

## Thermodynamics of the impure classical Heisenberg chain

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The thermodynamic properties (specific heat, spin-spin correlation function, magnetic susceptibility, and density-density correlation function) of an impure one-dimensional classical Heisenberg chain with nearest-neighbor exchange are calculated exactly in the thermodynamic limit. We consider both bond and site impurities and consider the quenched and annealed limits for each of these models. The present theory is an extension of Fisher's work for the pure case. In the bond model, the annealed and quenched limits lead to the same results. In the site model, the difference between the annealed and quenched limits is predominant at low temperatures. For various combinations of the exchange constants (both ferro- and antiferromagnetic) we examine analytically how the low-temperature behavior of the zero-field susceptibility varies with concentration. Numerical results are given as functions of temperature and concentration. It is found that in the annealed limit of the site model the specific heat versus temperature curve has a maximum at a finite temperature. The maximum comes from the short-range ordering of the constituent ions.

### I. INTRODUCTION

Impure magnetic insulators have received considerable theoretical and experimental attentions in recent years. There exist two models which describe such systems. One of them is the bond model where only one kind of magnetic ion is located on the cation sites but two kinds of nonmagnetic ions,  $I$  and  $H$ , are distributed on the anion sites. There are then two kinds of superexchange bonds which connect the nearest-neighboring magnetic ions, or equivalently two kinds of interaction constants between them, corresponding to whether they interact on each other via the  $I$  or  $H$  ion. The mixture  $\text{Co}(\text{S}, \text{Se})_2$ <sup>1</sup> is an example of a system which is described by the bond model. The site model has two kinds of magnetic ions (or magnetic and nonmagnetic ions),  $I$  and  $H$ , which are distributed on the cation sites. Here we have three kinds of nearest-neighboring interaction constants corresponding to  $I$ - $I$ ,  $I$ - $H$ , and  $H$ - $H$  pairs of ions. As examples of systems which are described by the site model we may enumerate the mixtures  $(\text{Mn}, \text{Co})\text{F}_2$ ,  $\text{K}(\text{Mn}, \text{Co})\text{F}_3$ , and  $(\text{Mn}, \text{Zn})\text{F}_2$ .<sup>2</sup>

On the other hand, the idealized methods for the preparation of magnetic mixtures can be classified into two limiting cases: the mixture is prepared by cooling infinitely slowly to a given temperature; the mixture is prepared by cooling infinitely rapidly to a given temperature. These cases are called the annealed and quenched limits, respectively. In

the annealed limit the true thermal equilibrium is realized and the  $I$  and  $H$  constituent ions are distributed at absolute zero temperature in such a way that the mixture has a minimum internal energy. On the contrary, in the quenched limit the true thermal equilibrium is not realized and the  $I$  and  $H$  constituent ions are distributed randomly even at absolute zero temperature. One might expect that the quenched limit is more realistic than the annealed limit, because the distribution of constituent ions is probably not controlled by the magnetic interactions. However, a typical sample must lie, more or less, between these two limiting cases.

Efforts to exactly treat one-dimensional<sup>3</sup> or two-dimensional<sup>4</sup> Ising mixtures have been discussed by many authors. In the present paper, we calculate exactly in the thermodynamic limit various thermodynamic and magnetic quantities in a one-dimensional classical Heisenberg mixture, assuming an open-linear-chain lattice. Exchange-interaction constants between classical spins are assumed to be nonzero only for nearest neighbors, and the signs of the nearest-neighboring exchange constants are assumed to be arbitrary. The present study is an extension of Fisher's work<sup>5</sup> for the pure case to the mixture. We consider both the quenched and annealed limits for each of the bond and site models. All the quantities such as the specific heat at constant concentration, the spin-spin correlation function, the zero-field suscepti-

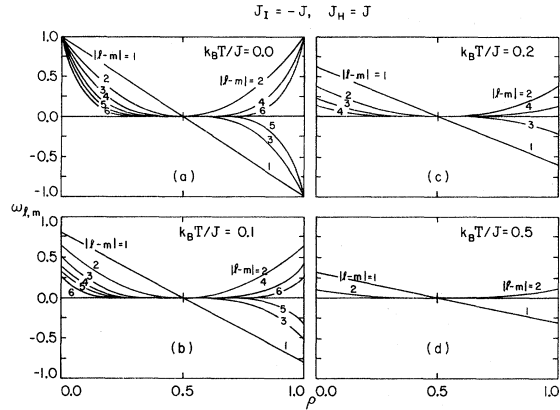


FIG. 1. Spin-spin correlation function  $\omega_{l,m}$  as a function of concentration of  $I$  bonds for  $J_I = -J$  and  $J_H = J$  in the bond model: (a)  $k_B T/J = 0.0$ ; (b)  $k_B T/J = 0.1$ ; (c)  $k_B T/J = 0.2$ ; (d)  $k_B T/J = 0.5$ . Labels on the individual curves denote the values of  $|l-m|$ . Note that  $\omega_{l,l} = 1$  for all temperatures.

bility,<sup>6</sup> etc. are obtained as functions of two (for the bond model) or three (for the site model) exchange constants, the concentrations of the constituent ions, and the temperature. The zero-field susceptibility in a pure one-dimensional classical Heisenberg ferromagnet and that in a noninteracting classical spin system diverge, respectively, as  $T^{-2}$  and  $T^{-1}$  in the limit of  $T \rightarrow 0$ , where  $T$  is the absolute temperature, whereas the zero-field susceptibility in a pure one-dimensional classical Heisenberg antiferromagnet is finite at  $T=0$ .<sup>5</sup> We show analytically how the low-temperature behavior of the zero-field susceptibility in a mixture of two of these three systems varies with concentration. It is also shown that for the bond model the specific heat at constant concentration, the spin-spin correlation function, the zero-field susceptibility, etc. in the annealed limit agree with those in the quenched limit. This is because in this model all of the configurations of the constituent ions for a given concentration have the same energy. As would be expected naturally, on the other hand, for the site model, the difference between the results in the annealed limit and those in the quenched limit is predominant at low temperatures. We calculate in the annealed limit of the site model the density-density correlation function for a given constituent ion, say, the  $I$  ion. This function seems to be a useful quantity to examine how the difference between the quenched limit and the annealed limit changes with the temperature, the concentration, etc. One more point to be mentioned here is that the temperature dependence of the specific heat at constant concentration in the annealed limit of the site model shows a maximum at a finite tempera-

ture, which arises from the short-range ordering of the constituent ions.

It is known that the compounds  $(\text{CH}_3)_4\text{NMnCl}_3$  (TMMC) and  $(\text{CH}_3)_4\text{NNiCl}_3$  (TMNC) are good examples of the one-dimensional Heisenberg antiferromagnet and ferromagnet, respectively.<sup>7</sup> The experimental data for the zero-field susceptibilities in TMMC<sup>8</sup> and TMNC<sup>9</sup> can be explained fairly well by the results (scaled to  $S=5/2$  and  $S=1$ , respectively) of Fisher's calculation<sup>5</sup> for the one-dimensional classical Heisenberg model over a wide range of temperature. Thus, we may expect that the results obtained especially for the zero-field susceptibility in the present work will be applicable to magnetic mixtures of TMMC and TMNC or of their isomorphs.

An outline of this paper is as follows. In Sec. II we formulate the bond model for both the annealed and quenched limits. Section III is devoted to the corresponding formulation for the site model. The results of the numerical calculation are given and discussed in the final section (Sec. IV).

## II. BOND MODEL

In this section we consider the bond model for a one-dimensional classical Heisenberg alloy with nearest-neighboring exchange interactions only. Assuming an open linear chain of  $N+1$  classical spins and using Fisher's definition of the exchange constant,<sup>10</sup> we may write the Hamiltonian  $\tilde{\mathcal{H}}$  for a given configuration of two kinds of bonds, i.e., the  $I$  and  $H$  bonds, as

$$\tilde{\mathcal{H}} = -\frac{J_I}{2} \sum_{i=1}^N p_{i-1,i} \vec{S}_{i-1} \cdot \vec{S}_i - \frac{J_H}{2} \sum_{i=1}^N (1-p_{i-1,i}) \vec{S}_{i-1} \cdot \vec{S}_i, \quad (2.1)$$

where  $J_I$  and  $J_H$  are, respectively, the exchange constants associated with the  $I$  and  $H$  bonds,  $\vec{S}_i$  is the (three-dimensional) unit vector at the  $i$ th site, and  $p_{i-1,i}$  is an occupation variable assuming the value of 1 or 0 depending on whether the bond between the  $(i-1)$ th and  $i$ th sites is the  $I$  or  $H$  bond. We note here that in the discussions given in this and following sections we confine ourselves to the thermodynamic limit, i.e., the limit of  $N \rightarrow \infty$ . The results which will be obtained in this paper are exact in this limit.

### A. Annealed limit

We first treat the annealed limit. The grand-partition function  $\Xi$  of the system is given by

$$\Xi = \int \frac{d\Omega_0}{4\pi} \int \frac{d\Omega_1}{4\pi} \dots \int \frac{d\Omega_N}{4\pi} \sum_{p_{0,1}=0}^1 \sum_{p_{1,2}=0}^1 \dots \sum_{p_{N-1,N}=0}^1 \exp \left( K_I \sum_{i=1}^N p_{i-1,i} \vec{S}_{i-1} \cdot \vec{S}_i + K_H \sum_{i=1}^N (1-p_{i-1,i}) \vec{S}_{i-1} \cdot \vec{S}_i + \ln \lambda \sum_{i=1}^N p_{i-1,i} \right), \tag{2.2}$$

with

$$K_I = J_I/2k_B T, \quad K_H = J_H/2k_B T. \tag{2.3}$$

In these equations  $d\Omega_i$  is the element of solid angle for the unit vector  $\vec{S}_i$ ,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\lambda$  is the absolute activity for the  $I$  bond.<sup>11</sup> By the use of Fisher's method,<sup>5</sup>  $\Xi$  is easily calculated to be

$$\Xi = (\lambda z_I + z_H)^N, \tag{2.4}$$

where

$$z_I = \sinh K_I / K_I, \quad z_H = \sinh K_H / K_H. \tag{2.5}$$

Let us denote by  $N_I$  the number of  $I$  bonds in the system. Then the absolute activity  $\lambda$  is determined from the equation

$$N_I = \lambda \left( \frac{\partial \ln \Xi}{\partial \lambda} \right)_T. \tag{2.6}$$

The result is

$$\lambda = \rho z_H / (1 - \rho) z_I, \tag{2.7}$$

where  $\rho (= N_I/N)$  is the concentration of the  $I$  bond. The Helmholtz free energy  $F^{(a)}$  in the annealed limit is calculated as

$$F^{(a)} = -k_B T (\ln \Xi - N_I \ln \lambda). \tag{2.8}$$

From Eqs. (2.4), (2.7), and (2.8), we have

$$F^{(a)} = -Nk_B T [\rho \ln z_I + (1 - \rho) \ln z_H - \rho \ln \rho - (1 - \rho) \ln(1 - \rho)]. \tag{2.9}$$

The internal energy  $U$  and the specific heat  $C$  at constant concentration of  $I$  bonds are then given, respectively, by<sup>12</sup>

$$U = -\frac{1}{2} N [\rho J_I u_I + (1 - \rho) J_H u_H], \tag{2.10}$$

$$C = Nk_B [\rho c_I + (1 - \rho) c_H], \tag{2.11}$$

with

$$u_I = \coth K_I - 1/K_I, \quad u_H = \coth K_H - 1/K_H, \tag{2.12}$$

and

$$c_I = 1 - K_I^2 / \sinh^2 K_I, \quad c_H = 1 - K_H^2 / \sinh^2 K_H. \tag{2.13}$$

