnetic phase.

We shall now consider specifically the case of a cubic lattice of spins $\vec{S}_i$ (the sc, bcc, and fcc lat-

TABLE I. $\langle S^\lambda : S^\lambda \rangle$ ($\lambda = \parallel, \perp$) from Eq. (2.3), for the case of spins $S=1$ to $\frac{7}{2}$ inclusive. $E(m) = \exp(-my)$; $y = D'/kT$.

S	$\langle S^\parallel : S^\parallel \rangle$
1	$\dfrac{2E(1)}{[1+2E(1)]}$
$\frac{3}{2}$	$\dfrac{[\frac{1}{4}E(\frac{1}{4})+\frac{9}{4}E(\frac{9}{4})]}{[E(\frac{1}{4})+E(\frac{9}{4})]}$
2	$\dfrac{2[E(1)+4E(4)]}{[1+2E(1)+2E(4)]}$
$\frac{5}{2}$	$\dfrac{\frac{1}{4}E(\frac{1}{4})+\frac{9}{4}E(\frac{9}{4})+\frac{25}{4}E(\frac{25}{4})}{E(\frac{1}{4})+E(\frac{9}{4})+E(\frac{25}{4})}$
3	$\dfrac{2[E(1)+4E(4)+9E(9)]}{1+2E(1)+2E(4)+2E(9)]}$
$\frac{7}{2}$	$\dfrac{\frac{1}{4}E(\frac{1}{4})+\frac{9}{4}E(\frac{9}{4})+\frac{25}{4}E(\frac{25}{4})+\frac{49}{4}E(\frac{49}{4})}{E(\frac{1}{4})+E(\frac{9}{4})+E(\frac{25}{4})+E(\frac{49}{4})}$
S	$\langle S^\perp : S^\perp \rangle$
1	$\dfrac{2y^{-1}[1-E(1)]}{1+2E(1)}$
$\frac{3}{2}$	$\dfrac{y^{-1}[(y+\frac{3}{4})E(\frac{1}{4})-\frac{3}{4}E(\frac{9}{4})]}{E(\frac{1}{4})+E(\frac{9}{4})}$
2	$\dfrac{2y^{-1}[3-\frac{7}{3}E(1)-\frac{2}{3}E(4)]}{1+2E(1)+2E(4)}$
$\frac{5}{2}$	$\dfrac{(\frac{9}{4}y+2)E(\frac{1}{4})-\frac{11}{8}E(\frac{9}{4})-\frac{5}{8}E(\frac{25}{4})}{y[E(\frac{1}{4})+E(\frac{9}{4})+E(\frac{25}{4})]}$
3	$\dfrac{2[6-\frac{13}{3}E(1)-\frac{16}{15}E(4)-\frac{3}{5}E(9)]}{y[1+2E(1)+2E(4)+2E(9)]}$
$\frac{7}{2}$	$\dfrac{(4y+\frac{15}{4})E(\frac{1}{4})-\frac{9}{4}E(\frac{9}{4})-\frac{11}{12}E(\frac{25}{4})-\frac{7}{12}E(\frac{49}{4})}{y[E(\frac{1}{4})+E(\frac{9}{4})+E(\frac{25}{4})+E(\frac{49}{4})]}$

tices will each be considered in turn) with nearest-neighbor ferromagnetic exchange J (only) and subject to a local crystal field at each site of the form

$$V_{ci} = DS_{iz}^2. \tag{2.6}$$

Since the resulting system is axially symmetric in a phase with unbroken symmetry (e.g., the paramagnetic phase), the transverse correlation parameters α^x and α^y are equal by symmetry and we can define parallel and perpendicular correlations with respect to the axis (z) as follows:

$$\alpha^x = \alpha^y = \alpha^\perp, \quad \alpha^z = \alpha^\parallel. \tag{2.7}$$

The CEF ith-site effective Hamiltonian (2.1) can now be diagonalized very simply, and it has eigenvalues

$$E(m) = D'm^2 \tag{2.8}$$

and eigenfunctions $|m\rangle$, where m is the quantum number of the z component of local angular momentum S_{iz}, and where

$$D' = D - zJ(\alpha_\parallel - \alpha_\perp), \tag{2.9}$$

in which z is the number of nearest-neighbor sites of any individual spin ($z = 6$, 8, 12, respectively, for the sc, bcc, and fcc lattices) and where we have dropped constant terms. This knowledge of local CEF eigenfunctions and eigenlevels now enables us to calculate explicit forms for $\langle S^\parallel : S^\parallel \rangle$ and $\langle S^\perp : S^\perp \rangle$ from Eq. (2.3) for any spin quantum number. We have obtained results up to and including $S = \frac{7}{2}$; the explicit forms are detailed in Table I.

The many-body problem for T_C in CEF approximation now reduces to the simultaneous solution of Eqs. (2.2) ($\lambda = \parallel, \perp$) and (2.5) for $\alpha_\parallel$, $\alpha_\perp$, and T_c. One of the correlations can be obtained analytically, as we shall now establish, so that the numerical problem for estimating T_C as a function of anisotropy reduces finally to the solution of a pair of implicit equations for two unknowns.

