Spherical Model of an Antiferromagnet*

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(Received March 31, 1954)

The sphericalization technique is adapted to the calculation of the partition function of a body-centered cubic lattice of spins with isotropic antiferromagnetic interactions between nearest neighbors and between second-nearest neighbors. Two transition points may be obtained. The usual Curie point transition from the paramagnetic state to the antiferromagnetic state (caused by the sticking of the saddle point) leads to an antiferromagnetic state with ordering either of the first kind or of the second kind, depending on the value of the ratio of the second-nearest neighbor interaction to the nearest-neighbor interaction. In addition a first-order transition from one kind of ordering to the other can occur if the ratio of the interactions varies with the specific volume in such a way that it moves through a critical value. Mathematically, this transition occurs because the largest eigenvalue of the interaction matrix becomes triply degenerate at the temperature at which the ratio of the interactions attains the critical value.

The long-range order is measured in terms of long-range order parameters, which are closely related to the sublattice magnetizations. The analog of the perpendicular susceptibility is also calculated.

Qualitative agreement with the molecular field theory is obtained for all those properties of the model which depend on the long-range order. In contrast to the molecular field theory, this model should give valid predictions for quantities depending on short-range order.

INTRODUCTION

In recent years, interest in the study of antiferromagnetism has grown steadily. Extensive experimental investigations have been paralleled by attempts to develop a theory of antiferromagnetism.[1–4] Considerable success has been achieved at very low temperatures, where the spin wave theory provides the necessary mathematical framework.[5–7] At higher temperatures, particularly in the vicinity of the critical points, the situation is far less satisfactory. While the phenomenological molecular field theory serves a useful heuristic purpose, it fails to give a consistent and reliable description of magnetic phenomena near the Curie point.

The Van Vleck molecular field theory starts out from the well-known physical result that short-range forces are responsible for antiferromagnetism. Physically, this clearly implies that the local field acting on each spin is determined by the local magnetic order. The molecular field theory, however, proceeds to set the local field proportional to the magnetization of a sublattice—a magnetization existing only when long-range order is present. This approximation has a measure of validity well below the Curie temperature, where long-range order is actually present; but it fails completely just above the Curie temperature, where local order persists even though long-range order is absent. In the entire region of the transition temperature, it is not always clear which predictions of the theory are consequences of the model and which are due to the approximations.

The purpose of this paper is to adapt the recently developed "sphericalization" technique to the study of antiferromagnetism.[8–12] This is a method which can be applied to a well-defined mathematical model, the "spherical" model of an antiferromagnet, and which permits the calculation of pertinent physical quantities without approximations other than that of letting the number of spins tend to infinity. The results of these calculations will, therefore, be rigorously true for the spherical model. The question still remains whether the spherical model is a good approximation to the physical antiferromagnet. We believe that it merits careful study because of its success in the treatment of ferromagnetism.

THE SPHERICAL MODEL

Let us define our model. Consider a body-centered[13] cubic lattice of N spins, each of which is a classical vector fixed at a point in space but free to rotate about it. We shall assume that there are isotropic antiferromagnetic interactions both between nearest neighbors and between next nearest neighbors. The spins will be required to obey the spherical condition

$$\sum_j \mathbf{S}_j^2 = NS(S+1), \tag{1}$$

where the summation extends over the N spins. This condition will be imposed rather than the more usual quantum condition,

$$\mathbf{S}_j^2 = S(S+1), \quad j=0, 1, 2, \cdots N-1, \tag{2}$$

in order to render the model tractable. The substitution

* This work was supported by the Bureau of Ordnance, Department of the Navy.

[1] J. H. Van Vleck, J. Chem. Phys. **9**, 85–90 (1941).
[2] P. W. Anderson, Phys. Rev. **79**, 705–710 (1950).
[3] J. H. Van Vleck, J. phys. radium **12**, 262 (1951).
[4] J. S. Smart, Phys. Rev. **90**, 55 (1953).
[5] P. W. Anderson, Phys. Rev. **86**, 694 (1952).
[6] Keffer, Kaplan, and Yafet, Am. J. Phys. **21**, 250 (1953).
[7] J. R. Tessman, Phys. Rev. **88**, 1132 (1952).
[8] T. H. Berlin and M. Kac, Phys. Rev. **86**, 821 (1952).
[9] E. W. Montroll, Nuovo cimento **6**, Supplement No. 2, 265 (1949).
[10] M. Lax, J. Chem. Phys. **20**, 1351 (1952).
[11] T. H. Berlin and J. S. Thomsen, J. Chem. Phys. **20**, 1368 (1952).
[12] An entirely different approach to the problem has been adopted by Y. Y. Li, Phys. Rev. **84**, 721 (1951). He uses the cluster method of Bethe, Peierls, and Weiss.
[13] The body-centered cubic lattice appeared to be somewhat easier to handle analytically than the more interesting case of the face-centered cubic.

of the continuum model (1) for the more conventional discrete model (2) leads to spurious effects at very low temperatures. Berlin and Kac[8] have shown, however, that at higher temperatures the spherical model (1) closely approximates the discrete model (2). It should, therefore, be no worse an approximation to the physical situation than is the discrete model (2).

The Hamiltonian of our system is of the form

$$H=-\sum_{jk} B_{jk}\mathbf{S}_j\cdot\mathbf{S}_k-g\beta_0\mathbf{H}\cdot\sum_j \mathbf{S}_j. \tag{3}$$

Here, $\mathbf{S}_j$ is the classical spin vector at the jth lattice point, B_{jk} the interaction coefficient between the jth and the kth spins, g the spectroscopic splitting factor, β_0 the Bohr magneton, and $\mathbf{H}$ the externally applied, uniform, static magnetic field.

Two types of properties of the model are of interest to us: the thermodynamic quantities, and the long-range magnetic order parameters. The former can be obtained from the partition function. The latter are closely related to the magnetizations of the sublattices, and are obtained from the expectation value of the absolute magnitude of a certain linear function of the $\mathbf{S}_j$.

The partition function can be written as

$$Z=\int d^3S_0\int d^3S_1\cdots\int d^3S_{N-1}\times\exp[\sum_{ij} A_{ij}\mathbf{S}_i\cdot\mathbf{S}_j+\mathfrak{K}\cdot\sum_j \mathbf{S}_j]\cdot\delta[\sum_j \mathbf{S}_j^2-NS(S+1)], \tag{4}$$

where

$$A_{ij}=(B_{ij}/kT),\quad \mathfrak{K}=(g\beta_0/kT)\mathbf{H}, \tag{5}$$

the integration is extended over all spin space, and constraint (1) is imposed by the introduction of the Dirac delta function under the integral sign. The multiple integral of (4) can be reduced to a single integral over an auxiliary variable t in the following steps.

(a) Replace the delta function by its Fourier integral representation,

$$\delta\{\textstyle\sum_j S_j^2-NS(S+1)\}=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} dt\exp\{-t[\textstyle\sum_j S_j^2-NS(S+1)]\}, \tag{6}$$

choose γ large and positive, and interchange the order of integrations.

(b) Introduce the new variables

$$\mathbf{S}_j=\boldsymbol{\sigma}_j+\mathbf{C},\quad \mathbf{C}=\mathbf{C}(t), \tag{7}$$

where $\mathbf{C}$ is chosen so as to eliminate the linear terms from the exponent. The explicit expression for $\mathbf{C}$ is given in Eq. (25).

