

find once again

$$E_0 = C \exp(-E/2V^2\rho). \quad (29)$$

Here, however, there is no question that the series is logarithmic, we have been able to calculate it explicitly.

The full implication of our performing-perturbation theory with a limited basis set is still being investi-

gated. The calculation is, however, a strong indication that our assumption of a geometric series in Eq. (24) is more than wishful thinking, but reflects correctly the basis dynamics of the problem.

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Approximate Free Energies for Heisenberg Ferromagnets*

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A systematic discussion is given of the approximate free energies and Curie temperatures that can be obtained by using trial density matrices (which describe various possible decompositions of the ferromagnet into clusters) in a variational calculation of the free energy. Single-spin clusters lead to the molecular-field model (as is well known) and two-spin clusters yield the Oguchi pair model. The relation of the "constant-coupling" method to these approximations is clarified. A rigorous calculation using three-spin clusters is found to give results differing from those of Oguchi. Finally, the Bethe-Peierls-Weiss approximation is considered within the framework of this paper.

I. INTRODUCTION

AN exact calculation of the free energy, and consequently of the thermodynamic properties of a Heisenberg ferromagnet, appears to be beyond the reach of present mathematical techniques, except at high temperatures where an expansion in powers of the exchange constant gives accurate results and at low temperatures when spin waves (possibly renormalized and weakly interacting) give a good description of the system. Assuming isotropic exchange between nearest neighbors, which greatly simplifies all the calculations, the Hamiltonian of the system of interacting spins is

$$\mathcal{H} = -2J \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B H \sum_i S_{i,z}. \quad (I1)$$

The exact density matrix is

$$\rho = \exp[\beta(N\mathcal{F} - \mathcal{H})], \quad \text{Tr}\{\rho\} = 1, \quad (I2)$$

where $\beta = 1/kT$ and the free-energy-per-spin \mathcal{F} is defined by

$$\exp(-\beta N\mathcal{F}) = Z = \text{Tr}\{\exp(-\beta\mathcal{H})\}. \quad (I3)$$

The essential difficulty in the way of an exact evaluation of Z is that there are important contributions to

it from very large rings of spins coupled by the nearest-neighbor interaction. Many approximate theories introduce some relatively small clusters of spins, tread exactly, whose interaction with other clusters is simulated by an effective field, so that the density matrix factorizes. A detailed account of many of these theories can be found in the book by Smart¹. These effective fields have been chosen on an intuitive *ad hoc* basis. It will be seen that in some cases these fields are not the optimum ones in the sense that they do not minimize the corresponding free energies. It must, however, be borne in mind that they may well lead to better descriptions of particular aspects of the properties of a ferromagnet, for example the location of the Curie temperature.

Calculations of the type given here can be done equally well using spin-wave variables. In these terms, the theory of Bloch² corresponds to employing an approximate density matrix diagonal in the spin-wave occupation numbers which automatically eliminates the off-diagonal parts of the truncated Holstein-Primakoff Hamiltonian. Brooks *et al.*³ have used the present technique to treat the temperature dependence of crystal-field effects in terbium.

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¹ J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Co., Phila., 1966).

² M. Bloch, *Phys. Rev. Letters* **9**, 286 (1962).

³ M. S. Brooks, D. A. Goodings, and H. I. Ralph, *Proc. Phys. Soc. (London)* (to be published).

II. VARIATIONAL PRINCIPLE AND CLUSTER DENSITY MATRICES

The well-known variational principle to be employed is that the mean-free-energy per spin \mathfrak{F} given by

$$\begin{aligned}\mathfrak{F} &= (1/N) \text{Tr}\{\rho \mathfrak{H}\} + (1/N\beta) \text{Tr}\{\rho \ln \rho\}, \\ \mathfrak{F} &= (1/N) \langle \mathfrak{H} \rangle + (1/N\beta) \langle \ln \rho \rangle,\end{aligned}\quad (\text{II1})$$

with $\text{Tr}\{\rho\} = 1$, is an absolute minimum for the true density matrix. Although a familiar case, it is convenient to begin with the single-spin cluster, since the form of the corresponding free energy will be needed in Sec. III.

A. Single-Spin Cluster

The density matrix described by this decomposition is

$$\rho = \prod_{\text{spins } i} \exp(-h_\sigma S_{i,z}) / Z_\sigma^N, \quad (\text{II2})$$

with

$$\begin{aligned}Z_\sigma &= \text{Tr}_1\{\exp(-h_\sigma S_{i,z})\} = \sum_{m=-S_0}^{S_0} \exp(-mh_\sigma) \\ &\equiv \exp(-\beta F_\sigma).\end{aligned}\quad (\text{II3})$$

This last equation defines the cluster free energy per spin F_σ and it follows directly that the mean z component of the spin is $\langle S_z \rangle_\sigma = \beta \partial F_\sigma / \partial h_\sigma$. It is then clear that the two terms in the approximate free energy per spin for the entire crystal, when each spin has n nearest neighbors, are

$$\begin{aligned}(1/N) \langle \mathfrak{H} \rangle_\sigma &= -Jn \langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle + g\mu_B H \langle S_z \rangle_\sigma \\ &= -Jn \langle S_z \rangle_\sigma^2 + g\mu_B H \langle S_z \rangle_\sigma,\end{aligned}$$

and

$$(1/N\beta) \langle \ln \rho \rangle_\sigma = -(1/\beta) h_\sigma \langle S_z \rangle_\sigma + F_\sigma, \quad (\text{II4})$$

and that the complete expression is

$$\mathfrak{F}_\sigma = (h - h_\sigma) \partial F_\sigma / \partial h_\sigma + F_\sigma - \beta j n (\partial F_\sigma / \partial h_\sigma)^2, \quad (\text{II5})$$

where $h = \beta g\mu_B H$ and $j = \beta J$.

