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Composite Ising Lattices. I. Bragg-Williams Approximation*

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The Bragg-Williams approximation for certain general classes of composite Ising lattices is worked out and discussed in detail. Our results suggest that the proximity effect may exist in composite ferromagnetic insulators.

1. INTRODUCTION

THE phenomena of composite systems are very interesting and useful for many practical applications. This is especially true for composite systems which exhibit a phase transition. They are known as proximity effects[1] in superconductors, and have been studied extensively for temperatures near the critical point. On the other hand, very little is known about composite magnetic systems. In particular, we are not aware of any theoretical study of composite Ising lattices. The Ising lattice has been unique in that both an exact solution and an effective-field approximation are known. The exact solution provides tests for various numerical approximation schemes, and improves our general understandings of phase transitions in short-range interaction systems. The approximate solution is simple in calculation, easy to interpret, and gives reasonably good descriptions of the magnetic behavior near the transition region. In this article, we shall discuss the Bragg-Williams approximation[2] for certain general classes of composite Ising lattices. The general formulation will be given in Sec. 2, upper and lower bounds derived in Sec. 3, analytical solutions in Sec. 4, and finally the connection of our results with the exact solution and with experiments will be discussed in Sec. 5.

2. GENERAL FORMULATION

Let us first consider an Ising lattice of two components. Let γ be the coordination number and N the total number of lattice sites. We assume a nearest-neighbor interaction with strength ϵ_{ij}, where $\epsilon_{ij}=\epsilon_1$ (ϵ_2) if both spins of the interacting pair come from component 1 (2), and $\epsilon_{ij}=\epsilon_3$ if they come from different components. It is physically reasonable to assume that ϵ_3 lies in between ϵ_1 and ϵ_2. We shall restrict ourselves to cases where the lattice can be built up be repetition of a finite unit cell; the distribution of components inside the unit cell is, however, arbitrary. (Regularly distributed impurities or holes are special cases of our model.) Some examples are shown in Fig. 1. Given the structure of the unit cell, one can easily find the volume fraction v_1 (v_2) of component 1 (2) and the fraction of interacting pairs $2u_1$ ($2u_2$) whose spins come from component 1 (2). Also, let $2u_3$ be the fraction of interacting pairs where the two spins come from different components.

Our problem is to compute the partition function Q as a function of the external magnetic field B and the temperature T:

$$Q(B,T)=\sum_{S_1}\cdots\sum_{S_N} e^{-\beta E\{S_i\}}. \tag{1}$$

S_i is either $+1$ or -1, $\beta=1/k_BT$, and E is the energy of the system for a given spin configuration $\{S_i\}$:

$$E\{S_i\}=-\sum_{\langle ij\rangle}\epsilon_{ij}S_iS_j-B\sum_{i=1}^{N}S_i. \tag{2}$$

$\langle ij\rangle$ indicates summation over nearest neighbors.

Since E is in general degenerate, it is convenient to reexpress E in terms of the following variables: N_{1+}, N_{1-}, N_{2+}, N_{2-}, N_{1++}, N_{1+-}, N_{1--}, N_{2++}, N_{2+-}, N_{2--}, N_{3++}, N_{3+-}, N_{3--}, N_+, and N_-. N_+ is the total number of up spins in a given configuration. N_{1+} is the total number of up spins in component 1. N_{1+-} is the total number of interacting pairs with one spin up and one spin down, and both spins come from component 1, etc. These 15 variables are related by the following 13 equations:

$$N_+=N_{1+}+N_{2+},\quad N_-=N_{1-}+N_{2-}; \tag{3}$$

$$N_{1+}+N_{1-}=v_1N,\quad N_{2+}+N_{2-}=v_2N; \tag{4}$$

$$N_{1++}+N_{1+-}+N_{1--}=u_1\gamma N,\quad N_{2++}+N_{2+-}+N_{2--}=u_2\gamma N,\quad N_{3++}+N_{3+-}+N_{3--}=u_3\gamma N; \tag{5}$$

$$\frac{N_{1++}}{u_1\gamma N}=\left(\frac{N_{1+}}{v_1N}\right)^2,\quad \frac{N_{2++}}{u_2\gamma N}=\left(\frac{N_{2+}}{v_2N}\right)^2,\quad \frac{N_{3++}}{u_3\gamma N}=\frac{N_{1+}}{v_1N}\frac{N_{2+}}{v_2N}; \tag{6}$$

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[1] G. Deutscher and P.-G. De Gennes, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1968), Chap. 17.

