PHYSICAL REVIEW VOLUME 168, NUMBER 2 10 APRIL 1968

Remarks on the Modified Potassium Dihydrogen Phosphate Model of a Ferroelectric

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(Received 4 December 1967)

The modified potassium dihydrogen phosphate (KDP) model of a two-dimensional ferroelectric with the inclusion of an arbitrary electric field $\mathcal{E}$ is considered. The nature of the phase transition is unaffected by the inclusion of an external field, whereas the transition temperature depends on $\mathcal{E}$ with $T_c \to \infty$ as $\mathcal{E} \to \infty$, and $T_c \to 0$ as $\mathcal{E} \to$ some special values. We also find that T_c is determined by different relations in different regions in the $\mathcal{E}$ plane, a property not shared by the Slater KDP model. Among the other thermodynamic properties discussed, the critical behavior of the polarizability is shown to be $\chi \sim (T-T_c)^{-1/2}$. It is shown that this model is identical to the problem of close-packed dimers on a hexagonal lattice.

I. INTRODUCTION

RECENTLY, the problem of the two-dimensional hydrogen-bonded crystals as soluble models in statistical mechanics has received considerable attention. After Lieb's celebrated evaluation of the residual entropy of the two-dimensional ice through the use of the method of transfer matrix,[1,2] the solutions have since been extended to include the F model[3] and the Slater potassium dihydrogen phosphate (KDP) model, both with a vertical field,[4,5] and to the general case when the energy parameters are arbitrary.[6,7] In these discussions, the partition function of the crystal is identified as the largest eigenvalue of a certain matrix, while the associated eigenvector proves to be identical to the ground state of a one-dimensional anisotropic Heisenberg chain. Use is then made of the properties of the latter problem which have been discussed extensively.[8–10] While in principle the thermodynamic properties of the hydrogen-bonded crystals follow from the ground-state properties of the linear chain, detailed studies of these properties involve the solution of an integral equation which is analytically soluble only in certain special instances. As a consequence, the partition functions of the F model and the Slater KDP model are given explicitly only when there is no external field.[3,4] With a finite external field, the integral equation cannot be solved in terms of known functions.

In a previous paper[11] (hereafter referred to as I), we have proposed a *modified* KDP model which exhibits the main features of the two-dimensional Slater KDP model, while mathematically it is much easier to deal with. This model is also interesting in that the inclusion of an external field does not present any mathematical problem. Explicit and closed expression can be obtained for the partition function and one has at least one model of a phase transition which is *explicitly* solvable when there is a finite external field. In this paper we shall obtain this solution. First, in Sec. II a generalized version of the modified KDP model is considered and it is shown that this model is equivalent to the problem of close-packed dimers on a hexagonal lattice, namely, the solution to this model is exactly the generating function for the related dimer problem. The modified KDP model in an arbitrary field now appears as a special case and is discussed in Sec. III with the complete thermodynamic properties derived and comparisons with the Slater KDP model given.

II. GENERALIZED MODEL

As is well known,[12] a simple picture of the structure of the KDP crystal (coordination number is 4) allows one hydrogen atom sitting off center on each lattice edge so that the crystal L can be represented by a directed graph. The ice condition (or the condition of local electrical neutrality) requires that there are precisely two arrows pointing into a vertex. Energy values are assigned to the crystal vertices according to the arrow configurations, and we are required to evaluate the partition function

$$Z = \sum_{\text{allowed configurations on } L} \exp\Big(-\beta \sum_{\alpha} \epsilon_\alpha\Big), \tag{1}$$

where ϵ_α is the energy of the αth lattice vertex and $\beta \equiv 1/kT$.

As pointed out in I, considerations relating to the directed graphs can always be transformed into the language of closed polygons. One simply compares an arbitrary directed graph with a standard one and observes that there is always an even number of arrows reversed at each vertex. Replacing these reversed arrows

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[1] E. H. Lieb, Phys. Rev. Letters **18**, 692 (1967).

[2] E. H. Lieb, Phys. Rev. **162**, 162 (1967).

[3] E. H. Lieb, Phys. Rev. Letters **18**, 1046 (1967).

[4] E. H. Lieb, Phys. Rev. Letters **19**, 108 (1967).

[5] B. Sutherland, Phys. Rev. Letters **19**, 103 (1967).

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[7] B. Sutherland, C. N. Yang, and C. P. Yang, Phys. Rev. Letters **19**, 588 (1967).