Suppose that the incipient direction of ferromagnetic ordering is $\lambda = \mu$. Writing $T = T_C^\mu = T_C$ in Eq. (2.2) with $\lambda = \mu$ and using Eq. (2.5) also with $\lambda = \mu$, we obtain

$$\alpha_C^\mu \equiv \alpha^\mu (T = T_C) = \frac{\sum_{\vec{q}} J(\vec{q})/[J(0) - J(\vec{q})]}{\sum_{\vec{q}} J(0)/[J(0) - J(\vec{q})]}, \tag{2.10}$$

which is independent of V_{ci} and is readily evaluated once $J(\vec{q})$ is specified. Inserting into Eq. (2.10) in turn the Fourier transforms relevant for the three nearest-neighbor cubic lattices under consideration, viz.,

$$\text{sc:} \quad J(\vec{q}) = 2J[\cos(q_x a) + \cos(q_y a) + \cos(q_z a)], \tag{2.11}$$

$$\text{bcc:} \quad J(\vec{q}) = 8J[\cos(\tfrac{1}{2}q_x a)\cos(\tfrac{1}{2}q_y a)\cos(\tfrac{1}{2}q_z a)], \tag{2.12}$$

$$\text{fcc:} \quad J(\vec{q}) = 4J[\cos(\tfrac{1}{2}q_x a)\cos(\tfrac{1}{2}q_y a) + (\text{cyclic perms.})], \tag{2.13}$$

where a is a linear dimension of the basic cubic unit cell in each case, we find values for α_C^μ equal to 0.34053, 0.28223, and 0.25632 for sc, bcc, and fcc, respectively.

In the present context, where we have only nearest-neighbor exchange, the correlation parameters α^λ take on a rather simple physical interpretation. They are defined, in general,[13] by replacing all operators $S_j^\lambda (j \neq i)$ in the paramagnetic zero-field equation-of-motion for $\vec{S}_i$ by $A_{ij}^\lambda S_i^\lambda$ and writing

$$\sum_i A_{ij}^\lambda J_{ij} = \alpha^\lambda \sum_j J_{ij}. \tag{2.14}$$

It follows that when J_{ij} are restricted to nearest neighbors which are all equivalent by symmetry, then $\alpha^\lambda = A_{ij}^\lambda$ (i, j nearest neighbors) and nearest-neighbor correlations $\langle S_i^\lambda S_j^\lambda \rangle$ in particular are ap-

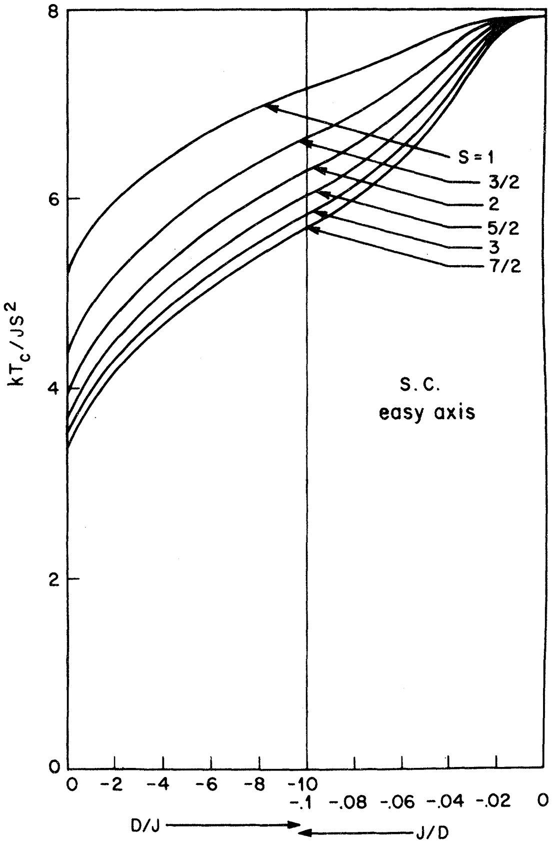

Fig. 1. Curie temperature as a function of anistropy D/J for the Heisenberg simple cubic system with an easy anisotropy axis (D negative) and for spin quantum numbers $S=1$ to $\frac{7}{2}$.

proximated as $\alpha^{\lambda}\langle(S_i^{\lambda})^2\rangle$. Thus the correlation parameters $\alpha^{\parallel}$ and $\alpha^{\perp}$ for our examples can be construed as a measure of nearest-neighbor spin correlations in the sense

$$\alpha^{\lambda}=\langle S_i^{\lambda}S_j^{\lambda}\rangle/\langle(S_i^{\lambda})^2\rangle,\quad \lambda=\parallel,\perp. \qquad (2.15)$$

