

# Theory of the Random Magnetic Mixture. I

—*Ising System*—

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A theory of the random magnetic mixture of some kinds of Ising spins is formulated in terms of distribution functions which are introduced for the thermal averages of each kind of spins. The distribution functions are determined from a simultaneous non-linear integral equation of order  $n$ , where  $n$  is the number of kinds of spins.

By the use of this theory, the magnetic properties of a honeycomb lattice with two kinds of magnetic atoms are investigated. The ferromagnetic phase, the ferrimagnetic phase and the antiferromagnetic phase are obtained with respect to the types and concentrations of those atoms. The possibility of a new phase with the infinite susceptibility without the spontaneous magnetization is also conjectured. The magnetization process and phase transition in each phase are studied in detail.

## § 1. Introduction and summary

In a previous paper<sup>1)</sup> (referred to as I hereafter), a theory to obtain the magnetic properties of the one-dimensional random mixture composed of some kinds of Ising spins was given in terms of distribution functions and was applied to some binary mixtures. It was shown that the low temperature magnetization curves of the binary mixture have some steps when antiferromagnetic elements are included, and they increase abruptly with external magnetic field when ferromagnetic elements are included. These were discussed in detail from random nature of the system.

The main purposes of this paper are to develop a general theory for the random mixture of Ising spins by generalizing the idea of the distribution functions, and to study ordered phases and the magnetization processes of the random binary mixtures. The theory will be extended to the Heisenberg system in a next paper.

In § 2, a mathematical formulation is given in terms of the distribution functions. Since the thermal average of each element of the random mixture such as each spin and each spin pair on the lattice sites is at random corresponding to the random arrangement of atoms, it is natural to introduce distribution functions for those elements and to consider equations for those functions. Following this idea, we develop two approximation theories which correspond to molecular field theory and Bethe approximation theory in the regular system. In

both theories, the distribution function  $g_\alpha(\sigma)$  is introduced for the thermal average of the spin  $\sigma$  of  $\alpha$  atom. A simultaneous non-linear integral equation for the distribution functions is obtained.

The paramagnetic phase is considered in §3. The simultaneous integral equation is reduced to a simultaneous linear equation when magnetic field is low.<sup>2),3)</sup> The magnetization process is numerically investigated. It is shown that shapes of the magnetization curves are dependent on concentrations of magnetic bonds rather than kinds of magnetic atoms. It is also shown that our theories are generally in agreement with the previous approximation theories for the regular system when the system is in the paramagnetic phase and magnetic field is low.<sup>4)</sup>

In §4, ordered phases and the magnetization processes of the random binary mixtures of  $A$  and  $B$  atoms in the loose-packed lattice are numerically studied. We take a honeycomb lattice for simplicity. The ordered phases obtained are as follows: The ferromagnetic one when  $J_{AA}, J_{BB}, J_{AB} > 0$ , and  $J_{AA} > 0, J_{BB} < 0$  for  $p_A > p_B$ , the ferrimagnetic one when  $J_{AA}, J_{BB} > 0, J_{AB} < 0$ , and the antiferromagnetic one when  $J_{AA}, J_{BB} < 0$ , and  $J_{AA} > 0, J_{BB} < 0$ , for  $p_A < p_B$ , where  $J_{AA}, J_{BB}$  and  $J_{AB}$  are the exchange integrals of each spin pair of  $A$ - $A$  atoms,  $B$ - $B$  atoms and  $A$ - $B$  atoms, and  $p_A$  and  $p_B$  are concentrations of  $A$  and  $B$  atoms, respectively.

The magnetization process of each system is investigated in detail. It has information of both the ordered phase and random nature. The spontaneous magnetization and the first order phase transition are found when  $J_{AA}, J_{BB} > 0$  (except the case  $J_{AA} = J_{BB}, J_{AB} < 0, m_A = m_B$  and  $p_A = p_B$ ), and  $J_{AA} > 0, J_{BB} < 0$  for  $p_A > p_B$ , while the sublattice magnetizations and the second order phase transition caused by sublattice structure when  $J_{AA}, J_{BB} < 0$ , and  $J_{AA} > 0, J_{BB} < 0$  for  $p_A < p_B$ . We also find the second order phase transition when  $J_{AA} = J_{BB} (> 0), J_{AB} < 0, m_A = m_B$  and  $p_A = p_B$ , which is due to the symmetry of two kinds of magnetic atoms. The behavior of saturation process is also discussed from random nature of the mixture.