[8] C. N. Yang and C. P. Yang, Phys. Rev. **150**, 321 (1966).

[9] C. N. Yang and C. P. Yang, Phys. Rev. **150**, 327 (1966).

[10] J. des Cloizeaux and M. Gaudin, J. Math. Phys. **7**, 1384 (1966).

[11] F. Y. Wu, Phys. Rev. Letters **18**, 605 (1967).

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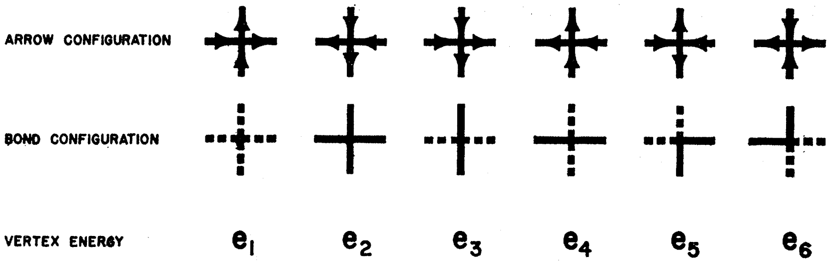

FIG. 1. The six kinds of arrow configurations allowed by the "ice condition" and the associated bond configurations. Configuration (1) is taken as the standard in obtaining the bond configurations.

by bonds, one recovers closed polygons consisting of bonds. These comparisons and correspondences are exhibited in Fig. 1 for the case of a rectangular lattice. Let e_i be the energy of a vertex having the ith ($i=1, 2, \cdots, 6$) configuration. The Slater KDP model corresponds to $e_1=e_2=0$, $e_3=e_4=e_5=e_6=\epsilon>0$; while the model we now proceed to solve has the following restrictions:

$$e_1=\infty \text{ [configuration (1) forbidden]},$$
$$e_3+e_4=e_5+e_6. \qquad (2)$$

On taking $e_2=0$ and $e_3=e_4=e_5=e_6=\epsilon>0$, one recovers the model considered in I.

It has been pointed out that the restriction $e_1=\infty$ is equivalent to taking a certain limit in the more general model considered by Sutherland, Yang, and Yang.[7] However, we shall proceed here with the method of Pfaffians because it allows us to see directly the equivalence of this model and the problem of dimers on a hexagonal lattice. The partition function we wish to evaluate is given by (1) with the summation now extending over all allowed bond configurations on L. Since it is well known[13–15] that such a sum can be transformed into a dimer generating function, we shall describe the procedures only briefly. As illustrated in Figs. 2 and 3, we first construct a terminal (dimer) lattice L^Δ by expanding each vertex on L into a city of internally connected points.[16] Next, we cover L^Δ by placing dimers along the edges so that (a) each dimer covers two (neighboring) points on L^Δ, and (b) each point on L^Δ is covered by one and only one dimer (close-packed configuration). For any allowed dimer configuration, we note that there are either two or four dimers leading into a city, corresponding to an allowed bond configuration on L (two or four bonds leading into a vertex). In fact, as shown in Fig. 4, the correspondence between the dimer configurations (within a city on L^Δ) and the allowed bond configurations (at a vertex on L) is actually one-to-one. Therefore to each dimer configuration on L^Δ, there corresponds a bond configuration on L, and vice versa. Now we assign weights (or activities) to the edges on L^Δ (according to Fig. 2) and consider the product of the activities of the covered edges as the configurational weight of a dimer configuration. It is then easy to verify, using the relation $[u_i\equiv\exp(-e_i/kT)]$

$$u_3u_4=u_5u_6, \qquad (3)$$

that the dimer configurational weights of L^Δ are just the needed Boltzmann factors for the corresponding bond configurations on L. It follows then the partition function Z is exactly the dimer generating (partition) function Δ defined by

$$Z=\Delta\equiv\sum_{\text{all dimer configurations on } L^\Delta}(\text{configurational weight of } L^\Delta). \qquad (4)$$

The dimer lattice L^Δ, as shown in Fig. 3, can still

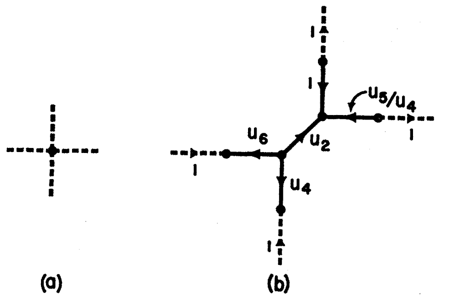

FIG. 2. The expansion of (a) a vertex point on L into (b) a city on L^Δ. The dotted lines denote the lattice edges originally on L and the solid lines denote those gererated by the expansion procedure.

