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Mobile-Electron Ising Ferromagnet

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The general mobile-electron Ising ferromagnet (introduced by Fisher) is described, and its properties discussed: Electrons migrate over a lattice of spin-$\frac{1}{2}$ ions; when there are k electrons on the bond (i,j), their energy is ϵ_k and they induce an Ising spin coupling between the spins i and j. The mean number of electrons per bond n is determined by the condition of electroneutrality. The model can be solved exactly in terms of the free energy of the underlying lattice and exhibits renormalized critical exponents: in the three-dimensional model, these are $\beta=0.33$–0.36, $\gamma\simeq1.43$, and $\alpha_s\simeq-0.14$. The behavior of the simplest ferromagnetic model with $k=0$, 1, or 2 and $n=2$ depends, for a fixed mode of electron-ion coupling, only on n and $\epsilon=2\epsilon_1-\epsilon_0-\epsilon_2$. The variation of the critical point with n, ϵ, and the coupling energies is studied, and the behavior of the energy, magnetization, specific heat, and susceptibility is investigated. For certain parametric ranges, it is found that the spontaneous magnetization initially *increases* with T. The model exhibits a critical concentration for ordering $(n=r_c)$, and also a lower critical temperature below which $M_0(T)$ again vanishes. A brief survey of related models exhibiting one or the other of these properties is presented.

I. INTRODUCTION

COMPARISONS of critical indices[1] obtained from three-dimensional Ising models with those from experimental observations in magnetic and fluid systems show small but definite discrepancies. As an example, consider β, the best experimentally determined exponent. In magnetic systems (where β describes the spontaneous magnetization) and in fluids (where β describes the coexistence curve), typical experimental values of β lie in the range 0.33–0.36. On the other hand, the best estimate of this exponent from the Ising model is $\beta\simeq\frac{5}{16}=0.3125$. This theoretical value is 7–15% lower than the experimental values and is well outside any possible interval of uncertainty. These discrepancies are not really surprising, since the Ising interactions cannot hope to describe the complexities of a real physical system. The additional degrees of freedom possessed by a real system might easily influence the behavior at a critical point.

Recently, Fisher[2] has considered this problem quite generally and has found that under certain circumstances the critical exponents are "renormalized." The abstraction underlying Fisher's analysis is as follows: In the attempt to describe a real system, we start with an "ideal" system with known variables and characterized by the ideal critical indices $\alpha, \beta, \gamma, \ldots$. The real system, however, may have some additional "hidden" variables which should be considered in the ideal system. These hidden variables will fluctuate but remain in equilibrium with the known variables, and they are subject to some over-all "constraint." To illustrate the validity of this abstraction, consider the following two cases. In the idealization of a real fluid system as a lattice gas at constant temperature and density, the extra degrees of freedom introduced by isotopic and other impurities are not considered. A hidden variable, in this case, would be the impurity concentration. Obviously, this will fluctuate, but it is constrained since the total number of impurity atoms is fixed. Similarly, the electronic degrees of freedom in a metallic ferromagnet are not considered in the Ising model where temperature and applied field are the known variables. The fact that the system must remain electrically neutral serves as a constraint over these hidden electronic variables. The situation is similar for other physical systems and their idealizations.

On the basis of certain very general thermodynamic assumptions, the behavior of such constrained systems at and near their critical points[3] is found to be renormalized relative to the behavior of the ideal system. It is the constraint of the additional freedoms which is essential in bringing this about. Where the specific heat of the ideal system was divergent with exponents α and α', the real system has a cusp at the critical temperature characterized by the renormalized exponents $\alpha_x=-\alpha/(1-\alpha)$ and $\alpha_x'=-\alpha'/(1-\alpha')$. The other exponents are also renormalized, in particular, $\beta_x=\beta/(1-\alpha')$, $\gamma_x=\gamma/(1-\alpha)$, $\gamma_x'=\gamma'/(1-\alpha')$. Using the three-dimensional Ising-model exponents, we find $\alpha_x\simeq-0.14$, $\gamma_x\simeq1.43$, and $\beta_x\simeq0.33$–0.36. The range in β_x results from the uncertainty in α'. Note that the renormalized value of β_x is seen to be the same as that for which experimental values are found.

The purpose of this paper is to study the effects brought about when an otherwise "stiff" Ising model is given greater flexibility and extra degrees of freedom. Our model is the mobile-electron Ising ferromagnet previously proposed by Fisher (although in a more simplified form than the one adopted here).[4] The

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[1] We use the standard critical-point exponent notation: see the review articles (a) M. E. Fisher, J. Appl. Phys. **38**, 981 (1967); (b) L. P. Kadanoff *et al.*, Rev. Mod. Phys. **39**, 395 (1967); (c) M. E. Fisher, Rept. Progr. Phys. **30**, 615 (1967).

[2] M. E. Fisher, Phys. Rev. **176**, 257 (1968).

[3] As shown by Fisher in Ref. 2, renormalization does not "set in" until the temperature is within some "transition region" about the critical point. This region, however, may be very small and for temperatures very close to T_c (yet outside the transition region) the real system can appear to follow the ideal behavior.

[4] In Ref. 2, Fisher proposed a spinless-electron version of this model with a specified ground state and fixed concentration of electrons. A preliminary account of the present work was given by M. E. Fisher and P. E. Scesney, J. Appl. Phys. **40**, 1534 (1969).

physical picture is one of a metallic ferromagnet in which spin-$\frac{1}{2}$ positive ions occupy the sites of a lattice with coordination number q. An ion is coupled magnetically to its nearest neighbor only when one or more free electrons are in the immediate vicinity of the particular ion-ion bond in question. The ionic spin coupling is then achieved via intermediate interactions with the electronic spins. Although the electrons are free to migrate through the lattice, we suppose that, at a given instant, every electron is associated with some inter-ion bond. Such a bond "occupied" by k electrons has an occupation energy ϵ_k. Unoccupied bonds $(k=0)$ do not couple the vertex ionic spins but do have a "hole" energy ϵ_0. Figure 1 illustrates a possible configuration of our model for a square lattice of ions. The electrons will be treated in a grand canonical ensemble. Their chemical potential $\mu=\xi k_B T$ is to be determined, as usual, by the constraint that, at all temperatures, the average number of electrons per bond is that constant n for which the over-all system of electrons plus ions is electrically neutral.

The mobile-electron Ising ferromagnet is one of a class of "bond decorated" models. Such models are intimately related to the Ising models, since only the form of the nearest-neighbor interaction has been changed. The underlying spin configurational problems arising in the determination of the partition function are identical. The general method of solution of these models[5] is first to consider that part of the partition function associated with the configurations of a single ion-ion bond. This "partial bond partition function" can be rewritten in an Ising from dependent only on the vertex spins. Mathematically, the decorated bond then looks like an undecorated or simple Ising bond, except the usual interaction and field parameters are now complicated functions of the temperature and of the field on the original bond. The partition function can then be rewritten in the usual Ising form which depends only on the spin configurations of the undecorated or reference lattice. This formalism depends only on the structure of the bond; it is independent of the dimensionality of the lattice.

Of prime importance in the determination of the properties of decorated lattices are the algebraic transformations relating the temperature and field variables of the decorated and undecorated bonds. It is quite possible to include in our model the additional complications of three-ion interactions and multiple energy and coupling states of a k bond (a bond occupied by k electrons). The corresponding transformations, however, become increasingly involved. In this paper, we consider only the simplest case in which a bond can accommodate only 0, 1, or 2 electrons and in which n is less than or equal to 2 electrons per bond.

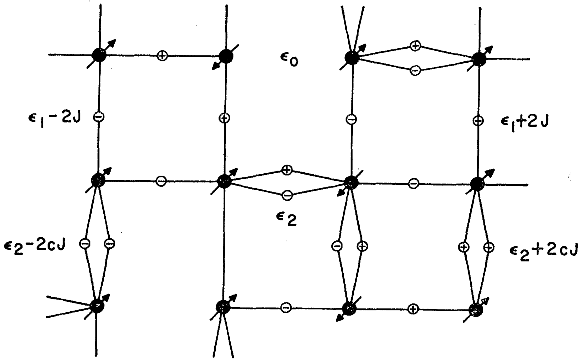

FIG. 1. A possible state of the mobile-electron Ising ferromagnet on a section of square lattice.

Our model, then, introduces additional degrees of freedom in a fairly natural way yet can be solved to the same extent as the corresponding Ising problem. Since the electroneutrality constraint will yield renormalized critical behavior, we have a system which permits us to study these effects quantitatively. In this paper, we display explicitly the factors governing renormalization and the resulting effects on the behavior of the magnetization and specific heat; a detailed numerical study of the renormalization effects is reserved for a following paper.

The model has several interesting features. For certain ranges of the parameters governing the electron behavior, both an upper and lower critical temperature are found, the magnetization being nonzero only for the intermediate temperatures. Binary fluid systems have been known to exhibit the analogous behavior of separating into distinct phases at temperatures between upper and lower consolute temperatures.[6] For other parametric ranges in our model, the magnetization is nonzero at $T=0$ but initially increases with temperature. These effects are a direct result of the additional degrees of freedom introduced in the model.

The simpler version of the mobile-electron ferromagnet in which multiple occupancy is excluded (k equals 0 or 1 only and n is less than or equal to 1) is essentially the same as the dilute ferromagnetic model proposed by Syozi[7] and recently studied in detail by Essam and Garelick.[8] In the Syozi model, the vertex spins are coupled only when the intermediate bond is occupied by a second kind of spin-$\frac{1}{2}$ particle. As in our model, the coupling is achieved via an intermediate interaction with the central spin. Since the number of occupied bonds is fixed, this model has the constraint needed for renormalization. Essam and Garelick show that renormalization does indeed occur, but they do not consider the quantitative behavior of the Syozi model near the critical point. The interesting effects mentioned

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[5] M. E. Fisher, Phys. Rev. **113**, 969 (1959).

[6] J. S. Rowlinson, *Liquids and Liquid Mixtures* (Academic Press Inc., New York, 1959), Chap. 5, 159 ff.

[7] I. Syozi, Progr. Theoret. Phys. (Kyoto) **34**, 189 (1965); I. Syozi and S. Miyozima, *ibid.* **36**, 1083 (1966).

[8] J. W. Essam and H. Garelick, Proc. Phys. Soc. (London) **92**, 136 (1967).