We now turn our attention to the spin-spin correlation function  $\omega_{l,m}$ <sup>12</sup> in the annealed limit which is defined by

$$\begin{aligned} \omega_{l,m} &= \langle \vec{S}_l \cdot \vec{S}_m \rangle_g = 3 \langle S_l^z S_m^z \rangle_g \\ &= \frac{3}{\Xi} \int \frac{d\Omega_0}{4\pi} \int \frac{d\Omega_1}{4\pi} \dots \int \frac{d\Omega_N}{4\pi} \sum_{p_{0,1}=0}^1 \sum_{p_{1,2}=0}^1 \dots \sum_{p_{N-1,N}=0}^1 \\ &\quad \times S_l^z S_m^z \exp \left( K_I \sum_{i=1}^N p_{i-1,i} \vec{S}_{i-1} \cdot \vec{S}_i + K_H \sum_{i=1}^N (1-p_{i-1,i}) \vec{S}_{i-1} \cdot \vec{S}_i + \ln \lambda \sum_{i=1}^N p_{i-1,i} \right). \end{aligned} \tag{2.14}$$

Here  $\langle \dots \rangle_g$  denotes, as is shown explicitly, the grand canonical ensemble average. Using again Fisher's method<sup>5</sup> for the pure case, we obtain the following expression for  $\omega_{l,m}$ :

$$\omega_{l,m} = \left( \frac{\lambda y_I + y_H}{\lambda z_I + z_H} \right)^{|l-m|}, \tag{2.15}$$

where

$$y_I = \frac{K_I \cosh K_I - \sinh K_I}{K_I^2}, \quad y_H = \frac{K_H \cosh K_H - \sinh K_H}{K_H^2}. \tag{2.16}$$

Note that  $\omega_{l,m}$  given by Eq. (2.15) depends only on  $|l - m|$ . Combining Eq. (2.15) with Eq. (2.7) yields

$$\omega_{l,m} = \bar{u}^{|l-m|}, \tag{2.17}$$

with

$$\bar{u} = \rho u_I + (1 - \rho) u_H. \quad (2.18)$$

The zero-field susceptibility  $\chi$ <sup>12</sup> is expressed in terms of  $\omega_{l,m}$  as

$$\chi = \frac{g^2 \mu_B^2}{12 k_B T} \sum_{i=0}^N \sum_{m=0}^N \omega_{i,m}, \quad (2.19)$$

$g$  and  $\mu_B$  being the  $g$  factor of the ion with the classical spin<sup>13</sup> and the Bohr magneton, respectively. If we substitute Eq. (2.17) into Eq. (2.19), perform summations over  $l$  and  $m$ , and then take the limit of  $N \rightarrow \infty$ , the zero-field susceptibility  $\chi$  in the thermodynamic limit is obtained to be

$$\chi = \frac{Ng^2 \mu_B^2}{12 k_B T} \frac{1 + \bar{u}}{1 - \bar{u}}. \quad (2.20)$$

### B. Quenched limit

Next we discuss the quenched limit. The partition function  $\bar{Z}$  for a given configuration of  $N_I$   $I$  bonds and  $(N - N_I)$   $H$  bonds is evaluated as

$$\bar{Z} = \int \frac{d\Omega_0}{4\pi} \int \frac{d\Omega_1}{4\pi} \cdots \int \frac{d\Omega_N}{4\pi} \exp \left( K_I \sum_{i=1}^N p_{i-1,i} \vec{S}_{i-1} \cdot \vec{S}_i + K_H \sum_{i=1}^N (1 - p_{i-1,i}) \vec{S}_{i-1} \cdot \vec{S}_i \right) = z_I^{N_I} z_H^{N - N_I}. \quad (2.21)$$

Thus the Helmholtz free energy  $F^{(q)}$  in the quenched limit is given by

$$\begin{aligned} F^{(q)} &= -k_B T \langle \ln \bar{Z} \rangle_{\text{conf}} \\ &= -N k_B T [\rho \ln z_I + (1 - \rho) \ln z_H], \end{aligned} \quad (2.22)$$

where  $\langle \cdots \rangle_{\text{conf}}$  stands for the arithmetic average over all the configurations for fixed  $N_I$  (or equivalently for fixed  $\rho$ ). From Eqs. (2.9) and (2.22) we see that the difference  $F^{(a)} - F^{(q)}$  is proportional to the temperature  $T$ . It is thus obvious that the internal energy and the specific heat at constant concentration in the quenched limit of the bond model agree with those in the annealed limit of this model.

On the other hand, the spin-spin correlation function  $\bar{\omega}_{l,m}$  for a given configuration of the  $I$  and  $H$  bonds is defined by

$$\bar{\omega}_{l,m} = \langle \vec{S}_l \cdot \vec{S}_m \rangle_c = \frac{3}{Z} \int \frac{d\Omega_0}{4\pi} \int \frac{d\Omega_1}{4\pi} \cdots \int \frac{d\Omega_N}{4\pi} S_l^z S_m^z \exp \left( K_I \sum_{i=1}^N p_{i-1,i} \vec{S}_{i-1} \cdot \vec{S}_i + K_H \sum_{i=1}^N (1 - p_{i-1,i}) \vec{S}_{i-1} \cdot \vec{S}_i \right), \quad (2.23)$$

where  $\langle \cdots \rangle_c$  denotes the canonical ensemble average. We have from Eq. (2.23)

$$\bar{\omega}_{l,m} = \begin{cases} \prod_{i=l+1}^m u_{i-1,i} & \text{for } l < m, \\ 1 & \text{for } l = m, \\ \bar{\omega}_{m,l} & \text{for } l > m, \end{cases} \quad (2.24)$$

where  $u_{i-1,i}$  takes one of two possible values,  $u_I$  and  $u_H$ , depending on whether the bond connecting the  $(i-1)$ th and  $i$ th sites is the  $I$  or  $H$  bond. The spin-spin correlation function  $\omega_{l,m}$ <sup>12</sup> in the quenched limit is nothing but the configurational average of  $\bar{\omega}_{l,m}$ , i. e.,

$$\omega_{l,m} = \langle \bar{\omega}_{l,m} \rangle_{\text{conf}}. \quad (2.25)$$

Since the probability that the bond connecting nearest-neighboring sites is the  $I$  or  $H$  bond is, respectively,  $\rho$  or  $1 - \rho$ , we can obtain the following recurrence relation for  $\omega_{l,m}$  with  $l < m$ :

$$\begin{aligned} \omega_{l,m} &= \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}} \\ &= \rho \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, I \in (m-1, m)} + (1 - \rho) \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, H \in (m-1, m)} \\ &= \rho u_I \left\langle \prod_{i=l+1}^{m-1} u_{i-1,i} \right\rangle_{\text{conf}} + (1 - \rho) u_H \left\langle \prod_{i=l+1}^{m-1} u_{i-1,i} \right\rangle_{\text{conf}} \end{aligned}$$

$$= \bar{u} \omega_{i,m-1} \quad (\text{for } m=l+1, l+2, \dots). \quad (2.26)$$

Here  $\langle \dots \rangle_{\text{conf}, I \in (m-1, m)}$  or  $\langle \dots \rangle_{\text{conf}, H \in (m-1, m)}$  stands for the arithmetic average over all the configurations of the  $I$  and  $H$  bonds subject to the condition that the bond between the  $(m-1)$ th and  $m$ th sites is the  $I$  or  $H$  bond, respectively. Iterating Eq. (2.26) and noting that  $\omega_{i,m} = 1$  and  $\omega_{m,i} = \omega_{i,m}$  leads us to

$$\omega_{i,m} = \bar{u}^{|l-m|}, \quad (2.27)$$

which is the same result as that given by Eq. (2.17).

### III. SITE MODEL

In the site model, for a given configuration of the  $I$  and  $H$  constituent ions the Hamiltonian  $\mathcal{H}$  may be written as

$$\begin{aligned} \mathcal{H} = & -\frac{J_{II}}{2} \sum_{i=1}^N p_{i-1} p_i \vec{S}_{i-1} \cdot \vec{S}_i \\ & -\frac{J_{IH}}{2} \sum_{i=1}^N (p_{i-1} - p_i)^2 \vec{S}_{i-1} \cdot \vec{S}_i \\ & -\frac{J_{HH}}{2} \sum_{i=1}^N (1 - p_{i-1})(1 - p_i) \vec{S}_{i-1} \cdot \vec{S}_i, \end{aligned} \quad (3.1)$$

where  $J_{II}$ ,  $J_{IH}$ , and  $J_{HH}$  are, respectively, the exchange constants (defined similarly to those in the bond model<sup>10</sup>) between the nearest-neighboring pairs of the

$I$  and  $I$ ,  $I$  and  $H$ , and  $H$  and  $H$  ions, and  $p_i$  is equal to 1 or 0 depending on whether the ion at the  $i$ th site is the  $I$  or  $H$  ion. The vector  $\vec{S}_i$  in Eq. (3.1) is the same unit vector as used in Eq. (2.1).

#### A. Annealed limit

Introducing the following dimensionless quantities similar to those defined in the preceding section:

$$K_{II} = J_{II}/2k_B T, \quad K_{IH} = J_{IH}/2k_B T, \quad K_{HH} = J_{HH}/2k_B T, \quad (3.2)$$

and

$$\begin{aligned} z_{II} &= \sinh K_{II}/K_{II}, \quad z_{IH} = \sinh K_{IH}/K_{IH}, \\ z_{HH} &= \sinh K_{HH}/K_{HH}, \end{aligned} \quad (3.3)$$

the grand-partition function  $\Xi$  of the system becomes

$$\begin{aligned} \Xi &= \int \frac{d\Omega_0}{4\pi} \int \frac{d\Omega_1}{4\pi} \dots \int \frac{d\Omega_N}{4\pi} \sum_{p_0=0}^1 \sum_{p_1=0}^1 \dots \sum_{p_N=0}^1 \exp \left( K_{II} \sum_{i=1}^N p_{i-1} p_i \vec{S}_{i-1} \cdot \vec{S}_i + K_{IH} \sum_{i=1}^N (p_{i-1} - p_i)^2 \vec{S}_{i-1} \cdot \vec{S}_i \right. \\ &\quad \left. + K_{HH} \sum_{i=1}^N (1 - p_{i-1})(1 - p_i) \vec{S}_{i-1} \cdot \vec{S}_i + \ln \lambda \sum_{i=0}^N p_i \right) \\ &= \text{Tr}(A_0 A^N). \end{aligned} \quad (3.4)$$

Here  $\lambda$  is the absolute activity for the  $I$  ion, and  $A_0$  and  $A$  are the  $2 \times 2$  transfer matrices defined by

$$A_0 = \begin{pmatrix} 1 & \sqrt{\lambda} \\ \sqrt{\lambda} & \lambda \end{pmatrix}, \quad (3.5)$$

$$A = \begin{pmatrix} z_{HH} & \sqrt{\lambda} z_{IH} \\ \sqrt{\lambda} z_{IH} & \lambda z_{II} \end{pmatrix}. \quad (3.6)$$

The eigenvalues  $a_{\pm}$  of the matrix  $A$  can be calculated easily and the results are

$$a_{\pm} = \frac{1}{2} \{ \lambda z_{II} + z_{HH} \pm [(\lambda z_{II} - z_{HH})^2 + 4\lambda z_{IH}^2]^{1/2} \}. \quad (3.7)$$

It is important to note here that

$$a_+ > |a_-|. \quad (3.8)$$

Since we are concerned in the thermodynamic limit and since we have the relation (3.8), the equation which determines the absolute activity  $\lambda$

becomes

$$\rho = \lambda \left( \frac{\partial \ln a_+}{\partial \lambda} \right)_T, \quad (3.9)$$