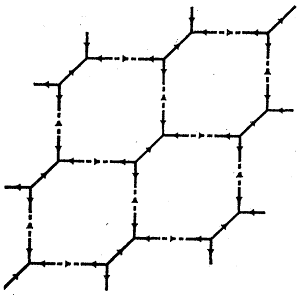

FIG. 3. The dimer lattice L^Δ generated by the expansion procedure shown in Fig. 2. The meaning of the arrows attached to the edges are explained in Ref. 19.

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[13] E. W. Montroll, in *Applied Combinatorial Mathematics*, edited by E. F. Beckenbach (John Wiley & Sons, Inc., New York, 1964), Chap. 4.

[14] H. S. Green and C. A. Hurst, in *Order-Disorder Phenomena*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1964).

[15] M. E. Fisher, J. Math. Phys. **7**, 1776 (1966).

[16] The structure of the city used here, which allows a direct identification with the problem of close-packed dimers on a hexagonal lattice, is simpler than the one adopted in I. This possible simplification is also observed by M. E. Fisher (private communication).

be further simplified. We observe that L^{Δ} consists of chains of three edges with activities 1, 1, u_4 and u_6, 1, u_5/u_4, respectively. Since the middle edge of these chains always has a unity activity, we may replace each chain by a single edge of activity u_4 or $u_6u_5/u_4=u_3$, respectively. The resulting dimer lattice is therefore a hexagonal (honeycomb) one (see Fig. 5) with activities u_2, u_3, and u_4 respectively along the directions of the three principle axes.[17] Therefore, we have established that the partition function of the generalized (modified) KDP model is identical to the generating (partition) function of the problem of close-packed dimers on a hexagonal lattice, with the dimer lattice containing twice as many vertex points.

The problem of dimers on a hexagonal lattice has been discussed by Kasteleyn.[18] The main feature of the solution is that the partition function is a smoothly varying function of the activities u_2, u_3, and u_4 whenever the activities satisfy the triangle inequalities $u_2+u_3>u_4$, etc.; otherwise the largest activity prevails resulting in a perfect ordering state. Since Kasteleyn did not write the partition function, and it has not been given in the existing literature, we shall supply it here. The derivation is through the use of Pfaffian and is quite straightforward, if one goes back to Fig. 2 and uses the dimer city and the associated activities given there. We refer the readers to Ref. 13 for details and only quote the result.[19] For an infinite lattice (N is the number of vertices on the KDP lattice or $2N$ is the number of vertices on the hexagonal lattice) wrapped around a torus, we find the free energy F per vertex (for the KCP lattice) given by

$$\begin{aligned}-\beta F&=\lim_{N\to\infty} N^{-1}\ln Z\\ &=\frac{1}{8\pi^2}\int_0^{2\pi}d\theta\int_0^{2\pi}d\phi\,\ln[u_2^2+u_3^2+u_4^2+2u_2u_3\cos\theta\\ &\qquad+2u_2u_4\cos\phi+2u_3u_4\cos(\theta-\phi)].\qquad(5)\end{aligned}$$

Equation (5) is obviously symmetric in u_2, u_3, and u_4. With the aid of the formula

$$\int_0^{2\pi}\ln[2a+2b\cos\phi+2c\sin\phi]d\phi=2\pi\ln[a+(a^2-b^2-c^2)^{1/2}],\qquad(6)$$

one of the integrations can be performed, yielding

$$-\beta F=\frac{1}{4\pi}\int_0^{2\pi}d\theta\,\ln\max\{u_4^2,\,u_2^2+u_3^2-2u_2u_3\cos\theta\}.\qquad(7)$$

Despite its apparent asymmetric appearance, Eq. (7) is still symmetric in u_2, u_3, and u_4. It is then clear that Z is a smoothly varying function in u_2, u_3, and u_4 whenever u_2, u_3, and u_4 satisfy the triangle inequalities $u_2+u_3>u_4$, $u_3+u_4>u_2$ and $u_4+u_2>u_3$. Suppose, on the other hand, $u_4>u_2+u_3$; then one has identically

$$Z=u_4^N,\qquad u_2+u_3<u_4.\qquad(8)$$

Kasteleyn has given the reason for this from the point of view of the dimer lattice.[18] It is also easy to see why an ordered state should occur from the considerations of the KDP lattice. If $e_2\neq e_3\neq e_4$, then, at a sufficiently low temperature, the configuration with the lowest energy dominates, thus forming an ordered state.[20]