(c) Then diagonalize the interaction matrix A_{ij} (which will be shown to be symmetric and cyclic) by the real orthogonal transformation T_{jk}. The partition function now becomes

$$Z=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} dt\varphi(t)\exp[NH^2G(t)+NS(S+1)t], \tag{8}$$

where

$$\varphi(t)=\int d^3u_0\int d^3u_1\cdots\int d^3u_{N-1}\times\exp\{-[\textstyle\sum_j(t-\Lambda_j)u_j^2]\}=\pi^{(3N/2)}\prod_{j=0}^{N-1}(t-\Lambda_j)^{-3/2},\quad \gamma>\mathrm{Max}(\Lambda_j). \tag{9}$$

Here, the $\mathbf{u}_j$ are related to the $\boldsymbol{\sigma}_k$ by the transformation equations:

$$\mathbf{u}_j=\textstyle\sum_k T_{kj}\boldsymbol{\sigma}_k. \tag{10}$$

They are the eigenvectors of A_{ij}. The Λ_j are the eigenvalues of A_{ij} and are given by

$$\Lambda_j=(\tilde{T}AT)_{jj}. \tag{11}$$

$G(t)$ is a function of t only, arising from the transformation of (b). Its explicit form will be given later [see Eq. (26)].

One major task of this paper is the evaluation of (8). The other is the calculation of the expectation value of the absolute magnitude of a Cartesian component of the eigenvector $\mathbf{u}_j$. It will be shown later that this expectation value is closely related to the magnetizations of the sublattices.

The actual evaluation of (8) is performed by a saddle point method. In order to be able to investigate the existence and location of the saddle point, we must know the explicit form of the eigenvalues. We shall proceed to deduce them presently.

THE INTERACTION MATRIX

In order to facilitate the interpretation of our results in terms of the sublattice picture, the following scheme is adopted for numbering the spins. The original body centered cubic lattice is divided into two simple cubic sublattices, the A and B sublattices.[3] Then the nearest neighbors of a spin on A are on sublattice B, and *vice versa*. Sublattice A is further subdivided into two face centered cubic sublattices A_1 and A_2, so that all the second nearest neighbors of a spin on A_1 are found on sublattice A_2 and *vice versa*. A similar subdivision is carried out on the B sublattice.

Analytically this subdivision is effected as follows. Assume a set of rectangular axes along the cube edges, and consider the three families of planes (see Fig. 1):

$$\begin{aligned} -x+y+z&=p, \quad p=0,1,2\cdots 2n_1-1;\\ +x-y+z&=q, \quad q=0,1,2\cdots 2n_2-1;\\ +x+y-z&=s, \quad s=0,1,2\cdots 2n_3-1. \end{aligned} \tag{12}$$

It is clear that the position of each spin can be specified by the triad of numbers (p,q,s) as well as by the Car-

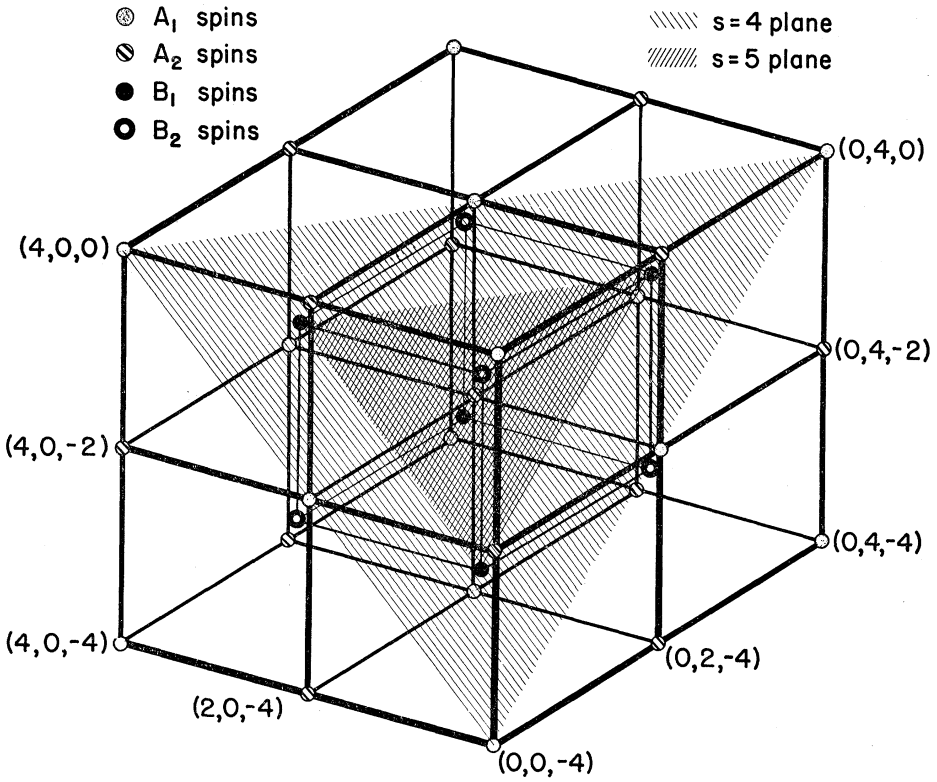

FIG. 1. Some of the $x+y-z=s$ planes.

tesian coordinates (x,y,z). In fact,

$$x=\tfrac{1}{2}(q+s),\quad y=\tfrac{1}{2}(s+p),\quad z=\tfrac{1}{2}(p+q). \tag{13}$$

In order that the Cartesian coordinates of each spin be integers, p,q, and s must be either all odd or all even. It is then possible to choose the sublattices so that

$$\begin{aligned} &s=4m && \text{for the } A_1 \text{ sublattice,}\\ &s=4m+1 && \text{for the } B_1 \text{ sublattice,}\\ &s=4m+2 && \text{for the } A_2 \text{ sublattice,}\\ &s=4m+3 && \text{for the } B_2 \text{ sublattice,} \end{aligned} \tag{14}$$

where m is an integer or zero. The total number of spins in the crystal is evidently

$$2n_1n_2n_3=N. \tag{15}$$

The position of each spin can also be designated by the single number j, where

$$\begin{aligned} &j=s+n_3q+n_2n_3p,\\ &j=0,\ 2,\ \cdots N-2 \text{ for even } p,\ q, \text{ and } s;\\ &j=1+(n_3+n_2n_3),\ 3+(n_3+n_2n_3),\ \cdots\\ &\qquad N-1+(n_3+n_2n_3) \text{ for odd } p,\ q, \text{ and } s. \end{aligned} \tag{16}$$

It is convenient to assume that n_3 is a multiple of 4. Then

$$\begin{aligned} &j=4m && \text{for } A_1,\\ &j=4m+1 && \text{for } B_1,\\ &j=4m+2 && \text{for } A_2,\\ &j=4m+3 && \text{for } B_2. \end{aligned} \tag{17}$$

Since the matrix A_{ij} is defined as the matrix of interactions between nearest neighbors and next-nearest neighbors, it must be symmetric and invariant under a translation of coordinates. Consequently,

$$A_{(i+k)(j+k)}=A_{ij}, \tag{18}$$

$$A_{ij}=A_{ji}. \tag{19}$$

In order to simplify the calculations, we also impose periodic boundary conditions on the crystal lattice by requiring

$$A_{(i+N)j}=A_{ij}. \tag{20}$$

The periodicity condition (20) permits us to change the range of j from the one given in (16) to

$$j=0,\ 1,\ 2,\ \cdots N-1. \tag{21}$$

This merely rearranges the order of appearance of the various terms, but does not affect their value. The resulting matrix has the form

$$A_{ij}=c_{j-i}=c_{i-j}=c_{j-i+N}. \tag{22}$$

The problem of determining the interaction matrix now reduces to that of finding $(j-i)$ for nearest and next-nearest neighbors. Let one spin be situated at (x,y,z) and have the index i, and let the other spin be at (x',y',z') and have the index j. Then Table I gives $(j-i)$ for nearest neighbors and for next-nearest neighbors. For nearest neighbors

$$c_{j-i}=-(J/kT)=-K, \tag{23}$$

and for next-nearest neighbors

$$c_{j-i}=-(J'/kT)=-K'. \tag{24}$$

J and J' are interaction coefficients given by the appropriate superexchange theory (in principle at least). From this table it is clear that the nearest neighbors of a spin on A_1 are distributed equally between B_1 and B_2. The next nearest neighbors of a spin on A_1 are all on A_2. Analogous statements hold for the other sublattices.