$\rho$  being the concentration of  $I$  ions. Substituting  $a_+$  given by Eq. (3.7) into Eq. (3.9) and performing some manipulations gives

$$\begin{aligned} \lambda &= \frac{z_{HH}}{z_{II}} + \frac{(1-2\rho)^2}{2\rho(1-\rho)} \frac{z_{IH}^2}{z_{II}^2} \\ &\quad - \frac{1-2\rho}{2\rho(1-\rho)} \frac{z_{IH}}{z_{II}^2} [4\rho(1-\rho) z_{II} z_{HH} + (1-2\rho)^2 z_{IH}^2]^{1/2}. \end{aligned} \quad (3.10)$$

It is straightforward to evaluate the internal energy  $U^{(a)}$  in the annealed limit and we finally have

$$U^{(a)} = - \frac{N(J_{II} \gamma_{II} \gamma_{II} + J_{IH} \gamma_{IH} \gamma_{IH} + J_{HH} \gamma_{HH} \gamma_{HH})}{\lambda z_{II} + z_{HH} + [(\lambda z_{II} - z_{HH})^2 + 4\lambda z_{IH}^2]^{1/2}}, \quad (3.11)$$

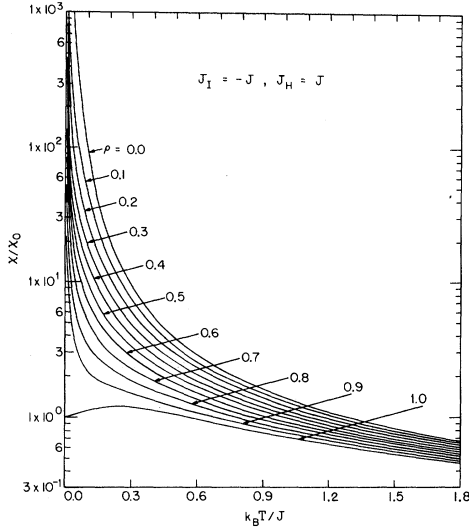


FIG. 2. Zero-field susceptibility  $\chi/\chi_0$  ( $\chi_0 = Ng^2\mu_B^2/12J$ ) as a function of temperature for  $J_I = -J$  and  $J_H = J$  in the bond model. Labels on the individual curves denote the values of  $\rho$ .

where

$$\begin{aligned} \gamma_{II} &= \frac{K_{II} \cosh K_{II} - \sinh K_{II}}{K_{II}^2}, \\ \gamma_{IH} &= \frac{K_{IH} \cosh K_{IH} - \sinh K_{IH}}{K_{IH}^2}, \\ \gamma_{HH} &= \frac{K_{HH} \cosh K_{HH} - \sinh K_{HH}}{K_{HH}^2}, \end{aligned} \quad (3.12)$$

and

$$\begin{aligned} \gamma_{II} &= \frac{\lambda}{2} \left( 1 + \frac{\lambda z_{II} - z_{HH}}{[(\lambda z_{II} - z_{HH})^2 + 4\lambda z_{IH}^2]^{1/2}} \right), \\ \gamma_{IH} &= \frac{2\lambda z_{IH}}{[(\lambda z_{II} - z_{HH})^2 + 4\lambda z_{IH}^2]^{1/2}}, \\ \gamma_{HH} &= \frac{1}{2} \left( 1 - \frac{\lambda z_{II} - z_{HH}}{[(\lambda z_{II} - z_{HH})^2 + 4\lambda z_{IH}^2]^{1/2}} \right). \end{aligned} \quad (3.13)$$

The specific heat  $C^{(a)}$  at constant concentration of  $I$  ions in the annealed limit can be calculated by

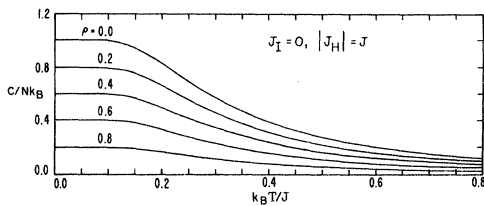


FIG. 3. Specific heat  $C/Nk_B$  at constant concentration of  $I$  bonds as a function of temperature for  $J_I = 0$  and  $|J_H| = J$  in the bond model. Labels on the individual curves denote the values of  $\rho$ .

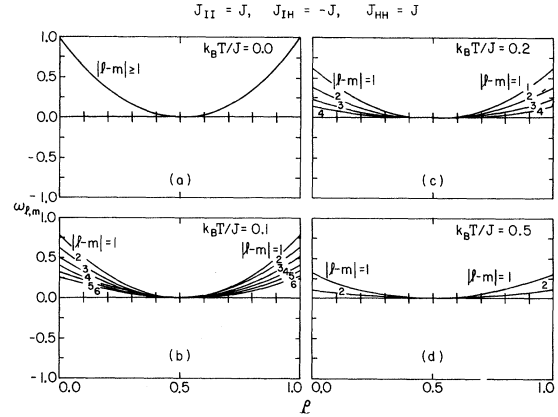


FIG. 4. Spin-spin correlation function  $\omega_{l,m}$  as a function of concentration of  $I$  ions for  $J_{II} = J$ ,  $J_{IH} = -J$ , and  $J_{HH} = J$  in the site model: (a)  $k_B T / J = 0.0$ ; (b)  $k_B T / J = 0.1$ ; (c)  $k_B T / J = 0.2$ ; (d)  $k_B T / J = 0.5$ . Labels on the individual curves denote the values of  $|l-m|$ . Note that  $\omega_{l,l} = 1$  for all temperatures. For the present combination of the exchange constants, the annealed and quenched limits lead to the same result for  $\omega_{l,m}$ , and  $\omega_{l,m}$  depends only on  $|l-m|$ . The spin-spin correlation function  $\omega_{l,m}$  for  $J_{II} = -J$ ,  $J_{IH} = J$ , and  $J_{HH} = -J$  is obtained by multiplying  $\omega_{l,m}$  shown in the figures by  $(-1)^{|l-m|}$ .

differentiating  $U^{(a)}$  with respect to the temperature  $T$  keeping  $\rho$  constant, i. e.,

$$C^{(a)} = \left( \frac{\partial U^{(a)}}{\partial T} \right)_\rho. \quad (3.14)$$

We next consider the spin-spin correlation function  $\omega_{l,m}^{(a)}$  in the annealed limit. This correlation function is calculated as

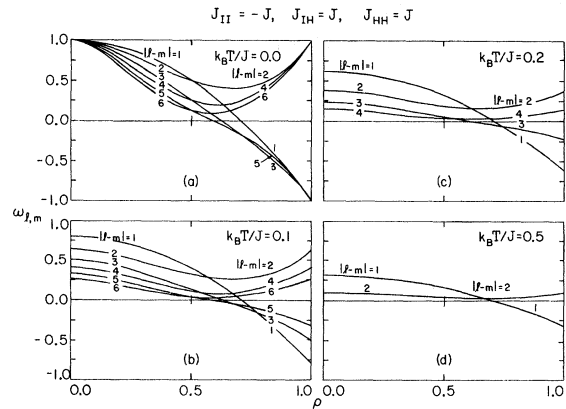


Fig. 5. Same as Fig. 4 but for  $J_{II} = -J$ ,  $J_{IH} = J$ , and  $J_{HH} = J$ . The spin-spin correlation function  $\omega_{l,m}$  for  $J_{II} = -J$ ,  $J_{IH} = -J$ , and  $J_{HH} = J$  is obtained by multiplying  $\omega_{l,m}$  shown in the figures by  $(-1)^{|l-m|}$  and then by replacing  $\rho$  by  $(1-\rho)$ .

$$\begin{aligned} \omega_{i,m}^{(a)} = \langle \vec{S}_i \cdot \vec{S}_m \rangle_{\mathcal{E}} &= \frac{3}{\Xi} \int \frac{d\Omega_0}{4\pi} \int \frac{d\Omega_1}{4\pi} \dots \int \frac{d\Omega_N}{4\pi} \sum_{p_0=0}^1 \sum_{p_1=0}^1 \dots \sum_{p_N=0}^1 S_i^z S_m^z \\ &\times \exp \left( K_{II} \sum_{i=1}^N p_{i-1} p_i \vec{S}_{i-1} \cdot \vec{S}_i + K_{IH} \sum_{i=1}^N (p_{i-1} - p_i)^2 \vec{S}_{i-1} \cdot \vec{S}_i + K_{HH} \sum_{i=1}^N (1 - p_{i-1})(1 - p_i) \vec{S}_{i-1} \cdot \vec{S}_i + \ln \lambda \sum_{i=0}^N p_i \right) \\ &= \begin{cases} \frac{1}{\Xi} \text{Tr}(A_0 A^l B^{m-l} A^{N-m}) & \text{for } l \leq m, \\ \omega_{m,i}^{(a)} & \text{for } l \geq m. \end{cases} \end{aligned} \quad (3.15)$$

Here we have introduced newly the  $2 \times 2$  matrix  $B$  which is defined by

$$B = \begin{pmatrix} y_{HH} & \sqrt{\lambda} y_{IH} \\ \sqrt{\lambda} y_{IH} & \lambda y_{II} \end{pmatrix}. \quad (3.16)$$

It is to be noted here that, since the two matrices  $A_0$  and  $A$  do not commute with one another,  $\omega_{i,m}^{(a)}$  depends independently on  $l$  and  $m$ . When  $J_{IH} = 0$ , i. e.,  $y_{IH} = 0$ , the matrix  $B$  is diagonal and has two eigenvalues  $b_{\pm}$  given by

$$b_+ = y_{HH}, \quad b_- = \lambda y_{II} \quad (\text{for } J_{IH} = 0). \quad (3.17)$$

On the other hand, the eigenvalues  $b_{\pm}$  of the matrix  $B$  for the case of  $J_{IH} \neq 0$  are expressed as

$$b_{\pm} = \frac{1}{2} \{ \lambda y_{II} + y_{HH} \pm [(\lambda y_{II} - y_{HH})^2 + 4\lambda y_{IH}^2]^{1/2} \} \quad (\text{for } J_{IH} \neq 0). \quad (3.18)$$

Let us now introduce two matrices  $P$  and  $Q$ , which are defined, respectively, by

$$P^{-1}AP = \begin{pmatrix} a_+ & 0 \\ 0 & a_- \end{pmatrix}, \quad P^{-1}P = PP^{-1} = E, \quad (3.19)$$

and

$$Q^{-1}BQ = \begin{pmatrix} b_+ & 0 \\ 0 & b_- \end{pmatrix}, \quad Q^{-1}Q = QQ^{-1} = E, \quad (3.20)$$

where  $E$  is the  $2 \times 2$  unit matrix. Then, the spin-spin correlation function  $\omega_{i,m}^{(a)}$  in the limit of  $1 \ll l$ ,  $m \ll N$  can be rewritten in the following form:

$$\begin{aligned} \omega_{i,m}^{(a)} &= [P^{-1}Q]_{11} [Q^{-1}P]_{11} (b_+/a_+)^{|l-m|} \\ &+ [P^{-1}Q]_{12} [Q^{-1}P]_{21} (b_-/a_+)^{|l-m|} \quad (\text{for } 1 \ll l, m \ll N), \end{aligned} \quad (3.21)$$

where, for example,  $[P^{-1}Q]_{11}$  is the (1, 1) element of the matrix product  $P^{-1}Q$ . In deriving Eq. (3.21), we have employed the fact that

$$a_+ > |b_{\pm}|. \quad (3.22)$$

It is natural that  $\omega_{i,m}^{(a)}$  in the limit of  $1 \ll l$ ,  $m \ll N$  depends only on  $|l - m|$ . The explicit expressions for  $P$ ,  $P^{-1}$ ,  $Q$ , and  $Q^{-1}$  are given by

$$\begin{aligned} P &= \begin{pmatrix} \sqrt{\lambda} z_{IH} & \sqrt{\lambda} z_{IH} \\ a_+ - z_{HH} & a_- - z_{HH} \end{pmatrix}, \\ P^{-1} &= \frac{1}{\sqrt{\lambda} z_{IH} (a_+ - a_-)} \begin{pmatrix} -a_+ + z_{HH} & \sqrt{\lambda} z_{IH} \\ a_+ - z_{HH} & -\sqrt{\lambda} z_{IH} \end{pmatrix}, \end{aligned} \quad (3.23)$$

and

$$Q = Q^{-1} = E \quad (\text{for } J_{IH} = 0), \quad (3.24)$$

$$Q = \begin{pmatrix} \sqrt{\lambda} y_{IH} & \sqrt{\lambda} y_{IH} \\ b_+ - y_{HH} & b_- - y_{HH} \end{pmatrix},$$

$$Q^{-1} = \frac{1}{\sqrt{\lambda} y_{IH} (b_+ - b_-)} \begin{pmatrix} -b_+ + y_{HH} & \sqrt{\lambda} y_{IH} \\ b_+ - y_{HH} & -\sqrt{\lambda} y_{IH} \end{pmatrix} \quad (3.25)$$

(for  $J_{IH} \neq 0$ ).