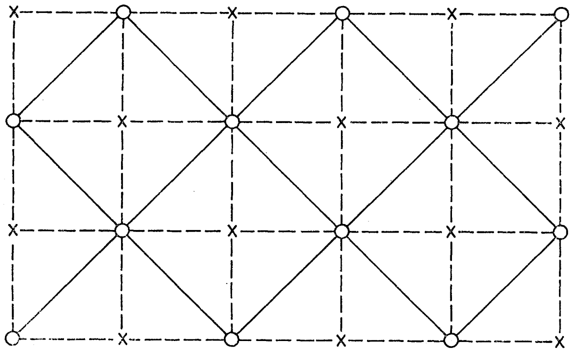

FIG. 2. The model of Vaks, Larkin, and Ovchinnikov with alternating second–nearest-neighbor interactions.

in the previous paragraph are not found in the Syozi model: These effects are dependent on the possibility of multiple occupancy (k equal to 2) incorporated in our model. As we shall see, the results for the Syozi model will be recovered in one special limit of the behavior of the mobile-electron ferromagnet.

Models for magnetic systems with multiple critical points have been found before. In 1965, Vaks, Larkin, and Ovchinnikov[9] studied the properties of a two-dimensional square lattice with nearest-neighbor and alternating second–nearest-neighbor interactions. Figure 2 shows the configuration of bonds in their model. The Ising coupling between nearest-neighbor spins (dotted lines connecting × and ○ sites) was assumed to be ferromagnetic with an energy of interaction J. The Ising interaction between alternating second nearest neighbors (solid lines connecting ○ sites) was given an energy cJ, where a negative value of c would denote an antiferromagnetic coupling. For c greater than -0.94, the model undergoes a unique ferromagnetic transition. In the corresponding ground state, all spins (× and ○) align parallel to one another. For c less than -1, there is a single transition to a low-temperature "antiferromagnetic" state in which ○ spins align antiparallel and × spins have no preferred orientation. In the rather narrow range of c values between -0.94 and -1, the model undergoes three successive phase transitions. With increasing temperature, the lattice passes through a ferromagnetic state to a disordered state, into the "antiferromagnetic" state, and finally into the high-temperature disordered state.

Concurrent with the present work on the mobile-electron ferromagnet, Syozi, Nakano, and Hattori[9] began to study a class of decorated lattice models which in certain circumstances, were also found to exhibit multiple phase transitions similar to that of the model of Vaks *et al.* A typical decorated bond in this class is shown in Fig. 3. It possesses a direct antiferromagnetic coupling (energy $-|c|J$) and an indirect coupling (energy J) via an intermediate interaction which tends to order the vertex spins. As also illustrated by Fig. 3, this type of bond is similar to the alternating nearest-neighbor–coupling scheme of the Vaks model. As in the Vaks model, over a certain range of c, these other decorated lattices can have a low-temperature ferromagnetic phase with all spins (× and ○) aligning parallel, and a higher-temperature antiferromagnetic phase with ○ spins aligning antiparallel and × spins having no preferred directions. It has been further found[10] that by "superdecoration" of lattice bonds with multiple spin systems of increased complexity, other combinations of multiple critical behavior are possible.

Unlike the mobile-electron ferromagnet, all these other models have bonds of fixed structure. Hence, they are just as rigid as the standard Ising model and possess the same ideal critical behavior. The multiple phase transitions that are found result from a competition between the direct and indirect couplings of the ○ spins. Associated with this competition are two ordered states of low energy. The ferromagnetic ground state is favored by a "binding energy" per ○ spin which is small $[2(|c|-1)J]$ for the Vaks model compared to the direct antiferromagnetic coupling energy $2cJ$. Note that in the antiferromagnetic state the × spins can take any orientation without influencing the energy of the configuration. The higher-temperature phase transitions arise from the possibility of establishing the second "excited" phase at temperatures low enough $(T\sim[2(|c|-1)J]/k_B)$ to maintain ○ spin ordering. This second phase is then disordered at still higher temperatures $(T\sim 2J/k_B)$. We shall see (i) that the upper and lower critical temperatures which are possible in the mobile-electron ferromagnet arise from quite a different mechanism; (ii) that they can occur for large energy ranges; and (iii) that, unlike some of the other models, they are possible in all two- and three-dimensional lattices.

The format for the rest of this paper is as follows. In Sec. II, we consider the derivation of the partition

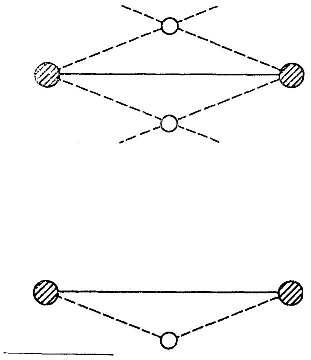

FIG. 3. The similarity between the bonds of a class of "decoration" models (bottom) and the Vaks model (top). Both possess an indirect ferromagnetic coupling (dashed lines) and a direct antiferromagnetic coupling (solid lines).

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[9] V. G. Vaks, A. I. Larkin, and Yu N. Ovchinnikov, Zh. Eksperim. i Teor. Fiz. **49**, 1180 (1965) [English transl.: Soviet Phys.—JETP **22**, 820 (1966)].

[10] (a) H. Nakano, Progr. Theoret. Phys. (Kyoto) **39**, 1121 (1968); (b) I. Syozi, *ibid.* **39**, 1367 (1968); (c) I. Syozi and H. Nakano, *ibid.* **40**, 236 (1969); (d) M. Hattori and H. Nakano, *ibid.* **40**, 958 (1969).

function for the mobile-electron Ising ferromagnet. We first deal with a specific form of interaction and then consider those properties of a general interaction which are necessary in the rest of the paper. Section III deals with the electroneutrality constraint and the derivation of the basic transformation equations mentioned earlier. Section IV deals with the solutions of the transformation equations with emphasis on critical point determination and elucidation of the upper and lower critical point solutions and discusses the approach of the real system to its critical temperature relative to that of the ideal system. The renormalized behavior of the internal energy, specific heat, spontaneous magnetization, and susceptibility of the system are displayed explicitly in Sec. V. A quantitative study of the effects of renormalization, including estimates of the apparent values of the critical exponents which would be found experimentally by different techniques of data analysis, will be presented in a following paper.

II. PARTITION FUNCTION

We consider a nearest-neighbor ionic bond which is occupied by 0, 1, or 2 electrons. The ionic spins can effect each other only via an intermediate interaction with an electronic spin. Several modes of this spin-spin coupling could be considered for the various states of the bond. In what follows, a specific case will be developed. Those parts of the analysis which are dependent on the form of the interaction will be isolated and generalized. The effect of changing the form of the coupling scheme can then be easily assessed.

Consider the (i,j) bond connecting nearest-neighbor sites i and j. The spin of the ith ion will be described by the variable σ_i which takes the values ± 1. In order to describe the electronic state of the bond, we introduce, as an algebraic convenience, two inter-ion sites with spin-occupancy variables μ_{ij} and ν_{ij}. These variables will be the usual spin variables taking the values ± 1 if the site is occupied by an electron but will equal zero if the site is unoccupied.

These electronic variables are somewhat artificial since they distinguish the electrons on doubly occupied bonds from one another and give double statistical weight to singly occupied bonds. They are not necessary for the analysis but do allow us to factorize the partition function in certain limits. They also give us a definite notation in which to describe the states of the bond.

The interaction energy for one form of coupling can be written as

$$E_{\text{int}} = -J[1+(\tfrac{1}{2}c-1)\mu_{ij}^2\nu_{ij}^2](\mu_{ij}+\nu_{ij})(\sigma_i+\sigma_j)\,. \quad (2.1)$$

In this scheme, empty bonds produce no ionic spin coupling, singly occupied bonds couple through a ferromagnetic electron-ion interaction of strengh J, and occupancy of both sites yields two independent but similar interactions, each with strength $\frac{1}{2}cJ$. The resulting ionic ordering for occupied bonds is ferromagnetic. The occupation energy of the bond may be written

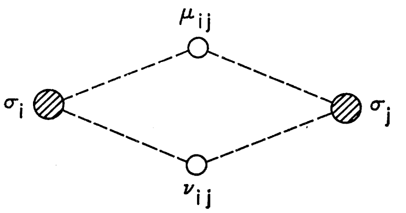

FIG. 4. Schematic of a bond adopted for the mobile-electron Ising ferromagnet.

$$E_{\text{occ}} = -J\{b_0(1-\mu_{ij}^2)(1-\nu_{ij}^2) + b_1[(1-\mu_{ij}^2)\nu_{ij}^2+(1-\nu_{ij}^2)\mu_{ij}^2] + b_2\mu_{ij}^2\nu_{ij}^2\}\,, \quad (2.2)$$

where

$$b_k = -\epsilon_k/J\,. \quad (2.3)$$

For simplicity, we will assume that the magnetic moment of both ions and electrons is m. The possibility of different moments can be accounted for later. Figure 4 shows a schematic of the bond we have adopted. Figure 1 shows a possible state of a lattice with these bonds.