[2] See, for example, K. Huang, in *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1963), Chap. 16.

$$\frac{N_{1--}}{u_1\gamma N}=\left(\frac{N_{1-}}{v_1N}\right)^2,$$

$$\frac{N_{2--}}{u_2\gamma N}=\left(\frac{N_{2-}}{v_2N}\right)^2, \tag{7}$$

$$\frac{N_{3--}}{u_3\gamma N}=\frac{N_{1-}}{v_1N}\,\frac{N_{2-}}{v_2N}.$$

Equations (3)–(5) are merely definitions. Equations (6) and (7) are generalizations of the Bragg-Williams approximation to the multiple-components case. It says that there is no short-range order apart from that which follows from long-range order within each component. Incidentally, $\frac{1}{2}\gamma N(N_+/N)^2$ is no longer equal to N_{++} $(\equiv N_{1++}+N_{2++}+N_{3++})$, because of the existence of different components. Since the total number of sites is N, and the total number of nearest-neighbor pairs is $\frac{1}{2}\gamma N$, we also have

$$\begin{aligned} v_1+v_2&=1,\\ u_1+u_2+u_3&=\tfrac{1}{2}. \end{aligned} \tag{8}$$

We use L_1 and L_2—the long-range-order parameters in components 1 and 2—as our independent variables. They are defined by

$$\begin{aligned} N_{1+}/v_1N&=(L_1+\tfrac{1}{2}),\\ N_{2+}/v_2N&=(L_2+\tfrac{1}{2}), \end{aligned} \tag{9}$$

with $|L_1|$, $|L_2|\leq\frac{1}{2}$. The other variables, as well as L (the magnetization per site), E and Q, can be expressed in terms of L_1 and L_2:

$$N_{1++}=u_1\gamma N(L_1+\tfrac{1}{2})^2,\quad N_{2++}=u_2\gamma N(L_2+\tfrac{1}{2})^2,\quad N_{3++}=u_3\gamma N(L_1+\tfrac{1}{2})(L_2+\tfrac{1}{2}); \tag{10}$$

$$N_{1+-}=2u_1\gamma N(\tfrac{1}{4}-L_1^2),\quad N_{2+-}=2u_2\gamma N(\tfrac{1}{4}-L_2^2),\quad N_{3+-}=2u_3\gamma N(\tfrac{1}{4}-L_1L_2); \tag{11}$$

$$N_{1--}=u_1\gamma N(L_1-\tfrac{1}{2})^2,\quad N_{2--}=u_2\gamma N(L_2-\tfrac{1}{2})^2,\quad N_{3--}=u_3\gamma N(L_1-\tfrac{1}{2})(L_2-\tfrac{1}{2}); \tag{12}$$

$$L=2(v_1L_1+v_2L_2), \tag{13}$$

$$E/N=-BL-4\gamma(\epsilon_1u_1L_1^2+\epsilon_2u_2L_2^2+\epsilon_3u_3L_1L_2), \tag{14}$$

$$Q=\sum_{L_1=-1/2}^{1/2}\ \sum_{L_2=-1/2}^{1/2}\frac{(v_1N)!(v_2N)!e^{-\beta E}}{[v_1N(L_1+\frac{1}{2})]![v_1N(\frac{1}{2}-L_1)]![v_2N(L_2+\frac{1}{2})]![v_2N(\frac{1}{2}-L_2)]!}. \tag{15}$$