Calculating the zero-field susceptibility  $\chi^{(a)}$  in the annealed limit, we assume that the  $g$  factor of the  $I$  ion is equal to that of the  $H$  ion and denote the  $g$  factor by  $g$ .<sup>13</sup> Thus, by following the same procedure that led us from Eqs. (2.17) and (2.19) to Eq. (2.20), we find

$$\chi^{(a)} = \frac{Ng^2 \mu_B^2}{12k_B T} \left( [P^{-1}Q]_{11} [Q^{-1}P]_{11} \frac{a_+ + b_+}{a_+ - b_+} + [P^{-1}Q]_{12} [Q^{-1}P]_{21} \frac{a_+ + b_-}{a_+ - b_-} \right). \quad (3.26)$$

Furthermore, it is interesting to discuss the density-density correlation function  $\psi_{i,m}^{(a)}$  for the  $I$  ion in the annealed limit. This correlation function is defined as

$$\psi_{i,m}^{(a)} = \langle p_i p_m \rangle_{\mathcal{E}} = \frac{1}{\Xi} \int \frac{d\Omega_0}{4\pi} \int \frac{d\Omega_1}{4\pi} \dots \int \frac{d\Omega_N}{4\pi} \sum_{p_0=0}^1 \sum_{p_1=0}^1 \dots \sum_{p_N=0}^1 p_i p_m \exp \left( K_{II} \sum_{i=1}^N p_{i-1} p_i \vec{S}_{i-1} \cdot \vec{S}_i + K_{IH} \sum_{i=1}^N (p_{i-1} - p_i)^2 \vec{S}_{i-1} \cdot \vec{S}_i \right)$$

$$+ K_{HH} \sum_{i=1}^N (1 - p_{i-1})(1 - p_i) \vec{S}_{i-1} \cdot \vec{S}_i + \ln \lambda \sum_{i=0}^N p_i \Big), \quad (3.27)$$

and is calculated to be

$$\psi_{l,m}^{(a)} = \begin{cases} \frac{1}{|l|} \text{Tr}(A_0 A^{l-1} A' A^{m-l-1} A' A^{N-m}) & \text{for } 1 \leq l < m \leq N, \\ \frac{1}{|l|} \text{Tr}(A_0 A^{l-1} A' A^{N-l}) & \text{for } 1 \leq l = m \leq N, \\ \psi_{m,l}^{(a)} & \text{for } 1 \leq m < l \leq N, \end{cases} \quad (3.28)$$

and

$$\psi_{0,m}^{(a)} = \begin{cases} \frac{1}{|l|} \text{Tr}(A'_0 A^{m-1} A' A^{N-m}) & \text{for } 1 \leq m \leq N, \\ \frac{1}{|l|} \text{Tr}(A'_0 A^N) & \text{for } m=0, \end{cases} \quad (3.29)$$

where  $A_0$  and  $A$  have already been defined by Eqs. (3.5) and (3.6), respectively, and

$$A'_0 = \begin{pmatrix} 0 & \sqrt{\lambda} \\ 0 & \lambda \end{pmatrix}, \quad (3.30)$$

$$A' = \begin{pmatrix} 0 & \sqrt{\lambda} z_{IH} \\ 0 & \lambda z_{II} \end{pmatrix}. \quad (3.31)$$

Note that  $\psi_{l,m}^{(a)}$  also depends independently on  $l$  and  $m$ . It is not difficult to show that  $\psi_{l,m}^{(a)}$  is expressed in the limit of  $1 \ll l, m \ll N$  as

$$\psi_{l,m}^{(a)} = \begin{cases} \frac{[P^{-1}A'P]_{12}[P^{-1}A'P]_{21}}{a_+^2} \left(\frac{a_-}{a_+}\right)^{|l-m|-1} + \rho^2 & \text{for } 1 \ll l \neq m \ll N, \\ \rho & \text{for } 1 \ll l = m \ll N, \end{cases} \quad (3.32)$$

which depends only on  $|l - m|$ .

### B. Quenched limit

The partition function  $\tilde{Z}$  for a given configuration of the  $I$  and  $H$  ions is expressed as

$$\begin{aligned} \tilde{Z} &= \int \frac{d\Omega_0}{4\pi} \int \frac{d\Omega_1}{4\pi} \cdots \int \frac{d\Omega_N}{4\pi} \exp\left(K_{II} \sum_{i=1}^N p_{i-1} p_i \vec{S}_{i-1} \cdot \vec{S}_i + K_{IH} \sum_{i=1}^N (p_{i-1} - p_i)^2 \vec{S}_{i-1} \cdot \vec{S}_i + K_{HH} \sum_{i=1}^N (1 - p_{i-1})(1 - p_i) \vec{S}_{i-1} \cdot \vec{S}_i\right) \\ &= \prod_{i=1}^N z_{i-1,i}. \end{aligned} \quad (3.33)$$

Here  $z_{i-1,i}$  is equal to  $z_{II}$ ,  $z_{IH}$ , or  $z_{HH}$ , depending on the species of ions at the  $(i-1)$ th and  $i$ th sites. The Helmholtz free energy  $F^{(a)}$  in the quenched limit is obtained from

$$F^{(a)} = -k_B T \langle \ln \tilde{Z} \rangle_{\text{conf}} = -k_B T \left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}}. \quad (3.34)$$

In this equation  $\langle \cdots \rangle_{\text{conf}}$  represents the arithmetic average over all the configurations of the  $I$  and  $H$  ions for given concentrations of these ions.

The Helmholtz free energy  $F^{(a)}$  can be calculated as follows. Since the probability of finding the  $I$  or  $H$  ion at a given site is, respectively,  $\rho$  or  $1 - \rho$ , we have

$$\left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}} = \rho \left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}, I \in N} + (1 - \rho) \left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}, H \in N}, \quad (3.35)$$



$$\begin{aligned}
\left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}, I \in N} &= \rho \left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}, I \in (N-1), I \in N} + (1-\rho) \left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}, H \in (N-1), I \in N} \\
&= \rho \ln z_{II} + (1-\rho) \ln z_{IH} + \rho \left\langle \ln \prod_{i=1}^{N-1} z_{i-1,i} \right\rangle_{\text{conf}, I \in (N-1)} + (1-\rho) \left\langle \ln \prod_{i=1}^{N-1} z_{i-1,i} \right\rangle_{\text{conf}, H \in (N-1)} \\
&= \rho \ln z_{II} + (1-\rho) \ln z_{IH} + \left\langle \ln \prod_{i=1}^{N-1} z_{i-1,i} \right\rangle_{\text{conf}}, \tag{3.36}
\end{aligned}$$

$$\begin{aligned}
\left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}, H \in N} &= \rho \left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}, I \in (N-1), H \in N} + (1-\rho) \left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}, H \in (N-1), H \in N} \\
&= \rho \ln z_{IH} + (1-\rho) \ln z_{HH} + \rho \left\langle \ln \prod_{i=1}^{N-1} z_{i-1,i} \right\rangle_{\text{conf}, I \in (N-1)} + (1-\rho) \left\langle \ln \prod_{i=1}^{N-1} z_{i-1,i} \right\rangle_{\text{conf}, H \in (N-1)} \\
&= \rho \ln z_{IH} + (1-\rho) \ln z_{HH} + \left\langle \ln \prod_{i=1}^{N-1} z_{i-1,i} \right\rangle_{\text{conf}}, \tag{3.37}
\end{aligned}$$

where, for example,  $\langle \dots \rangle_{\text{conf}, I \in N}$  denotes the arithmetic average over all the configurations of the  $I$  and  $H$  ions subject to the condition that the  $I$  ion occupies the  $N$ th site and  $\langle \dots \rangle_{\text{conf}, I \in (N-1), I \in N}$  the arithmetic average over all the configurations of the  $I$  and  $H$  ions subject to the condition that the  $I$  ions occupy the  $(N-1)$ th and  $N$ th sites. Substituting Eqs. (3.36) and (3.37) into (3.35) gives

$$\begin{aligned}
\left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}} &= \rho^2 \ln z_{II} + 2\rho(1-\rho) \ln z_{IH} + (1-\rho)^2 \ln z_{HH} \\
&\quad + \left\langle \ln \prod_{i=1}^{N-1} z_{i-1,i} \right\rangle_{\text{conf}}. \tag{3.38}
\end{aligned}$$

In a similar way we can obtain

$$\begin{aligned}
\left\langle \ln \prod_{i=1}^{N-1} z_{i-1,i} \right\rangle_{\text{conf}} &= \rho^2 \ln z_{II} + 2\rho(1-\rho) \ln z_{IH} \\
&\quad + (1-\rho)^2 \ln z_{HH} + \left\langle \ln \prod_{i=1}^{N-2} z_{i-1,i} \right\rangle_{\text{conf}}. \tag{3.39}
\end{aligned}$$

From Eqs. (3.38) and (3.39) we have

$$\begin{aligned}
\left\langle \ln \prod_{i=1}^N z_{i-1,i} \right\rangle_{\text{conf}} &= 2[\rho^2 \ln z_{II} + 2\rho(1-\rho) \ln z_{IH} \\
&\quad + (1-\rho)^2 \ln z_{HH}] + \left\langle \ln \prod_{i=1}^{N-2} z_{i-1,i} \right\rangle_{\text{conf}}. \tag{3.40}
\end{aligned}$$

Substituting the result obtained by repeating this procedure and by noting that

$$\langle \ln z_{01} \rangle_{\text{conf}} = \rho^2 \ln z_{II} + 2\rho(1-\rho) \ln z_{IH} + (1-\rho)^2 \ln z_{HH}$$

into Eq. (3.34) expresses finally the Helmholtz free energy  $F^{(a)}$  as

$$\begin{aligned}
F^{(a)} &= -Nk_B T [\rho^2 \ln z_{II} + 2\rho(1-\rho) \ln z_{IH} \\
&\quad + (1-\rho)^2 \ln z_{HH}]. \tag{3.41}
\end{aligned}$$