The condition for \mathfrak{F}_σ to be a minimum is that

$$\partial \mathfrak{F}_\sigma / \partial h_\sigma = 0, \quad (\text{II6})$$

and the solution (or more precisely a solution) of this equation is

$$h - h_\sigma = 2\beta j n (\partial F_\sigma / \partial h_\sigma) = 2j n \langle S_z \rangle_\sigma. \quad (\text{II7})$$

This is just the Weiss formula for the molecular field, and its properties are well known. We note here only that in this model a phase transition occurs when the parameter j takes the value $j_c = \frac{3}{2} n S_0 (S_0 + 1)$, where S_0 is the spin of an individual atom.

B. Two-Spin (Pair) Clusters

Any ferromagnet with spins on the sites of a Bravais lattice can be decomposed into pairs of nearest neighbors so that no spin belongs to two pairs and every spin

belongs to some pair. The corresponding density matrix is

$$\rho = \prod_{\text{pairs}} \exp(G_\pi) / Z_\pi^{N/2}, \quad (\text{II8})$$

where

$$Z_\pi = \text{Tr}_{1,2}\{\exp[G_\pi(1, 2)]\} \equiv \exp[-2\beta F_\pi], \quad (\text{II9})$$

which defines the cluster free energy per spin, F_π . The most general form for G_π which we shall consider is

$$G_\pi(1, 2) = 2j' \mathbf{S}_1 \cdot \mathbf{S}_2 + 2\lambda S_{1,z} S_{2,z} - h_\pi (S_{1,z} + S_{2,z}). \quad (\text{II10})$$

It follows from Eqs. (II9) and (II10) that the mean spin in the z direction is

$$\langle S_z \rangle_\pi = \beta \partial F_\pi / \partial h_\pi. \quad (\text{II11})$$

The mean energy per spin for the entire crystal can then be written as

$$\begin{aligned}(1/N) \langle \mathfrak{H} \rangle &= -J \langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle_\pi - J(n-1) \langle S_z \rangle_\pi^2 \\ &= j \partial F_\pi / \partial j' - \beta j (n-1) (\partial F_\pi / \partial h_\pi)^2,\end{aligned}\quad (\text{II12})$$

since only spins in the same cluster are correlated. The corresponding free energy per spin is

$$\begin{aligned}\mathfrak{F}_\pi &= (j - j') \partial F_\pi / \partial j' - \lambda \partial F_\pi / \partial \lambda + (h - h_\pi) \partial F_\pi / \partial h_\pi + F_\pi \\ &\quad - \beta j (n-1) (\partial F_\pi / \partial h_\pi)^2.\end{aligned}\quad (\text{II13})$$

The conditions for \mathfrak{F}_π to be a minimum are

$$\frac{\partial \mathfrak{F}_\pi}{\partial j'} = \frac{\partial \mathfrak{F}_\pi}{\partial \lambda} = \frac{\partial \mathfrak{F}_\pi}{\partial h_\pi} = 0,$$

with the solutions

$$j' = j,$$

$$\lambda = 0,$$

$$h_\pi = h - 2\beta j (n-1) \partial F_\pi / \partial h_\pi = h - 2j (n-1) \langle S_z \rangle_\pi. \quad (\text{II14})$$

These are in fact just the equations defining the Oguchi pair model,⁴ and they yield a somewhat lower free energy, and also a lower value for j_c , than the single-spin model. This pair model also shows some short-range order even above the Curie point.

At this juncture, rather than going on immediately to discuss clusters containing three or more spins, it is appropriate to consider the "constant-coupling" approximation⁵ to these models.

III. CONSTANT-COUPPING APPROXIMATION

In Secs. I and II, two approximations to the free energy of the real ferromagnet were obtained by using trial density matrices including clusters of one and two spins, respectively, and the free energies were expressed in terms of the cluster free energies per spin $F_\sigma(h_\sigma)$ and $F_\pi(h_\pi)$. With those results available, consider the func-

⁴ T. Oguchi, Progr. Theoret. Phys. (Kyoto) **13**, 148 (1955).