Digressing from our subject for a moment, we note that it is now evident that $\mathbf{C}$ in Eq. (7) is

$$\mathbf{C}=\mathfrak{C}/[2(t+8K+6K')], \tag{25}$$

and that $G(t)$ is given by

$$G(t)=\left(\frac{g\beta_0}{2kT}\right)^2\frac{1}{t+8K+6K'}. \tag{26}$$

When the external field is zero, $\mathbf{S}_k=\boldsymbol{\sigma}_k$.

We now return to the determination of the eigenvalues of the interaction matrix. It is shown in the literature[8] that the cyclic, symmetric matrix A_{ij} can be diagonalized by the real orthogonal transformation T_{jk}, where the T_{jk} are given by

$$T_{jk}=(2/N)^{\frac{1}{2}}\cos[(2\pi jk/N)+\tfrac{1}{4}\pi]. \tag{27}$$

The eigenvalues become

$$\Lambda_m=\sum_{k=0}^{N-1}c_k\cos(2\pi km/N)=\Lambda_{N-m}. \tag{28}$$

It is evident from Eq. (28) that all but two of the eigenvalues are doubly degenerate. The two nondegenerate eigenvalues are Λ_0 and $\Lambda_{N/2}$. The degeneracy derives from the symmetry and periodicity of the matrix (A_{ij}). Substituting the values of the c_k, we obtain the explicit form of the eigenvalues.

$$\begin{aligned}\Lambda_m=&-2K[\cos(\Omega_1+\Omega_2+\Omega_3)+\cos(-\Omega_1+\Omega_2+\Omega_3)\\&+\cos(+\Omega_1-\Omega_2+\Omega_3)+\cos(+\Omega_1+\Omega_2-\Omega_3)]\\&-2K'(\cos2\Omega_1+\cos2\Omega_2+\cos2\Omega_3)\\=&-8K\cos\Omega_1\cos\Omega_2\cos\Omega_3\\&-2K'(\cos2\Omega_1+\cos2\Omega_2+\cos2\Omega_3),\end{aligned} \tag{29}$$

$$\begin{aligned}\Omega_1&=(2\pi m/N)(n_2n_3-n_3-1),\\\Omega_2&=(2\pi m/N)(n_2n_3+n_3-1),\\\Omega_3&=(2\pi m/N)(n_2n_3-n_3+1).\end{aligned} \tag{30}$$

THE PARTITION FUNCTION

It will be convenient to define

$$z=t/2K, \tag{31}$$

$$\rho=K'/K=J'/J, \tag{32}$$

$$\lambda_m=\Lambda_m/2K. \tag{33}$$

In this notation, the partition function becomes

$$Z=\frac{K}{\pi i}\int_{\gamma'-i\infty}^{\gamma'+i\infty}dz\exp\{N[H^2G(2Kz)+S(S+1)2Kz]\}\varphi(2Kz),\quad\gamma'>\mathrm{Max}(\lambda_m). \tag{34}$$

TABLE I. Values of $(j-i)$ for nearest neighbors and next-nearest neighbors.

$x'-x$	$y'-y$	$z'-z$	$p'-p$	$q'-q$	$s'-s$	$(j-i)$
			Nearest neighbors			
1	1	1	1	1	1	$1+n_3+n_2n_3$
−1	1	1	3	−1	−1	$-1-n_3+3n_2n_3$
1	−1	1	−1	3	−1	$-1+3n_3-n_2n_3$
1	1	−1	−1	−1	3	$+3-n_3-n_2n_3$
−1	−1	1	1	1	−3	$-3+n_3+n_2n_3$
−1	1	−1	1	−3	1	$1-3n_3+n_2n_3$
1	−1	−1	−3	1	1	$1+n_3-3n_2n_3$
−1	−1	−1	−1	−1	−1	$-1-n_3-n_2n_3$
			Next-nearest neighbors			
2	0	0	−2	2	2	$+2+2n_3-2n_2n_3$
−2	0	0	2	−2	−2	$-2-2n_3+2n_2n_3$
0	2	0	2	−2	2	$2-2n_3+2n_2n_3$
0	−2	0	−2	2	−2	$-2+2n_3-2n_2n_3$
0	0	2	2	2	−2	$-2+2n_3+2n_2n_3$
0	0	−2	−2	−2	2	$2-2n_3-2n_2n_3$

In order to perform the saddle point integration, it will be necessary to obtain a more manageable expression for $\varphi(t)$ than the one given by Eq. (9). This is done in Appendix I. A tractable expression is obtained for the product in Eq. (9), after first factoring out the terms containing the largest eigenvalue. Let

$$\begin{aligned}\lambda(\omega_1,\omega_2,\omega_3)=&-\cos(\omega_1+\omega_2+\omega_3)-\cos(-3\omega_1+\omega_2+\omega_3)\\&-\cos(\omega_1-3\omega_2+\omega_3)-\cos(\omega_1+\omega_2-3\omega_3)\\&-\rho[\cos2(-\omega_1+\omega_2+\omega_3)+\cos2(\omega_1-\omega_2+\omega_3)\\&+\cos2(\omega_1+\omega_2-\omega_3)],\end{aligned} \tag{35}$$

and

$$\lambda_M=\mathrm{Max}(\lambda_m). \tag{36}$$

Note that $\mathrm{Max}(\lambda_m)=\mathrm{Max}[\lambda(\omega_1,\omega_2,\omega_3)]$. The expression for $\varphi(2Kz)$ can take on one of two forms, depending on the value of ρ. Case I: $\rho<\frac{2}{3}$.

$$\lambda_M=4-3\rho=\lambda', \tag{37}$$

corresponding to

$$m=N/2\quad\text{or}\quad\omega_1=\omega_2=0,\quad\omega_3=\pi. \tag{38}$$

Then

$$\exp[NS(S+1)2Kz]\varphi(2Kz)=(\pi/2K)^{3N/2}\exp[Nf(z)]/(z-\lambda')^{\frac{3}{2}}, \tag{39}$$

where

$$f(z)=S(S+1)2Kz-\tfrac{3}{2}(1/2\pi)^3\times\int_0^{2\pi}d\omega_1\int_0^{2\pi}d\omega_2\int_0^{2\pi}d\omega_3\ln[z-\lambda(\omega_1,\omega_2,\omega_3)]. \tag{40}$$

Case II: $\rho>\frac{2}{3}$.

$$\lambda_M=3\rho=\lambda'', \tag{41}$$

corresponding to

$$m=N/2\quad\text{or}\quad3N/2,\quad\text{or}\quad\omega_1=\omega_2=0,\quad\omega_3=\pi/2\quad\text{or}\quad3\pi/2. \tag{42}$$

The largest eigenvalue is doubly degenerate in this case.

$$\exp[NS(S+1)2Kz]\varphi(2Kz)=(\pi/2K)^{3N/2}\exp[Nf(z)]/(z-\lambda'')^3. \tag{43}$$

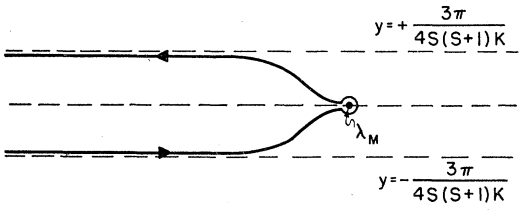

FIG. 2. Path of integration above T_c.