It is straightforward to evaluate the internal energy  $U^{(a)}$  and the specific heat  $C^{(a)}$  at constant concen-

tration of  $I$  ions from the Helmholtz free energy obtained above, and the results are

$$U^{(a)} = -\frac{1}{2}N[\rho^2 J_{II} u_{II} + 2\rho(1-\rho) J_{IH} u_{IH} + (1-\rho)^2 J_{HH} u_{HH}], \tag{3.42}$$

$$C^{(a)} = Nk_B [\rho^2 c_{II} + 2\rho(1-\rho) c_{IH} + (1-\rho)^2 c_{HH}], \tag{3.43}$$

where

$$\begin{aligned}
u_{II} &= \coth K_{II} - 1/K_{II}, \\
u_{IH} &= \coth K_{IH} - 1/K_{IH}, \\
u_{HH} &= \coth K_{HH} - 1/K_{HH}, \tag{3.44}
\end{aligned}$$

and

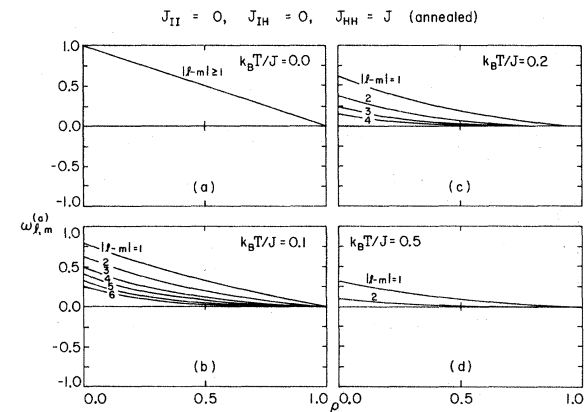


FIG. 6. Spin-spin correlation function  $\omega_{l,m}^{(a)}$  ( $1 \ll l \neq m \ll N$ ) as a function of concentration of  $I$  ions for  $J_{II}=0$ ,  $J_{IH}=0$ , and  $J_{HH}=J$  in the annealed limit of the site model: (a)  $k_B T/J=0.0$ ; (b)  $k_B T/J=0.1$ ; (c)  $k_B T/J=0.2$ ; (d)  $k_B T/J=0.5$ . Labels on the individual curves denote the values of  $|l-m|$ . Note that  $\omega_{l,l}^{(a)}=1$  for all temperatures. The spin-spin correlation function  $\omega_{l,m}^{(a)}$  ( $1 \ll l, m \ll N$ ) for  $J_{II}=0$ ,  $J_{IH}=0$ , and  $J_{HH}=-J$  is obtained by multiplying  $\omega_{l,m}^{(a)}$  shown in the figures by  $(-1)^{|l-m|}$ .

$$\begin{aligned} c_{II} &= 1 - K_{II}^2 / \sinh^2 K_{II}, \\ c_{IH} &= 1 - K_{IH}^2 / \sinh^2 K_{IH}, \\ c_{HH} &= 1 - K_{HH}^2 / \sinh^2 K_{HH}. \end{aligned} \quad (3.45)$$

The spin-spin correlation function  $\omega_{i,m}^{(\alpha)}$  in the

quenched limit is calculated from

$$\omega_{i,m}^{(\alpha)} = \langle \tilde{\omega}_{i,m} \rangle_{\text{conf}}, \quad (3.46)$$

where  $\tilde{\omega}_{i,m}$  is the spin-spin correlation function for a given configuration of the  $I$  and  $H$  ions which is given by

$$\begin{aligned} \tilde{\omega}_{i,m} &= \langle \vec{S}_i \cdot \vec{S}_m \rangle_c = \frac{3}{Z} \int \frac{d\Omega_0}{4\pi} \int \frac{d\Omega_1}{4\pi} \cdots \int \frac{d\Omega_N}{4\pi} S_i^z S_m^z \exp \left( K_{II} \sum_{i=1}^N p_{i-1} p_i \vec{S}_{i-1} \cdot \vec{S}_i + K_{IH} \sum_{i=1}^N (p_{i-1} - p_i)^2 \vec{S}_{i-1} \cdot \vec{S}_i \right. \\ &\quad \left. + K_{HH} \sum_{i=1}^N (1 - p_{i-1})(1 - p_i) \vec{S}_{i-1} \cdot \vec{S}_i \right) \\ &= \begin{cases} \prod_{i=l+1}^m u_{i-1,i} & \text{for } l < m, \\ 1 & \text{for } l = m, \\ \tilde{\omega}_{m,l} & \text{for } l > m. \end{cases} \end{aligned} \quad (3.47)$$

Here  $u_{i-1,i}$  equals to  $u_{II}$ ,  $u_{IH}$ , or  $u_{HH}$ , depending on the ions at the  $(i-1)$ th and  $i$ th sites. By following the method similar to that used in deriving Eq. (3.41) from Eq. (3.34),  $\omega_{i,m}^{(\alpha)}$  can be evaluated as follows. Since  $\omega_{i,m}^{(\alpha)} = \omega_{m,i}^{(\alpha)}$ , we consider only the case where  $l < m$ . First we note that  $\omega_{i,m}^{(\alpha)}$  can be written as

$$\omega_{i,m}^{(\alpha)} = \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}} = \rho \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, I \in m} + (1 - \rho) \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, H \in m} \quad (\text{for } m = l+1, l+2, \dots). \quad (3.48)$$

Furthermore  $\langle \prod_{i=l+1}^m u_{i-1,i} \rangle_{\text{conf}, I \in m}$  and  $\langle \prod_{i=l+1}^m u_{i-1,i} \rangle_{\text{conf}, H \in m}$  are expressed as

$$\begin{aligned} \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, I \in m} &= \rho \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, I \in (m-1), I \in m} + (1 - \rho) \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, H \in (m-1), I \in m} \\ &= \rho u_{II} \left\langle \prod_{i=l+1}^{m-1} u_{i-1,i} \right\rangle_{\text{conf}, I \in (m-1)} + (1 - \rho) u_{IH} \left\langle \prod_{i=l+1}^{m-1} u_{i-1,i} \right\rangle_{\text{conf}, H \in (m-1)} \quad (\text{for } m = l+2, l+3, \dots), \end{aligned} \quad (3.49)$$

$$\begin{aligned} \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, H \in m} &= \rho \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, I \in (m-1), H \in m} + (1 - \rho) \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, H \in (m-1), H \in m} \\ &= \rho u_{IH} \left\langle \prod_{i=l+1}^{m-1} u_{i-1,i} \right\rangle_{\text{conf}, I \in (m-1)} + (1 - \rho) u_{HH} \left\langle \prod_{i=l+1}^{m-1} u_{i-1,i} \right\rangle_{\text{conf}, H \in (m-1)} \quad (\text{for } m = l+2, l+3, \dots), \end{aligned} \quad (3.50)$$

or equivalently in the matrix form as

$$\begin{bmatrix} \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, I \in m} \\ \left\langle \prod_{i=l+1}^m u_{i-1,i} \right\rangle_{\text{conf}, H \in m} \end{bmatrix} = D \begin{bmatrix} \left\langle \prod_{i=l+1}^{m-1} u_{i-1,i} \right\rangle_{\text{conf}, I \in (m-1)} \\ \left\langle \prod_{i=l+1}^{m-1} u_{i-1,i} \right\rangle_{\text{conf}, H \in (m-1)} \end{bmatrix} \quad (\text{for } m = l+2, l+3, \dots), \quad (3.51)$$

where

$$D = \begin{bmatrix} \rho u_{II} & (1 - \rho) u_{IH} \\ \rho u_{IH} & (1 - \rho) u_{HH} \end{bmatrix}. \quad (3.52)$$

Note that the matrix  $D$  is not Hermitian. Using

$$\begin{bmatrix} \langle u_{i,i+1} \rangle_{\text{conf}, I \in (i+1)} \\ \langle u_{i,i+1} \rangle_{\text{conf}, H \in (i+1)} \end{bmatrix} = D \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \quad (3.53)$$

substituting the result obtained by iterating Eq.

(3.51) into Eq. (3.48), and noting  $\omega_{i,i}^{(\alpha)} = 1$  and  $\omega_{m,i}^{(\alpha)} = \omega_{i,m}^{(\alpha)}$ , we obtain for  $\omega_{i,m}^{(\alpha)}$

$$\omega_{i,m}^{(\alpha)} = [\rho, 1 - \rho] D^{l-m} \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \quad (3.54)$$

which, as in the case of the bond model, depends only on  $|l - m|$ .

We now introduce the matrix  $R$  which diagonalizes the matrix  $D$ , i.e.,

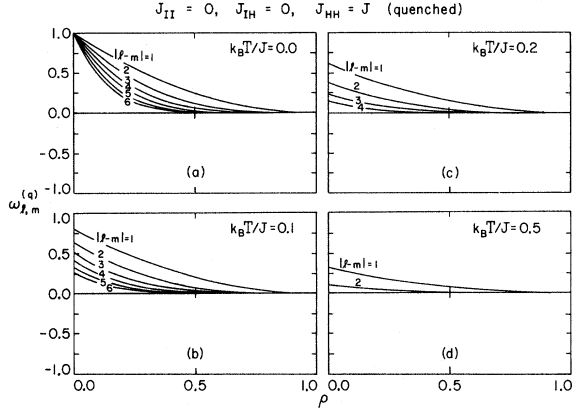


FIG. 7. Same as Fig. 6 but for  $\omega_{l,m}^{(q)}$  ( $1 \ll l \neq m \ll N$ ) in the quenched limit.

$$R^{-1}DR = \begin{bmatrix} d_+ & 0 \\ 0 & d_- \end{bmatrix}, \quad R^{-1}R = RR^{-1} = E, \quad (3.55)$$

where  $d_{\pm}$  are the eigenvalues of the matrix  $D$  and  $E$  is, as before, the  $2 \times 2$  unit matrix. The eigenvalues  $d_{\pm}$  are given by

$$d_+ = \rho u_{II}, \quad d_- = (1 - \rho)u_{HH} \quad (\text{for } J_{IH} = 0), \quad (3.56)$$

and

$$d_{\pm} = \frac{1}{2}(\rho u_{II} + (1 - \rho)u_{HH} \pm \{[\rho u_{II} - (1 - \rho)u_{HH}]^2 + 4\rho(1 - \rho)u_{IH}^2\}^{1/2}) \quad (\text{for } J_{IH} \neq 0). \quad (3.57)$$

Note that the absolute values of  $d_{\pm}$  are smaller than unity. The explicit expressions for  $R$  and  $R^{-1}$  are

$$R = R^{-1} = E \quad (\text{for } J_{IH} = 0) \quad (3.58)$$

and

$$R = \begin{bmatrix} (1 - \rho)u_{IH} & (1 - \rho)u_{IH} \\ d_+ - \rho u_{II} & d_- - \rho u_{II} \end{bmatrix},$$

$$R^{-1} = \frac{1}{(1 - \rho)u_{IH}(d_+ - d_-)} \begin{bmatrix} -d_- + \rho u_{II} & (1 - \rho)u_{IH} \\ d_+ - \rho u_{II} & -(1 - \rho)u_{IH} \end{bmatrix} \quad (\text{for } J_{IH} \neq 0). \quad (3.59)$$

The spin-spin correlation function  $\omega_{l,m}^{(q)}$  of Eq. (3.54) can be rewritten in terms of  $R$ ,  $R^{-1}$ , and  $d_{\pm}$  as

$$\omega_{l,m}^{(q)} = [\rho R_{11} + (1 - \rho)R_{21}][R_{11}^{-1} + R_{21}^{-1}]d_+^{l-m-1} + [\rho R_{12} + (1 - \rho)R_{22}][R_{21}^{-1} + R_{22}^{-1}]d_-^{l-m-1}. \quad (3.60)$$

It is now easy to calculate the zero field susceptibility  $\chi^{(q)}$  in the quenched limit. The result is given by

$$\chi^{(q)} = \frac{Ng^2 \mu_B^2}{12k_B T} \left( [\rho R_{11} + (1 - \rho)R_{21}][R_{11}^{-1} + R_{12}^{-1}] \frac{1 + d_+}{1 - d_+} \right. \quad (3.61)$$

$$\left. + [\rho R_{12} + (1 - \rho)R_{22}][R_{21}^{-1} + R_{22}^{-1}] \frac{1 + d_-}{1 - d_-} \right), \quad (3.61)$$

where we have again assumed that the  $g$  factor of the  $I$  ion and that of the  $H$  ion are equal to one another.