III. EASY-AXIS CASE

When the anisotropy parameter D of Eq. (2.6) is negative, the parallel susceptibility diverges first as temperature T is decreased in the paramagnetic phase. The systems therefore order along the z axis and α_C^{μ} of Eq. (2.10) is equal to $\alpha^{\parallel}$. The "unknowns" are therefore $\alpha_C^{\perp}$ and $T_C^{\parallel}=T_C$ and are obtained by the numerical simultaneous solution of Eq. (2.2) with $T=T_C$, $\lambda=\perp$ and Eq. (2.5) with $\lambda=\parallel$, i.e., of

$$\alpha_C^{\perp}=\frac{\sum_{\vec{q}}J(\vec{q})\{kT_C-2[J(\vec{q}-\alpha_C^{\perp}J(0)]\langle S^{\perp}:S^{\perp}\rangle_{T=T_C}\}^{-1}}{\sum_{\vec{q}}J(0)\{kT_C-2[J(\vec{q})-\alpha_C^{\perp}J(0)]\langle S^{\perp}:S^{\perp}\rangle_{T=T_C}\}^{-1}} \qquad (3.1)$$

and

$$kT_C=kT_C^{\parallel}=2J(0)(1-\alpha_C^{\parallel})\langle S^{\parallel}:S^{\parallel}\rangle_{T=T_C}, \qquad (3.2)$$

where $\langle S^{\perp}:S^{\perp}\rangle$ and $\langle S^{\parallel}:S^{\parallel}\rangle$ for $T=T_C$ can be taken from Table I and where $\alpha_C^{\parallel}$ is independent of anisotropy and spin quantum number and is equal to 0.34053, 0.28223, and 0.25632 for the sc, bcc, and fcc lattices, respectively.

We have solved these equations numerically for the complete easy-axis anisotropy range $-\infty \leq D/J \leq 0$. The results for Curie temperature as a function of D/J are shown in Figs. 1–3 for the sc, bcc, and fcc lattices, respectively, and for $S=1$ to $S=\frac{7}{2}$ inclusive for each case. The corresponding curves for critical ($T=T_C$) correlation $\alpha_C^{\perp}$ as a function of anisotropy are detailed (for brevity) only for the sc lattice (Fig. 4). The nature of the curves for the other lattices is qualitatively similar.

For the isotropic $D=0$ limit the method gives the same estimates for T_C as the RPA Green's-function approach.[8] These are within a few percent of the best known (high-temperature series) values for all spin values. The other value of anisotropy for which we have good series expansion estimates is the opposite limit $D/J\to-\infty$ for which the system goes over to an Ising extreme $\mathcal{H}=-\langle S^2\rangle\sum_i\sum_j J\sigma_i^z\sigma_j^z$ in which i and j run over nearest neighbors and σ^z can take only the two values ±1. In this limit the RPA Green's-function approximation becomes equal to the molecular-field theory and gives estimates of T_C between 23% (fcc) and 33% (sc) too high. In this same limit the

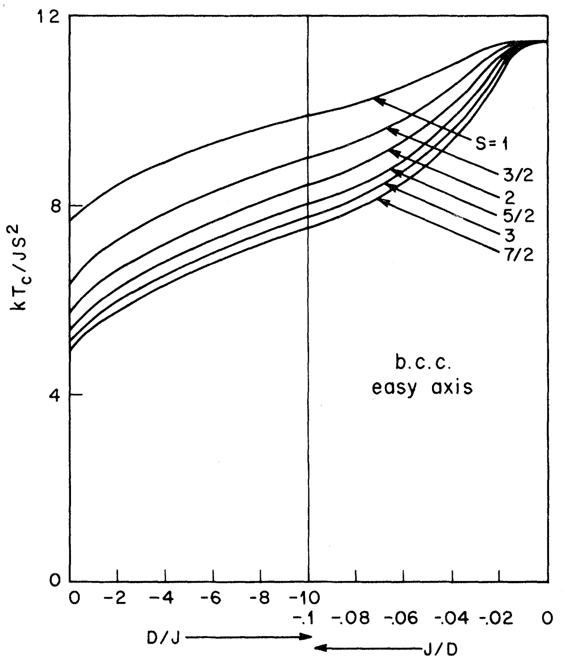

FIG. 2. As Fig. 1 but for a bcc lattice.