It is interesting to find a new phase where the susceptibility diverges while the spontaneous magnetization disappears when  $J_{AA} = -J_{BB}, m_A = m_B$  and  $p_A = p_B$ . This property resembles to that in the two-dimensional Heisenberg ferromagnet conjectured by Stanley and Kaplan.<sup>5)</sup> The origin of our phase is the cancellation of antiparallel two unstable magnetic moments contrary to the instability of the ferromagnetism in the Heisenberg system. It should be noted, however, the existence of this new phase is still open question, because we have used an assumption that the ordered phase is either ferromagnetic or antiferromagnetic in addition to use of an approximation theory.

Finally it is to be noted that our theory is one for the random mixtures (the quenched systems), and it is completely satisfied with requirements of the quenched system, i.e., the free energy of the quenched system is given as an average of free energies of various systems each of which has a possible con-

figuration of atoms.<sup>9)</sup> Our theory is exact so long as the thermal average is exactly treated. The Bethe approximation in our theory gives the exact result for the Bethe lattice (it contains the previous exact result for the one-dimensional mixture). The limits and the efficiencies of our theory are also dependent on the properties of approximation for the thermal average.

## § 2. Formulation

In this section an idea of the distribution functions for the problem of the random magnetic mixture is given and two approximation theories are developed.

We first consider the thermal averages of the spins on the lattice sites of a random binary mixture. The magnetization per lattice site of this mixture is given as an average of these thermal averages. The thermal averages have random values corresponding to the random arrangement of atoms. Therefore, it is necessary to take account of fluctuations of those values. Then we introduce distribution functions for the thermal averages of some elements of the system and consider equations for those functions. These correspond to some theories for the cooperative phenomena such as molecular field theory and Bethe approximation theory where some parameters are introduced with some consistency equations. These generalize the idea of the distribution functions used in I where the distribution functions are introduced as a technique of calculations.

To make this idea concrete, we firstly consider a zero-order approximation which corresponds to molecular field theory in the regular system (we call it the molecular field theory in the random mixture).

### (1) *Molecular field theory*

We consider an  $\alpha$  atom on a lattice site and  $\beta_1, \beta_2, \dots, \beta_z$  atoms on  $z$  neighboring sites. The thermal averages of the spins of those atoms are expressed as  $\sigma_0, \sigma_1, \dots, \sigma_z$ . They are connected by molecular field theory as

$$\sigma_0 = \tanh\left(C_\alpha + \sum_{i=1}^z K_{\alpha\beta_i} \sigma_i\right), \quad (2.1)$$

where  $C_\alpha = m_\alpha H/kT$ ,  $K_{\alpha\beta} = J_{\alpha\beta}/2kT$ , and  $m_\alpha, J_{\alpha\beta}, H, k$  and  $T$  are used in usual meaning (see I). The spins of those atoms are assumed as  $S=1/2$  and  $\sigma = 2\langle S^z \rangle$ . Equation (2.1) is the well known molecular field theory's when  $K_{\alpha\beta} = K$ ,  $C_\alpha = C$  and  $\sigma_i = \sigma$ .

Next, we introduce a distribution function  $g_\alpha(\sigma)$  for the thermal average of the spin  $\sigma$  of  $\alpha$  atom. The distribution function is normalized as

$$\int g_\alpha(\sigma) d\sigma = 1. \quad (2.2)$$

Using this distribution function, we obtain the average value of the spin of  $\alpha$  atom as

$$\bar{\sigma}_\alpha = \int \sigma g_\alpha(\sigma) d\sigma. \tag{2.3}$$

The magnetization per lattice site of the mixture is given by

$$\langle m\sigma \rangle = \sum_\alpha m_\alpha p_\alpha \bar{\sigma}_\alpha, \tag{2.4}$$

where  $p_\alpha$  is concentration of  $\alpha$  atoms.