#### IV. RESULTS OF THE CALCULATION AND DISCUSSION

##### A. Bond model

We first discuss the results of the calculation for the bond model. In Fig. 1 the numerical results of the spin-spin correlation function  $\omega_{l,m}$  obtained for the case where two exchange constants  $J_I$  and  $J_H$  are given by  $J_I = -J$  and  $J_H = J$  (hereafter we use  $J$  which is always positive as the unit of energy) at representative values of the distance  $|l - m|$  between two sites,  $l$  and  $m$ , and of the reduced temperature  $k_B T/J$  are plotted as functions of the concentration  $\rho$  of the  $I$  bond. We also plot in Fig. 2 as functions of  $k_B T/J$  the numerical results of the zero-field susceptibility  $\chi$  for this case at representative values of  $\rho$ . The low-temperature expansion of  $\chi$  for this case is given by

$$\chi = \begin{cases} \chi_0 \left( \frac{2(1 - \rho)}{\rho} K - \frac{1 - 2\rho}{\rho^2} + \frac{(1 - 2\rho)^2}{2\rho^3} \frac{1}{K} + \dots \right) & \text{for } 0 < \rho \leq 1, \\ \chi_0 (4K^2 - 2K + \dots) & \text{for } \rho = 0, \end{cases} \quad (4.1)$$

where  $\chi_0 = Ng^2 \mu_B^2 / 12J$  and  $K = J / 2k_B T$ . It is to be noted here that  $\omega_{l,m}$  and  $\chi$  for  $\rho = \frac{1}{2}$  of this case are expressed as

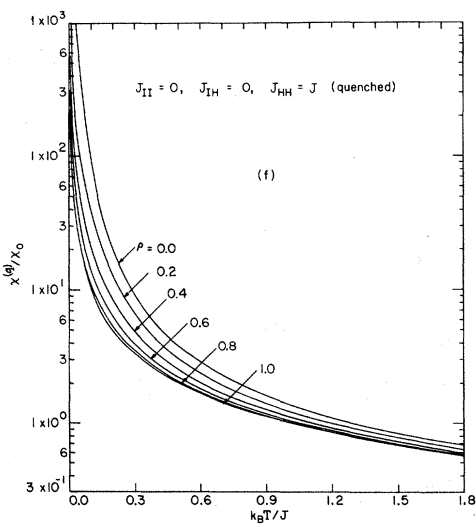
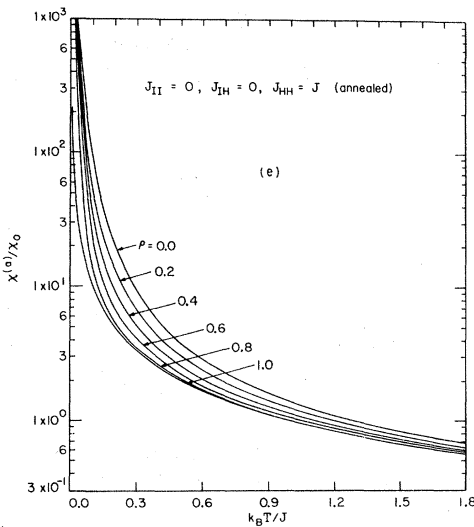
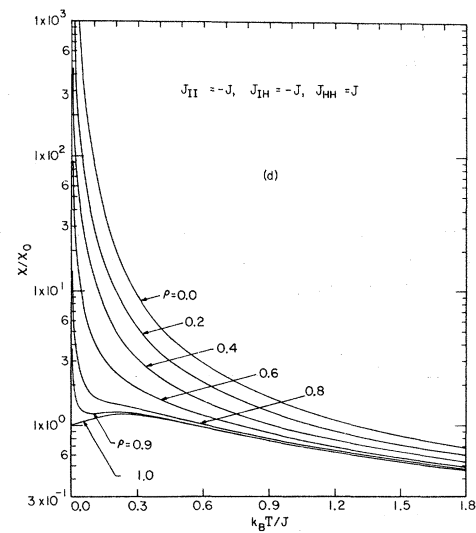
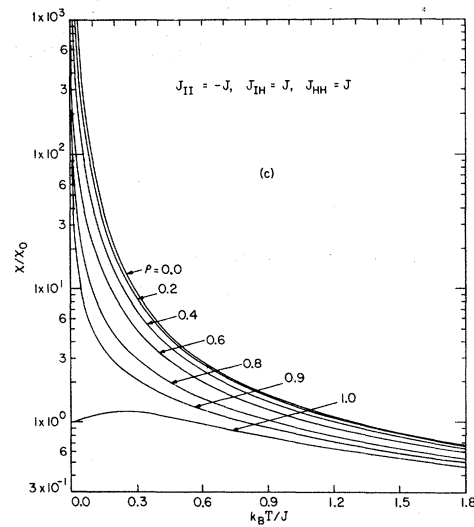
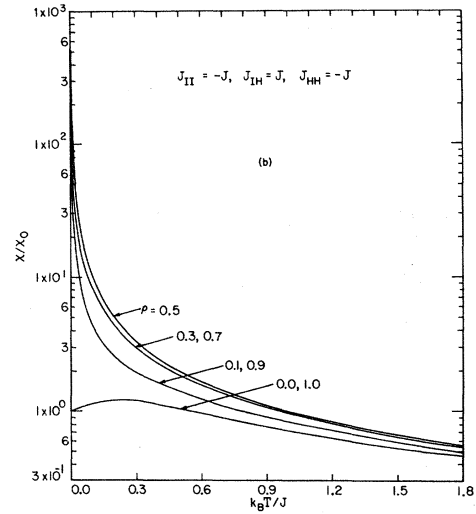
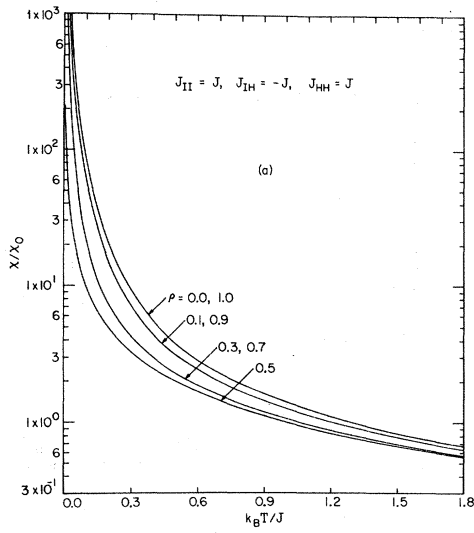
$$\omega_{l,m} = \begin{cases} 1 & \text{for } l = m, \\ 0 & \text{for } l \neq m, \end{cases} \quad (4.2)$$

and

$$\chi = \frac{Ng^2 \mu_B^2}{12k_B T}, \quad (4.3)$$

and that these results agree precisely with those for the noninteracting spin system in which  $J_I = J_H = 0$ . Since the specific heat at constant concentration depends only on the absolute values of  $J_I$  and  $J_H$ , the result of the specific heat for the case of  $J_I = -J$  and  $J_H = J$  is equal, for all values of  $\rho$ , to that of the specific heat for the pure ferro- or antiferromagnetic case with the exchange constant  $J$  or  $-J$ , respectively, which has already been obtained by Fisher.<sup>5</sup>

As can be easily seen from Eqs. (2.17), (2.18), and (2.20) and the fact that if  $J_I = 0$ , then  $u_I = 0$ , the spin-spin correlation function  $\omega_{l,m}$  and the zero-field susceptibility  $\chi$  for the case of  $J_I = 0$  and  $J_H = J$  are obtained, respectively, by replacing  $\rho$  (with the values of  $0 \leq \rho \leq \frac{1}{2}$ ) in  $\omega_{l,m}$  and  $\chi$  for the case of  $J_I = -J$  and  $J_H = J$ , which we have discussed above, by  $\frac{1}{2}\rho$ . Similarly,  $\omega_{l,m}$  and  $\chi$  for the case of  $J_I = 0$  and  $J_H = -J$  can be obtained, respectively, by replacing  $\rho$  (with the values of  $\frac{1}{2} \leq \rho \leq 1$ ) in  $\omega_{l,m}$  and  $\chi$  for the



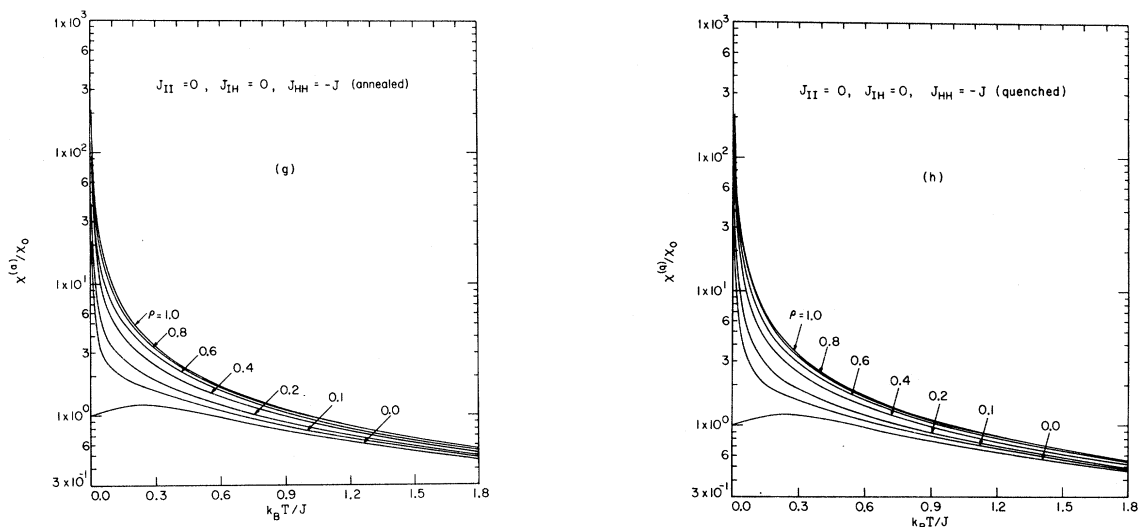


FIG. 8. Zero-field susceptibility  $\chi^{(a)}/\chi_0$  or  $\chi^{(a)}/\chi_0$  ( $\chi_0 = Ng^2\mu_B^2/12J$ ) as a function of temperature in the site model: (a)  $J_{II}=J$ ,  $J_{IH}=-J$ , and  $J_{HH}=J$ ; (b)  $J_{II}=-J$ ,  $J_{IH}=J$ , and  $J_{HH}=-J$ ; (c)  $J_{II}=-J$ ,  $J_{IH}=J$ , and  $J_{HH}=J$ ; (d)  $J_{II}=-J$ ,  $J_{IH}=-J$ , and  $J_{HH}=J$ ; (e)  $J_{II}=0$ ,  $J_{IH}=0$ , and  $J_{HH}=J$  in the annealed limit; (f)  $J_{II}=0$ ,  $J_{IH}=0$ , and  $J_{HH}=J$  in the quenched limit; (g)  $J_{II}=0$ ,  $J_{IH}=0$ , and  $J_{HH}=-J$  in the annealed limit; (h)  $J_{II}=0$ ,  $J_{IH}=0$ , and  $J_{HH}=-J$  in the quenched limit. Labels on the individual curves denote the values of  $\rho$ . Note that when  $|J_{II}| = |J_{IH}| = |J_{HH}|$ ,  $\chi^{(a)} = \chi^{(a)}$  ( $=\chi$ ) (a, b, c, d).

case of  $J_I = -J$  and  $J_H = J$  by  $1 - \frac{1}{2}\rho$ . The specific heat  $C$  at constant concentration for the cases of  $J_I = 0$  and  $|J_H| = J$  is shown in Fig. 3 as a function of  $k_B T/J$  for representative values of  $\rho$ .