The energy per vertex E can now be computed for all temperatures. However, it is easier (for $T>T_c$) to start from the expression of the free energy given by Eq. (5). We obtain (assuming $e_2<e_3$, e_4)

$$\begin{aligned}E&=\partial(\beta F)/\partial\beta\\ &=\tfrac{1}{2}(e_3+e_4)+(4\pi)^{-1}(e_3-e_2)\\ &\qquad\times\int_0^{2\pi}d\phi\,\operatorname{sgn}(2u_2u_4\cos\phi+u_3^2-u_4^2-u_2^2)\\ &\quad+(4\pi)^{-1}(e_4-e_2)\int_0^{2\pi}d\phi\,\operatorname{sgn}(2u_2u_3\cos\phi+u_4^2-u_3^2-u_2^2)\qquad(9)\\ &=e_2\qquad u_3+u_4<u_2\\ &=e_2+[(e_3-e_2)/\pi]\cos^{-1}[(u_4^2-u_3^2+u_2^2)/2u_2u_4]\\ &\quad+[(e_4-e_2)/\pi]\cos^{-1}[(u_3^2-u_4^2+u_2^2)/2u_2u_3],\\ &\qquad\qquad u_3+u_4>u_2.\qquad(10)\end{aligned}$$

Here we have used the following identity in obtaining the expression (9):

$$\begin{aligned}\int_0^{2\pi}\frac{d\theta}{A+B\cos\theta+c\sin\theta}&=2\pi/(A^2-B^2-C^2)^{1/2},\qquad\text{for } A^2>B^2+C^2\\ &=0,\qquad\text{for } A^2<B^2+C^2.\qquad(11)\end{aligned}$$

As concluded in I, a second-order phase transition (without latent heat) occurs at T_c defined by

$$\exp(-e_3/kT_c)+\exp(-e_4/kT_c)=\exp(-e_2/kT_c).\qquad(12)$$

This is in contrast to the result on the Slater KDP model with zero field (phase change with latent heat).[4]

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[17] It is easy to see why the result does not depend on e_5 or e_6. This is because the configurations (5) and (6) always occur in pairs with energy $e_5+e_6=e_3+e_4$.

[18] P. W. Kasteleyn, J. Math. Phys. **4**, 287 (1963).

[19] We mention only one important point in the evaluation of the dimer generating function Δ through the use of Pfaffians. In order to transform Δ directly and correctly into a Pfaffian, it suffices to orient the edges of the dimer lattice L^{Δ} such that if one traces around any closed path (cycle) on L^{Δ} according to the two rules: (a) The number of edges contained in the cycle is even, and (b) the number of lattice points enclosed by the cycle is also even; one always finds an odd number of edges oriented in the clockwise (or the counterclockwise) direction. This is the key step involved in the evaluation of Δ, and it can be shown that this proper orientation can always be realized for planar lattices (Ref. 15). Interested readers may check that this is indeed the case for the oriented dimer lattice shown in Fig. 3.

[20] Provided that this energy is also lower than $\frac{1}{2}(e_5+e_6)$. Otherwise, we have an antiferroelectric.

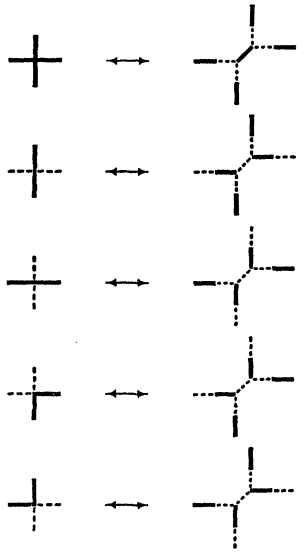

FIG. 4. The one-to-one correspondence between the bond configurations on L and the dimer configurations on L^{Δ}.