The grand partition function for a lattice of N ions at temperature T and in an external field H is now

$$\Xi(K,L,\xi,b_0,b_1,b_2,c) = \sum_{\mu_{12}=0}^{\pm 1}\sum_{\nu_{12}=0}^{\pm 1}\cdots\sum_{\sigma_N=\pm 1}\exp\{\sum_{(i,j)}[-(K/J)(E_{\text{int}}+E_{\text{occ}}) + \xi(\mu_{ij}^2+\nu_{ij}^2)+L(\mu_{ij}+\nu_{ij})]+\sum_i L\sigma_i\}\,, \quad (2.4)$$

where

$$K=J/k_BT \quad \text{and} \quad L=mH/k_BT\,.$$

We begin the decoration transformation by performing the sum over the variables μ_{ij} and ν_{ij} independently and writing the resulting partial-bond partition functions in an Ising form.

$$\psi(\sigma_i,\sigma_j) = \sum_{\mu_{ij}=0}^{\pm 1}\sum_{\nu_{ij}=0}^{\pm 1}\exp[-(K/J)(E_{\text{int}}+E_{\text{occ}}) + \xi(\mu_{ij}^2+\nu_{ij}^2)+L(\mu_{ij}+\nu_{ij})]\,, \quad (2.5)$$

$$\psi(\sigma_i,\sigma_j) = e^{b_0K}+e^{\xi}e^{b_1K}\{4\cosh[K(\sigma_i+\sigma_j)+L]\} + e^{2\xi}e^{b_2K}\{2+2\cosh[cK(\sigma_i+\sigma_j)+2L]\}\,, \quad (2.6)$$

$$\psi(\sigma_i,\sigma_j) = \phi\exp(K'\sigma_i\sigma_j+L_i^*\sigma_i+L_j^*\sigma_j)\,. \quad (2.7)$$

Denoting the signs of σ_i, σ_j by $+$ and $-$ and requiring (2.7) to hold identically for the four possible states gives, in general,[5]

$$\phi^4 = \psi_{++}\psi_{--}\psi_{+-}\psi_{-+}\,, \quad (2.8)$$

$$\exp(4K') = \psi_{++}\psi_{--}/\psi_{+-}\psi_{-+}\,, \quad (2.9)$$

$$\exp(4L_1^*) = \psi_{++}\psi_{+-}/\psi_{--}\psi_{-+}\,, \quad (2.10)$$

$$\exp(4L_2^*) = \psi_{++}\psi_{-+}/\psi_{--}\psi_{+-}\,. \quad (2.11)$$

For our symmetric bond, we have

$$\psi(\sigma_i,\sigma_j)=\psi(\sigma_j,\sigma_i)\,, \tag{2.12}$$

hence,

$$L_i^*=L_j^*=L^* \tag{2.13}$$

and

$$\exp(4L^*)=\psi_{+\,+}/\psi_{-\,-}\,. \tag{2.14}$$

Substitution back into the grand partition function gives

$$\Xi(K,L,\xi,b_0,b_1,b_2,c)=\phi^{qN/2}Z(K',L')\,, \tag{2.15}$$

where

$$Z(K',L') = \sum_{\sigma_1=\pm 1}\cdots\sum_{\sigma_N=\pm 1}\exp\Big(K'\sum_{(i,j)}\sigma_i\sigma_j+L'\sum_i\sigma_i\Big) \tag{2.16}$$

and

$$L'=L+qL^*. \tag{2.17}$$

Evidently, $Z(K',L')$ is the partition function of the reference Ising lattice with interaction and field parameters determined by Eqs. (2.9), (2.14), and (2.17).

Generalization of these formulas for an arbitrary coupling scheme involves only certain parts of the partial-bond partition functions. Obviously, (2.6) can be rewritten as

$$\psi(\sigma_i,\sigma_j)=e^{b_0k}f_0+e^{\xi}e^{b_1k}f_1+e^{2\xi}e^{b_2k}f_2\,, \tag{2.18}$$

where the f_k are functions of σ_i, σ_j, K, and L and contain everything arising out of the form of the interaction. In our general model, empty bonds produce no coupling, so

$$f_0(\sigma_i,\sigma_j,K,L)\equiv 1\,. \tag{2.19}$$

Proceeding as before to consider the four possible orientations of the vertex spins, each of the remaining functions $f_k(\sigma_i,\sigma_j,K,L)$ can be thought of as a set of functions, namely $f_{k+\,+}$, $f_{k+\,-}$, $f_{k-\,+}$, $f_{k-\,-}$, which are dependent only on K and L. For our specific choice of interaction given by (2.1), we obtain explicitly

$$f_{1\pm\,\pm}(K,L)=4\cosh(2K\pm L)\,, \tag{2.20}$$

$$f_{2\pm\,\pm}(K,L)=4\cosh^2(cK\pm L)\,, \tag{2.21}$$

$$f_{1+\,-}(K,L)=4\cosh(L)=f_{1-\,+}(K,L)\,, \tag{2.22}$$

$$f_{2+\,-}(K,L)=4\cosh^2(L)=f_{2-\,+}(K,L)\,. \tag{2.23}$$

Equations (2.22) and (2.23), which show the equivalence of the $(+,-)$ and $(-,+)$ configurations, are a direct result of the symmetry of our bond. For any symmetric-bond scheme, we can write

$$f_{k+\,-}(K,L)=h_k(K,L)=f_{k-\,+}(K,L)\,. \tag{2.24}$$

Furthermore, as illustrated by Eqs. (2.20) and (2.21), arbitrary bond schemes can possess an additional symmetry. If the decorating spins have no preferred orientations, the $(+,+)$ and $(-,-)$ configurations will always be equivalent in zero field;

$$f_{k+\,+}(K,0)=g(K)=f_{k-\,-}(K,0)\,. \tag{2.25}$$

If, in addition to these symmetries, we assume that all the states of occupied bonds have a ferromagnetic character, then for $k=1$, 2, we expect

$$f_{k+\,+}(K,L)>f_{k-\,-}(K,L)\,, \tag{2.26}$$

when the external field is greater than zero.

Making use of these general properties, we find that, as in the case of the Ising model, the mobile-electron Ising ferromagnet can have a critical point only in zero field. This follows since the critical point will be any K, L point mapping onto the critical point of the reference Ising lattice and a ferromagnetic transition can occur only when L', the field on this lattice, is zero. By (2.14) and (2.17), and the properties mentioned, L' equals zero only when L equals zero.

To determine the critical points, then, we only have to consider the zero-field case for which L' equals zero. For a symmetric bond, the number of functions determining ϕ and K' is now reduced to two, namely,

$$\begin{aligned}\psi_+(K)&=\psi_{+\,+}(K,0)=\psi_{-\,-}(K,0)\\&=e^{b_0k}+e^{\xi}e^{b_1k}g_1(K)+e^{2\xi}e^{b_2k}g_2(K),\end{aligned} \tag{2.27}$$

$$\begin{aligned}\psi_-(K)&=\psi_{+\,-}(K,0)=\psi_{-\,+}(K,0)\\&=e^{b_0k}+e^{\xi}e^{b_1k}h_1(K,0)+e^{2\xi}e^{b_2k}h_2(K,0)\,.\end{aligned} \tag{2.28}$$

ϕ and K' are then given by

$$\phi^2=\psi_+\psi_-\,, \tag{2.29}$$

$$e^{2K'}=\psi_+/\psi_-\,. \tag{2.30}$$

We shall see that the right-hand side of Eqs. (2.29) and (2.30) depend on K' through e^{ξ}, so that Eq. (2.30) actually represents an involved relationship between K and K'. We will refer to (2.30) as the transformation equation. Before considering the solutions of this equation, we mention a few more general properties associated with the zero-field coupling functions g_k and h_k.

Since all spin configurations of finite energy are equally probable at infinite temperature, we must have for $k=1$, 2

$$g_k(0)=h_k(0,0)=\eta\,, \tag{2.31}$$

where η is a positive constant. In addition, $g_k(K)/h_k(K,0)$ must be a positive monotonically increasing function of K because of the ferromagnetic nature of the bonds. We will assume that the parameter c always describes the ferromagnet strength of a $k=2$ bond relative to a $k=1$ bond. We can then write that, as $K\to\infty$,

$$g_1(K)/e^{2K}\to v_1 \tag{2.32}$$

and

$$g_2(K)/e^{2cK}\to v_2\,, \tag{2.33}$$

where v_k is the number of distinct states of a k-electron bond.

III. CHEMICAL POTENTIAL

The chemical potential of the electrons must be determined by the constraint of over-all electroneutrality. The average number of electrons per bond is n, a number determined by the average ionic charge per bond of the lattice. Thus, we require that

$$n=\lim_{N\to\infty}\left[(\tfrac{1}{2}qN)^{-1}\frac{\partial}{\partial\xi_{K,L}}\ln\Xi\right] \tag{3.1}$$

$$=\frac{\partial\ln\phi}{\partial\xi_{K,L}}+\omega(K',L')\frac{\partial K'}{\partial\xi_{K,L}}+(\tfrac{1}{2}q)^{-1}\sigma(K',L')\frac{\partial L'}{\partial\xi_{K,L}}, \tag{3.2}$$

where $\omega(K',L')$ and $\sigma(K',L')$ are related to the energy and magnetization of the reference lattice; namely,

$$\omega(K',L')=\lim_{N\to\infty}\left[(\tfrac{1}{2}qN)^{-1}\frac{\partial}{\partial K'}\ln Z\right], \tag{3.3}$$

$$\sigma(K',L')=\lim_{N\to\infty}\left(N^{-1}\frac{\partial}{\partial L'}\ln Z\right). \tag{3.4}$$

Using the definitions in Sec. II, we have

$$\frac{\partial\ln\phi}{\partial\xi_{K,L}}=\frac{1}{4}\left[\frac{\psi_{++}{}^{(\xi)}}{\psi_{++}}+\frac{\psi_{--}{}^{(\xi)}}{\psi_{--}}+\frac{2\psi_{+-}{}^{(\xi)}}{\psi_{+-}}\right], \tag{3.5}$$

$$\frac{\partial K'}{\partial\xi_{K,L}}=\frac{1}{4}\left[\frac{\psi_{++}{}^{(\xi)}}{\psi_{++}}+\frac{\psi_{--}{}^{(\xi)}}{\psi_{--}}+\frac{2\psi_{+-}{}^{(\xi)}}{\psi_{+-}}\right], \tag{3.6}$$

$$\frac{\partial L'}{\partial\xi_{K,L}}=\tfrac{1}{4}q\left[\frac{\psi_{++}{}^{(\xi)}}{\psi_{++}}-\frac{\psi_{--}{}^{(\xi)}}{\psi_{--}}\right], \tag{3.7}$$

where the superscript notation is defined by

$$\psi(\sigma_i,\sigma_j)^{(\xi)}=(\partial\psi(\sigma_i,\sigma_j)/\partial\xi_{\mathrm{K},L}). \tag{3.8}$$

In zero field, (3.5)–(3.7) become

$$\frac{\partial\ln\phi}{\partial\xi_{K,L}}=\frac{1}{2}\left[\frac{\psi_{+}{}^{(\xi)}}{\psi_{+}}+\frac{\psi_{-}{}^{(\xi)}}{\psi_{-}}\right], \tag{3.9}$$

$$\frac{\partial K'}{\partial\xi_{K,L}}=\frac{1}{2}\left[\frac{\psi_{+}{}^{(\xi)}}{\psi_{+}}-\frac{\psi_{-}{}^{(\xi)}}{\psi_{-}}\right], \tag{3.10}$$

$$\frac{\partial L'}{\partial\xi_{K,L}}=0, \tag{3.11}$$

so that (3.2) becomes

$$n=\tfrac{1}{2}[(1+\omega)\psi_{+}{}^{(\xi)}/\psi_{+}+(1-\omega)\psi_{-}{}^{(\xi)}/\psi_{-}]. \tag{3.12}$$

Equation (3.12) could be solved directly for e^{ξ}, since it is a quadratic expression in that quantity. However, by making the substitutions

$$(\psi_{+})^{-1}=(1-e^{-2K'})/(\psi_{+}-\psi_{-}), \tag{3.13}$$

$$(\psi_{-})^{-1}=(e^{2K'}-1)/(\psi_{+}-\psi_{-}), \tag{3.14}$$

which arise from Eq. (2.30), it is possible to generate an expression linear in e^{ξ}. This expression is

$$n=(r\psi_{+}{}^{(\xi)}+s\psi_{-}{}^{(\xi)})/(\psi_{+}-\psi_{-}), \tag{3.15}$$

where r and s are functions of K' given by

$$r(K')=\tfrac{1}{2}(1-e^{-2K'})[1+\omega(K')], \tag{3.16}$$

$$s(K')=\tfrac{1}{2}(e^{2K'}-1)[1-\omega(K')]. \tag{3.17}$$

Finally, solving for e^{ξ}, we get

$$e^{\xi}=[e^{b_1K}F_1(K,K')]/[e^{b_2K}F_2(K,K')], \tag{3.18}$$

with

$$F_1(K,K')=[r(K')-n]g_1(K)+[s(K')+n]h_1(K), \tag{3.19}$$

$$F_2(K,K')=[n-2r(K')]g_2(K)-[n+2s(K')]h_2(K). \tag{3.20}$$

Note that the numerator and denominator of e^{ξ} involve only $k=1$ and $k=2$ bonds, respectively.