As $N\rightarrow\infty$, the logarithm of Q approaches the logarithm of the largest term in the summand. Using Sterling's approximation for $N!$, we find that

$$\begin{aligned} A/N&=-(1/\beta N)\ln Q\\ &=+4\gamma(\epsilon_1u_1\bar{L}_1^2+\epsilon_2u_2\bar{L}_2^2+\epsilon_3u_3\bar{L}_1\bar{L}_2)\\ &\quad+(1/2\beta)[v_1\ln(\tfrac{1}{4}-\bar{L}_1^2)+v_2\ln(\tfrac{1}{4}-\bar{L}_2^2)], \end{aligned} \tag{16}$$

$$U/N=-4\gamma(\epsilon_1u_1\bar{L}_1^2+\epsilon_2u_2\bar{L}_2^2+\epsilon_3u_3\bar{L}_1\bar{L}_2)-B\bar{L}, \tag{17}$$

where U is the internal energy and A is the free energy. $\bar{L}_1$ and $\bar{L}_2$ are the values of L_1 and L_2 that maximize the summand of Eq. (15). They satisfy

$$\begin{aligned} 2\bar{L}_1&=\tanh[\beta B+4\beta\epsilon_1\gamma(u_1/v_1)\bar{L}_1+2\beta\epsilon_3\gamma(u_3/v_1)\bar{L}_2],\\ 2\bar{L}_2&=\tanh[\beta B+4\beta\epsilon_2\gamma(u_2/v_2)\bar{L}_2+2\beta\epsilon_3\gamma(u_3/v_2)\bar{L}_1]. \end{aligned} \tag{18}$$

Without any danger of confusion, we shall remove the bars from $\bar{L}_1$ and $\bar{L}_2$ from now on. We note that all our equations reduce to those of the single-component case in the proper limit. The generalization to composites with more than two components is straightforward.

3. UPPER AND LOWER BOUNDS

Theorem. For a given cell structure (i.e., for fixed u's and v's), and with a zero external magnetic field, L_1 and L_2 of Eq. (18) are monotonically increasing functions of ϵ_1, ϵ_2, ϵ_3, β, and γ.

To prove this theorem, we first note that if $f(x)=(1/x)\tanh^{-1}x$, then $f(x)$ is a monotonically increasing function of x in the domain $1>x>0$. Next, we rewrite

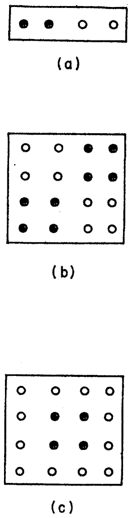

FIG. 1. Some examples of composite Ising lattices: ●, component 1; ○, component 2. (a) $\gamma=2$, $v_1=v_2=\frac{1}{2}$, $u_1=u_2=\frac{1}{2}u_3=\frac{1}{8}$. (b) $\gamma=4$, $v_1=v_2=\frac{1}{2}$, $u_1=u_2=\frac{1}{2}u_3=\frac{1}{8}$. (c) $\gamma=4$, $v_1=\frac{1}{4}$, $v_2=\frac{3}{4}$, $u_1=\frac{1}{16}$, $u_2=\frac{5}{16}$, $u_3=\frac{1}{8}$.

Eq. (18) (with $B=0$) as

$$\frac{\epsilon_3 u_3}{v_1}=\frac{L_1}{L_2}\left(\frac{f(2L_1)}{\beta\gamma}-\frac{2u_1\epsilon_1}{v_1}\right), \tag{19a}$$

$$\frac{\epsilon_3 u_3}{v_2}=\frac{L_2}{L_1}\left(\frac{f(2L_2)}{\beta\gamma}-\frac{2u_2\epsilon_2}{v_2}\right). \tag{19b}$$

From the product of Eqs. (19a) and (19b), we see that L_1 and L_2 cannot both decrease as we increase ϵ_3 or β or γ. Furthermore, if L_1 is increasing while L_2 is decreasing, this would violate Eq. (19b). The reverse case violates Eq. (19a). Hence both L_1 and L_2 must increase monotonically as we increase ϵ_3 or β or γ.

Now rewrite Eq. (19a) as

$$\epsilon_3\gamma\beta\frac{u_3 L_2}{v_1 L_1}=f(2L_1)-2\frac{u_1}{v_1}\beta\epsilon_1\gamma. \tag{20a}$$

So for fixed ϵ_1, ϵ_3, β, and γ, if we increase L_1 (say, by changing ϵ_2), L_2 must also increase. Next, we find L_2/L_1 by solving Eq. (20a), and substitute it into Eq. (19b); we find that

$$\frac{2u_2\beta\gamma\epsilon_2}{v_2}=f(2L_1A(L_1))-\frac{\epsilon_3\gamma\beta u_3}{A(L_1)v_2}, \tag{20b}$$

$$A(L_1)=[v_1 f(2L_1)-2\epsilon_1 u_1\beta\gamma]/\epsilon_3 u_3\beta\gamma.$$

From Eq. (20b), it is clear that for fixed ϵ_1, ϵ_3, β, and γ, L_1 (hence L_2) is a monotonically increasing function of ϵ_2. Similar arguments imply that for fixed ϵ_2, ϵ_3, β, and γ, L_2 (hence L_1) is a monotonically increasing function of ϵ_1. This completes our proof of the theorem.