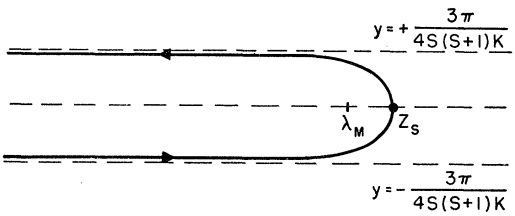

FIG. 3. Path of integration below T_c.

The expression for the partition function becomes, therefore,

$$Z=(1/2i)(\pi/2K)^{3N/2-1}\times\int dz\,\exp[NH^2G(2Kz)+Nf(z)]/(z-\lambda_M)^r, \quad (44)$$

where $r=\frac{3}{2}$ in case I and $r=3$ in case II.

At the point $\rho=\frac{2}{3}$, $\lambda'=\lambda''$. The largest eigenvalue becomes triply degenerate. We shall later show that a transition from one kind of antiferromagnetic ordering to another can take place at this point.

The susceptibility per spin at zero field is given by

$$\chi=\frac{kT}{H}\frac{\partial}{\partial H}\left(\frac{\ln Z}{N}\right)=2kT\frac{\int dz(z-\lambda_M)^{-r}G(2Kz)\exp[Nf(z)]}{\int dz(z-\lambda_M)^{-r}\exp[Nf(z)]}. \quad (45)$$

We shall be interested in the properties of our model in an infinitesimal applied field. A finite external field may shift the position of the Curie point, or, if the applied field is strong enough to saturate the material, it may prevent the transition from taking place. Most of these effects, however, cannot be observed except when a material with a very low Curie point is placed in a strong field. The influence of a finite field may be calculated by the methods used by Berlin and Thomsen[11] and by Lax.[10] In this paper, however, we shall evaluate (44) and (45) only in the limit of vanishing external field.

The existence and location of the saddle point are determined by the equation

$$f'(z)=0=S(S+1)2K-\tfrac{3}{2}(1/2\pi)^3\times\int d\omega_1\int d\omega_2\int d\omega_3[z-\lambda(\omega_1,\omega_2,\omega_3)]^{-1}. \quad (46)$$

Since the integral converges for all values of z, this equation can have a solution z_s only for $K<K_c$, where

$$K_c=\frac{3}{4S(S+1)}(1/2\pi)^3\int d\omega_1\int d\omega_2\int d\omega_3\times[\lambda_M-\lambda(\omega_1,\omega_2,\omega_3)]^{-1}. \quad (47)$$

In this temperature region, $T>T_c$; there exists one normal saddle point. It lies on the real axis, to the right of λ_M. The path of integration is deformed into the path of steepest descent given by $\mathrm{Im}[f(z)]=0$ (see Fig. 2). The saddle point integration is carried through in the usual manner, giving

$$Z=\frac{1}{2}\left(\frac{\pi}{2K}\right)^{3N/2-1}\left[\frac{2\pi}{Nf''(z_s)}\right]^{\frac{1}{2}}\frac{\exp[Nf(z_s)]}{(z_s-\lambda_M)^r}. \quad (48)$$

If $K>K_c(T<T_c)$, on the other hand, the saddle point equation has no solution, and no normal saddle point exists. A path of steepest descent can still be found, however, by setting $\mathrm{Im}[f(z)]=0$. Somewhere along this path (which is shown in Fig. 3), $f'(z)$ must have a branch point. This is the point which now replaces the saddle point and from whose vicinity come most of the contributions to the integral. In Appendix II it is shown that in the vicinity of the point λ_M, $f'(z)$ takes the form

$$f'(z)=2S(S+1)(K-K_c)+(z-\lambda_M)^{\frac{1}{2}}F(0), F(0)>0; \quad (49)$$

and

$$f(z)=f(\lambda_M)+2S(S+1)(K-K_c)(z-\lambda_M)+\tfrac{2}{3}(z-\lambda_M)^{\frac{3}{2}}F(0). \quad (50)$$

Using the first two terms of (50) and remembering the contour integral representation of the gamma function, one obtains

$$Z=\pi\left(\frac{\pi}{2K}\right)^{3N/2-1}\frac{[2S(S+1)(K-K_c)N]^{r-1}}{\Gamma(r)}\times\exp[Nf(\lambda_M)]. \quad (51)$$

The evaluation of (45) is carried out in the same manner, remembering that $G(2Kz)$ is a slowly varying function in the region of the saddle point (or the branch point). The result is

$$\chi=2kTG(2Kz_s), \quad \text{above the Curie point,} \quad (52)$$

and

$$\chi=2kTG(2K\lambda_M), \quad \text{below.} \quad (53)$$

THE THERMODYNAMIC PROPERTIES AND THE NATURE OF THE PHASE TRANSITIONS

We shall define F and U, respectively, as limiting values of the Helmholtz free energy and the internal

energy per spin as N approaches infinity. Then,

$$-F/kT=\tfrac{3}{2}\ln(\pi/2K)+f(z'), \tag{54}$$

where $z'=z_s$ above the Curie point and $z'=\lambda_M$ below.

Before proceeding with the calculation, we must note that J and J' are functions of the interatomic distances in the solid. They are, therefore, functions of the specific volume, and possibly also explicit functions of the temperature. In the following, the calculation will be simplified by the assumption that J and J' are explicit functions of the specific volume only. The specific volume itself, of course, is a function of the temperature and pressure. The implicit dependence of ρ on the temperature gives rise to the possibility of transition from one kind of antiferromagnetic ordering to another. It has been demonstrated already that the analytical form of λ_M changes at $\rho=\frac{2}{3}$. This will be shown to lead to a transition of the first order at $\rho=\frac{2}{3}$. Such a transition can occur in a given substance only if the interaction coefficients J and J' vary with the specific volume in such a way that ρ passes through the value $\frac{2}{3}$ for some temperature below the Curie point. In this section, we shall study the thermodynamic characteristics of the transitions. In the next section, we shall investigate the changes in magnetic order which occur at the transition temperatures.

The internal energy is

$$U=T^2\left[\frac{d}{dT}\left(-\frac{F}{T}\right)\right]_v=\tfrac{3}{2}kT-2S(S+1)Jz', \tag{55}$$

where we have made use of the fact that above the Curie point $f'(z_s)=0$,[14] because of the existence of the saddle point; and below the Curie point,

$$(d\lambda_M/dT)_v=0. \tag{56}$$

From (54) we obtain for the pressure

$$\frac{p}{kT}=\left[\frac{\partial}{\partial v}\left(\frac{-F}{kT}\right)\right]_T=\frac{\partial f(z')}{\partial z'}\left(\frac{\partial z'}{\partial v}\right)_T+\frac{\partial f(z')}{\partial \rho}\left(\frac{\partial \rho}{\partial v}\right)_T+\left(\frac{\partial J}{\partial v}\right)_T\left[\frac{2S(S+1)z'}{kT}-\frac{3}{2J}\right]. \tag{57}$$

The order of the Curie point transition is now readily established. We note that the right-hand member of (57) and its first partial derivatives are continuous through the Curie point. From (54) and (55), we can easily obtain the entropy and show that it and its first partials are also continuous through the Curie point. The second partials are discontinuous, however. Thus the Curie point transition is of the third order. It is clear, therefore, that the inclusion of the next-nearest neighbor interaction in the Hamiltonian has not changed the order of the Curie point transition.