B. Site model

Let us now turn to the site model. Before going into the discussion of the numerical results, we

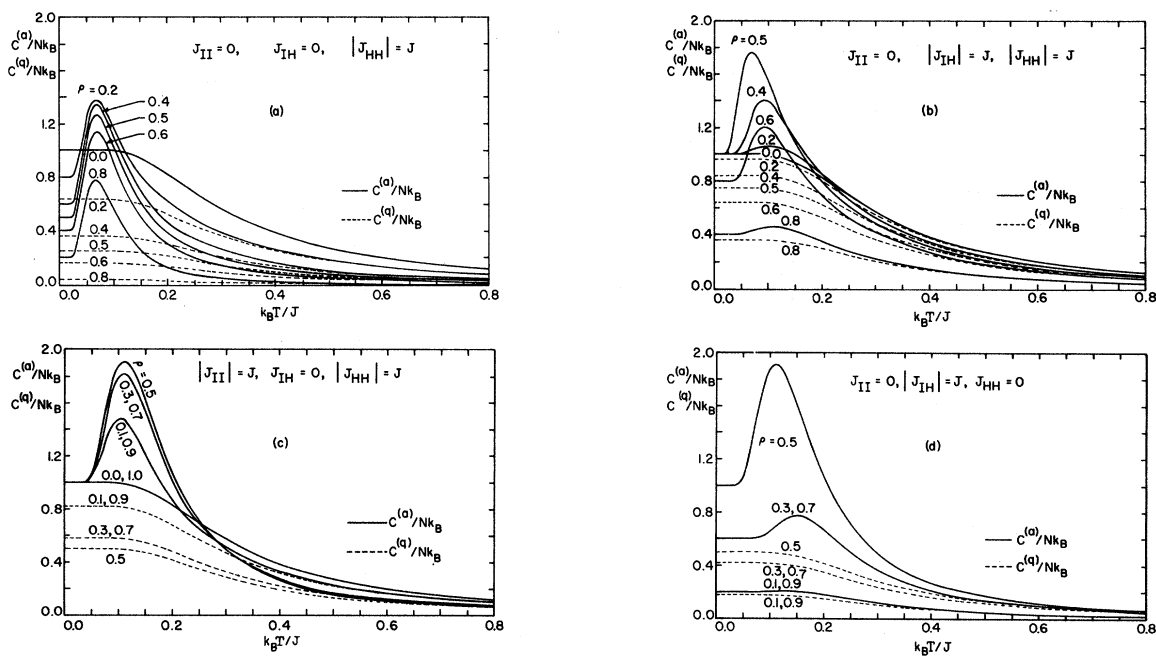


FIG. 9. Specific heat  $C^{(a)}/Nk_B$  at constant concentration of  $I$  ions in the annealed limit of the site model (solid lines) and specific heat  $C^{(a)}/Nk_B$  at constant concentration of  $I$  ions in the quenched limit of this model (dotted lines) as functions of temperature: (a)  $J_{II}=0$ ,  $J_{IH}=0$ , and  $|J_{HH}|=J$ ; (b)  $J_{II}=0$ ,  $|J_{IH}|=J$ , and  $|J_{HH}|=J$ ; (c)  $|J_{II}|=J$ ,  $J_{IH}=0$ , and  $|J_{HH}|=J$ ; (d)  $J_{II}=0$ ,  $|J_{IH}|=J$ , and  $J_{HH}=0$ . Labels on the individual curves denote the values of  $\rho$ .

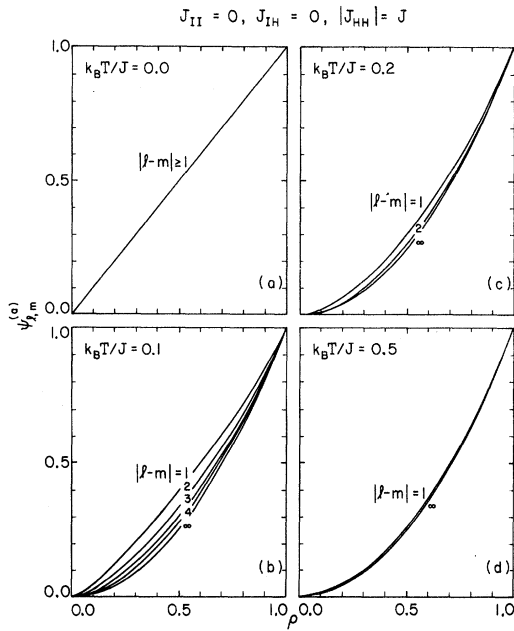


FIG. 10. Density-density correlation function  $\psi_{l,m}^{(a)}$  ( $1 \ll l \neq m \ll N$ ) for the  $I$  ion as a function of concentration of  $I$  ions for  $J_{II}=0$ ,  $J_{IH}=0$ , and  $|J_{HH}|=J$  in the annealed limit of the site model: (a)  $k_B T/J=0.0$ ; (b)  $k_B T/J=0.1$ ; (c)  $k_B T/J=0.2$ ; (d)  $k_B T/J=0.5$ . Labels on the individual curves denote the values of  $|l-m|$ . The curves for  $|l-m|=\infty$  are the  $\rho^2$  curves. Note that  $\psi_{l,l}^{(a)}=\rho$  for all temperatures.

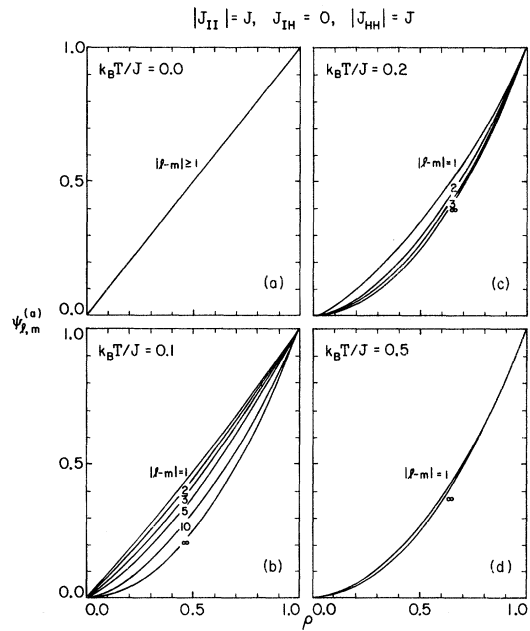


FIG. 12. Same as Fig. 10 but for  $|J_{II}|=J$ ,  $J_{IH}=0$ , and  $|J_{HH}|=J$ .

mention that for the special cases where  $|J_{II}| = |J_{IH}| = |J_{HH}|$ , the annealed and quenched limits lead to the same results, even in the site model, for the internal energy, the specific heat at constant concentration, the spin-spin correlation function, and the zero-field susceptibility. In connec-

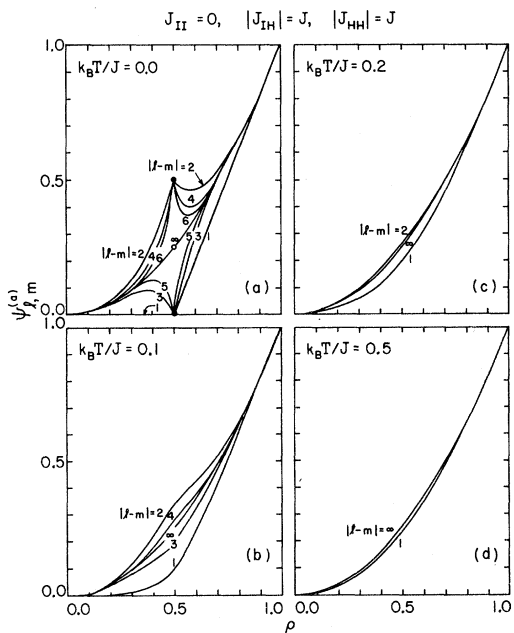


FIG. 11. Same as Fig. 10 but for  $J_{II}=0$ ,  $|J_{IH}|=J$ , and  $|J_{HH}|=J$ . We note that  $\psi_{l,m}^{(a)}$  in Fig. 11(a) coincides with that in Fig. 13(a).

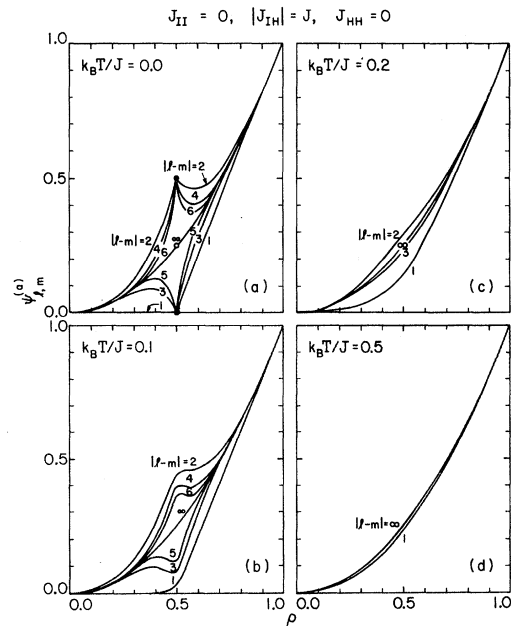


FIG. 13. Same as Fig. 10 but for  $J_{II}=0$ ,  $|J_{IH}|=J$ , and  $J_{HH}=0$ . We note that  $\psi_{l,m}^{(a)}$  in Fig. 13(a) coincides with that in Fig. 11(a).

TABLE I. Low-temperature expansion of the zero-field susceptibility  $\chi^{(a)}/\chi_0$  ( $\chi_0 = Ng^2 \mu_B^2 / 12J$ ) in the annealed limit of the site model and that of the zero-field susceptibility  $\chi^{(a)}/\chi_0$  in the quenched limit of this model. Here  $K = J/2k_B T$ . Note that when  $|J_{II}| = |J_{IH}| = |J_{HH}|$ ,  $\chi^{(a)} = \chi^{(a)}$ .