We should comment that when this procedure is used in the solution of the Syozi model, the analysis would be essentially complete at this stage. In the Syozi model, the equation analogous to (3.12) is linear in e^{ξ} and the equation analogous to (3.15) would define the relationship between K and K' and would be independent of e^{ξ}. To continue the analysis of our model, however, we must substitute our expression for e^{ξ} back into the transformation (2.30). Before doing this, we define a reduced activity in which the occupation energies do not enter; namely,

$$z=F_1(K,K')/F_2(K,K'). \tag{3.21}$$

The basic zero-field transformation (2.30), relating K and K', then becomes

$$e^{2K'}=[e^{b_0K}+ze^{(b_1-b_2)K}e^{b_1K}g_1+(ze^{(b_1-b_2)K})^2e^{b_2K}g_2]\times[e^{b_0K}+ze^{(b_1-b_2)K}e^{b_1K}h_1+(ze^{(b_1-b_2)K})^2e^{b_2K}h_2]^{-1}, \tag{3.22}$$

$$e^{2K'}=(e^{bK}+zg_1+z^2g_2)(e^{bK}+zh_1+z^2h_2)^{-1}. \tag{3.23}$$

The bond occupation energies enter only in the one combination,

$$b=b_0+b_2-2b_1=(2\epsilon_1-\epsilon_0-\epsilon_2)/J=\epsilon/J. \tag{3.24}$$

Evidently, ϵ is the energy for preference of one-electron relative to zero- or two-electron bonds. In the limit $\epsilon\to-\infty$, as many bonds as possible will be $k=1$ bonds, while for $\epsilon\to+\infty$, only $k=2$ and $k=0$ bonds will be found.

The solution of Eq. (3.23) tells us how the interaction parameters K and K' of the decorated and reference

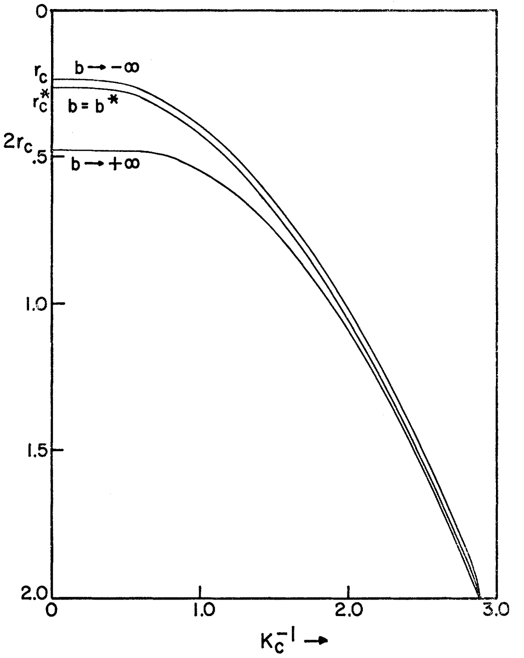

FIG. 5. Dependence of critical temperature on electron concentration for a simple cubic lattice with a coupling constant c of 2.

Ising lattices depend on one another. One problem which arises at this point is that the transformation relation K and K' is found to have several branches. That is, a single arbitrary value of K corresponds, in general, to distinctly different values of K'. The determination of that correspondence reflecting the true physical behavior of the system is accomplished by considering the value of e^{ξ} for a given K, K'. Since the chemical potential must be real valued, e^{ξ} must be real and greater than or equal to zero. In Sec. IV, we discuss the family of physically significant solutions.

IV. TRANSFORMATION EQUATION AND CRITICAL POINT

The zero-field transformation (3.23), relating K and K', is dependent on the underlying lattice through the presence of the energy $\omega(K')$ in the functions F_1, F_2, r, and s which are imbedded in z. Indeed, it is because of this dependence that the critical exponents are renormalized. However, when given a specific lattice and the bond functions g_k and h_k, it is not normally possible to generate simple explicit expressions for the relationship between K and K' because of this dependence. Since $\omega(K')$ has a similar qualitative behavior for all lattices of interest, however, the behavior of the solutions with b, c, n should likewise be similar. We now consider these common features.

It is immediately observed that high temperatures always map onto high temperatures since, when $K=0$, $K'=0$ by (2.31). To study what happens for large K, we rewrite (3.23) so as to isolate the effects of the preferential energy ϵ. That is, we isolate the b dependence:

$$e^{bK}=z[g_1-h_1e^{2K'}+z(g_2-h_2e^{2K'})]/(e^{2k'}-1). \quad (4.1)$$

We now proceed to analyze the solution of this equation for the limiting values of b for which we understand the electronic behavior.

A. Infinite Values of $b=\epsilon/J$

In the limit $b\to\infty$, the existence of singly occupied bonds becomes energetically impossible, coupling of the ionic spins occurs only through doubly occupied bonds, and the probability p of a nearest-neighbor pair being coupled is $\frac{1}{2}n$. Hence, the relation between K and K' should be independent of the $k=1$ bond functions. This is indeed the case since, for an arbitrary value of K and e^{bK} tending to infinity, (4.1) can only be satisfied if z tends to infinity. Equation (3.21) then gives the $b\to\infty$ solution as

$$F_2(K,K')=0, \quad (4.2)$$

which, by (3.20), becomes

$$g_2(K)/h_2(K)=[\tfrac{1}{2}n+s(K')]/[\tfrac{1}{2}n-r(K')]. \quad (4.3)$$

In the opposite limit $b\to-\infty$, singly occupied bonds are preferred. We must, however, distinguish two different possibilities of electron behavior dependent on the average number of electrons per bond. For $n\leq 1$, coupling will occur only through $k=1$ bonds with a probability n and the K, K' relation should be independent of the $k=2$ functions. For $1<n<2$, the situation becomes more complicated. Although $k=1$ bonds are preferred, a fraction $n-1$ of the bonds must be doubly occupied to accommodate all the electrons, and there are no uncoupled empty bonds. Obviously, the solution must involve both the $k=1$ and $k=2$ functions with the dependence on the $k=1$ functions becoming very small as n approaches 2.

In the limit $b\to-\infty$, then, we must have $e^{bK}\to 0$ for an arbitrary K value. Equation (4.1) now has two possible solutions, namely,

$$z=0, \quad (4.4)$$

$$g_1-h_1e^{2K'}+z(g_2-h_2e^{2K'})=0. \quad (4.5)$$

Now, Eq. (4.4) holds for an arbitrary K value if

$$F_1(K,K')=0, \quad (4.6)$$

which gives

$$g_1(K)/h_1(K)=[n+s(K')]/[n-r(K')]. \quad (4.7)$$

This is the solution involving only $k=1$ functions and which is physically significant for $n\leq 1$. The second solution given by (4.5) and involving both types of coupling functions is the proper limit for $1\leq n\leq 2$. It can be verified that, for $n=1$, (4.4) and (4.5) are identical and that, for $n=2$, (4.5) is independent of $k=1$ functions and agrees with (4.3).

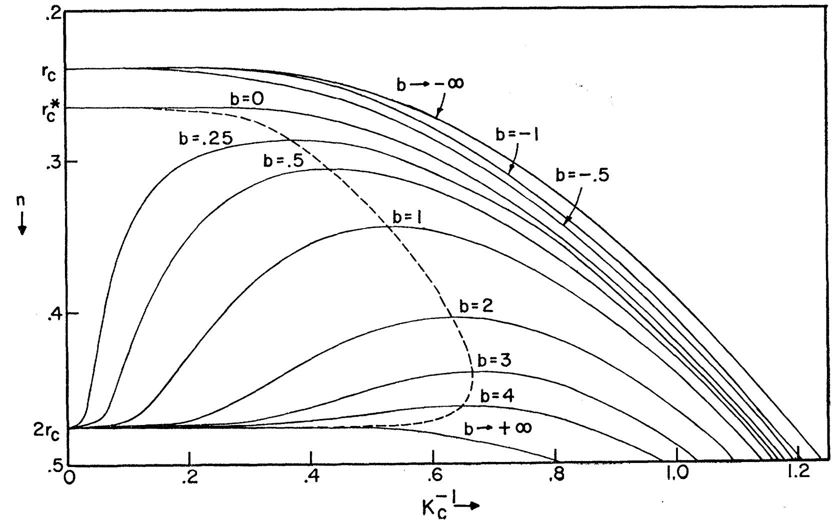

FIG. 6. Enlarged section of Fig. 5 illustrating the region in which both upper and lower critical points are possible and showing the variation with b, the bond energy parameter. The dashed line is the locus of critical concentration and corresponding unique critical points for the parametrically indicated b values.