The other transition point (whenever it occurs), however, exhibits quite different characteristics. Here the first term on the right-hand side of (57) is not zero at the transition temperature, for no saddle point exists in this temperature region. It is now easy to show that this transition is of the first order by demonstrating that p, v, and T cannot all be continuous through the transition. This is established by supposing that p, v, T are all continuous in Eq. (57) and considering the increment in the right-hand member as we pass through the transition temperature. Since this increment must be zero, we have

$$0=\left[2KS(S+1)-\frac{3}{2}\left(\frac{1}{2\pi}\right)^3\int_0^{2\pi}d\omega_1\int_0^{2\pi}d\omega_2\times\int_0^{2\pi}d\omega_3\frac{1}{z'-\lambda(\omega_1,\omega_2,\omega_3)}\right]_{\rho=2/3}\left(\frac{d\rho}{dv}\right)_{\rho=2/3}. \tag{58}$$

Since no saddle point exists in this region, the term in the bracket cannot vanish. We have, therefore,

$$(d\rho/dv)_{\rho=2/3}=0. \tag{59}$$

This is obviously a condition which cannot be expected to hold in all materials under all circumstances. Thus it is clear that, in general, p, v, and T cannot all remain constant through this order-order transition. The transition is, therefore, a first order transition.

One other macroscopic property of the model which can be readily obtained is the susceptibility corresponding to the equilibrium configuration of the spin system in a vanishingly small external field. Since no anisotropy has been introduced into the model, the spins tend to assume fixed orientations with respect to each other, but not with respect to a fixed direction in space. When a vanishingly small external magnetic field is applied, the intrinsic magnetizations retain their orientation with respect to each other, but the entire configuration rotates to assume minimum energy. In the molecular field theory, this corresponds to the perpendicular susceptibility. From (52), (53), and (26),

$$\chi=2kTG(2Kz')=\frac{g^2\beta_0^2}{4J}\frac{1}{(z'+4+3\rho)}. \tag{60}$$

From (46), it is clear that far above the Curie point,

$$T=4S(S+1)Jz'/3k. \tag{61}$$

We write, therefore,

$$\chi=\frac{S(S+1)g^2\beta_0^2}{3k}\cdot\frac{1}{\tau+\theta}, \tag{62}$$

where

$$\tau=4S(S+1)Jz'/3k, \tag{63}$$

and

$$\theta=4S(S+1)(4J+3J')/3k. \tag{64}$$

At very high temperatures, $\tau\rightarrow T$. Below the Curie point, τ and θ depend on the temperature only through

[14] We shall continue to use the notation $f'(z)$ for $(df/dz)_{\rho,K}$.

the temperature dependence of J and J'. At $\rho=\frac{2}{3}$, the susceptibility at constant pressure suffers a discontinuous change because of the jump in z'.

LONG-RANGE ORDER PARAMETERS AND SUBLATTICE MAGNETIZATIONS

The commonly used measure of long-range order is the sublattice magnetization per spin, defined by the equation

$$\mathfrak{y}(p)=\frac{4\beta_0 g}{N}\sum_j \mathbf{S}_j, \quad p=A_1, B_1, A_2, B_2, \tag{65}$$

j summed over the p'th sublattice.

The expectation values of these sublattice magnetizations are obviously zero, for our model is spherically symmetric. The calculation of the expectation values of the absolute magnitudes of the $\mathfrak{y}(p)$ is not feasible. Consequently, it is inconvenient to use the sublattice magnetizations directly as a measure of long-range order.

Below the Curie point, the model is predominantly in one eigenstate, the eigenstate of lowest energy, which determines the prevailing long-range magnetic order. The corresponding eigenvector may be expressed as a linear combination of the sublattice magnetizations. It is a simple matter to calculate the expectation value of the absolute magnitude of a Cartesian component of an eigenvector of the interaction matrix. These quantities are also easily obtainable from molecular field theory, and we shall therefore use them as our long-range order parameters.

Our first task is, then, to express some of the eigenvectors in terms of the sublattice magnetizations. Clearly,

$$\frac{\mathbf{u}_0}{\sqrt{N}}=\frac{1}{N}\sum_{l=0}^{N-1}\boldsymbol{\sigma}_l$$

$$=\frac{1}{4g\beta_0}[\mathfrak{y}(A_1)+\mathfrak{y}(A_2)+\mathfrak{y}(B_1)+\mathfrak{y}(B_2)], \tag{66}$$

$$\frac{\mathbf{u}_{N/2}}{\sqrt{N}}=\frac{1}{N}\sum_{l=0}^{N-1}\boldsymbol{\sigma}_l\cos(\pi l)$$

$$=\frac{1}{4g\beta_0}[\{\mathfrak{y}(A_1)+\mathfrak{y}(A_2)\}-\{\mathfrak{y}(B_1)+\mathfrak{y}(B_2)\}]. \tag{67}$$

From (28) we recall that the two eigenvalues $\lambda_{N/4}$ and $\lambda_{3N/4}$ are degenerate. Thus, any linear combination of the eigenvectors $\mathbf{u}_{N/4}$ and $\mathbf{u}_{3N/4}$ is an eigenvector of the interaction matrix. We use, therefore, the linear combinations

$$\frac{1}{\sqrt{N}}\mathbf{v}_{N/4}\equiv\frac{1}{\sqrt{(2N)}}(\mathbf{u}_{3N/4}+\mathbf{u}_{N/4})$$

$$=\frac{\sqrt{2}}{N}\sum_{l=0}^{N-1}\boldsymbol{\sigma}_l\cos\left(\frac{\pi l}{2}\right)=\frac{\sqrt{2}}{4\beta_0 g}[\mathfrak{y}(A_1)-\mathfrak{y}(A)_2], \tag{68}$$

$$\frac{1}{\sqrt{N}}\mathbf{v}_{3N/4}=\frac{1}{\sqrt{(2N)}}(\mathbf{u}_{3N/4}-\mathbf{u}_{N/4})$$

$$=\frac{\sqrt{2}}{N}\sum_{l=0}^{N-1}\boldsymbol{\sigma}_l\sin\left(\frac{\pi l}{2}\right)=\frac{\sqrt{2}}{4\beta_0 g}[\mathfrak{y}(B_1)-\mathfrak{y}(B_2)] \tag{69}$$

which have a simple meaning in terms of the sublattice magnetizations. Defining $\mathbf{v}_0=\mathbf{u}_0$ and $\mathbf{v}_{N/2}=\mathbf{u}_{N/2}$, we introduce the long-range order parameters L_i ($i=0$, $N/4$, $N/2$, $3N/4$), where

$$L_i=\frac{\int d^3\sigma_0\cdots\int d^3\sigma_{N-1}\left|\frac{1}{\sqrt{N}}v_{ix}\right|\delta(\sum_j \boldsymbol{\sigma}_j^2-NS(S+1))\exp(\sum_{jk}A_{jk}\boldsymbol{\sigma}_j\cdot\boldsymbol{\sigma}_k)}{\int d^3\sigma_0\cdots\int d^3\sigma_{N-1}\delta(\sum_j \boldsymbol{\sigma}_j^2-NS(S+1))\exp(\sum_{jk}A_{jk}\boldsymbol{\sigma}_j\cdot\boldsymbol{\sigma}_k)}=\left\langle\left|\frac{1}{\sqrt{N}}v_{ix}\right|\right\rangle. \tag{70}$$

Note that we are considering the case where no external field is applied.