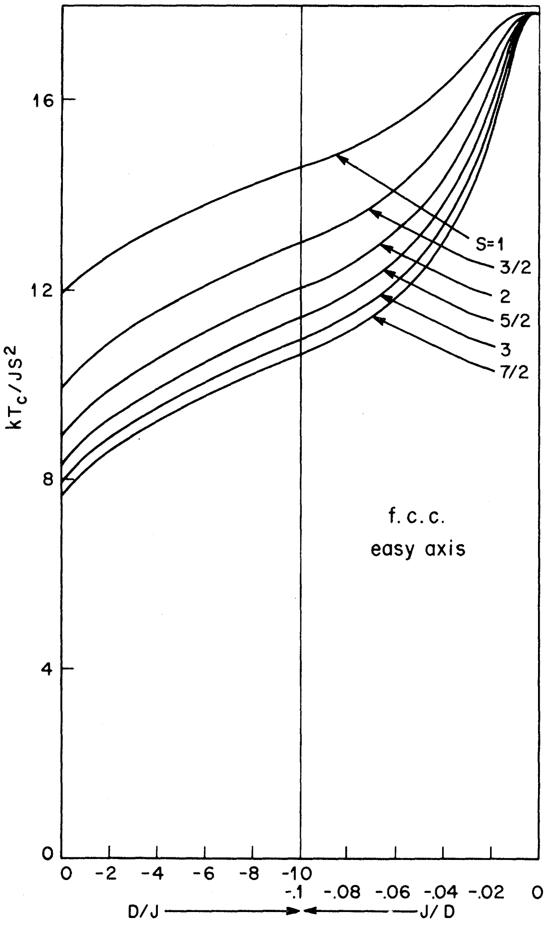

FIG. 3. As Fig. 1 but for a fcc lattice.

CEF theory goes over to the spherical approximation[14] with T_C estimates from 8% (fcc) to 12% (sc) low. In the case of spin $S=1$, which is the only case for which a major body of existing literature is available, it is possible to do a more careful comparison of methods. The quantity which has received most attention is the ratio $T_C(D/J)/T_C(0)$, i.e., the enhancement of Curie temperature by the presence of the easy-axis crystal field. In Fig. 5 we show a full calculation of this quantity for the sc lattice over the complete range $-\infty \leq D/J \leq 0$ using the molecular field theory, the RPA Green's-function approximation, the present work, and finally the Green's-function diagrammatic technique of Yang and Wang.[10] It is apparent that of these methods the RPA Green's-function approach is the least satisfactory, seemingly overestimating the sensitivity of Curie temperature to anisotropy very seriously. The molecular-field theory is surprisingly good in its estimate (although of course it overestimates the actual values of $T_C(D/J)$, rather than the ratio, very considerably). If we take Yang and Wang's calculation to be the most accurate yet available, and probably[10] accurate to within a few percent over the entire anisotropy range, then it is apparent that the CEF method of the present paper (which in terms of $T_C(D/J)/T_C(0)$ never deviates from the Yang and Wang value by more than ~5%) is a very useful representation in this context.

From Fig. 5 we see that the molecular-field theory probably somewhat underestimates the sensitivity of Curie temperature to easy-axis anisotropy. At first sight this is in conflict with the high temperature series results of Brankov *et al.*,[12] who find that for $|D|/J$ up to ~10 the molecular-field and series estimates for $T_c(D/J)/T_C(0)$ agree, while for larger anisotropy values the molecular field estimates are a little too large. The explanation is contained in the fact that, in order to avoid the mathematical complexities introduced by noncommutation of operators, the series work was performed for an Ising exchange $-\sum_i\sum_j JS_i^z S_j^z$ (i, j, nearest neighbors).

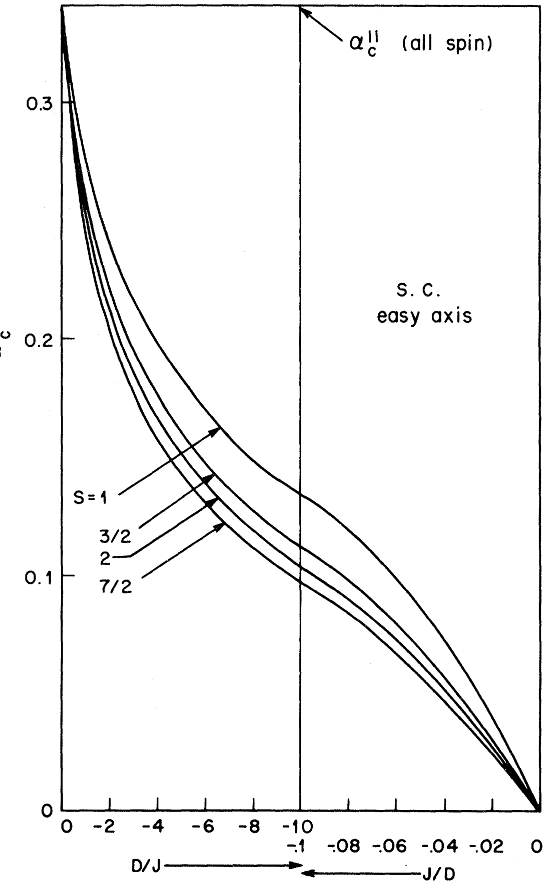

FIG. 4. Correlation parameters $\alpha_C^{\parallel}$ and $\alpha_C^{\perp}$ of the CEF theory as a function of anisotropy D/J for the Heisenberg simple cubic system with easy-axis anisotropy.