The first two of these limits ($b=\infty$; $b=-\infty$, $n\leq 1$) are modifications of the Syozi model. In both cases, coupling occurs with a specified probability through only one type of bond. The similarity between (4.3) and (4.7) is then obvious. These equations represent a general solution for the Syozi model involving only the coupling bond functions and the corresponding probability of coupling. When the $k=1$ coupling is through the central spin, as in (2.1), (4.7) is identical to the Syozi solution since the zero-field coupling functions give

$$g_1(K)/h_1(K)=\cosh(2K)\,. \tag{4.8}$$

In both these Syozi-like limits, the solution only makes sense if $r(K')$ is less than or equal to p, the probability for coupling. There is no possible ambiguity involved here, since $r(K')$ is an increasing function of K' with values between 0 and 1. Evidently, $r(K')=p$ denotes the largest value of K' attainable at $T=0$ with a given concentration of electrons. When $p=1$, all ions are identically coupled to their neighbors and we have, in effect, a standard Ising lattice. The right-hand side of (4.3) and (4.7) reduces simply to

$$[1+s(K')]/[1-r(K')]=e^{2K'}\,. \tag{4.9}$$

In these Ising limits, $K=\infty$ corresponds to $K'=\infty$ and complete ionic spin ordering occurs at $T=0$. The standard Ising critical exponents are found in these limits.

The final limiting solution (4.5) valid for $b\to-\infty$, $1\leq n\leq 2$ coincides with the $k=1$ Ising limit, when $n=1$, and to the $k=2$ Ising limit, when $n=2$. For intermediate values of n, this solution represents a smooth transition from one Ising limit to another arising from the filling of the bonds. $K=\infty$ will correspond to $K'=\infty$ but, because $\omega(K')$ enters when all bonds are all bonds are no longer identical, the critical behavior will be renormalized.

B. Finite Values of $b=\varepsilon/J$

A feature suggested by the above discussion is that $n=2$ is always an Ising limit and that the solution

$$g_2(K)/h_2(K)=e^{2K'}\,, \tag{4.10}$$

which is valid for the infinite values of b, should also be valid for any finite b. This is verified by substitution into (3.23).

For other values of n, the finite b solution lies between the limiting solutions, and for finite K it changes from (4.3) to (4.5) and (4.7) in a continuous manner as b goes from $+\infty$ to $-\infty$. For values of b greater than a value b^*, however, two different values of K can correspond to the same K'.

To illustrate this discontinuous behavior as a function of b, consider those values of K which correspond to a specific value of K'. In particular, consider the critical points K_c given by (4.1) with $K'=K_c'$, K_c' being the critical point of the reference Ising lattice (the subscript c will denote the critical value of any quantity). Figures 5 and 6 show the (b,n) behavior of a simple cubic lattice for our choice of interaction as given in (2.1). The $k=2$ coupling parameter c was chosen to be 2 so that all electrons couple the ions with the same strength. The picture is similar for other lattices, only the parameters K_c' and $\omega_c=\omega(K_c')$ being different.

Before discussing the critical-point solutions, we consider the finite b, large K limit of (4.1). From (2.32) and (2.33), we have, for $K\to\infty$,

$$e^{bK}=\{(n-r)rv_1^2/[(n-2r)^2(e^{2K'}-1)v_2]\}e^{b^*K}+\cdots\,, \tag{4.11}$$

where

$$b^*=4-2c=\epsilon^*/J\,. \tag{4.12}$$

The limiting values of K' then depend on b. They are given by

$$r(K')=\tfrac{1}{2}n\,,\quad (b>b^*) \tag{4.13}$$

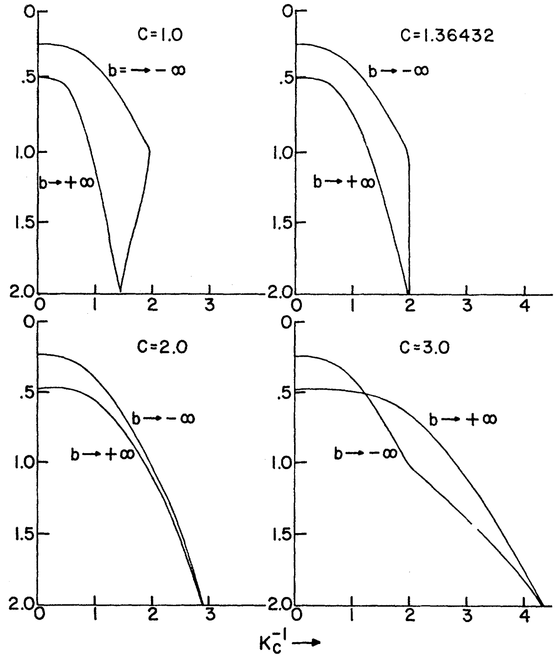

FIG. 7. Variation of critical-point behavior with the coupling constant c.

$$r(K')=n, \quad (b<b^*) \tag{4.14}$$

and, for $b=b^*$,

$$r^*(K')=2r(K')\{1+[1+4v_2(e^{2K'}-1)/v_1{}^2]^{1/2}\}^{-1}=n, \tag{4.15}$$

where $r\leq r^*\leq 2r$, with its exact value dependent on v_k, the number of distinct states of a k bond. Note that (4.13) and (4.14) are the same limits found in the corresponding infinite b cases.

C. Upper and Lower Critical Points

To understand the critical-point solutions illustrated by Fig. 6, we must first understand the significance of the equality $b=b^*$. When rewritten in terms of the occupation and coupling energies of the bonds at $T=0$, the equality becomes

$$2(\epsilon_1-2J)=\epsilon_0+(\epsilon_2-2cJ). \tag{4.16}$$

In other words, at $T=0$, two electrons may either occupy separate bonds or pair up on the same bond leaving the other vacant, the energies for the two possibilities being equal.

For $b<b^*$, the ground state would contain as many unpaired electrons as possible. For $n\leq 1$, this is identical to the Syozi ground state and the critical concentration is the same, $p_c=n_c=r_c$. Note that, for $r_c{}^*>n>r_c$, the critical temperature decreases from a maximum when $b=-\infty$ down to zero as b approaches b^*. The reason for this is that, for $T>0$, there is a finite probability for the pairing of electrons. This probability increases to a maximum as the energy per electron $(\frac{1}{2}\epsilon-\frac{1}{2}\epsilon^*)$, favoring the unpaired ground state approaches zero. Increasing temperature, then, disorders the lattice in two ways; thermal disorder of coupled ionic spins and self-dilution through creation of $k=2$ bonds. It is this self-diluting effect which is responsible for the fall of T_c to zero as $b\rightarrow b^*$. For $n>r_c{}^*$, there are always enough bonds to support low-temperature ordering, and the critical temperature is always greater than zero.

All the electrons for the $b>b^*$ ground state will be on $k=2$ bonds, and the $T=0$ critical concentration is again $p_c=\frac{1}{2}n_c=r_c$. At finite temperatures, there will be a definite probability of splitting a $k=2$ bond and creating two singly occupied bonds. The energy per electron involved in this process is $\frac{1}{2}(\epsilon-\epsilon^*)$. It is because of this splitting that an ordered state is possible at finite temperature for $r_c{}^*<n<2r_c$, even though the ground state is disordered.

The criterion for the establishment of an ordered state is whether enough extra bonds can be produced before the connected ionic spins are disordered by the rising temperature. In this ground state, the probability of a bond coupling its ions is $\frac{1}{2}n$, but the probability needed for ordering at $T=0$ is r_c. At finite temperatures, a slightly greater probability would be needed, but, for $T\ll J/k_B$, the probability increase needed for order would be approximately $(r_c-\frac{1}{2}n)$. This increase is to be attained by bond splitting. Equation (4.11) gives

$$(r_c-\tfrac{1}{2}n)\propto\exp[-\tfrac{1}{2}(\epsilon-\epsilon^*)/k_BT]+\cdots, \tag{4.17}$$

which could have been expected. From this we easily see that for $n\lesssim 2r_c$ there are almost enough bonds to give order at $T=0$ and lower critical points are possible even for very large values of $b-b^*$, since few bonds need be split. Similarly, as b approaches b^*, more bonds will be split at a given temperature and an ordered state could be established for lower electron concentrations. When n is in this range from $r_c{}^*$ to $2r_c$, then, order is possible at finite temperature for b values up to some maximum value, at which the upper and lower critical temperatures concide. This unique value of $K_c{}^{-1}$ versus n_c is shown by the dashed line is Fig. 6. The corresponding b values must be read along the line.

Summarizing, we found that, when the ground state favored one-electron bonds, there was a range of $n(r_c<n<r_c{}^*)$ over which it was possible to fall to zero. When the ground state favored $k=2$ bonds, there was an analogous range of $n(r_c{}^*<n<2r_c)$, over which it was possible to have upper and lower critical points. In both cases, the energy favoring the ground state $(\frac{1}{2}|\epsilon-\epsilon^*|)$ controlled the processes which were, in fact, very similar. In the first case, the mechanism was self-dilution with heating, and, in the second case, it was self-dilution accompanying cooling.

The ground state for $b=b^*$ contains a mixture of bonds since all configurations of pair of electrons have the same energy. If v_k is the number of distinct states of a k bond, then two electrons can occupy separate bonds in $\frac{1}{2}v_1^2$ ways and can pair up on one bond in v_2 ways. It is the magnitude of these degeneracies that determines the critical concentration r_c^*. For $\frac{1}{2}v_1^2 \gg v_2$, there will be many more unpaired configurations than paired ones. The ground state will then have mostly $k=1$ bonds, and r_c^* approaches r_c. Similarly, if $v_2 \gg \frac{1}{2}v_1^2$, r_c^* approaches $2r_c$. More electrons are needed for ordering because of the increased likelihood of pairing in the ground state.

D. Effect of Coupling Ratio

Referring back to Fig. 5 and the shape of the critical region, we now consider the effect of varying c, the relative coupling strength of a $k=2$ bond. The $b=-\infty$, $n=1$ curve involving only $k=1$ bonds will remain the same, but the other limiting curves and the enclosed solutions do change. The behavior of the finite b solutions within the limiting curves is similar to that of the $c=2$ case. Figure 7 shows the limits of the critical temperatures for various c values.

As illustrated in Fig. 7, the limiting curves can cross for large values of c. In these cases, for large enough n, the $b=\infty$ critical temperature is greater than that for $b=-\infty$. That is, at a high temperature, a few strong bonds can order more effectively than a larger number of weaker bonds. The smallest value of c for which this crossing can occur is c^*. It is included in Table I, which lists the critical parameters of various lattices. The values of r_c^* are those for $v_1=2$, $v_2=1$ as in E_{int}, given by (3.1). The critical values of K' and ω used in compiling Table I are those found in Ref. 1(c).