By methods similar to those used in the evaluation of the partition function,[8] we reduce (70) to the form

$$L_i(2\pi K)^{\frac{1}{2}}\int_{\gamma'-i\infty}^{\gamma'+i\infty}dz(z-\lambda_M)^{-r}\exp[Nf(z)]$$

$$=\frac{1}{\sqrt{N}}\int_{\gamma'-i\infty}^{\gamma'+i\infty}dz(z-\lambda_M)^{-r}(z-\lambda_i)^{-1/2}\exp[Nf(z)]. \tag{71}$$

It is now easy to show that above the Curie point, L_i goes to zero as N tends toward infinity. Below the Curie point, there are two cases to be considered. If $i\neq M$,

$$L_i=\lim_{N\to\infty}[2\pi KN(\lambda_M-\lambda_i)]^{-1/2}, \tag{72}$$

this quantity vanishes in the limit. On the other hand, if $i=M$,

$$L_M=\frac{\Gamma(r)}{\Gamma(r+\frac{1}{2})}\left[\frac{S(S+1)}{\pi}\left(1-\frac{T}{T_c}\right)\right]^{\frac{1}{2}}. \tag{73}$$

Above the Curie temperature there is no long-range order. This follows from the fact that the L_i are all zero.

$$\begin{aligned}
L_0=0&=\frac{1}{4g\beta_0}\langle|\mu_x(A_1)+\mu_x(A_2)+\mu_x(B_1)+\mu_x(B_2)|\rangle,\\
L_{N/2}=0&=\frac{1}{4g\beta_0}\langle|\mu_x(A_1)+\mu_x(A_2)-\mu_x(B_1)-\mu_x(B_2)|\rangle,\\
L_{N/4}=0&=\frac{\sqrt{2}}{4g\beta_0}\langle|\mu_x(A_1)-\mu_x(A_2)|\rangle;\\
L_{3N/4}=0&=\frac{\sqrt{2}}{4g\beta_0}\langle|\mu_x(B_1)-\mu_x(B_2)|\rangle.
\end{aligned}\tag{74}$$

According to the sublattice picture, this implies that all the sublattice magnetizations vanish.

Below the Curie temperature, there are two cases to be distinguished. In Case I, $\rho<\frac{2}{3}$, and only $L_{N/2}\neq 0$.

$$\begin{aligned}
&L_0=L_{N/4}=L_{3N/4}=0,\\
L_{N/2}&=\frac{1}{2}\left[S(S+1)\left(1-\frac{T}{T_c}\right)\right]^{\frac{1}{2}}\\
&=\frac{1}{4g\beta_0}\langle|\mu_x(A_1)+\mu_x(A_2)-\mu_x(B_1)-\mu_x(B_2)|\rangle.
\end{aligned}\tag{75}$$

In terms of the sublattice picture, this implies antiferromagnetic ordering of the first kind. This means that most of the spins on the A sublattice are parallel and most of the spins on the B sublattice are parallel, but the A spins are antiparallel to the B spins. In Case II, on the other hand, $\rho>\frac{2}{3}$ and $L_{N/4}=L_{3N/4}\neq 0$. In fact,

$$\begin{aligned}
&L_0=L_{N/2}=0,\\
L_{N/4}&=\frac{16}{15\pi}\left[S(S+1)\left(1-\frac{T}{T_c}\right)\right]^{\frac{1}{2}}\\
&=\frac{\sqrt{2}}{4g\beta_0}\langle|\mu_x(A_1)-\mu_x(A_2)|\rangle,\\
L_{3N/4}&=\frac{16}{15\pi}\left[S(S+1)\left(1-\frac{T}{T_c}\right)\right]^{\frac{1}{2}}\\
&=\frac{\sqrt{2}}{4g\beta_0}\langle|\mu_x(B_1)-\mu_x(B_2)|\rangle.
\end{aligned}\tag{76}$$

The interpretation is that ordering of the second kind prevails. The net magnetization of the A sublattice and the net magnetization of the B sublattice vanish. The magnetization of the A_1 sublattice is equal and opposite to the magnetization of the A_2 sublattice, and similarly for the B_1 and B_2 sublattices. The magnetizations of A_1 and B_1 (or B_2) appear to be completely uncorrelated.

DISCUSSION

The range of validity of the classical spherical model of the antiferromagnet is bounded at the low temperature end by the omission of quantum effects. The quantum conditions have been violated in two ways: On the one hand, the operator $\mathbf{S}_i\cdot\mathbf{S}_j$ has been treated as a c number; on the other hand, the use of the spherical condition means that the quantization of each $\mathbf{S}_j^2$ has been relaxed. Practically, this limitation is probably less serious in the case of antiferromagnetism than it is in ferromagnetism. In ferromagnetism, interest is usually centered on the behavior of the saturation magnetization, a quantity best observed at very low temperatures where quantum effects are paramount. In antiferromagnetism, on the other hand, interest is usually centered on the behavior of the susceptibility in the vicinity of the transition temperature where quantum effects are probably less important and the sphericalization procedure may be expected to hold.

The spherical model combines into one formalism many of the advantages of the molecular field theory and the Bethe-Peierls-Weiss-Li (B.P.W.L.) cluster theory. It retains much of the simplicity of the molecular field theory below the Curie point and yet it holds in the region of the transition temperature and above. It predicts a transition of higher order at the Curie point, the local order smoothing the way for the onset of long-range order. A more thorough investigation of the local order can be easily performed by calculating the correlation function $\langle\mathbf{S}_i\cdot\mathbf{S}_j\rangle$. The onset of local order well above the Curie point is predicted by the spherical model and the B.P.W.L. theory, and is confirmed by experiment, but is not envisaged by the molecular field theory.

Below the Curie point, long-range order parameters L_i are introduced to furnish a quantitative measure of long-range order. The L_i are expressed in terms of the sublattice magnetizations for convenience in comparison with molecular field theory. It should be noted, of course, that the sublattice concept facilitates interpretation, but is not essential to the spherical model.

Two kinds of antiferromagnetic ordering can occur below the Curie point. A first-order transition between the two kinds of order is predicted, in agreement with the thermodynamic theory of Smart.[4]

The susceptibility corresponding to the equilibrium configuration of the spin system in a vanishingly small external field has been calculated on the spherical model. It agrees qualitatively with the perpendicular susceptibility of the molecular field theory, to which it corresponds. Below the Curie temperature, it assumes a constant value for a given kind of long-range order, if the interaction coefficients J and J' do not vary with the volume. Above the Curie temperature, it follows a modified Curie-Weiss law. The analog of the parallel susceptibility cannot be calculated from an isotropic model with a single spherical constraint.

The qualitative features of the sphericalized antiferromagnet agree well with the available experimental information.[1,3,4] A quantitative comparison with the experimental data was not attempted because the authors are not aware of any data on body-centered antiferromagnets. For the same reason we have not carried through the discussion of the case of one ferromagnetic and one antiferromagnetic interaction, or the evaluation of the integral for K_c. The latter quantity is required for the numerical calculation of (θ/T_c), a ratio convenient for the quantitative comparison of theory and experiment. The present theory appears to be easily adaptable to the somewhat more complicated case of a face-centered cubic lattice, for which experimental data are available.