It is straightforward to compute the specific heat $c=\partial E/\partial T$. We find $c=0$ below T_c and $c\sim(T-T_c)^{-1/2}$ near and above the Curie temperature, in agreement with the previous conclusions.[4,11]

III. MODIFIED KDP MODEL IN AN ARBITRARY FIELD

We now turn to the modified KDP model in the presence of an arbitrary external field $\boldsymbol{\mathcal{E}}=(\mathcal{E}_x, \mathcal{E}_y)$.[21] In addition to the vertex energies, we now also have bond energies due to the dipole moment d of each arrow. However, one may split the bond energy into two halves and associate one half to each of the two vertices the bond connects. Thus for the modified KDP model in an external field $\boldsymbol{\mathcal{E}}$, one makes the substitutions

$$e_2=(\mathcal{E}_x+\mathcal{E}_y)d, \qquad e_3=\epsilon-(\mathcal{E}_x-\mathcal{E}_y)d,$$

$$e_4=\epsilon+(\mathcal{E}_x-\mathcal{E}_y)d, \qquad e_5=e_6=\epsilon.$$

Since condition (2) is satisfied, the results of the last section apply and the following conclusions are immediate: The transition temperature T_c now depends on the external field and, with the $\boldsymbol{\mathcal{E}}$ plane divided into three regions (Fig. 6), the critical condition takes different forms in each of the three regions. They are $[K\equiv e^{\beta\epsilon}, X\equiv\exp(2\beta\mathcal{E}_x d), Y\equiv\exp(2\beta\mathcal{E}_y d)]$.

$$\begin{aligned} K&=X+Y, &&(\epsilon>2\mathcal{E}_x d,\ \epsilon>2\mathcal{E}_y d;\ \text{region I})\\ K&=X-Y, &&(\epsilon<2\mathcal{E}_x d,\ \mathcal{E}_x>\mathcal{E}_y;\ \text{region II}) \qquad (13)\\ K&=Y-X, &&(\epsilon<2\mathcal{E}_y d,\ \mathcal{E}_y>\mathcal{E}_x;\ \text{region III}). \end{aligned}$$

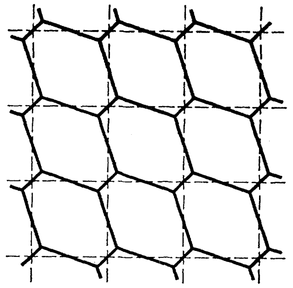

FIG. 5. The hexagonal dimer lattice superimposed on the original lattice L (denoted by the thin lines).

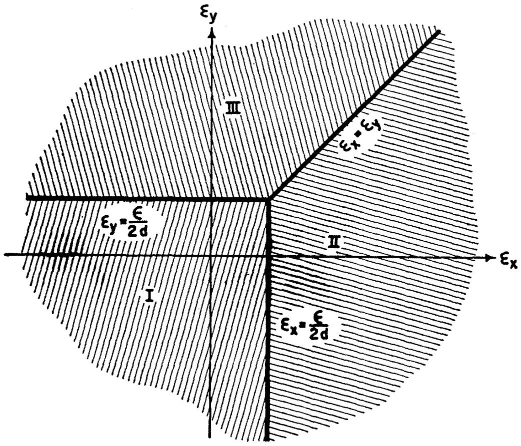

FIG. 6. The three regions in $\boldsymbol{\mathcal{E}}$ the plane and the equations for the boundaries.

We observe that $T_c\rightarrow\infty$ as $\mathcal{E}\rightarrow\infty$ and $T_c\rightarrow 0$ as $\boldsymbol{\mathcal{E}}$ approaches the boundaries between the three regions. That T_c may go to zero is a unique property of this model and is also what we expect on physical grounds. On these boundaries two or more of the five allowed vertex configurations have the lowest energy and one no longer has a unique, energetically preferred state. The relation analogous to (13) for the Slater KDP model in a vertical field only is[22]

$$K=1+\exp(-2\beta\,|\,\mathcal{E}_y\,|\,d), \qquad (14)$$

which agrees with our expression when $\mathcal{E}_y<0$ $(\mathcal{E}_x=0)$. This reflects the fact that our model does not possess the up-down symmetry of the Slater KDP model. It is also straightforward to compute the polarization per vertex $\mathbf{P}=-\partial F/\partial\boldsymbol{\mathcal{E}}$. Again using (11), one finds

$T>T_c$:

$$P_x=\left[\frac{2}{\pi}\cos^{-1}\frac{Y^2-X^2+K^2}{2KY}-1\right]d,$$

$$P_y=\left[\frac{2}{\pi}\cos^{-1}\frac{X^2-Y^2+K^2}{2KX}-1\right]d, \qquad (15)$$

$T<T_c$:

$$\begin{aligned} \mathbf{P}&=(-d,\,-d), &&(\text{region I})\\ &=(+d,\,-d), &&(\text{region II})\\ &=(-d,\,+d), &&(\text{region III}). \qquad (16) \end{aligned}$$

Below T_c, all vertices take the configurations (2), (3),

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[21] We may also consider the model specified by relation (2) with the inclusion of a field. The conclusions are unchanged except the differences in energy values.