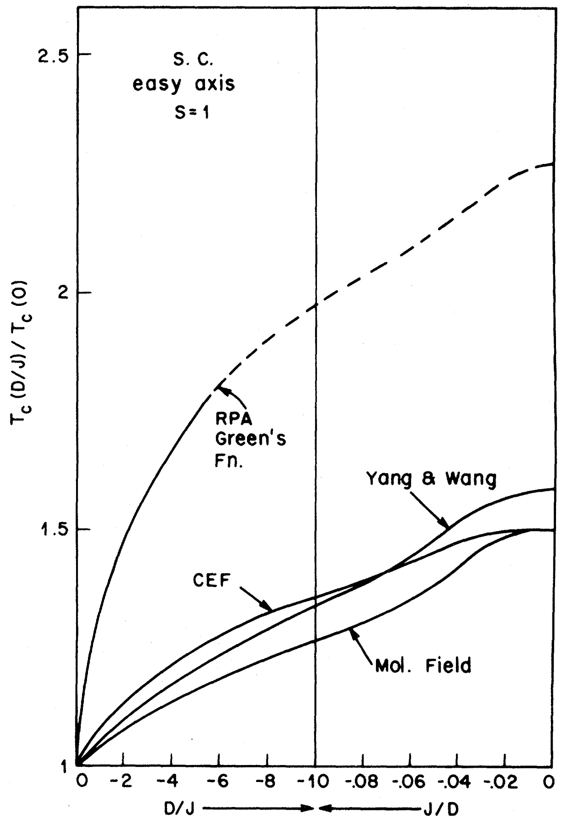

FIG. 5. Ratio of easy-axis Curie temperature $T_C(D/J)$ to its value in the isotropic limit $T_C(0)$ as a function of easy-axis anisotropy D/J for the simple cubic lattice with spin $S=1$. The simple molecular-field estimate is compared with those of the RPA Green's-function theory, the diagrammatic Green's-function theory of Yang and Wang (Ref. 10), and the CEF approximation of the present paper. We have not been able to find a published RPA Green's-function curve for all D/J, and the dashed part of the relevant curve in this figure is an interpolation between published values $|D|/J<6$ and the known $|D|/J \to \infty$ limit.

Via the CEF method we can easily demonstrate the effect which the removal of the transverse spin operators from the problem has on the sensitivity results.

For an Ising exchange Hamiltonian subject to an easy-axis crystal field $V_{ci} = DS_{iz}^2$ (D negative), the local ith site CEF Hamiltonian still has the form of Eq. (2.1), but now the perpendicular correlation parameters $\alpha^x = \alpha^y = \alpha^\perp$ are zero by definition. The resulting problem therefore involves the single correlation parameter $\alpha^z = \alpha^{\parallel}$ which, from Eq. (2.15), is a measure of z component nearest-neighbor correlations. The CEF Hamiltonian again has eigenvalues $D'm^2$ and eigenfunctions $|m\rangle$ but now

$$D'(\text{Ising}) = D - zJ\alpha_{\parallel}. \tag{3.3}$$

The Curie temperature is now determined from (2.2) ($\lambda = \parallel$) and (2.5) ($\lambda = \parallel$). Substituting the latter into the former we find

$$\alpha_C^{\parallel}(\text{Ising}) = \frac{\sum_{\vec{q}} J(\vec{q})/[J(0)-J(\vec{q})]}{\sum_{\vec{q}} J(0)/[J(0)-J(\vec{q})]} , \tag{3.4}$$

which is independent of anisotropy D and takes on the values cited earlier for the sc, bcc, and fcc lattices with nearest-neighbor exchange. Thus, for the easy-axis Ising problem, the correlation determination is trivial with $\alpha_C^{\parallel} \approx 0.341$ (sc), 0.282 (bcc), 0.256 (fcc), and $\alpha_C^{\perp} = 0$ for all values of D/J. The resulting Curie temperature is

$$kT_C = 2J(0)(1-\alpha_C^{\parallel})\langle S^{\parallel} : S^{\parallel}\rangle_{D'/kT_C}, \tag{3.5}$$

where we have now labeled the ensemble average with that parameter (i.e., D'/kT_C) of which it is a variable at the Curie point.

Let us now compare the Curie temperature findings for the CEF Heisenberg (T_C^H), CEF Ising (T_C^I), and molecular-field Heisenberg or Ising (T_C^{MF}) approximations. They can be written as the solutions of

$$kT_C^H = 2J(0)(1-\alpha_C^{\parallel})\langle S^{\parallel} : S^{\parallel}\rangle_{D'/kT_C^H} ,$$