E. Approach to Critical Point

To determine the relationship between K and K' away from the critical point, we must know the energy function $\omega(K')$. For two-dimensional lattices, exact solutions are known but, in three dimensions, only high- and low-temperature series are available. However, for the three-dimensional lattices, it is possible to construct approximate analytic functions for $\omega(K')$ which have a specified critical-point behavior and which agree with the limiting series away from the critical point.[11] With these functions (see Appendix), plots of K versus K', such as those shown in Fig. 8, can be constructed.

TABLE I. Critical-point parameters for various lattices.

Lattice	q	$\exp(-2K_c')$	ω_c	s_c	r_c	r_c^*	c^*
Hexagonal	3	0.2679492	0.7698003	0.3145	0.6478	0.8246	2.256
Kagomé	4	0.3933198	0.7440169	0.1175	0.5369	0.6599	2.191
Square	4	0.4142136	0.7071068	0.2071	0.5000	0.6084	2.154
Triangular	6	0.5773503	0.6666667	0.1220	0.3522	0.4003	2.092
Diamond	4	0.47729	0.432	0.311	0.374	0.443	2.06
s.c.	6	0.64183	0.3284	0.1874	0.2379	0.2642	2.102
b.c.c.	8	0.72985	0.270	0.135	0.172	0.185	2.02
f.c.c.	12	0.8153	0.245	0.086	0.115	0.121	2.01

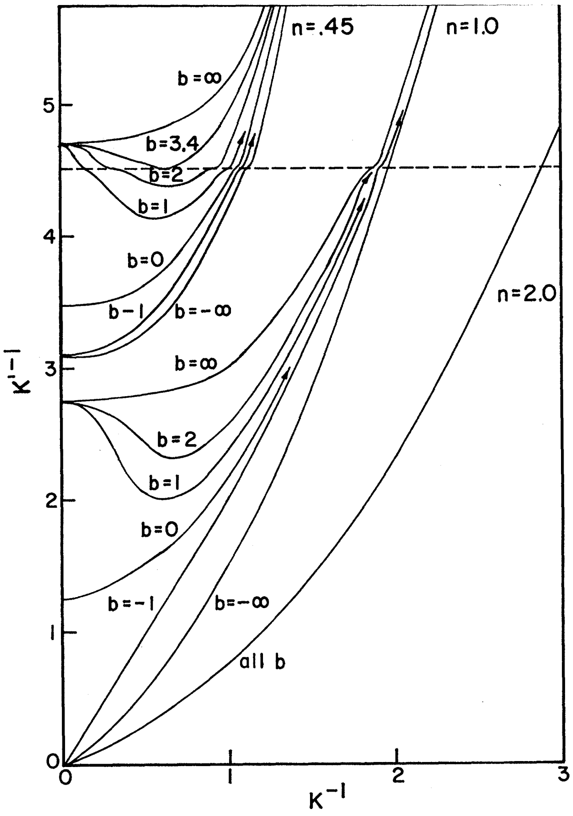

FIG. 8. The dependence of K' on K. Note that with the exception of the Ising limits ($n=1$, $b=\infty$; $n=2$, all b) the curves have zero slope at the critical point.

From Fig. 8, it is observed that in the Ising limits [which are independent of $\omega(K')$], the function $K(K')$ has a definite slope at the critical point. In these cases, the critical behaviors of the decorated and reference lattices are similar. The corresponding reduced temperatures

$$t=1-(T/T_c)$$
$$=1-(K_c/K) \tag{4.18}$$

and

$$t'=1-(T'/T_c')$$
$$=1-(K_c'/K') \tag{4.19}$$

are proportional near the critical point.

In the non-Ising cases, $K(K')$ is a smooth continuous function but its derivative diverges at the critical point. For these cases, t and t' will no longer be proportional and decorated lattice will be different from that of the reference lattice. To see how this comes about, we note that, except in the Ising limits, we can always write

$$(\partial K/\partial K')=\Sigma_K(K',n,b)+\Pi_K(K',n,b)(\partial\omega/\partial K'), \tag{4.20}$$

where, here and in Sec. V, Σ and Π will be used to denote smooth functions of K', n, b. At the critical

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[11] These exponents are generally agreed [see Ref. 1(c)] to describe the behavior of the three-dimensional Ising model.

point, $(\partial\omega/\partial K')$ becomes infinite so that asymptotically we can ignore Σ_{K} and integrate (4.20) to produce

$$t\simeq[\omega(K')-\omega_c]/\Psi(n,b)\,, \tag{4.21}$$

where Ψ is again a smooth function.

On using the asymptotic expressions[12]

$$\omega(K')-\omega_c\simeq a^- t'^{(1-\alpha')}\,, \qquad K_c'/K'\lesssim 1 \tag{4.22}$$

$$\simeq -a^+|t'|^{(1-\alpha)}\,, \quad K_c'/K'\gtrsim 1 \tag{4.23}$$

for three dimensions, and

$$\omega(K')-\omega_c\simeq -at'\ln|t'|\,, \quad K_c'/K'\sim 1\,. \tag{4.24}$$

For the two-dimensional Ising models, we can determine the relationship between t and t' at the critical point. In ordered temperature regions, for three-dimensional lattices, one then has

$$t'\simeq(\psi|t|/a^-)^{1/(1-\alpha)}\,, \tag{4.25}$$

$$(\partial\omega/\partial K')\simeq[a^-(1-\alpha')/K_c'](\psi|t|/a^-)^{-\alpha'/(1-\alpha')}\,. \tag{4.26}$$

The corresponding formulas for disordered regions are obtained by the substitution of α for α' and a^+ for a^-. In two dimensions, we find

$$t'\simeq-(\psi/a)t/\ln|t|+\cdots\,, \tag{4.27}$$

$$(\partial\omega/\omega K')\simeq-(a/K_c')\ln|t|+\cdots\,. \tag{4.28}$$

It is interesting to consider the isolated case of $n=2r_c$ and $b>b^*$. For this case, the upper critical point is finite and the above comments hold. The ground state, however, is one of critical concentration. A special treatment is needed since we now have $T_c=0$. The relevant variable for measuring the proximity to the critical point is not T, but the probability for producing additional ion-ion bonds, namely $\exp[-\frac{1}{2}(b-b^*)K]$.

The formulas analogous to the three-dimensional result (4.25) and the two-dimensional result (4.27) are, respectively,

$$t'\propto y^{1/(1-\alpha')}+\cdots \quad \text{as } y\to 0 \tag{4.29}$$

and

$$t'\propto y/\ln y+\cdots \quad \text{as } y\to 0\,, \tag{4.30}$$

where, again,

$$y=e^{-(1/2)(b-b^*)K}\,. \tag{4.31}$$

Equations (4.25) and (4.27) represent the asymptotic relation between t and t' near the critical points of dilute lattices of three and two dimensions. The manner and rate of approach to these asymptotic expressions is determined by the form and relative size of higher terms in the expansions. These higher terms are best studied in specific examples.

Consider a specific model as studied in Sec. V with E_{int} as in (2.1), $b=0$, $c=2$. The relation between t and t' in ordered regions is given by

$$t[2K_c\tanh 2K_c] =(n-2)C_L'(t'K_c')^{1-\alpha'}+t'K_c'+\cdots\,, \tag{4.32}$$

where C_L' is a constant dependent on the reference lattice. A similar relation holds for disordered regions if the primes are removed from C_L' and α'.

It is obvious from (4.32) that, for almost filled lattices ($n\lesssim 2$), the true asymptotic relation (4.25) will become evident only at exceedingly small values of t' and t. As suggested by Fisher,[2] a "transition region" is defined as that t range within which the true asymptotic behavior is "felt." The size of this region is given by a "cross-over temperature" t_X. The value of t_X could, for instance, be determined by equality of the first two terms on the right-hand side of (4.32).

As we shall see in a following paper, this transition region can be so small as to be beyond experimental reach, especially if α or α' is small.

V. THERMODYNAMIC FUNCTIONS

In this section, we will give general formulas for some thermodynamic functions but will not attempt to describe their variation for all b, c, and n. Instead, we confine our attention to the simplest case of our model with

$$\epsilon_1=\epsilon_2=0\,, \tag{5.1}$$

$$b=\epsilon/J=-\epsilon_0/J=b_0\,, \tag{5.2}$$

$$e^{\xi}=z-F_1/F_2\,, \tag{5.3}$$

$$c=2\,, \tag{5.4}$$

$$b^*=0\,. \tag{5.5}$$

In view of (3.23) and (3.24), we lose no generality in the K, K' relationship, yet this choice of parameters relieves the activity from an unimportant b_1 and b_2 dependence and, hence, simplifies calculations. The behavior of this special system will be quite similar to that of systems with other parameters. As in the solution of the transformation (4.1), the values of the thermodynamic functions will depend on ϵ, the energy favoring one-electron bonds. The possible solutions will range from the $\epsilon\to-\infty$ limit to the $\epsilon\to+\infty$ limit in a continuous manner as ϵ increases. For this system, we know the K, K' relation explicitly in three cases, namely,

(i) $b=-\infty$,

$$\cosh 2K'=[n+s(K')]/[n-r(K')]\,, \tag{5.6}$$

(ii) $b=b^*=0$,

$$\cosh(2K')=[n+s^*(K')]/[n-r^*(K')]\,, \tag{5.7}$$

where

$$r^*(K')=(1-e^{-K'})[1+\omega(K')]\,, \tag{5.8}$$

$$s^*(K')=(e^{K'}-1)[1-\omega(K')]\,, \tag{5.9}$$

(iii) $b=+\infty$,

$$\cosh(2K')=\{[\tfrac{1}{2}n+s(K')]/[\tfrac{1}{2}n-r(K')]\}\,. \tag{5.10}$$

As illustrated in Fig. 8, the solutions for $b<b^*$ lie

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[12] See the review article by Fisher cited in Ref. 1(c).

between (i) and (ii), while the solutions for $b > b^*$ lie between (ii) and (iii).