Now, we consider an equation for the distribution functions. The probability of finding the thermal average of the spin of  $\alpha$  atom in an interval  $(\sigma, \sigma + \Delta\sigma)$  is given by  $g_\alpha(\sigma) \Delta\sigma$  from the definition of the distribution functions. On the other hand, it is also given by  $\sum_{\beta_1} p_{\beta_1} \cdots \sum_{\beta_z} p_{\beta_z} \int \cdots \int_{\mathcal{A}\sigma} \prod_{i=1}^z g_{\beta_i}(\sigma_i) d\mathcal{V}^*$  from Eq. (2.1), where  $\mathcal{A}\sigma$  is a region in  $(\sigma_1, \sigma_2, \dots, \sigma_z)$  space which is projected to the interval  $(\sigma, \sigma + \Delta\sigma)$  by the function (2.1). Then, in the limit  $\Delta\sigma \rightarrow 0$ , we obtain

$$g_\alpha(\sigma) = \sum_{\beta_1} \cdots \sum_{\beta_z} p_{\beta_1} \cdots p_{\beta_z} \lim_{\Delta\sigma \rightarrow 0} \frac{1}{\Delta\sigma} \int \cdots \int_{\mathcal{A}\sigma} \prod_{i=1}^z g_{\beta_i}(\sigma_i) d\mathcal{V}. \tag{2.5}$$

Equation (2.5) is a simultaneous non-linear integral equation for the distribution functions. This corresponds to consistency equations in molecular field theory. It requires the consistency of the distributions of molecular fields instead of the consistency of some definite values of molecular fields.

It is obvious that our theory contains ordinary molecular field theory in special case. A simultaneous equation for the average values of the spins of each kind of atoms in molecular field theory is given by

$$\bar{\sigma}_\alpha = \tanh(C_\alpha + z \sum_\beta p_\beta K_{\alpha\beta} \bar{\sigma}_\beta). \tag{2.6}$$

On the other hand, we have

$$\bar{\sigma}_\alpha = \sum_{\beta_1} \cdots \sum_{\beta_z} p_{\beta_1} \cdots p_{\beta_z} \int \cdots \int \tanh(C_\alpha + \sum_{i=1}^z K_{\alpha\beta_i} \sigma_i) \prod_{i=1}^z g_{\beta_i}(\sigma_i) d\mathcal{V} \tag{2.7}$$

from Eq. (2.5). Equation (2.7) reproduces Eq. (2.6) when  $K_{\alpha\beta} = K$  and  $C_\alpha = C$ , and both are rewritten as

$$\bar{\sigma}_\alpha = C_\alpha + z \sum_\beta p_\beta K_{\alpha\beta} \bar{\sigma}_\beta, \tag{2.8}$$

when  $T > T_c$  and  $H \sim 0$ . These facts shows that two theories may give qualitatively the same results when the system is composed of similar kinds of atoms, i.e.,  $C_\alpha \doteq C$  and  $J_{\alpha\beta} \doteq J$ , or when the system is in the paramagnetic phase and  $H \sim 0$ . The latter fact is discussed again in the next section.

(2) *Bethe approximation theory*

Next, we consider a first-order approximation which corresponds to the Bethe approximation. Here we consider the exact formulation for the Bethe

\*) Since the correlation of spins is neglected in the molecular field theory, the integrand is given as a product of independent  $z$  functions  $\prod_{i=1}^z g_{\beta_i}(\sigma_i)$ .

lattice, because of the simplicity of the succeeding calculations. The framework of the Bethe approximation will be given in the Appendix.

We consider an  $\alpha$  atom and neighboring  $\beta_1, \beta_2, \dots, \beta_z$  atoms on the Bethe lattice. The thermal average of the spin of the  $\alpha$  atom is given by

$$\sigma_0 = \frac{[\tanh C_\alpha + \sum_{i=1}^z x_i \tanh K_{\alpha\beta_i} + \sum_{i \neq j} x_i x_j \tanh K_{\alpha\beta_i} \tanh K_{\alpha\beta_j} \tanh C_\alpha + \dots + x_1 x_2 \dots x_z \tanh K_{\alpha\beta_1} \tanh K_{\alpha\beta_2} \dots \tanh K_{\alpha\beta_z} \tanh^{n(z)} C_\alpha]}{[1 + \sum_{i=1}^z x_i \tanh K_{\alpha\beta_i} \tanh C_\alpha + \sum_{i \neq j} x_i x_j \tanh K_{\alpha\beta_i} \tanh K_{\alpha\beta_j} + \dots + x_1 x_2 \dots x_z \tanh K_{\alpha\beta_1} \tanh K_{\alpha\beta_2} \dots \tanh K_{\alpha\beta_z} \tanh^{n(z-1)} C_\alpha]} \quad (2.9)$$