ACKNOWLEDGMENTS

We are indebted to Professor T. H. Berlin and Professor E. W. Montroll and to Dr. J. S. Smart and Dr. R. K. Wangsness for informative and stimulating discussions. This research would not have been accomplished without the encouragement of Dr. F. T. McClure and Dr. C. K. Jen.

APPENDIX I

In part I of this appendix, we shall obtain the maximum eigenvalues of the interaction matrix. In part II, we derive a tractable expression for $\varphi(t)$.

Part I. It is clear from part II that the Ω's may be regarded as independent variables. We therefore determine $\lambda_{\max}$[15] by regarding the Ω's as continuous variables, and verify that $\lambda_{\max}$ actually occurs for an integral m. It is now clear from Eq. (29) that the equations $\partial\lambda/\partial\Omega_r=0$, $(r=1,2,3)$, become

$$\begin{aligned}&\sin\Omega_1[\cos\Omega_2\cos\Omega_3+\rho\cos\Omega_1]=0,\\&\sin\Omega_2[\cos\Omega_3\cos\Omega_1+\rho\cos\Omega_2]=0,\\&\sin\Omega_3[\cos\Omega_1\cos\Omega_2+\rho\cos\Omega_3]-0.\end{aligned}\qquad\text{(A-I-1)}$$

The two roots which can be absolute maxima correspond to the following two cases:

Case I

$$\cos\Omega_1=\cos\Omega_2=\cos\Omega_3=-1.$$

The maximum eigenvalue for this case (λ') is given by

$$\lambda'=4-3\rho. \qquad \text{(A-I-2)}$$

To determine the value of m corresponding to this case, note that each Ω is an odd multiple of π, i.e., $\Omega_1=(2\nu_1+1)\pi$, $\Omega_2=(2\nu_2+1)\pi$, $\Omega_3=(2\nu_3+1)\pi$ where ν_1, ν_2, ν_3, are integers or zero. From Eq. (30),

$$m=(N/4\pi)(\Omega_3-\Omega_1). \qquad \text{(A-I-3)}$$

For this case, the above equation can be rewritten in terms of the ν's as

$$m=(N/2)(\nu_3-\nu_1). \qquad \text{(A-I-4)}$$

It is evident that the two possible values of $\nu_3-\nu_1$ which are consistent with $0\leq m\leq N-1$ are the values 0 and 1. The unique value of m for which the three conditions $(\cos\Omega_1=\cos\Omega_2=\cos\Omega_3=-1)$ are satisfied is readily determined by substituting the above possibilities into Eq. (30). The result is that the value of m corresponding to $\lambda'=4-3\rho$ is

$$m=N/2. \qquad \text{(A-I-5)}$$

Case II

$$\cos\Omega_1=\cos\Omega_2=\cos\Omega_3=0.$$

The maximum eigenvalue for this case (λ'') is given by

$$\lambda''=3\rho. \qquad \text{(A-I-6)}$$

To determine the value of m for which these conditions on $\cos\Omega$ are satisfied, note that each Ω must be an odd half-integer multiple of π, i.e.,

$$\Omega_1=(\nu_1+\tfrac{1}{2})\pi,\quad \Omega_2=(\nu_2+\tfrac{1}{2})\pi,$$

and

$$\Omega_3=(\nu_3+\tfrac{1}{2})\pi.$$

It follows from Eq. (A-I-3) that

$$m=\frac{N}{4}(\nu_3-\nu_1), \qquad \text{(A-1-7)}$$

which limits $(\nu_3-\nu_1)$ to the possible values 0, 1, 2, 3. It follows from Eq. (30) that only the values $\nu_3-\nu_1=1$, 3 are consistent with (A-I-6), so that the values of m corresponding to case II are

$$m=N/4, \qquad \text{(A-I-8)}$$

and

$$m=3N/4. \qquad \text{(A-I-9)}$$

The two roots are plotted in Fig. 4. From this plot it is clear that for $\rho<\frac{2}{3}$, λ' is the largest eigenvalue while for $\rho>\frac{2}{3}$, λ'' is the largest. The two eigenvalues are degenerate when $\rho=\frac{2}{3}$.

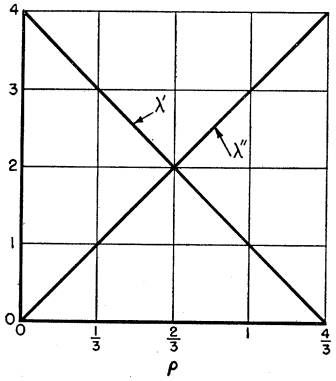

FIG. 4. The roots.

[15] See Eq. (36).

Part II

For the purpose of performing the saddle point integration in the text, it is convenient to put the rapidly varying part of the integrand into the exponent. Consider the product

$$\prod_{m=0}^{N-1}(t-\Lambda_m)^{-3/2}=(2K)^{-3N/2}(z-\lambda_M)^{-r}\times\exp\left(\frac{-3}{2}\sum_{m=0}^{N-1}{}'\ln[z-\lambda_m]\right), \quad \text{(A-I-10)}$$

where the prime on the sum indicates that the maximum eigenvalue(s) is (are) omitted from the summand. The reason for treating the term(s) containing the maximum eigenvalue separately is that the summation in the exponent will be replaced by an integration. In this limiting process, each term in the sum loses its identity: the density of terms is what counts. Consequently, this replacement can be legitimate only if the summand does not contain terms whose singularities lie arbitrarily close to the path of integration. Since (as is readily shown) the separation between adjacent eigenvalues near λ_M is of order $N^{-2/3}$, the path of steepest descents can not come arbitrarily close to any singularity except λ_M, and this term(s) is (are), therefore, removed from the summand before converting it to an integral.

We write m in the form

$$m=p_1+n_1p_2+n_1n_2p_3, \quad \begin{aligned} &p_1=0,\,1,\,2\cdots 2n_1-1,\\ &p_2=0,\,1,\,2\cdots 2n_2-1,\\ &p_3=0,\,1,\,2\cdots 2n_3-1,\\ &(\text{all } p\text{'s even or all odd}); \end{aligned} \quad \text{(A-I-11)}$$

and introduce the variables

$$\omega_r=\pi p_r/n_r, \quad r=1,\,2,\,3, \quad \text{(A-I-12)}$$

which will become continuous as N approaches infinity. It is clear that since the p's are independent, the ω's, too, are independent variables.

For convenience, we shall let n_2 be even. Then

$$\begin{aligned} \Omega_1&=\omega_1-\omega_2-\omega_3+\pi(n_2p_3+p_2-p_3)-\frac{\omega_1}{n_2}-\frac{\omega_2}{n_3}-\frac{\omega_1}{n_2n_3},\\ \Omega_2&=\omega_1+\omega_2-\omega_3+\pi(n_2p_3+p_2+p_3)\\ &\quad+\frac{\omega_1}{n_2}+\frac{\omega_2}{n_3}+\frac{\omega_1}{n_2n_3}, \quad \text{(A-I-13)}\\ \Omega_3&=\omega_1-\omega_2+\omega_3+\pi(n_2p_3+p_2-p_3)-\frac{\omega_1}{n_2}+\frac{\omega_2}{n_3}+\frac{\omega_1}{n_2n_3}. \end{aligned}$$