⁵ P. W. Kasteleijn and J. Van Kranendonk, Physica **22**, 317 (1956).

tion $\tilde{F}(\tilde{S})$ defined by

$$\tilde{F}(\tilde{S}) = aF_\pi(\tilde{S}) - bF_\sigma(\tilde{S}), \quad (\text{III1})$$

where the arguments of the F 's are chosen to be

$$h_\pi = h - 2jb\tilde{S}, \quad h_\sigma = h - 2ja\tilde{S}. \quad (\text{III2})$$

It then follows immediately that

$$\begin{aligned} \partial\tilde{F}/\partial\tilde{S} &= a \partial F_\pi/\partial\tilde{S} - b \partial F_\sigma/\partial\tilde{S} \\ &= -2abj[\partial F_\pi/\partial h_\pi - \partial F_\sigma/\partial h_\sigma] \\ &= -2abJ[\langle S_z \rangle_\pi - \langle S_z \rangle_\sigma]. \end{aligned} \quad (\text{III3})$$

The condition for \tilde{F} to be a minimum, or at least stationary, is that

$$\langle S_z \rangle_\pi = \langle S_z \rangle_\sigma, \quad (\text{III4})$$

an equation which determines \tilde{S} as a function of β and h . There remains the question of how to choose the parameters a and b so that \tilde{F} is in some sense a good approximation to the true free energy of the real ferromagnet and can also be analyzed into components which have a natural interpretation in terms of entropy, mean exchange energy, and magnetic moment. Expressed in terms of the \mathfrak{F} 's, the function \tilde{F} is

$$\begin{aligned} \tilde{F} &= a\mathfrak{F}_\pi - b\mathfrak{F}_\sigma - 2Jab\tilde{S}[\langle S_z \rangle_\pi - \langle S_z \rangle_\sigma] \\ &\quad + J[a(n-1)\langle S_z \rangle_\pi^2 - bn\langle S_z \rangle_\sigma^2]. \end{aligned} \quad (\text{III5})$$

At the minimum of \tilde{F} ,

$$\langle S_z \rangle_\pi = \langle S_z \rangle_\sigma = \langle S_z \rangle,$$

and there,

$$\tilde{F}_{\min} = a\mathfrak{F}_\pi - b\mathfrak{F}_\sigma + J[a(n-1) - bn]\langle S_z \rangle^2.$$

The last term vanishes if

$$a(n-1) = bn, \quad (\text{III6})$$

and this will be used as one condition on a and b .

As the first step in analyzing \tilde{F} we define the entropy \mathfrak{s} by

$$\mathfrak{s} = -\partial\tilde{F}/\partial T. \quad (\text{III7})$$

Now \tilde{F} depends on T both explicitly and through the temperature dependence of \tilde{S} . Explicitly,

$$\mathfrak{s} = -\partial\tilde{F}/\partial T = -a\dot{F}_\pi + b\dot{F}_\sigma - \partial\tilde{F}/\partial\tilde{S}(\partial\tilde{S}/\partial T).$$

But at the minimum, $\partial\tilde{F}/\partial\tilde{S} = 0$, and there,

$$T\mathfrak{s} = aTS_\pi - bTS_\sigma. \quad (\text{III8})$$

Using the results of Sec. II, and putting $j' = j$, we know that

$$\begin{aligned} TS_\pi &= j\partial F_\pi/\partial j + h_\pi\partial F_\pi/\partial h_\pi - F_\pi, \\ TS_\sigma &= j\partial F_\sigma/\partial j + h_\sigma\partial F_\sigma/\partial h_\sigma - F_\sigma. \end{aligned} \quad (\text{III9})$$

Combining Eqs. (III8) and (III9),

$$T\mathfrak{s} = j\partial\tilde{F}/\partial j - \tilde{F} + (1/\beta)(ah_\pi - bh_\sigma)\langle S_z \rangle.$$

Using Eq. (III2), this reduces to

$$T\mathfrak{s} = j\partial\tilde{F}/\partial j - \tilde{F} + (1/\beta)(a-b)h\langle S_z \rangle,$$

and, alternatively, to

$$\tilde{F} = j\partial\tilde{F}/\partial j + (1/\beta)(a-b)h\langle S_z \rangle - T\mathfrak{s}. \quad (\text{III10})$$

This equation has a direct, natural, and self-consistent physical interpretation, with $\langle \mathcal{J}\mathcal{C}_{\text{exoh}} \rangle = j(\partial\tilde{F}/\partial j)$, for instance, if it is arranged that

$$a - b = 1,$$

so that, using (III6), the coefficients are determined to be

$$a = n, \quad b = n - 1. \quad (\text{III11})$$

The function

$$\tilde{F}_{\text{o.e.}} = nF_\pi - (n-1)F_\sigma \quad (\text{III12})$$

is in fact the free-energy function in the constant-coupling approximation. It should be emphasized that it is not in any sense a rigorous upper bound to the free energy of the physical ferromagnet (or any system of interacting spins with Heisenberg interactions). However, it does have the useful stationary property of Eq. (III3), and, as shown here, it also has a self-consistent thermodynamic interpretation. It is perhaps also worth noting that the first term in $\tilde{F}_{\text{o.e.}}$ is the exact free energy for a pseudocrystal with sheaves of n spins at every lattice site, each spin interacting with only one spin in a sheaf at a nearest-neighbor site. The function $\tilde{F}_{\text{o.e.}}$ was also obtained by Strieb *et al.*⁶ in the second order of a graphical cluster expansion of the free energy. For a pseudocrystal of sheaves of n spins, this second-order term is the exact result.