This theorem also implies that $L(T)$ is bounded by the magnetization curves of pure ϵ_1 and pure ϵ_2 cases. In particular, T_c is bounded by T_{c1} and T_{c2}. For the special case of $v_1=v_2$, $u_1=u_2$, Eq. (19) implies that if $\epsilon_1>\epsilon_2$, then $L_1>L_2$. We expect this result to hold for arbitrary u's and v's.

4. ANALYTICAL SOLUTIONS

For arbitrary temperatures, Eq. (18) can be solved only by numerical methods. However, analytical solutions exist in various limits. If $T>T_c$ and $B=0$, we have $L_1=L_2=0$, hence $U=L=C=0$, $A/N=(1/2\beta)\ln\frac{1}{4}$. The transition temperature T_c can easily be solved explicitly from

$$(\epsilon_3 u_3\beta\gamma)^2-(2\epsilon_1 u_1\beta\gamma-v_1)(2\epsilon_2 u_2\beta\gamma-v_2)=0. \tag{21}$$

If both solutions are positive, the larger one should be used, because T_c should change continuously with the parameters of the system.

To be very specific, let us consider examples (a) and (b) of Fig. 1, where $v_1=v_2=\frac{1}{2}$, $u_1=u_2=\frac{1}{2}u_3=\frac{1}{8}$, and set $\epsilon_3=(\epsilon_1\epsilon_2)^{1/2}$. For this case, we find that $k_BT_c=\gamma\times\frac{1}{2}(\epsilon_1+\epsilon_2)$. Thus the value of T_c coincides with that for the single-component case with $\epsilon=\frac{1}{2}(\epsilon_1+\epsilon_2)$. L_1 and L_2 are now determined in terms of $Y=(\surd\epsilon_1)L_1+(\surd\epsilon_2)L_2$ by

$$\begin{aligned}2L_1&=\tanh(\beta B+\beta\gamma\epsilon_1^{1/2}Y),\\ 2L_2&=\tanh(\beta B+\beta\gamma\epsilon_2^{1/2}Y),\end{aligned} \tag{22}$$

and Y satisfies

$$\begin{aligned}2Y=(\surd\epsilon_1)&\tanh(\beta B+\beta\gamma\epsilon_1^{1/2}Y)\\ &+(\surd\epsilon_2)\tanh(\beta B+\beta\gamma\epsilon_2^{1/2}Y).\end{aligned} \tag{23}$$

We also find that

$$\begin{aligned}U/N&=-\tfrac{1}{2}\gamma Y^2-BL,\\ E/N&=-BL-\tfrac{1}{2}\gamma Y^2,\end{aligned} \tag{24}$$

$$\begin{aligned}L=L_1+L_2&\approx\frac{\epsilon_1^{1/2}+\epsilon_2^{1/2}}{2}\left(\frac{\epsilon_1+\epsilon_2}{\epsilon_1^2+\epsilon_2^2}\right)^{1/2}\\ &\quad\times\left[3\left(1-\frac{T}{T_c}\right)\right]^{1/2}\quad(T\lesssim T_c)\\ &\approx1-\exp\left(-\frac{2T_c}{T}(\surd\epsilon_2)\frac{\epsilon_1^{1/2}+\epsilon_2^{1/2}}{\epsilon_1+\epsilon_2}\right)\\ &\quad-\exp\left(-\frac{2T_c}{T}(\surd\epsilon_1)\frac{\epsilon_1^{1/2}+\epsilon_2^{1/2}}{\epsilon_1+\epsilon_2}\right),\quad(T\gtrsim0)\end{aligned} \tag{25}$$

$$\frac{C}{Nk_B}=\frac{3}{2}\frac{(\epsilon_1+\epsilon_2)^2}{2(\epsilon_1^2+\epsilon_2^2)}\leq\frac{3}{2},\quad(T=T_c) \tag{26}$$