$$n(z) = [1 + (-1)^z] / 2,$$

where the  $x_i$  is the thermal average of the spin of the  $\beta_i$  atom when the  $\alpha$  atom on the central site is removed. The  $x_i$  is also determined by a recurrence relation

$$x_i = \frac{[\tanh C_{\beta_i} + \sum_{j=1}^{z-1} x_j \tanh K_{\beta_i\gamma_j} + \sum_{j \neq k} x_j x_k \tanh K_{\beta_i\gamma_j} \tanh K_{\beta_i\gamma_k} \tanh C_{\beta_i} + \dots + x_1 x_2 \dots x_{z-1} \tanh K_{\beta_i\gamma_1} \tanh K_{\beta_i\gamma_2} \dots \tanh K_{\beta_i\gamma_{z-1}} \tanh^{n(z-1)} C_{\beta_i}]}{[1 + \sum_{j=1}^{z-1} x_j \tanh K_{\beta_i\gamma_j} \tanh C_{\beta_i} + \sum_{j \neq k} x_j x_k \tanh K_{\beta_i\gamma_j} \tanh K_{\beta_i\gamma_k} + \dots + x_1 x_2 \dots x_{z-1} \tanh K_{\beta_i\gamma_1} \tanh K_{\beta_i\gamma_2} \dots \tanh K_{\beta_i\gamma_{z-1}} \tanh^{n(z-2)} C_{\beta_i}]} \quad (2.10)$$

Next, we also introduce a distribution function  $g_\alpha(x)$  for the thermal average  $x$  of  $\alpha$  atom. Using the similar discussion as in (1), we obtain a simultaneous integral equation

$$g_\alpha(x) = \sum_{\beta_1} \dots \sum_{\beta_{z-1}} p_{\beta_1} \dots p_{\beta_{z-1}} \lim_{\Delta x \rightarrow 0} \frac{1}{\Delta x} \int \dots \int_{\Delta v} \prod_{i=1}^{z-1} g_{\beta_i}(x_i) dv, \quad (2.11)$$

where  $\Delta v$  is a region in  $(x_1, x_2, \dots, x_{z-1})$  space which is projected to an interval  $(x, x + \Delta x)$  by the function (2.10). The average value of the spin of  $\alpha$  atom is given by

$$\bar{\sigma}_\alpha = \sum_{\beta_1} \dots \sum_{\beta_z} p_{\beta_1} \dots p_{\beta_z} \int \dots \int \sigma_\alpha(x_1, x_2, \dots, x_z) \prod_{i=1}^z g_{\beta_i}(x_i) dv, \quad (2.12)$$

where  $\sigma_\alpha(x_1, x_2, \dots, x_z)$  is the thermal average of the spin of the  $\alpha$  atom given by Eq. (2.9). The magnetization per lattice site of the mixture is given by Eq. (2.4). Equations (2.9) ~ (2.12) are completely in agreement with previous results when  $z=2$ .

The formulation developed in this section is more complicated than that in the Bethe approximation theory (Appendix). However it is more useful in the practical applications, because of the simplicity of the integral equation (2.11).

It is also to be noted that the formulation mentioned above is one for the ferromagnetic mixtures where  $J_{\alpha\alpha} > 0$ , i.e., each kind of atoms is ferromagnetic but interactions of them are not always ferromagnetic. The sublattice structure must be taken into account in the other cases. For those systems sublattice

distribution functions  $g_\alpha^u(x)$  and  $g_\alpha^d(x)$  are introduced. The simultaneous integral equation for those functions is given as follows:

$$\left. \begin{aligned} g_\alpha^u(x) &= \sum_{\beta_1} \cdots \sum_{\beta_{z-1}} p_{\beta_1} \cdots p_{\beta_{z-1}} \lim_{\Delta x \rightarrow 0} \frac{1}{\Delta x} \int \cdots \int \prod_{i=1}^{z-1} g_{\beta_i}^d(x_i) dv, \\ g_\alpha^d(x) &= \sum_{\beta_1} \cdots \sum_{\beta_{z-1}} p_{\beta_1} \cdots p_{\beta_{z-1}} \lim_{\Delta x \rightarrow 0} \frac{1}{\Delta x} \int \cdots \int \prod_{i=1}^{z-1} g_{\beta_i}^u(x_i) dv. \end{aligned} \right\} \quad (2.13)$$

We use Eqs. (2.9) ~ (2.13) in later sections.