IV. THREE-SPIN CLUSTERS

The natural way to extend the work of Sec. II is to consider clusters containing three spins. There are only two essentially distinct types of cluster, namely, Λ clusters, having end spins which are not nearest neighbors of each other, and triangle clusters. The latter can only occur in the hexagonal and close-packed lattices. It is not difficult to see that simple cubic (sc), body-centered cubic (bcc), and face centered cubic (fcc) lattices can all be decomposed into Λ clusters in such a way that no spin belongs to more than one cluster and every spin belongs to some cluster. The fcc lattice can also be decomposed into triangles. Examples of such decompositions are shown schematically in Figs. 1-4. As it happens, the two decompositions shown for the sc lattice in Fig. 1 lead to the same approximate free energy, but it may well be that other decompositions, leading to lower free energies, can be found. The density matrix has the same form for any

⁶ B. Strieb, H. B. Callen, and G. Horwitz, Phys. Rev. 130, 1798 (1963).

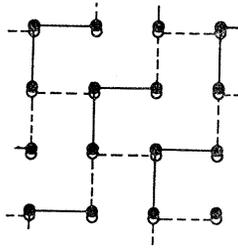
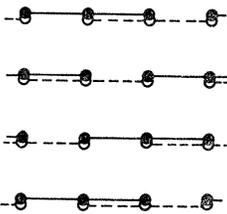


FIG. 1. Two equivalent decompositions of the sc lattice into Λ clusters.



●—SPINS IN BASAL PLANE
○---SPINS IN NEXT PLANE

decomposition into Λ clusters, namely,

$$\rho = \prod_{\text{clusters}} \exp[G_\lambda]/Z_\lambda^{N/\lambda}, \quad (\text{IV1})$$

where the cluster partition function is

$$Z_\lambda = \text{Tr}_{1,2,3} \{ \exp[G_\lambda(1, 2, 3)] \} \equiv \exp[-3\beta F_\lambda], \quad (\text{IV2})$$

also defining the cluster free energy per spin F_λ . The most general form for G_λ which we shall consider is

$$G_\lambda(1, 2, 3) = 2j\mathbf{S}_1 \cdot (\mathbf{S}_2 + \mathbf{S}_3) - h_\lambda S_{1,z} - h'_\lambda (S_{2,z} + S_{3,z}), \quad (\text{IV3})$$

where we have used the facts, easily verified, that the optimum coefficient of the exchange term is the actual

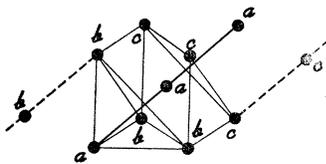
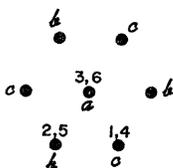


FIG. 2. A decomposition of the bcc lattice into Λ clusters.



coupling coefficient $j = \beta J$ and that the optimum coefficient of the Ising term is zero, precisely as it happened in Sec. II. It follows directly from Eqs. (IV2) and (IV3) that the mean z components of the spin of atoms at the center and ends of the cluster are given by

$$\langle S_{c,z} \rangle = 3\beta \partial F_\lambda / \partial h_\lambda, \quad \langle S_{e,z} \rangle = \frac{3}{2}\beta \partial F_\lambda / \partial h'_\lambda, \quad (\text{IV4})$$

respectively. We are now in a position to treat the three lattices in turn. The corresponding free energies differ only in the coefficients of the terms describing the exchange interaction between spins in different clusters.

A. sc Lattice

Inspection of Fig. 1 shows that each center spin interacts with the two end spins in its own cluster and four end spins in other clusters, while each end spin interacts with the central spin in its own cluster, with three end spins in other clusters and with two central spins in other clusters. The corresponding mean ex-

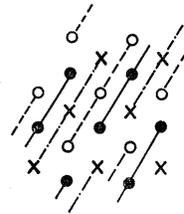


FIG. 3. A decomposition of the fcc lattice into Λ clusters.

●—SPINS IN BASAL PLANE
○---SPINS IN PLANE BELOW
×---SPINS IN PLANE ABOVE

change energy per spin is

$$\begin{aligned} N^{-1} \langle \mathcal{H}_{\text{exch}} \rangle &= j \partial F_\lambda / \partial j - \frac{3}{2} J \langle S_{e,z} \rangle \langle S_{c,z} \rangle - 2J \langle S_{e,z} \rangle^2 \\ &= j \frac{\partial F_\lambda}{\partial j} - 12\beta j \frac{\partial F_\lambda}{\partial h'_\lambda} \frac{\partial F_\lambda}{\partial h_\lambda} - \frac{9}{2} (\beta j) \left(\frac{\partial F_\lambda}{\partial h'_\lambda} \right)^2. \end{aligned} \quad (\text{IV5})$$