$$D' = D - zJ(\alpha_C^{\parallel} - \alpha_C^{\perp}), \tag{3.6}$$

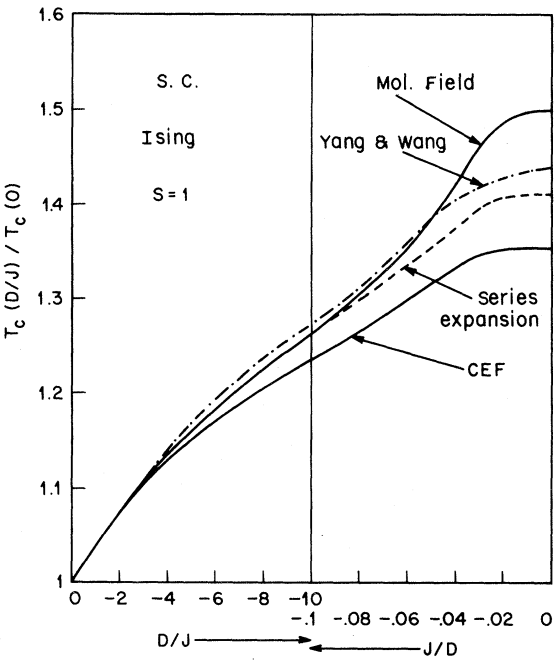

FIG. 6. As Fig. 5 but for the case of an Ising rather than a Heisenberg exchange form. For this case the RPA Green's-function and molecular field curves are identical. Also shown on this plot are the estimates from a high-temperature-series expansion extrapolation as calculated by Brankov *et al.* (Ref. 12).

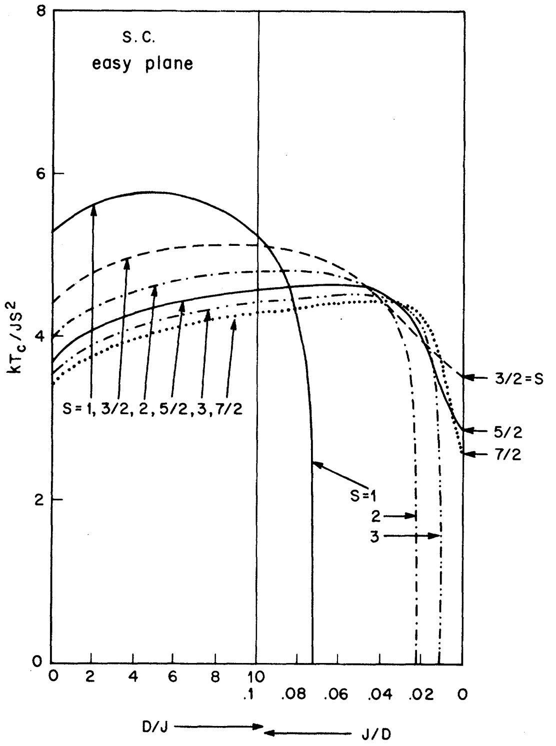

FIG. 7. T_C as a function of anisotropy D/J for the Heisenberg simple cubic system with easy-plane anisotropy (D positive) and for spin quantum numbers 1 to $\frac{7}{2}$.

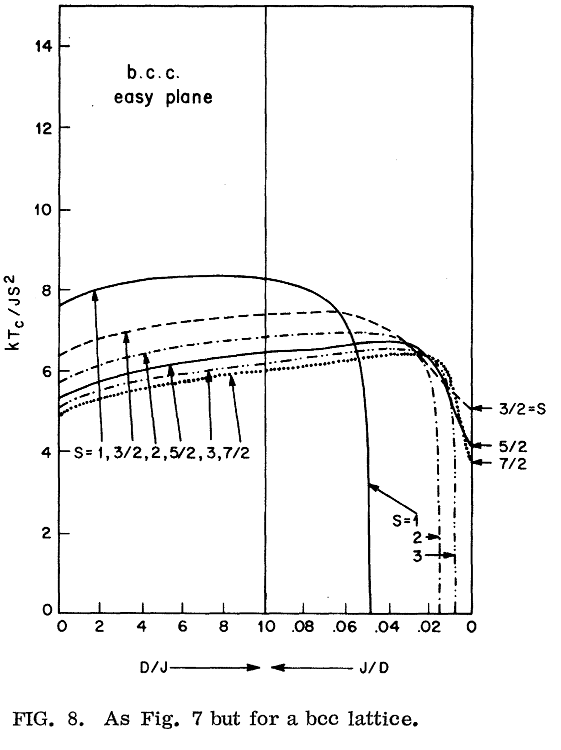

FIG. 8. As Fig. 7 but for a bcc lattice.

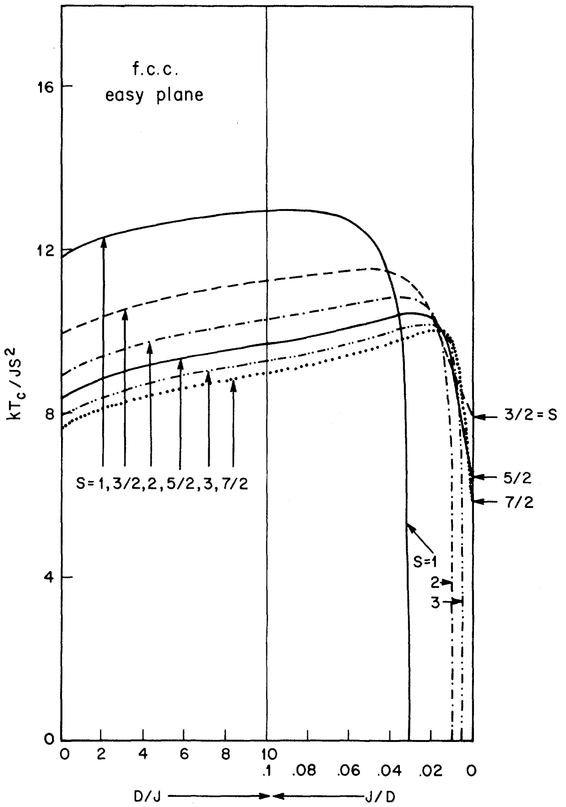

FIG. 9. As Fig. 7 but for a fcc lattice.