### § 3. Disordered phase

We first consider the paramagnetic phase at  $H \sim 0$ . Equations (2.9) and (2.10) are rewritten as

$$\sigma_0 = \tanh C_\alpha + \sum_{i=1}^z x_i \tanh K_{\alpha\beta_i} \quad (3.1)$$

and

$$x_i = \tanh C_{\beta_i} + \sum_{j=1}^{z-1} x_j \tanh K_{\beta_i\gamma_j}. \quad (3.2)$$

Then using Eqs. (2.11) and (2.12), we obtain

$$\bar{\sigma}_\alpha = \tanh C_\alpha + z \sum_{\beta} p_\beta \bar{x}_\beta \tanh K_{\alpha\beta} \quad (3.3)$$

and

$$\bar{x}_\beta = \tanh C_\beta + (z-1) \sum_{\gamma} p_\gamma \bar{x}_\gamma \tanh K_{\beta\gamma}, \quad (3.4)$$

where

$$\bar{x}_\beta = \int x g_\beta(x) dx. \quad (3.5)$$

Equation (3.4) is a simultaneous linear equation for  $\bar{x}_\beta$ . Hence we can obtain the paramagnetic magnetization at  $H \sim 0$ . These equations are completely in agreement with those in previous papers where the paramagnetic susceptibility and the phase transition of the binary mixture are discussed in detail.<sup>2),3)</sup>

The integral equation is numerically solved when  $H \neq 0$ . The magnetization processes of the random mixtures of A and B atoms are shown in Fig. 1. Since the effect of the long range correlation

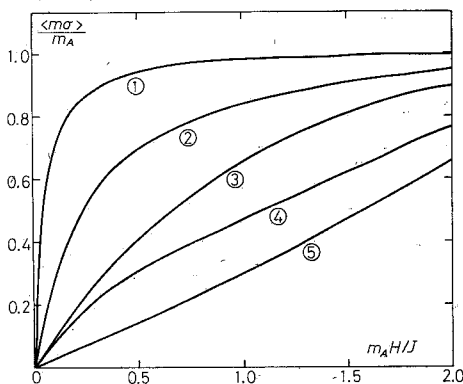


Fig. 1. The magnetization curves of random binary honeycomb lattices of  $m_A = m_B$  and  $p_A = p_B = 0.5$  when  $kT/J = 1$ . ① denotes the case  $J_{AA} = J_{BB} = J_{AB} = J (> 0)$ , ② the case  $J_{AA} = J_{AB} = -J_{BB} = J$ , ③ the case  $J_{AA} = J_{BB} = -J_{AB} = \pm J$ , ④ the case  $J_{AA} = -J_{BB} = -J_{AB} = J$ , ⑤ the case  $J_{AA} = J_{BB} = J_{AB} = -J$ .

does not play an important role in the paramagnetic phase, each magnetization curve increases smoothly with  $H$  and its shape is mainly dependent on concentrations of magnetic bonds. The shapes of the magnetization curves in the ordered phase have some patterns corresponding to the kinds of the magnetic atoms. These are discussed in detail in the next section.

Here we give a comment for the relation between our and previous approximation theories. It is already shown that ordinary molecular field theory gives the same results as ours when  $T > T_c$  and  $H \sim 0$ . It can be also shown that Eqs. (3.3) and (3.4) are also in agreement with those in ordinary Bethe approximation theory. These are not accidental. In both our and the previous theories, nature of randomness is taken into account as fluctuations of molecular fields which are small when  $T > T_c$  and  $H \sim 0$ . Then it gives the linear effects which are independent of the order of the averaging process (the thermal average for spins and the configurational average for atoms). Thus the equivalences are recognized. These may be also found in some of the other approximation theories.

#### § 4. Ordered phase

Let us next consider ordered phases of the random binary mixture in the loose-packed lattice. It was shown that the binary systems are distinguished to two groups with respect to the signs of the exchange integrals: (A)  $J_{AA}J_{BB}|J_{AB}| \geq 0$  and (B)  $J_{AA}J_{BB} < 0$ .<sup>2)</sup>