The first term corresponds to exchange within the cluster and the others to exchange between clusters. The corresponding approximate free energy is

$$\begin{aligned} \mathcal{F}_\lambda &= (h - h_\lambda) \partial F_\lambda / \partial h'_\lambda + (h - h'_\lambda) \partial F_\lambda / \partial h_\lambda + F_\lambda \\ &\quad - 12\beta j \frac{\partial F_\lambda}{\partial h_\lambda} \frac{\partial F_\lambda}{\partial h'_\lambda} - \frac{9}{2} (\beta j) \left(\frac{\partial F_\lambda}{\partial h'_\lambda} \right)^2. \end{aligned} \quad (\text{IV6})$$

Again, the conditions for \mathcal{F}_λ to be a minimum are

$$\partial \mathcal{F}_\lambda / \partial h_\lambda = \partial \mathcal{F}_\lambda / \partial h'_\lambda = 0, \quad (\text{IV7})$$

of which the solutions are

$$\begin{aligned} h_\lambda &= h - 12\beta j \partial F_\lambda / \partial h'_\lambda \\ &= h - 8j \langle S_{e,z} \rangle, \end{aligned} \quad (\text{IV8a})$$

and

$$\begin{aligned} h'_\lambda &= h - 12\beta j \partial F_\lambda / \partial h_\lambda - 9\beta j \partial F_\lambda / \partial h'_\lambda \\ &= h - 4j \langle S_{c,z} \rangle - 6j \langle S_{e,z} \rangle. \end{aligned} \quad (\text{IV8b})$$

It should be noted that, in general, the two mean z components of spin will not be equal and Eqs. (IV8a) and (IV8b) will lead to results different from those found by Oguchi, who assumed that they were the same. In particular, the value for the critical coupling constant j_c is slightly different in this theory.

In general, Eqs. (IV8a) and (IV8b) are coupled, nonlinear, equations for the effective fields h_λ and $h_{\lambda'}$. However, the critical value of j can be located simply in terms of a series expansion of $F_\lambda(h_\lambda; h_{\lambda'})$ in powers of its arguments, namely,

$$F_\lambda(h_\lambda; h_{\lambda'}) = F_\lambda(0; 0) + \frac{1}{2}F_{11}h_\lambda^2 + F_{12}h_\lambda h_{\lambda'} + \frac{1}{2}F_{22}h_{\lambda'}^2 + \dots, \quad (\text{IV9})$$

and where higher powers can be neglected at temperatures near and/or above the Curie point. The mean spin over all atoms is then

$$\langle S_z \rangle = \beta \partial F_\lambda / \partial h_\lambda + \beta \partial F_\lambda / \partial h_{\lambda'} \\ = \beta(F_{11} + F_{12})h_\lambda + \beta(F_{12} + F_{22})h_{\lambda'}. \quad (\text{IV9a})$$

In this region of small effective fields, the defining Eqs. (IV8a) and (IV8b) reduce to the coupled linear equations

$$[1 + 12\beta j F_{12}]h_\lambda + 12\beta j F_{22}h_{\lambda'} = h, \\ [12\beta j F_{11} + 9\beta j F_{12}]h_\lambda + [1 + 12\beta j F_{12} + 9\beta j F_{22}]h_{\lambda'} = h. \quad (\text{IV10})$$

The critical value of j is that for which the determinant of the coefficients vanishes, and the equation defining j_c is thus

$$(12\beta j)^2[F_{11}F_{12} - F_{12}^2] - 24\beta j F_{12} - 9\beta j F_{22} = 1. \quad (\text{IV11})$$

In practice, the calculation is done by way of an expansion of the cluster partition function $Z_\lambda(h_\lambda; h_{\lambda'})$ in powers of its arguments,

$$Z_\lambda(h_\lambda; h_{\lambda'}) = Z_0 + \frac{1}{2}Z_{11}h_\lambda^2 + Z_{12}h_\lambda h_{\lambda'} + \frac{1}{2}Z_{22}h_{\lambda'}^2 + \dots.$$

The equation for j_c is then

$$(16j^2/Z_0^2)[Z_{11}Z_{22} - Z_{12}^2] + 8jZ_{12}/Z_0 + 3jZ_{22}/Z_0 = 1. \quad (\text{IV12})$$

Convenient expressions for the coefficients Z_{ij} can be

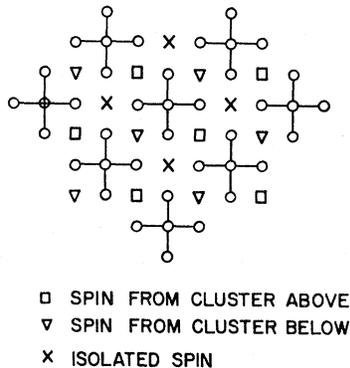


FIG. 4. A decomposition of the sc lattice into BPW clusters and isolated spins.

TABLE I. Values of j_c for ferromagnets with $S_0 = \frac{1}{2}$.

Method	Lattice		
	sc	bcc	fcc, hcp
Molecular field	0.333	0.250	0.167
Oguchi 2-spin	0.357	0.269	0.169
Oguchi 3-spin	0.356	0.260	0.170
Present Λ cluster	0.355	0.259	0.170
Triangle cluster	0.155
BPW	0.541	0.344	...
Present BPW	...	0.262	...
Constant coupling	0.549	0.347	...
High temp. expansion	0.529	0.379	0.245

found in the paper by Brown and Luttinger⁷. The value of j_c for $S_0 = \frac{1}{2}$ is included in Table I.