$$kT_C^I = 2J(0)(1-\alpha_C^{\parallel})\langle S^{\parallel} : S^{\parallel}\rangle_{D'/kT_C^I},$$

$$D' = D - zJ\alpha_C^{\parallel}, \qquad (3.7)$$

$$kT_C^{\mathrm{MF}} = 2J(0)\langle S^{\parallel} : S^{\parallel}\rangle_{D'/kT_C^{\mathrm{MF}}},$$

$$D' = D. \qquad (3.8)$$

Only the first needs additional information (viz., Eq. (3.1) for the calculation of perpendicular correlations) and a computer for solution. At the extreme easy-axis limit $D/J \rightarrow -\infty$ we verify by simple examination of Eqs. (3 6)–(3.8) that $T_C^H = T_C^I = T_C^{\mathrm{MF}}(1-\alpha_C^{\parallel})$. At the opposite isotropic crystal-field limit $D/J \rightarrow 0$ we again simply verify that $T_C^H = T_C^{\mathrm{MF}}(1-\alpha_C^{\parallel})$, but the equality of T_C^H and T_C^I no longer holds, since whereas $D' \rightarrow 0$ in this limit for the Heisenberg problem (with parallel and perpendicular correlations becoming equal), $D' \rightarrow -zJ\alpha_C^{\parallel}$ for the Ising system (the inherent anisotropy of the Ising exchange still splitting the local spin levels $|m\rangle$ even when the crystal-field anisotropy has vanished). The resulting $T_C^I(D=0)$ is higher than $T_C^H(D=0)$ and, since $T_C^I(D=-\infty) = T_C^H(D=-\infty)$, this suggests that the Ising system will be less sensitive to crystal-field anisotropy than its Heisenberg counterpart. Such is indeed established by numerical solution, as we show in Fig. 6 for $S=1$

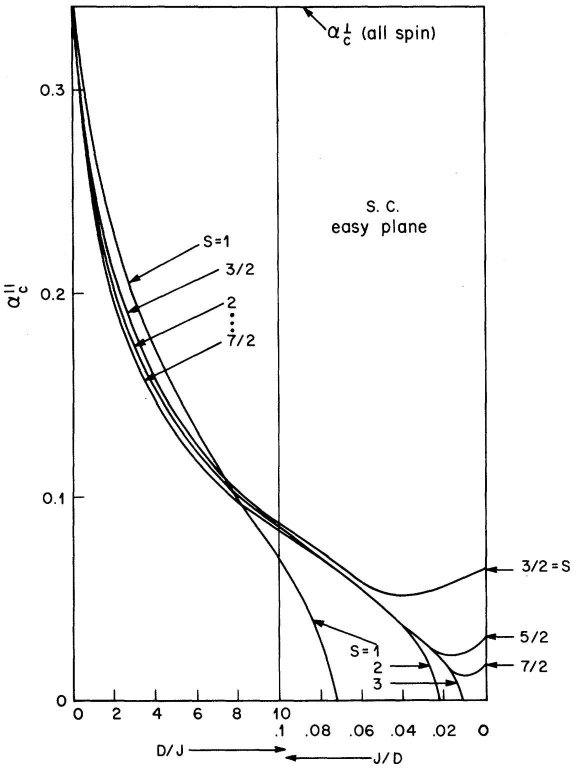

FIG. 10. Correlation parameters $\alpha_C^{\parallel}$ and $\alpha_C^\perp$ of the CEF theory as a function of anisotropy D/J for the Heisenberg simple cubic system with easy-plane anisotropy.

and the sc lattice. Thus, whereas the CEF and Yang and Wang estimates for $T_C(D/J)/T_C(0)$ are generally greater than the molecular-field curve for the Heisenberg problem, they are both very close to the molecular-field estimate for the Ising case except at higher anisotropies, where they fall below molecular field. This is in qualitative accord with the series expansion findings of Brankov *et al.*[12] for the Ising system, which are also plotted in Fig. 6.