The group (A) is rather simple. The ground state can be easily determined. The transition temperature is generally independent of the signs of the exchange integrals, and is approximately given by

$$\{1 - p_A(z-1) \tanh |K_{AA}|\} \{1 - p_B(z-1) \tanh |K_{BB}|\} = p_A p_B (z-1)^2 \tanh^2 K_{AB}, \quad (4.1)$$

when  $H=0$ . The ordered phases are as follows: (1) the case  $J_{AA}, J_{BB}, J_{AB} > 0$ ; the ferromagnetic one, (2) the case  $J_{AA}, J_{BB} > 0, J_{AB} < 0$ ; the ferrimagnetic one where almost all spins of  $A$  atoms are arranged upward and almost all spins of  $B$  atoms downward, (3) the case  $J_{AA}, J_{BB}, J_{AB} < 0$ ; the antiferromagnetic one with  $\alpha$  and  $\beta$  sublattices, (4) the case  $J_{AA}, J_{BB} < 0, J_{AB} > 0$ ; the antiferromagnetic one where almost all spins of  $A$  atoms are arranged upward when they are on  $\alpha$  sublattice and downward when they are on  $\beta$  sublattice, while those of  $B$  atoms downward when they are on  $\alpha$  sublattice and upward when they are on  $\beta$  sublattice.

On the other hand, the group (B) is complex. The ground state has not yet been determined. The studies have been developed under an assumption that the ordered phase is either ferromagnetic or antiferromagnetic.<sup>3)</sup> The Curie temperature was approximately given by

$$\{1 - p_A(z-1) \tanh K_{AA}\} \{1 - p_B(z-1) \tanh K_{BB}\} = p_A p_B (z-1)^2 \tanh^2 K_{AB}, \quad (4.2)$$

and the Néel temperature by

$$\{1 + p_A(z-1)\tanh K_{AA}\} \{1 + p_B(z-1)\tanh K_{BB}\} = p_A p_B (z-1)^2 \tanh^2 K_{AB}. \quad (4.3)$$

In this paper, we discuss features of those phases from the magnetization process obtained from Eqs. (2.4), (2.11), (2.12) and (2.13). We take a honeycomb lattice ( $z=3$ ) for simplicity. The integral equation is numerically solved.

(1) The case  $J_{AA}, J_{BB}, J_{AB} > 0$ : The magnetization curves resemble to those of the ferromagnetic regular system with effective exchange integrals and effective magnetic moments.

(2) The case  $J_{AA}, J_{BB} > 0, J_{AB} < 0$ : Since the ordered phase is ferrimagnetic, the mixture has the spontaneous magnetization except when  $J_{AA} = J_{BB}, m_A = m_B$  and  $p_A = p_B$ . The magnetization curves are shown in Figs. 2 and 3. They have linear slopes and small hollows in addition to ferrimagnetic shapes when the temperature is low. These are due to successive flips of spin clusters of various sizes. The spontaneous magnetization disappears when  $J_{AA} = J_{BB}, m_A = m_B$  and  $p_A = p_B$ , because of the cancellation of antiparallel two magnetic moments. The first order phase transition is only possible in the former case (which is found at  $H=0$ ), while the second order phase transition is also possible in the latter case, because of possibility of a change of symmetry of two kinds of magnetic atoms. In fact, as shown in Fig. 6, we have the second order phase transition in the latter case.

(3) The case  $J_{AA}, J_{BB}, J_{AB} < 0$ : Since the ordered phase is completely antiferromagnetic when  $H=0$ , the magnetization curves behave as the antiferromagnetic ones at  $H \sim 0$ . The second order phase transition is found because of existence of sublattice structure. The magnetization curves are shown in Fig. 4. The linear slopes and the small hollows are also due to the flips of various spins.

(4) The case  $J_{AA}, J_{BB} < 0, J_{AB} > 0$ : The ordered phase is also antiferro-

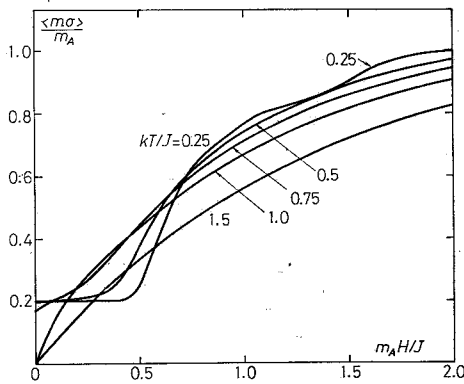


Fig. 2. The magnetization curves of a random binary honeycomb lattice of  $J_{AA} = J_{BB} = -J_{AB} = J (>0), m_A = m_B$  and  $p_A = 0.6, p_B = 0.4$ .