B. bcc Lattice

The decomposition of this lattice into Λ clusters is perhaps most easily analyzed by viewing the lattice along a body diagonal. The projection onto a plane normal to this axis shows a hexagonal pattern, with three distinct sites (Fig. 2). Six (111) atomic planes cut across each unit cell, and the decomposition can be represented by the following scheme which tabulates the location of spins in these layers for the three sites:

Site	Occupation
a	$e \ c \ e \ e \ c \ e \ e \ c \ e \ e \ c \ e \ e \ c$...6123456123456123456123456123456123456123
b	$c \ e \ e \ c \ e \ e \ c \ e \ e \ c \ e \ e \ c \ e$ 16123455123456123456123456123456123456123
c	$e \ e \ c \ e \ e \ c \ e \ e \ c \ e \ e \ c \ e$ 16123456123456123456123456123456123456123

The nearest neighbors of a spin at an a site in plane n are as follows:

- 3 on b sites in plane $(n-1) \text{ Mod } 6$,
- 3 on c sites in plane $(n+1) \text{ Mod } 6$,
- 1 on a sites in plane $(n \pm 3) \text{ Mod } 6$.

Inspection of Fig. 2 shows that the center spin in a cluster, taken without loss of generality to be at an a site in plane N , has as its nearest neighbors the two end spins in its own cluster, three end spins from other clusters at b sites in plane $(n-1) \text{ Mod } 6$. The nearest neighbors of an end spin at an a site in plane n are the center spin of its own cluster, also on an a site, one end spin of another cluster at an a site, three other ends at b sites, and three center spins from other clusters at c sites. The mean exchange energy per spin is then im-

⁷H. A. Brown and J. M. Luttinger, Phys. Rev. 100, 685 (1955).

mediately seen to be

$$\begin{aligned} (1/N) \langle \mathcal{H}_{\text{exch}} \rangle &= j \partial F_{\lambda} / \partial j - 4J \langle S_{c,z} \rangle \langle S_{e,z} \rangle - (8J/3) \langle S_{e,z} \rangle^2 \\ &= j \partial F_{\lambda} / \partial j - 18\beta j \partial F_{\lambda} / \partial h_{\lambda}' - 6\beta j (\partial F_{\lambda} / \partial h_{\lambda}')^2, \end{aligned} \quad (\text{IV13})$$

and the corresponding free energy is

$$\begin{aligned} \mathcal{F}_{\lambda} &= (h - h_{\lambda}) \partial F_{\lambda} / \partial h_{\lambda} + (h - h_{\lambda}') \partial F_{\lambda} / \partial h_{\lambda}' + F_{\lambda} \\ &\quad - 18\beta j \partial F_{\lambda} / \partial h_{\lambda} \cdot \partial F_{\lambda} / \partial h_{\lambda}' - 6\beta j (\partial F_{\lambda} / \partial h_{\lambda}')^2. \end{aligned} \quad (\text{IV14})$$

The solutions of the minimum conditions $(\partial \mathcal{F}_{\lambda} / \partial h_{\lambda}) = (\partial \mathcal{F}_{\lambda} / \partial h_{\lambda}') = 0$, are

$$\begin{aligned} h_{\lambda} &= h - 18\beta j \partial F_{\lambda} / \partial h_{\lambda}' \\ &= h - 12j \langle S_{e,z} \rangle, \end{aligned} \quad (\text{IV15})$$

and

$$\begin{aligned} h_{\lambda}' &= h - 12\beta j \partial F_{\lambda} / \partial h_{\lambda}' - 18\beta j \partial F_{\lambda} / \partial h_{\lambda} \\ &= h - 8j \langle S_{e,z} \rangle - 6j \langle S_{c,z} \rangle. \end{aligned} \quad (\text{IV15a})$$

As in the case of the sc lattice, the mean spin components $\langle S_{c,z} \rangle$ and $\langle S_{e,z} \rangle$ will not be equal in general. The critical value j_c can be found in exactly the same way as before, and the corresponding equation is

$$(18\beta j)^2 [F_{11} F_{22} - F_{12}^2] - 36\beta j F_{12} - 12\beta j F_{22} = 1. \quad (\text{IV16})$$

In terms of the coefficients in the expansion of the cluster partition function, this becomes

$$36j^2 / Z_0^2 [Z_{11} Z_{22} - Z_{12}^2] + 12j Z_{12} / Z_0 + 4j Z_{22} / Z_0 = 1. \quad (\text{IV17})$$

The value of j_c for $S_0 = \frac{1}{2}$ is included in Table I.