IV. EASY-PLANE CASE

When the anisotropy parameter D takes on positive values it favors a divergence of perpendicular susceptibility (in the xy plane). This situation creates a more difficult decoupling problem for Green's-function techniques and to my knowledge has not yet been attempted in the literature, although there have been some efforts (e.g., Lines[15]) to discuss the easy-plane problem for exchange anisotropy. From Eq. (2.8) it is immediately evident that for positive D' [or equivalently positive D, since $\alpha_\perp > \alpha_\parallel$ in Eq. (2.9) for the easy-plane situation] the problem takes on a different character for integral or half-integral spins. In the former case the lowest local CEF crystal-field is a singlet $|0\rangle$, with energy $E(0) = 0$, and for large enough values of D/J the exchange interaction is unable to induce a spontaneous moment into this singlet single-ion ground state even in the limit of temperature T going to zero. For this case there will exist a "critical" value of D/J which marks the limit of stability of the singlet-ground-state ferromagnetic order. For half-integer spins the lowest CEF crystal-field level is the doubly degenerate $|\pm\frac{1}{2}\rangle$, $E(\pm\frac{1}{2}) = \frac{1}{4}D'$ which can be split at low enough temperatures by even an infinitesimal exchange field for any D'. It follows that a finite Curie temperature exists for the whole range $0 < D/J < \infty$ for the case of half-integer spins.

For positive D the direction μ of incipient ordering, when a susceptibility divergence occurs, is $\perp z$. For this case, therefore, from Eq. (2.10), $\alpha_C^\mu = \alpha_C^\perp$. This leaves as "unknowns" the Curie temperature $T_C^\perp = T_C$ and $\alpha_C^{\parallel}$. They are obtained from the numerical solution of the simultaneous Eqs. (2.2), with $T = T_C$ and $\lambda = \parallel$, and (2.5), with $\lambda = \perp$, i.e., of

$$\alpha_C^{\parallel} = \frac{\sum_{\vec{q}} J(\vec{q})\{kT_C - 2[J(\vec{q}) - \alpha_C^{\parallel} J(0)]\langle S^{\parallel} : S^{\parallel}\rangle_{T=T_C}\}^{-1}}{\sum_{\vec{q}} J(0)\{kT_C - 2[J(\vec{q}) - \alpha_C^{\parallel} J(0)]\langle S^{\parallel} : S^{\parallel}\rangle_{T=T_C}\}^{-1}} \tag{4.1}$$

and

$$kT_C = kT_C^\perp = 2J(0)(1 - \alpha_C^\perp)\langle S^\perp : S^\perp\rangle_{T=T_C}, \tag{4.2}$$

where $\langle S^{\parallel} : S^{\parallel}\rangle$ and $\langle S^\perp : S^\perp\rangle$ are taken from Table I and $\alpha_C^\perp \approx 0.341$ (sc), 0.282 (bcc), and 0.256 (fcc).

These equations have been solved numerically for the complete easy-plane range of anisotropy $0 < D/J < \infty$. The results for Curie temperature are shown in Figs. 7–9 for the sc, bcc, and fcc lattices, respectively, and for $S = 1$ to $S = \frac{7}{2}$ inclusive for each case. The corresponding curves for critical ($T = T_C$) correlation $\alpha_C^{\parallel}$ as a function of anisotropy are shown only for the sc lattice (Fig. 10). The correlation curves for the other lattices are qualitatively similar to those shown for the sc case.

We see, in general, that the transition temperature increases at first as a function of D/J, but then goes through a maximum and falls off at higher anisotropy values. For half-integral spin the falloff is to finite T_C values in the infinite D/J limit, while for integer spin, T_C as a function of D/J falls continuously to zero at a large, but finite and

TABLE II. Critical values of D/J for which singlet-ground-state ferromagnetism is just stable at $T_C = 0$, as calculated in the CEF approximation.

$(D/J)_{T_C \to 0}$	$S=1$	$S=2$	$S=3$
sc	13.784	45.439	92.921
bcc	20.711	66.648	135.55
fcc	32.621	104.01	211.10

spin-dependent, value of D/J.

The limiting case of $D/J \to \infty$ and half-integer spin is not difficult to probe analytically within the theory. Restricting the calculation to only the lowest degenerate pair of local spin states we readily establish that

$$T_C(S) = (S+\tfrac{1}{2})^2 T_C(S=\tfrac{1}{2}), \quad D/J \to \infty, \tag{4.3}$$

where $T_C(S=\frac{1}{2})$ is the Curie temperature for the equivalent spin-$\frac{1}{2}$ system, which is unaffected by single spin anisotropy and in CEF approximation is

$$kT_C(S=\tfrac{1}{2}) = \tfrac{1}{2}J(0)(1-\alpha_C^{\mu}), \tag{4.4}$$

with α_C^{μ} given by Eq. (2.10).

The "critical" D/J value for the vanishing of singlet-ground-state magnetism with integer S can also be probed analytically using Eqs. (4.1) and (4.2). Writing $\langle S^{\perp} : S^{\perp} \rangle = (2/y)\phi_S$ from Table I, where $y = D'/kT_C$ we find that $\alpha_C^{\parallel} \to 0$ and $T_C \to 0$ when

$$D/J = z[4\phi_S - \alpha_C^{\perp}(4\phi_S + 1)]. \tag{4.5}$$

Using the relevant values of $\alpha_C^{\perp}$ and the fact that $\phi_1 = 1$, $\phi_2 = 3$, $\phi_3 = 6$, ..., from Table I we calculate the critical values of D/J within CEF theory as shown in Table II.

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