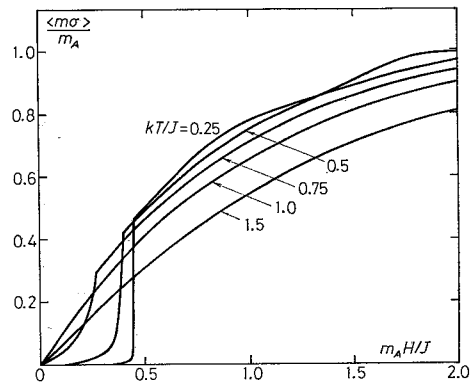


Fig. 3. The magnetization curves of a random binary honeycomb lattice of  $J_{AA} = J_{BB} = -J_{AB} = J (>0), m_A = m_B$  and  $p_A = p_B = 0.5$ .



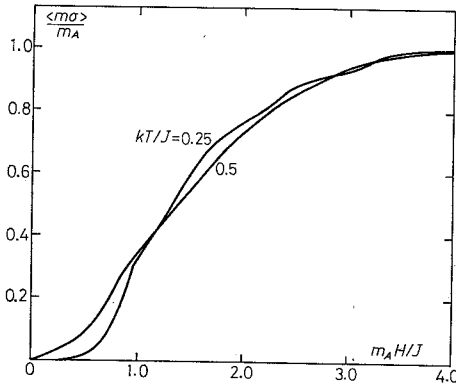


Fig. 4. The magnetization curves of a random binary honeycomb lattice of  $-J_{AA}/2 = -J_{BB} = -2J_{AB} = J (>0)$ ,  $m_A = m_B$  and  $p_A = p_B = 0.5$ .

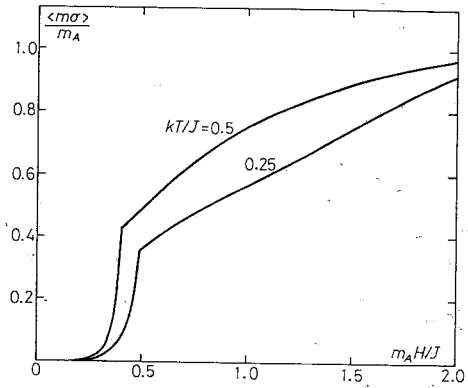


Fig. 5. The magnetization curves of a random binary honeycomb lattice of  $-J_{AA} = -J_{BB} = J_{AB} = J (>0)$ ,  $m_A = m_B$  and  $p_A = p_B = 0.5$ .

magnetic. The system has not spontaneous magnetization. The second order phase transition is also due to the existence of the sublattice structure. The magnetization curves are shown in Fig. 5. The low slopes of them in the paramagnetic phase ( $H > H_c$ ,  $H_c$  is the critical field) are due to successive flips of various spin clusters.

(5) The case  $J_{AA} > 0$ ,  $J_{BB} < 0$ : This case is most interesting. We calculate the magnetization curves through the assumption that the ordered phase is either ferromagnetic or antiferromagnetic. This assumption is supported from two ways; (1) it may be true when  $p_A \gg p_B$  or  $p_A \ll p_B$ , (2) the ordered phase with more complex sublattice structure may be unrealizable because of random arrangement of atoms. However, the possibility of more complex structures

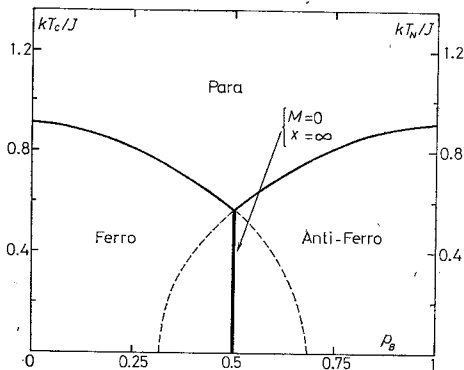


Fig. 6. The phase diagram of random binary mixtures of  $J_{AA} = -J_{BB} = |J_{AB}| = J (>0)$  and  $p_A + p_B = 1$  when  $H = 0$ .