C. fcc and hcp Lattices

A decomposition of the fcc lattice into Λ clusters is shown in Fig. 3. [The hexagonal close-packed (hcp) lattice possesses a similar one which yields the same free energy.] The nearest neighbors of a center spin are the two end spins in its own cluster, four other end spins in the same plane, two end spins in the planes above and below, and lastly, a center spin in the planes above and below. The nearest neighbors of an end spin are the center spin of its own cluster, two other center spins in the same plane, and a center spin in the plane above and below, three end spins in the same plane and two end spins in the planes above and below. The mean exchange energy per spin is

$$\begin{aligned} (1/N) \langle \mathcal{H}_{\text{exch}} \rangle &= j \partial F_{\lambda} / \partial j - \frac{2}{3} J \langle S_{c,z} \rangle^2 \\ &\quad - (16J/3) \langle S_{c,z} \rangle \langle S_{e,z} \rangle - (14J/3) \langle S_{e,z} \rangle^2 \\ &= j \partial F_{\lambda} / \partial j - 6\beta j (\partial F_{\lambda} / \partial h_{\lambda})^2 \\ &\quad - 24\beta j (\partial F_{\lambda} / \partial h_{\lambda}) (\partial F_{\lambda} / \partial h_{\lambda}') - \frac{2}{3} \beta j (\partial F_{\lambda} / \partial h_{\lambda}')^2, \end{aligned} \quad (\text{IV18})$$

and the approximate free energy is

$$\begin{aligned} \mathcal{F}_{\lambda} &= (h - h_{\lambda}) \partial F_{\lambda} / \partial h_{\lambda} + (h - h_{\lambda}') \partial F_{\lambda} / \partial h_{\lambda}' + F_{\lambda} \\ &\quad - 6\beta j \left(\frac{\partial F_{\lambda}}{\partial h_{\lambda}} \right)^2 - 24\beta j \frac{\partial F_{\lambda}}{\partial h_{\lambda}} \frac{\partial F_{\lambda}}{\partial h_{\lambda}'} - \frac{21}{2} \left(\frac{\partial F_{\lambda}}{\partial h_{\lambda}'} \right)^2. \end{aligned} \quad (\text{IV19})$$

The solutions of the minimum conditions $(\partial \mathcal{F}_{\lambda} / \partial h_{\lambda}) = (\partial \mathcal{F}_{\lambda} / \partial h_{\lambda}') = 0$, are

$$\begin{aligned} h_{\lambda} &= h - 12\beta j \partial F_{\lambda} / \partial h_{\lambda} - 24\beta j \partial F_{\lambda} / \partial h_{\lambda}' \\ &= h - 4j \langle S_{c,z} \rangle - 16j \langle S_{e,z} \rangle, \end{aligned}$$

and

$$\begin{aligned} h_{\lambda}' &= h - 24\beta j \partial F_{\lambda} / \partial h_{\lambda} - 21\beta j \partial F_{\lambda} / \partial h_{\lambda}' \\ &= h - 8j \langle S_{c,z} \rangle - 14j \langle S_{e,z} \rangle. \end{aligned} \quad (\text{IV20})$$

Using these equations and the notation Secs. I-III, it is easy to show that the critical coupling coefficient j_c is determined by

$$324(\beta j)^2 [F_{11} F_{22} - F_{12}^2] - 12\beta j F_{11} - 48\beta j F_{12} - 21\beta j F_{22} = 1,$$

or the alternative form

$$\frac{36j^2}{Z_0^2} [Z_{11} Z_{22} - Z_{12}^2] + 4j \frac{Z_{11}}{Z_0} + 16j \frac{Z_{12}}{Z_0} + 7j \frac{Z_{22}}{Z_0} = 1. \quad (\text{IV21})$$

The solution for $S_0 = \frac{1}{2}$ is given in Table I. These lattices clearly also possess decompositions into triangles, and the corresponding value of j_c is included in the table.

V. BETHE-PEIERLS-WEISS (BPW) CLUSTER

Clearly, any cluster theory will become more accurate as the size of the cluster increases, and, in particular, it will give a reliable approximation to such physical quantities as the magnetization over increasingly wide ranges of temperature. The difficulties of calculations using large clusters are, first, that the cluster free energy itself can become quite hard to evaluate and, second, that it may be necessary to introduce several molecular fields, satisfying nonlinear coupled equations.

The first obstacle in attempting to construct a theory using the BPW cluster of $(n+1)$ spins,⁹⁻¹⁰ that is a central spin plus n nearest neighbors on the periphery, is that of finding a decomposition of the lattice into these clusters. We have not been able to find such a decomposition for the sc or fcc lattices. The latter is in any case not a very suitable lattice for BPW calculations since each peripheral spin has four other peripheral spins in the same cluster as nearest neighbors and the cluster partition function itself is hard to evaluate. The best decomposition of the simple cubic lattice that we have been able to construct is shown schematically in Fig. 4. In this decomposition, $\frac{7}{8}$ of the spins are in BPW clusters and $\frac{1}{8}$ are isolated single spins. A theory using this decomposition can be constructed along the lines developed in this paper by using two effective fields, one for the peripheral spins and one for the isolated single spins.

The bcc lattice ($n=8$) does possess a decomposition into BPW clusters as shown in Fig. 5. The density

⁹ H. A. Bethe, Proc. Roy. Soc. (London) A150, 552 (1935).

⁹ R. E. Peierls, Proc. Cambridge Phil. Soc. 32, 477 (1936).