$J_{II}$	$J_{IH}$	$J_{HH}$	$\chi^{(a)}/\chi_0$	$\chi^{(a)}/\chi_0$
$J$	$J$	$J$	$4K^2 - 2K + \dots$	
$-J$	$-J$	$-J$	$1 + 1/2K + \dots$	
$J$	$-J$	$J$	$4(1-2\rho)^2 K^2 - 2[1-8\rho(1-\rho)]K + \dots$	
$-J$	$J$	$-J$	$8\rho(1-\rho)K + (1-2\rho)^2 + \dots$	
$-J$	$J$	$J$	$\begin{cases} \frac{2(1-\rho)(1+3\rho)}{\rho^2} K - \frac{1+4\rho-2\rho^2-8\rho^3+4\rho^4}{\rho^4} + \dots & (0 < \rho \leq 1) \\ 4K^2 - 2K + \dots & (\rho = 0) \end{cases}$	
$-J$	$-J$	$J$	$\begin{cases} \frac{2(1-\rho)^2}{\rho^2} K - \frac{1-6\rho^2+8\rho^3-4\rho^4}{\rho^4} + \dots & (0 < \rho \leq 1) \\ 4K^2 - 2K + \dots & (\rho = 0) \end{cases}$	
0	0	$J$	$(1-\rho)(4K^2 - 2K + \dots) + \rho(2K + \dots)$	$\begin{cases} \frac{2(2-3\rho+2\rho^2)}{\rho} K - \frac{4(1-\rho)^2}{\rho^2} + \dots & (0 < \rho \leq 1) \\ 4K^2 - 2K + \dots & (\rho = 0) \end{cases}$
0	0	$-J$	$\rho(2K + \dots) + (1-\rho)(1+1/2K + \dots)$	$\frac{2\rho(3-2\rho)}{2-\rho} K + \frac{4(1-\rho)^2}{(2-\rho)^2} + \dots$
0	$J$	$J$	$\begin{cases} 4K^2 - 2K + \dots & (0 \leq \rho \leq 1/2) \\ -\frac{2(1+4\rho-4\rho^2)}{1-2\rho} K - \frac{16\rho(1-\rho)}{(1-2\rho)^2} + \dots & (1/2 < \rho \leq 1) \end{cases}$	$\begin{cases} \frac{2(2+2\rho-3\rho^2)}{\rho^2} K - \frac{4(1-\rho^2)(1+2\rho-\rho^2)}{\rho^4} + \dots & (0 < \rho \leq 1) \\ 4K^2 - 2K + \dots & (\rho = 0) \end{cases}$
0	$J$	$-J$	$\begin{cases} \frac{8\rho(1-\rho)}{1-2\rho} K + \frac{1-8\rho+8\rho^2}{(1-2\rho)^2} + \dots & (0 \leq \rho < 1/2) \\ 4K^2 - 2K + \dots & (\rho = 1/2) \\ -\frac{2(1+4\rho-4\rho^2)}{1-2\rho} K - \frac{16\rho(1-\rho)}{(1-2\rho)^2} + \dots & (1/2 < \rho \leq 1) \end{cases}$	$\frac{2\rho(8-7\rho)}{2-2\rho+\rho^2} K + \frac{4(1-\rho^2)(1-6\rho+3\rho^2)}{4-8\rho+8\rho^2-4\rho^3+\rho^4} + \dots$
0	$-J$	$J$	$\begin{cases} 4(1-2\rho)^2 K^2 - 2(1-2\rho)(1-6\rho+4\rho^2)K + 16\rho^2(1-\rho)^2 + \dots & (0 \leq \rho \leq 1/2) \\ -2(1-2\rho)K - \frac{4\rho(1-\rho)}{1-2\rho} \frac{1}{K} + \dots & (1/2 < \rho \leq 1) \end{cases}$	$\begin{cases} \frac{2(2-6\rho+5\rho^2)}{\rho^2} K - \frac{4(1-\rho)^2(1-3\rho^2)}{\rho^4} + \dots & (0 < \rho \leq 1) \\ 4K^2 - 2K + \dots & (\rho = 0) \end{cases}$
0	$-J$	$-J$	$\begin{cases} 1 + \frac{1}{2K} + \dots & (0 \leq \rho \leq 1/2) \\ -2(1-2\rho)K - \frac{4\rho(1-\rho)}{1-2\rho} \frac{1}{K} + \dots & (1/2 < \rho \leq 1) \end{cases}$	$\frac{2\rho^2}{2-2\rho+\rho^2} K + \frac{4(1-\rho)^2(1+\rho^2)}{4-8\rho+8\rho^2-4\rho^3+\rho^4} + \dots$
$J$	0	$J$	$4K^2 - 2K + \dots$	$\begin{cases} \frac{2[2-5\rho(1-\rho)]}{\rho(1-\rho)} K - \frac{4[\rho^4+(1-\rho)^4]}{\rho^2(1-\rho)^2} + \dots & (0 < \rho < 1) \\ 4K^2 - 2K + \dots & (\rho = 0, 1) \end{cases}$
$-J$	0	$J$	$(1-\rho)(4K^2 - 2K + \dots) + \rho(1+1/2K + \dots)$	$\begin{cases} \frac{2(1-\rho)(2+\rho)}{\rho(1+\rho)} K - \frac{4(1-2\rho^2)}{\rho^2(1+\rho)^2} + \dots & (0 < \rho \leq 1) \\ 4K^2 - 2K + \dots & (\rho = 0) \end{cases}$
$-J$	0	$-J$	$1 + 1/2K + \dots$	$\frac{6\rho(1-\rho)}{(1+\rho)(2-\rho)} K + \frac{4[1+2\rho^2(1-\rho)^2]}{(1+\rho)^2(2-\rho)^2} + \dots$
0	$J$	0	$\begin{cases} \frac{2[1+4\rho(1-\rho)]}{ 1-2\rho } K - \frac{16\rho(1-\rho)}{(1-2\rho)^2} + \dots & (\rho \neq 1/2) \\ 4K^2 - 2K + \dots & (\rho = 1/2) \end{cases}$	$\frac{2[1+5\rho(1-\rho)]}{1-\rho(1-\rho)} K - \frac{8\rho(1-\rho)[2+\rho(1-\rho)]}{[1-\rho(1-\rho)]^2} + \dots$
0	$-J$	0	$\begin{cases} 2 1-2\rho K + \frac{4\rho(1-\rho)}{ 1-2\rho } \frac{1}{K} + \dots & (\rho \neq 1/2) \\ 1 + \frac{1}{2K} + \dots & (\rho = 1/2) \end{cases}$	$\frac{2[1-3\rho(1-\rho)]}{1-\rho(1-\rho)} K + \frac{8\rho^2(1-\rho)^2}{[1-\rho(1-\rho)]^2} + \dots$

tion with this fact we note that the density-density correlation function  $\psi_{l,m}^{(a)}$  ( $1 \ll l \neq m \ll N$ ) for the  $I$  ion in the annealed limit, which is given by Eq. (3.32), becomes for these special cases as

$$\psi_{l,m}^{(a)} = \rho^2 \quad (\text{for } 1 \ll l \neq m \ll N), \quad (4.4)$$

where  $\rho$  is the concentration of the  $I$  ion. Furthermore, we mention here that the specific heats at constant concentration for the special cases of  $|J_{II}| = |J_{IH}| = |J_{HH}| = J$  are the same, for all values of  $\rho$ , as that for the pure ferro- or antiferromagnet with the exchange constant  $J$  or  $-J$ , respectively.

The numerical calculation in the site model is performed for the cases of  $|J_{II}| = |J_{IH}| = |J_{HH}| = J$ ;  $J_{II} = J_{IH} = 0$  and  $|J_{HH}| = J$ ;  $J_{II} = 0$  and  $|J_{IH}| = |J_{HH}| = J$ ;  $|J_{II}| = J$ ,  $J_{IH} = 0$ , and  $|J_{HH}| = J$ ; and  $J_{II} = 0$ ,  $|J_{IH}| = J$ , and  $J_{HH} = 0$  both in the annealed and in the quenched limit. A part of the results is summarized in Figs. 4(a)–7(d) (spin-spin correlation function), Figs. 8(a)–(h) (zero-field susceptibility), Figs. 9(a)–(d) (specific heat at constant concentration), and in Figs. 10(a)–13(d) (density-density correlation function for the  $I$  ion). Table I tabulates the low-temperature expansions of the zero-field susceptibilities for various combinations of the exchange constants mentioned above. We are now ready to discuss the results obtained in the site model.

(i) It is interesting to look at Table I to examine, by attention to the difference between the annealed and quenched limits, how the low-temperature behavior of the zero-field susceptibility in the mixtures varies with concentration. This point will be further discussed for special cases in (v).

(ii) Note that when  $\rho = \frac{1}{2}$ , as in the case of the bond model with  $J_I = -J$  and  $J_H = J$ , the spin-spin correlation function and the zero-field susceptibility in the case of  $J_{II} = J$ ,  $J_{IH} = -J$ , and  $J_{HH} = J$  coincide with those in the noninteracting spin system. This is because when  $\rho = \frac{1}{2}$  the probability that the exchange constant associated with an arbitrarily given nearest-neighboring pair of sites is  $J$  (or  $-J$ ) is  $\frac{1}{2}$  also for the random arrangement of the  $I$  and  $H$  ions. For the same reason, the spin-spin correlation function and the zero-field susceptibility in the case of  $J_{II} = -J$ ,  $J_{IH} = J$ , and  $J_{HH} = -J$  with  $\rho = \frac{1}{2}$  agree with those in the noninteracting spin system.

(iii) Here we consider the cases of  $J_{II} = J_{IH} = 0$

and  $|J_{HH}| = J$ ;  $J_{II} = 0$  and  $|J_{IH}| = |J_{HH}| = J$ ;  $|J_{II}| = J$ ,  $J_{IH} = 0$ , and  $|J_{HH}| = J$ ; and  $J_{II} = 0$ ,  $|J_{IH}| = J$ , and  $J_{HH} = 0$ . The results of the numerical calculations show that for all of these cases, roughly speaking, the difference between the annealed and quenched limits becomes predominant at temperatures lower than  $T \sim J/2k_B$ . This feature is seen most clearly from Figs. 10(d), 11(d), 12(d), and 13(d), which demonstrate that when  $T = J/2k_B$ , the density-density correlation function  $\psi_{l,m}^{(a)}$  of the  $I$  ion in the limit of  $1 \ll l \neq m \ll N$  is almost equal to  $\rho^2$  even for  $|l - m| = 1$ .

(iv) We consider again the same cases as those in (iii). Figures 9(a)–(d) show that the specific heat at constant concentration for  $0 < \rho < 1$  in the annealed limit has a maximum at a finite temperature. We believe that this maximum is due to the short-range ordering of the  $I$  and  $H$  constituent ions. Note that the difference between the maximum value of the specific heat and its value at absolute zero temperature becomes largest at  $\rho = \frac{1}{2}$ .

(v) Finally we discuss the cases of  $J_{II} = 0$  and  $|J_{IH}| = |J_{HH}| = J$  with  $\rho = \frac{1}{2}$  and of  $J_{II} = 0$ ,  $|J_{IH}| = J$ , and  $J_{HH} = 0$  with  $\rho = \frac{1}{2}$ . In these cases the system has a minimum energy when the  $I$  and  $H$  ions are arranged alternately. Thus, as far as these cases are concerned, in the annealed limit where the true thermal equilibrium is realized, the system becomes at  $T = 0$  purely ferromagnetic when  $J_{IH} = J$  and purely antiferromagnetic when  $J_{IH} = -J$  irrespective of the values of  $J_{HH}$ . It should be noted that under these considerations we can understand very well the low-temperature behaviors of various quantities, which are shown in Figs. 9(b), 9(d), 11, and 13 and in Table I, for the cases of  $J_{II} = 0$  and  $|J_{IH}| = |J_{HH}| = J$  with  $\rho = \frac{1}{2}$  and of  $J_{II} = 0$ ,  $|J_{IH}| = J$ , and  $J_{HH} = 0$  with  $\rho = \frac{1}{2}$  in the annealed limit.

In conclusion, we mention that, as discussed in Sec. I, the results obtained here in the bond model as well as in the site model may be applied to mixtures of TMMC and TMNC or of their isomorphs. We hope that the present theory is helpful to understand the thermodynamic and magnetic properties of real one-dimensional magnetic alloys.

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- <sup>12</sup>Since, as will be shown later, the internal energy and the specific heat at constant concentration in the annealed limit of the bond model agree with those in the quenched limit of this model, we denote these without adding the superscript ( $a$ ) or ( $q$ ). Similar abbreviation will be also used later for the spin-spin correlation function and the zero-field susceptibility in the bond model.
- <sup>13</sup>Note that we have used Fisher's definition of the  $g$  factor (See Ref. 10).