[22] Equation (14) is implicit in Ref. 4.

or (4) for $\mathcal{E}$ in the regions I, II, or III, respectively. It is also interesting to note that there is a finite polarization for $T > T_c$ in the absence of an external field, again a consequence of the lack of symmetry of the model. The polarizability $\chi \equiv \partial \mathbf{P}/\partial \mathcal{E}$ can now be computed exactly. We note only its critical behavior $\chi \sim (T-T_c)^{-1/2}$ as compared to the $(T-T_c)^{-1}$ singularity of the Slater KDP model.[4]

ACKNOWLEDGMENT

I should like to thank Professor Elliott H. Lieb for useful comments.

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Statistical Effects of Superexchange in Binary Mixtures with One Magnetic Component

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(Received 21 September 1967)

The statistical thermodynamics of a binary solid mixture of a ferromagnetic or antiferromagnetic component A and a nonmagnetic component B is developed theoretically. The nearest-neighbor interaction and exchange energies and a superexchange energy between any two A atoms sharing one B atom as a nearest neighbor are introduced. In addition to magnetic spin ordering, long-range A-B sublattice ordering of a type appropriate to a body-centered cubic lattice is considered, using the zeroth-order statistical approximation. The effects of dilution and long-range component ordering on the onset of magnetic ordering are calculated for several sets of parameter values over the whole range of mole fractions. If the superexchange integral is large enough relative to the direct exchange integral, the curves of Curie (or Néel) temperature against mole fraction are convex upwards, and a maximum may be observed. The interaction of long-range ordering with magnetization is considered in both equilibrium (annealed) and frozen (quenched) mixtures.

I. INTRODUCTION

In a series of three papers, Bell and Lavis,[1] Lavis and Fairbairn,[2] and Lavis and Bell[3] investigated the effects of long-range component ordering on the occurence of magnetization in a binary mixture with a magnetic component A and a nonmagnetic component B. In Refs. 1 and 2, the lattice was divided into two equivalent sublattices, and in Ref. 3, into four equivalent sublattices. Nonmagnetic pair-interaction energies and direct-exchange–magnetic-interaction energies for AA pairs were postulated for nearest-neighbor pairs in Ref. 2 and for all pairs (varying with the distance between the two members of the pair) in Refs. 1 and 3. For both the zeroth-order approximation used in Refs. 1 and 3 and the Bethe-pair approximation used in Ref. 2, the Curie temperature was seriously affected by the presence of component order, and in Ref. 1, the sign and magnitude of the exchange interaction between magnetic pairs on the same sublattice were shown to be significant. In all cases, however, the Curie temperature was seen to be a monotonically increasing function of the percentage of magnetic atoms present. In practice, exceptions occur in, for instance, mixtures of ferromagnetic with semiconducting elements.[4]

The present paper introduces superexchange in the form of an exchange interaction between two second-neighbor A atoms, with a B atom as a common nearest neighbor. The existence of such an interaction in certain paramagnetic salts was first proposed by Kramers[5] and has since been discussed by many authors, including Anderson,[6] for nonmetallic B. As far as we know, the statistical consequences of superexchange in an incompletely ordered mixture have not previously been discussed, and we shall use the simplest, or zeroth-order, approximation. While our analysis is not applicable to the face-centered cubic lattice, it is likely that similar results could be obtained.

As in Refs. 1–3, we shall assume that the magnetic moments of the A atoms are unaffected by the concentration. We shall also assume that the lattice structure of the mixture is unchanged either in dimension or type by redistribution of the atoms upon it. This tends to confine us to limited ranges of concentration when comparing with experiment.

II. FREE ENERGY AND INTERNAL VARIABLES

We make the following assumptions:

(i) The lattice divides into a pair of equivalent sublattices, and each lattice site has z nearest neighbors in the other sublattice and none in its own sublattice.

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