$$\begin{aligned}\chi=\left.\frac{\partial L}{\partial B}\right|_{B=0}&\approx\frac{1}{k_B(T-T_c)}\left(1-\frac{\gamma}{4k_BT}(\epsilon_1^{1/2}-\epsilon_2^{1/2})^2\right)\\ &\qquad(T\gtrsim T_c)\\ &\approx\frac{1}{2k_B(T_c-T)}\left(1-\frac{\gamma}{4k_BT}(\epsilon_1^{1/2}-\epsilon_2^{1/2})^2\right),\\ &\qquad(T\lesssim T_c)\end{aligned} \tag{27}$$

$$\begin{aligned}L\simeq\frac{\epsilon_1^{1/2}+\epsilon_2^{1/2}}{2}&\left(\frac{\epsilon_1^{1/2}+\epsilon_2^{1/2}}{\epsilon_1^2+\epsilon_2^2}\right)^{1/3}(3\beta_cB)^{1/3}\\ &(T=T_c,\ B\rightarrow0).\end{aligned} \tag{28}$$

All our results reduce to the single-component case for the limit $\epsilon_1=\epsilon_2$. We also note that in our model, the specific-heat jump is no longer a constant. The same is true for the ratio $L/[3(1-T/T_c)]^{1/2}$ and the coefficient of the Curie-Weiss law [Eq. (27)].

In the Bragg-Williams approximation for the single-component case, free energy can be expanded in terms of the order parameter L:

$$\frac{A}{N}=\frac{A_0}{N}+\frac{\epsilon\gamma}{2}L^2-\frac{k_BT}{2}\left(\sum_{n=1}^{\infty}\frac{L^{2n}}{n}\right),$$
$$\frac{A_0}{N}=\frac{k_BT}{2}\ln\tfrac{1}{4}. \tag{29}$$

(For multiple-components cases, it is more convenient to expand A in terms of both L_1 and L_2.) In terms of critical indices,[3] our above results give $\beta=\frac{1}{2}$, $\delta=3$, $\gamma=\gamma'=1$, and $\alpha=\alpha'=0$. All these are in agreement with the prediction of Landau's theory of second-order phase transition. This is not surprising, since both the Bragg-Williams approximation and Landau's theory are expected to work well in the presence of very long-range forces.[4] We speculate that Baker's proof[4] still goes through for composite systems.

All the above conclusions still hold for the more general cases of arbitrary v's and u's, although the corresponding formulas are too clumsy to write down.

5. DISCUSSION

The Bragg-Williams approximation is useful because many times it simulates the behavior of the exact solution. The transition temperature obtained by the Bragg-Williams approximation is an upper bound of the exact T_c.[5] This is probably still true for composite lattices. Applying a recent theorem of Griffiths,[6] we easily see that T_c of the exact solution of a composite lattice is also bounded by T_c of the exact solution of corresponding single-component systems. There is some doubt about whether the Griffiths theorem can be generalized to the Heisenberg model,[7] although we expect from physical grounds that the same kind of upper and lower bounds still hold true. This means that, for composite ferromagnetic insulators (for which the Heisenberg model works), the whole system will undergo a magnetic phase transition at $T_{c2}<T_c<T_{c1}$. This effect should be observable even in composite thin films (i.e., proximity effects exist). Experiments[8] to search for such an effect in metallic ferromagnetic composites have not been successful, although factors like interfacial structures, domain walls, etc., may have influenced the outcome.

From previous sections, other features that we expect to see from experiments are the possibility of structures (various shapes and slopes) in $L(T)$, $C(T)$ curves. Furthermore, since there is no definite correlation between the magnitude of the magnetic moment and the magnitude of the exchange integral, a rough calculation based on the Bragg-Williams approximation suggests the following interesting possibility: If one component has a high saturation magnetization and a low T_c, and the other has a low saturation magnetization and a high T_c, then the composite may, in a certain temperature range, have a magnetization higher than those of its components.

Note added in proof. We thank Professor M. E. Fisher for sending us one of his recent reprints, which is related to the problem of composite magnetic lattices. The reference is M. E. Fisher, J. Phys. Soc. Japan Suppl. **26**, 87 (1969).

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