A. Internal Energy

The internal energy per bond in units of J is

$$U(T,H,n,b) = \lim_{N\to\infty} \left[-(\tfrac{1}{2}qN)^{-1} (\partial/\partial K_{L,\xi}) \ln \Xi \right], \qquad (5.11)$$

which can be written in terms of the partial bond partition functions, as ($H=0$)

$$U(T,0,n,b) = -(r\psi_+^{(K)} + s\psi_-^{(K)})/(\psi_+ - \psi_-), \qquad (5.12)$$

where the superscript (K) denotes $\partial/\partial K_{L,\xi}$. We see that the energy is a sum of two contributions arising from parallel and antiparallel alignment of the bond vertex spins. These contributions are proportional to r and s, respectively. Note that (5.12) can be written more generally as

$$U = U_{\text{occ}} + U_{\text{int}}, \qquad (5.13)$$

where

$$U_{\text{occ}} = (\epsilon_0/J)\rho_0 + (\epsilon_1/J)\rho_1 + (\epsilon_2/J)\rho_2 \qquad (5.14)$$

and

$$U_{\text{int}} = \{ U_+ = r(g_1^{(K)} + e^{\xi} g_2^{(K)}) [g_1 - h_1 + e^{\xi}(g_2 - h_2)]^{-1} \} + \{ U_- = s(h_1^{(K)} + e^{\xi} h_2^{(K)}) + [g_1 - h_1 + e^{\xi}(g_2 - h_2)]^{-1} \}. \qquad (5.15)$$

In our model, the energy of an occupied bond connecting two antiparallel ionic spins is zero for any orientation of the decorating spins, hence, these bonds do not contribute to the interaction energy. Mathematically, this shows up in the statements

$$h_1^{(K)} = h_2^{(K)} = 0, \quad U_- = 0. \qquad (5.16)$$

For the specific model defined by (5.1)–(5.5), we have

$$U = (\epsilon_0/J)\rho_0 + U_+, \qquad (5.17)$$

with

$$\rho_0 = (r+s)\{ (1-r)/(r+s) - (1+z) \times [(1+z2\cosh^2 K)2\sinh^2 K]^{-1} \}, \qquad (5.18)$$

$$U_+ = -2r[1 + z2\coth(2K)][\tanh(K) + Z]^{-1}. \qquad (5.19)$$

The activity is given by

$$z = [(n+s) - (n-r)\cosh^2(2K)]/[(n-2r) \times \cosh^2(2K) - (n+2s)], \qquad (5.20)$$

which can have any value from 0 to $+\infty$, depending on b and n. It is the magnitude of z which determines the actual value of ρ_0 and U_+, which must lie between the limits as shown in Table II.

TABLE II. Limiting energy functions and specific-heat amplitudes.

Limit	Function: $\Lambda^+ = \dfrac{K_c'}{(1-\alpha)a^+}\left(\dfrac{\psi}{a^+}\right)^{\alpha/(1-\alpha)}$, $\Lambda^- = \dfrac{K_c'}{(1-\alpha')a^-}\left(\dfrac{\psi}{a^-}\right)^{\alpha'/(1-\alpha')}$
$b \to +\infty$ all c $2 \geq n \geq 2r$	$\rho_0 = 1 - \frac{1}{2}n$ $U_+ = -cr2\coth(ck)$ $A = \dfrac{4(n-2r_c)}{(r_c+s_c)}\left(\dfrac{2(n+2s_c)(1-r_c)}{(2-n)} - r_c\right)$ $B^\pm = \dfrac{32(n+2s_c)(n-2r_c)^2(1-r_c)^2(1+s_c)^2\Lambda^\pm}{(r_c+s_c)^3(2-n)^2}$ $\psi = \dfrac{8k_c'(n-2r_c)^{3/2}(n+2s_c)^{1/2}(1-r_c)(1+s_c)}{(r_c+s_c)(2-n)}$
$b = b^* = 0$ $c = 2$ $2 \geq n \geq r^*$	ρ_0 produces no contribution to energy ($\epsilon_0 = 0$) $U_+ = -r^*2\coth(K)$ $A = \dfrac{4(n-r_c^*)}{(r_c^*+s_c^*)}\left(\dfrac{(2n+s_c^*-r_c^*)(2-r_c^*)}{(2-n)} - r_c^*\right)$ $B^\pm = \dfrac{4(2n+s_c^*-r_c^*)(n-r_c^*)(2+s_c^*)^2(2-r_c^*)\Lambda^\pm}{(r_c^*+s_c^*)^3(2-n)^2}$ $\psi = \dfrac{2K_c'(2n+s_c^*-r_c^*)^{1/2}(n-r_c^*)(2-r_c^*)(2+s_c^*)}{(r_c^*+s_c^*)^{3/2}(2-n)}$
$b \to -\infty$ all c $1 \geq n \geq r$	$\rho_0 = 1 - n$ $U_+ = -r2\coth(K)$ $A = \dfrac{4(n-r_c)}{(r_c+s_c)}\left(\dfrac{(2n+s_c-r_c)(1-r_c)}{(1-n)} - r_c\right)$ $B^\pm = \dfrac{16(2n+s_c-r_c)(1+s_c)^2(1-r_c)^2(n-r_c)^2\Lambda^\pm}{(r_c+s_c)^3(1-n)^2}$ $\psi = \dfrac{4K_c'(2n+s_c-r_c)^{1/2}(n-r_c)(1-r_c)(1+s_c)}{(r_c+s_c)^{3/2}(1-n)}$

The behavior of U at the critical point is similar, but not identical to the behavior of its reference lattice counterpart $\omega(K')$ at K_c'. Both are finite but, as hinted at in Sec. IV, the behavior of the slope of U is not the same as $\partial\omega/\partial K'$, which becomes infinite. For a general b, we can write

$$(\partial U/\partial K) = (\partial\omega/\partial K')(\partial K'/\partial K). \qquad (5.21)$$

B. Specific Heat

The reduced specific heat per bond is

$$C_H(T,n,b) = -(\partial/\partial K_{n,b})U. \qquad (5.22)$$

Using (4.20) and (5.21) yields

$$C_H = \Sigma + \Pi(\Sigma_K/\omega' + \Pi_K)^{-1} \qquad (5.23)$$

($\omega' = \partial\omega/\partial K'$), and we see that, although ω' and the specific heat of the reference lattice are divergent at T_c', the specific heat of the decorated model is finite

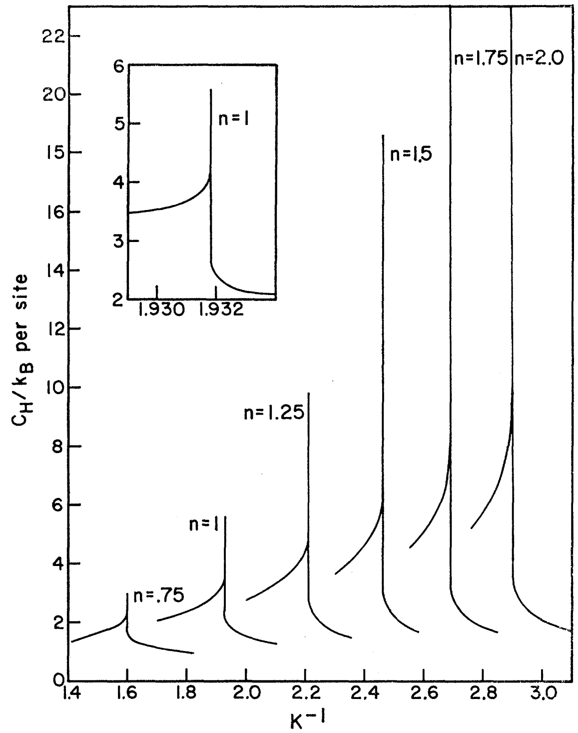

FIG. 9. Specific heat versus K^{-1} showing variation of cusped behavior with concentration. The height of the cusp for $n=1.75$ is 44.6. Only the specific heat of the filled lattice ($n=2$) diverges at the critical point. Both α and α' are assumed to be $\frac{1}{8}$.

with a cusp at T_c.[2] For three-dimensional lattices near T_c, we find

$$C_H \simeq A(n,b) - B^-(n,b)\,|t|^{\alpha'/(1-\alpha')} \tag{5.24}$$

in ordered regions and

$$C_H \simeq A(n,b) - B^+(n,b)\,|t|^{\alpha/(1-\alpha)} \tag{5.25}$$

in disordered regions. For two-dimensional lattices near T_c, we have

$$C_H \simeq A(n,b) - B(n,b)/\ln|t|\,. \tag{5.26}$$

The function A gives us the maximum value of the specific-heat cusp. It is a complicated function of n which can be explicitly evaluated only in certain cases ($b=\pm\infty$, 0). The important behavior which is found is that A diverges as the Ising limits are approached [e.g., $A \propto (n-2)^{-1}$ as $n \to 2$] and it decreases to zero as the electron concentration approaches the minimum value for ordering for a given b value [e.g., $A \propto (n-r^*)$ for $b=b^*=0$]. The functions B, $B^{\pm}$ have behaviors similar to that of A. Limiting values of $A(n,b)$, $B^+(n,b)$, and $B^-(n,b)$ are given in Table II.

Figure 9 illustrates the behavior of the specific heat of a simple cubic lattice with various electron concentrations. In order to generate these curves, the value of α' was assumed to be $\frac{1}{8}$ and, as shown in the Appendix, approximate functions were generated.

C. Magnetization

The reduced magnetization in units of m is

$$M(T,H,n,b) = \lim_{N\to\infty} [(1/N)(\partial/\partial L_{K,\xi}) \ln\Xi] \tag{5.27}$$

$$= \tfrac{1}{2}q[(\partial \ln\phi/\partial L_{K,\xi}) + \omega(\partial K'/\partial L_{K,\xi})] + \sigma(\partial L'/\partial L_{K,\xi})\,. \tag{5.28}$$

For a symmetric bond,

$$\begin{aligned} M = \tfrac{1}{2}q[\tfrac{1}{2}(1+\omega)(\psi_{+\,+}{}^{(L)}/\psi_{+\,+} + \psi_{-\,-}{}^{(L)}/\psi_{-\,-}) \\ + \tfrac{1}{2}(1-\omega)\psi_{+\,-}{}^{(L)}/\psi_{+\,-}] \\ + \sigma[1+\tfrac{1}{4}q(\psi_{+\,+}{}^{(L)}/\psi_{+\,+} - \psi_{-\,-}{}^{(L)}/\psi_{-\,-})], \end{aligned} \tag{5.29}$$

where the superscript (L) denotes that the operation $(\partial/\partial L_{K,\xi})$ has been applied. As a consequence of the ferromagnetic nature of the bonds, we must have, in addition to (2.27), the zero-field results that

$$\begin{aligned} \psi_{+\,+}{}^{(L)} &= -\psi_{-\,-}{}^{(L)}, \quad (L=0) \\ \psi_{+\,-}{}^{(L)} &= 0, \qquad\quad (L=0)\,. \end{aligned} \tag{5.30}$$

Thus, the spontaneous magnetization is given by

$$M_0(T,n,b) = [1+\tfrac{1}{2}q(\psi_{++}{}^{(L)}|_{L=0})/\psi_{++}]\sigma_0(K')\,. \tag{5.31}$$

The first term in the bracket is the contribution from the ionic spins, while the second term is the contribution from the decorating electronic spins. We originally assumed the magnetic moments of ions and electrons to be equal. If the magnetic moment of the electron had been m and that of the ion $g_{\text{ion}}m$, the first term in the bracket of (5.31) would be the constant g_{ion} rather than unity. For our specific model,

$$\begin{aligned} (\psi_{++}{}^{(L)}|_{L=0})/\psi_{++} = (r+s)[(1+s)\tanh(K)]^{-1} \\ \times[1+z2\cosh(2K)]\{1+z[\cosh(2K)+1]\}^{-1}, \end{aligned} \tag{5.32}$$

which is continuous and finite at the critical point.