The sum in the exponent can now be rewritten in the form

$$\begin{aligned} &\frac{1}{N}\sum_{m=0}^{N-1}{}'\ln(z-\lambda_m)\\ &=\frac{1}{2n_1n_2n_3}\sum_{p_1=0}^{2n_1-2}\sum_{p_2=0}^{2n_2-2}\sum_{p_3=0}^{2n_3-2}{}'\ln[z-\lambda(\omega_1,\omega_2,\omega_3)]\\ &\qquad\text{even } p\text{'s only}\\ &\quad+\frac{1}{2n_1n_2n_3}\sum_{p_1=1}^{2n_1-1}\sum_{p_2=1}^{2n_2-1}\sum_{p_3=1}^{2n_3-1}\ln[z-\lambda(\omega_1,\omega_2,\omega_3)]. \quad \text{(A-I-14)}\\ &\qquad\text{odd } p\text{'s only} \end{aligned}$$

As $n_1\to\infty$, $n_2\to\infty$, $n_3\to\infty$, this becomes

$$\left(\frac{1}{2\pi}\right)^3\int_0^{2\pi}d\omega_1\int_0^{2\pi}d\omega_2\int_0^{2\pi}d\omega_3\ln[z-\lambda(\omega_1,\omega_2,\omega_3)], \quad \text{(A-I-15)}$$

where

$$\begin{aligned} \lambda(\omega_1,\omega_2,\omega_3)&=-\cos(\omega_1+\omega_2+\omega_3)\\ &\quad-\cos(-3\omega_1+\omega_2+\omega_3)-\cos(\omega_1-3\omega_2+\omega_3)\\ &\quad-\cos(\omega_1+\omega_2-3\omega_3)-\rho[\cos2(-\omega_1+\omega_2+\omega_3)\\ &\quad+\cos2(\omega_1-\omega_2+\omega_3)+\cos2(\omega_1+\omega_2-\omega_3)]. \quad \text{(A-I-16)} \end{aligned}$$

Thus,

$$e^{NS(S+1)2Kz}\varphi(2Kz)=\left(\frac{\pi}{2K}\right)^{3N/2}\frac{e^{Nf(z)}}{(z-\lambda_M)^r}, \quad \text{(A-I-17)}$$

where

$$f(z)=S(S+1)2Kz-\frac{3}{2}\left(\frac{1}{2\pi}\right)^3\int_0^{2\pi}d\omega_1\int_0^{2\pi}d\omega_2\int_0^{2\pi}d\omega_3\times\ln[z-\lambda(\omega_1,\omega_2,\omega_3)]. \quad \text{(A-I-18)}$$

APPENDIX II

Our problem is to determine the behavior of $f(z)$ in the neighborhood of the point $z=+\lambda_M$. This can be done without actually evaluating the integral. We shall introduce the notation

$$\Delta=(z-\lambda_M)^{\frac{1}{2}}, \quad \text{(A-II-1)}$$

positive and real for $z-\lambda_M>0$.

$$D(\omega_1,\omega_2,\omega_3)=[\lambda_M-\lambda(\omega_1,\omega_2,\omega_3)]^{\frac{1}{2}}.$$

Then

$$\begin{aligned} \frac{1}{z-\lambda}&=\frac{1}{\Delta^2+D^2}=\frac{1}{D^2}+\frac{i\Delta}{2}\left\{\frac{1}{D^2(D-i\Delta)}-\frac{1}{D^2(D+i\Delta)}\right\}\\ &=\frac{1}{\lambda_M-\lambda}+\frac{i\Delta}{2}\left\{\frac{1}{D^2(D-i\Delta)}-\frac{1}{D^2(D+i\Delta)}\right\}, \quad \text{(A-II-2)} \end{aligned}$$

$$f'(z)=2S(S+1)K-\frac{3}{2}\left(\frac{1}{2\pi}\right)^3\int_0^{2\pi}d\omega_1\int_0^{2\pi}d\omega_2 \times\int_0^{2\pi}d\omega_3\frac{1}{\lambda_M-\lambda(\omega_1,\omega_2,\omega_3)} -\frac{3i\Delta}{4}\left(\frac{1}{2\pi}\right)^3\int_0^{2\pi}d\omega_1\int_0^{2\pi}d\omega_2\int_0^{2\pi}d\omega_3 \times\left[\frac{1}{D^2(D-i\Delta)}-\frac{1}{D^2(D+i\Delta)}\right] =2S(S+1)(K-K_c)+\Delta F(\Delta). \quad \text{(A-II-3)}$$

Here,

$$F(\Delta)=\frac{3}{4}\left(\frac{1}{2\pi}\right)^3(-i)\int d\omega_1\int d\omega_2\int d\omega_3 \times\left[\frac{1}{D^2(D-i\Delta)}-\frac{1}{D^2(D+i\Delta)}\right]. \quad \text{(A-II-4)}$$

We can readily show that $F(0)\equiv\lim_{\Delta\to 0^+}F(\Delta)\neq 0$, and we can also determine its sign. This will suffice to indicate that $f'(z)$ has a branch point at $+\lambda_M$, and also to show the direction of the path of integration.

We note that the largest contribution to the integral in (A-II-4) will come from the region where D^2 is very small. Since the zero of D^2 is also its minimum value, we expand D^2 about this point in a Taylor's series in $(\omega_1-\omega_1^0)$, $(\omega_2-\omega_2^0)$, and $(\omega_3-\omega_3^0)$, retaining only the first terms, which give a positive definite quadratic form in the $(\omega_i-\omega_i^0)$'s. We now introduce the spherical coordinates R, θ, and φ, defined by the equations

$$\begin{aligned}\omega_1-\omega_1^0&=R\sin\theta\cos\varphi,\\ \omega_2-\omega_2^0&=R\sin\theta\sin\varphi,\\ \omega_3-\omega_3^0&=R\cos\theta.\end{aligned} \quad \text{(A-II-5)}$$

The quadratic form now factors into

$$D^2=R^2\Phi^2(\theta,\varphi), \quad \text{(A-II-6)}$$

where Φ is positive for all values of θ and φ. We first perform the integration over R. This gives

$$F(\Delta)\doteq\frac{-3i}{4}\left(\frac{1}{2\pi}\right)^3\int_0^{\pi}d\theta\sin\theta\int_0^{2\pi}d\varphi\Phi^{-3}(\theta,\varphi) \times\int_0^{R_0}R^2dR\cdot\left[\frac{1}{R^2(R-i\Delta/\Phi)}-\frac{1}{R^2(R+i\Delta/\Phi)}\right] =-\frac{3i}{4}\left(\frac{1}{2\pi}\right)^3\int_0^{\pi}d\theta\sin\theta\int_0^{2\pi}d\varphi\Phi^{-3}(\theta,\varphi) \times\left[\ln\left(\frac{R_0-i\Delta/\Phi}{R_0+i\Delta/\Phi}\right)+\pi i\right], \quad \text{(A-II-7)}$$

where R_0 is the upper limit of the validity of the approximate expansion. If we now let $\Delta\to 0$, we obtain

$$F(0)=\frac{3\pi}{4}\left(\frac{1}{2\pi}\right)^3\int_0^{2\pi}d\varphi\int_0^{\pi}d\theta\frac{\sin\theta}{\Phi^3(\theta,\varphi)}>0. \quad \text{(A-II-8)}$$

The first three terms in the expansion of $f(z)$ about $+\lambda_M$ are, therefore,

$$f(z)=f(+\lambda_M)+2S(S+1)(K-K_c)(z-\lambda_M) +\tfrac{2}{3}(z-\lambda_M)^{\frac{3}{2}}F(0), \quad \text{(A-II-9)}$$

where $F(0)>0$.

Setting $\mathrm{Im}[f(z)]=0$, we can now find the path of integration near the branch point of the integrand of Eq. (44).