¹⁰ P. R. Weiss, Phys. Rev. 74, 1493 (1948).

matrix corresponding to this decomposition is

$$\rho = \prod_{\text{clusters}} \exp[G_\alpha] / Z_\alpha^{N/(n+1)}, \quad (\text{V1})$$

where the cluster partition function Z_α is given by

$$Z_\alpha = \text{Tr}_{1, \dots, n+1} \{ \exp[G_\alpha(1, \dots, n+1)] \} \\ \equiv \exp[-\beta(n+1)F_\alpha], \quad (\text{V2})$$

and this equation defines the cluster free energy per spin F_α . The most general form for the operator G_α which we shall consider is

$$G_\alpha = 2j\mathbf{S}_c \cdot \sum_{p=2}^{n+1} \mathbf{S}_p - h_\alpha S_{c,z} - h'_\alpha \sum_{p=2}^{n+1} S_{p,z}, \quad (\text{V3})$$

and it then follows directly that the mean z components of spin are $\langle S_{c,z} \rangle = \beta(n+1) \partial F_\alpha / \partial h_\alpha$ for the core spins, and $\langle S_{p,z} \rangle = \beta[(n+1)/n] \partial F_\alpha / \partial h'_\alpha$ for the peripheral spins. Each core spin interacts only with its own peripheral spins, whereas a peripheral spin interacts with its own core spin and $(n-1)$ peripheral spins on other clusters. The mean exchange energy per spin is

$$N^{-1} \langle \mathcal{H}_{\text{exch}} \rangle = j \partial F_\alpha / \partial j - J[n(n-1)/(n+1)] \langle S_{p,z} \rangle^2 \\ = j \partial F_\alpha / \partial j - \beta j [(n^2-1)/n] (\partial F_\alpha / \partial h'_\alpha)^2, \quad (\text{V4})$$

and the corresponding free energy per spin is

$$\mathcal{F}_\alpha = (h - h_\alpha) \partial F_\alpha / \partial h_\alpha + (h - h'_\alpha) \partial F_\alpha / \partial h'_\alpha + F_\alpha \\ - \beta j [(n^2-1)/n] (\partial F_\alpha / \partial h'_\alpha)^2. \quad (\text{V5})$$

The minimum value of \mathcal{F}_α occurs when $\partial \mathcal{F}_\alpha / \partial h_\alpha = \partial \mathcal{F}_\alpha / \partial h'_\alpha = 0$ and the solutions of these equations are

$$h_\alpha = h,$$

and

$$h'_\alpha = h - 2\beta j [(n^2-1)/n] \partial F_\alpha / \partial h'_\alpha \\ = h - 2j(n-1) \langle S_{p,z} \rangle. \quad (\text{V6})$$

It will be noted that these constraints are not generally equivalent to those imposed in the BPW method, namely,

$$\text{BPW:} \quad h_\alpha = h, \\ \langle S_{c,z} \rangle = \langle S_{p,z} \rangle, \quad (\text{V7})$$

or in alternative form

$$\text{BPW:} \quad h_\alpha = h, \\ \partial F_\alpha / \partial h_\alpha = n^{-1} \partial F_\alpha / \partial h'_\alpha. \quad (\text{V7a})$$

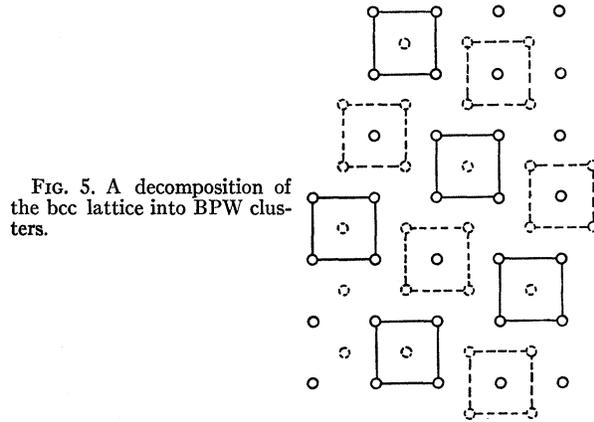


FIG. 5. A decomposition of the bcc lattice into BPW clusters.

The critical coupling coefficient can be located in exactly the same way as before, and the equation determining j_c is found to be

$$-[2\beta j(n^2-1)/n] F_{22} = 1, \quad (\text{V8})$$

or, alternatively,

$$2j[(n-1)/n] Z_{22}/Z_0 = 1. \quad (\text{V9})$$

For comparison, the equation determining the critical coupling coefficient in the standard BPW approximation is, using the same notation,

$$\text{BPW:} \quad F_{22} = nF_{12}, \quad \text{or} \quad Z_{22} = nZ_{12}. \quad (\text{V10})$$

The solution of Eq. (V9) for $S_0 = \frac{1}{2}$ is given in Table I and is seen to be only marginally better than that for the Weiss molecular field model. The reason appears to be that the peripheral spins and their interactions among themselves dominate the partition function, and if the core-contribution is neglected, then Eq. (V6) reduces to the Weiss molecular field equation for a lattice with $(n-1)$ nearest neighbors. A formal advantage of the present model is that it does not manifest an anti-Curie point, in contrast to the standard BPW approximation.

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