In ordered regions near the critical point, we write

$$M_0(T,n,b) \propto \sigma_0(K') \propto t'^{\beta}, \tag{5.33}$$

which, by (4.25), yields

$$M_0(T,n,b) \propto |t|^{\beta/(1-\alpha')} \tag{5.34}$$

in three dimensions, but, by (4.27),

$$M_0(T,n,b) \propto [\,|t|\ln|t|\,]^{\beta} \tag{5.35}$$

in two dimensions. We see that the renormalized value of β is $\beta/(1-\alpha')$ in three dimensions.[2]

As discussed in Sec. IV, the multiple-bond states lead to a great variety of critical behavior. In particular, a lower critical point is possible. There is an even greater variety of behavior in the magnetization. Corresponding to the case with upper and lower critical points, we find that M_0 is zero initially, increases, then decreases between the critical points, and is zero again above the upper point. This and other possible types of behavior are illustrated in Fig. 10 for the simple cubic lattice.

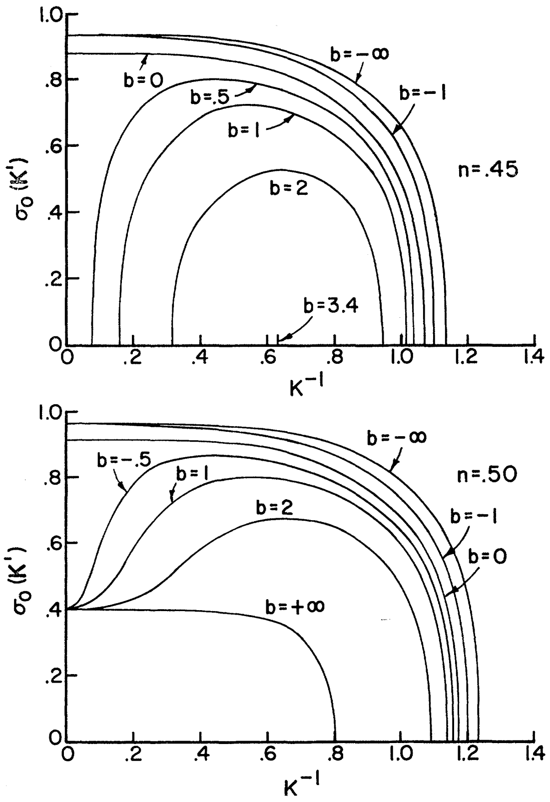

FIG. 10. Magnetization versus K^{-1}. For $n=0.45$ $(2r_c>n>r_c^*)$, a single critical point is found for $b\leq b^*$ whereas an additional lower critical point appears for $b^*<b<b_{\max}$ (for $n=0.45$, $b_{\max}=3.4$). For $n=0.5(n>2r_c)$, a unique critical point is found for all b, and, for $b>b^*$, the magnetization initially increases with temperature.

Only the ionic contribution $\sigma_0(K')$ is plotted. The values are based on Padé approximants to the low-temperature magnetization and energy series with the assumptions that $\alpha'=\frac{1}{8}$ and $\beta=\frac{5}{16}$.[11]

D. Susceptibility

The reduced susceptibility is given by

$$\xi(T,H,n,b)=\partial M(T,H,n,b)/\partial L_{n,b,T}. \qquad (5.36)$$

As in previous work,[8] the zero-field susceptibility ξ_0 in three dimensions is found to vary as

$$\xi_0\propto|t|^{-\gamma'/(1-\alpha')} \qquad (5.37)$$

on the ordered side of a critical point and as

$$\xi_0\propto|t|^{-\gamma/(1-\alpha)} \qquad (5.38)$$

on the disordered side. The two-dimensional case is given by

$$\xi_0\propto(|t|\ln|t|)^{-\gamma',-\gamma}, \qquad (5.39)$$

with the primed and unprimed exponents corresponding to the ordered and disordered side of the critical point, respectively.

TABLE III. Renormalization of critical exponents.

Thermodynamic function	Ideal Ising exponent	Renormalized exponent
Specific heat, constant H disordered region	α	$-\alpha/(1-\alpha)$
Specific heat, constant H ordered region	α'	$-\alpha/(1-\alpha')$
Spontaneous magnetization	β	$\beta/(1-\alpha')$
Susceptibility disordered region	γ	$\gamma/(1-\alpha)$
Susceptibility ordered region	γ'	$\gamma'/(1-\alpha')$

VI. SUMMARY

As predicted by Fisher[2] and as shown in this paper, the critical exponents are renormalized as summarized in Table III. It must be stressed that these renormalized exponents represent the behavior of the thermodynamic functions asymptotically close to the critical point. The crossover temperature t_x marking the onset of renormalized behavior can be much smaller than experimentally attainable values.

The question then remains of exactly how renormalization would be felt in an experimental situation. The answer to this question is reserved for a following paper.

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APPENDIX: APPROXIMATE THERMODYNAMIC FUNCTIONS FOR ISING FERROMAGNET ON SIMPLE CUBIC LATTICE

In order to calculate the properties of the mobile-electron Ising ferromagnet, it was necessary to generate approximate functions for the energy, specific heat, magnetization, and susceptibility for the reference Ising lattice.

The low-temperature $(K'>K_c')$ forms assumed for these functions for the simple cubic lattice are, for the energy,

$$\omega=\omega_c+\tfrac{1}{3}[1-(x/x_c)]^{1-\alpha'}A_1, \qquad (A1)$$

for the specific heat,

$$C_H=(32/6)x^3[1-(x/x_c)]^{-\alpha'}A_3, \qquad (A2)$$

and, for the magnetization,

$$\sigma_0=[1-(x/x_c)]^{\beta}A_5, \qquad (A3)$$

TABLE IV. Padé approximant coefficients.

	$A_1(\alpha'=\frac{1}{8})$	$A_2(\alpha=\frac{1}{8})$	$A_3(\alpha'=\frac{1}{8})$	$A_4(\alpha=\frac{1}{8})$	$A_5(\beta=\frac{5}{16})$	$A_6(\gamma=5/4)$
c_0	2.014 8000	0.3284	9.0	1.0	1.0	1.0
c_1	7.508 6969	−0.4104 9081	28.39 9652	−0.0050 24293	3.208 4380	2.692 9731
c_2	−4.716 7163	−7.656 2319	−12.34 6349	12.34 7675	−6.858 9583	4.244 4597
c_3	−24.78 8439	11.72 9123	−99.50 5752	−0.0881 68245	−19.43 6787	17.47 4689
c_4	−12.67 2356	35.67 3309	−66.89 3786	−96.58 6009	8.915 0085	
c_5	−45.77 4808	−58.03 2411	−13.66 5983		23.85 5077	
c_6	−19.06 0652		−145.2 4550		52.00 6214	
c_7	−57.18 0744				−9.115 6928	
d_0	1.0	1.0	1.0	1.0	1.0	1.0
d_1	1.602 7262	−2.215 9060	3.280 5169	0.1199 7571	2.449 8508	2.422 9761
d_2	−10.57 9114	−26.19 6836	−9.162 3325	1.495 4252	−9.925 8383	4.686 9843
d_3	−2.869 1075	61.09 7574	−23.86 0554	−0.4221 5089	−15.12 8944	1.730 4204
d_4	28.67 1431	148.8 7637	32.76 7416	−298.8 8911	28.71 8069	
d_5	−39.92 0916	−359.1 2013	35.07 3888	−26.37 7590	20.42 5852	
d_6	31.17 0122	−19.90 7284	−44.42 3595		26.99 2695	
d_7	−1.033 6985				−57.43 0494	

where

$$x=\exp(-4K')\,. \tag{A4}$$

The corresponding high-temperature ($K'<K_c'$) forms are, for the energy,

$$\omega=\omega_c-[1-(x/x_c)]^{1-\alpha}A_2\,, \tag{A5}$$

for the specific heat,

$$C_H=[1-(x/x_c)]^{-\alpha}A_4\,, \tag{A6}$$

and, for the susceptibility,

$$\chi_0=[1-(x/x_c)]^{-\gamma}A_6\,, \tag{A7}$$

where

$$x=\tanh(K')\,. \tag{A8}$$

Values for the critical exponents consistent with known numerical estimates [see Ref. 1(c)] were chosen. These values were

$$\alpha=\alpha'=\tfrac{1}{8}\,,\quad \beta=\tfrac{5}{16}\,,\quad \gamma=5/4\,.$$

Next, the multiplying functions A were determined using standard Padé approximant techniques [see Ref. 1(c)]. The form of these approximants is

$$A=\Big(\sum_{j=0}^{n} c_j x^j\Big)\Big/\Big(\sum_{i=0}^{m} d_i x^i\Big)\,. \tag{A9}$$

The constants d_i, c_j are listed in Table IV.[13]

In the determination of these approximants, the series expansion for the magnetization contained 16 terms, the expansion for the susceptibility contained 10 terms, and the low- and high-temperature expansions for the partition function contained 15 and 6 terms, respectively.[14] The series for energy and specific heat were generated from those of the partition function.

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[13] A_1 and A_5 are previously unpublished Padé approximants by W. J. Camp.

[14] For the actual coefficients, see M. F. Sykes, J. W. Essam, and D. S. Gaunt, J. Math. Phys. **6**, 283 (1965); C. Domb and M. F. Sykes, Proc. Roy. Soc. (London) **A240**, 214 (1957) (susceptibility); C. Domb, Advan. Phys. **9**, 149 (1960) (high-T partition function).