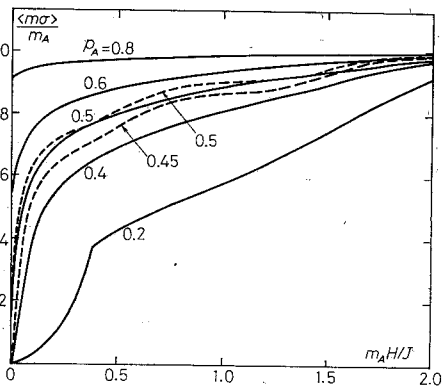


Fig. 7. The magnetization curves of random binary honeycomb lattices of  $J_{AA} = -J_{BB} = J_{AB} = J (>0)$ ,  $m_A = m_B$  and  $p_A + p_B = 1$  when  $kT/J = 0.5$  (solid curves) and  $0.25$  (dotted curves).

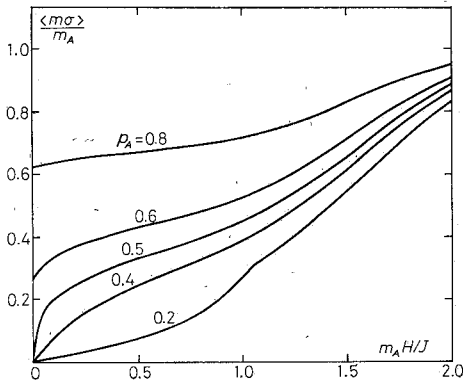


Fig. 8. The magnetization curves of random binary honeycomb lattices of  $J_{AA} = -J_{BB} = -J_{AB} = J (>0)$ ,  $m_A = m_B$  and  $p_A + p_B = 1$  when  $kT/J = 0.5$ .

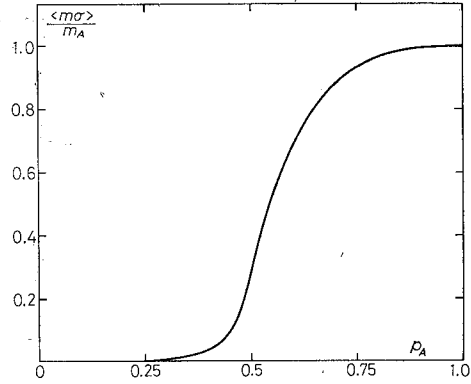


Fig. 9. The magnetizations of various random binary honeycomb lattices of  $J_{AA} = -J_{BB} = J_{AB} = J (>0)$ ,  $m_A = m_B$  and  $p_A + p_B = 1$  when  $kT/J = 0.25$  and  $m_A H/J = 0.01$ .

cannot be forbidden. In fact, the glass-like phase may be also one of the most realizable ones when  $p_A \neq p_B$ . The problems of the ground state and the structure of the ordered phase are still open questions. The phase diagram and the magnetization curves of binary mixtures with  $J_{AA} = -J_{BB} (>0)$  and  $m_A = m_B$  are shown in Figs. 6, 7 and 8. The magnetization curves have the spontaneous magnetizations when  $p_A > p_B$ , and the sublattice magnetization when  $p_A < p_B$ . The first order phase transition is found at  $H = 0$  in the former case, while the second order phase transition in the latter case. The bending of the magnetization curve at the critical field becomes smaller with  $p_A$  owing to the destruction of the sublattice structure. It is most interesting to observe that the zero field susceptibility increases anomalously with  $p_A$  near  $p_A \lesssim p_B$ , and diverges when  $p_A = p_B$  (see also Fig. 9). The latter fact generally indicates the possibility of a new ordered phase with the infinite susceptibility without the spontaneous magnetization. The critical temperature of this new phase may be approximately given by

$$p_A p_B (z - 1)^2 (\tanh K_{AA} \tanh |K_{BB}| + \tanh^2 K_{AB}) = 1. \quad (4.4)$$

This property resembles to that in the two-dimensional Heisenberg ferromagnet conjectured by Stanley and Kaplan. The origin of our new phase is, however, the cancellation of two unstable magnetic moments in contradiction to the thermal instability of the ferromagnetism in the Heisenberg system.

We have explained the magnetic behavior of the random binary Ising mixture in the loose-packed lattice with an example of a honeycomb lattice by using a new approximation theory. Although the honeycomb lattice is the simplest two-dimensional one and the reliability of our theory is the same as that of the Bethe approximation, the qualitative results mentioned above may be yet available for many of loose-packed lattices, for theories of the cooperative phenomena show a close resemblance of the magnetic behavior of the loose-packed lattices

and the qualitatively high validity of the Bethe approximation in the Ising system.

The numerical calculation has been done as follows: The continuous space  $x(-1 \leq x \leq 1)$  is replaced by the discontinuous space consisting of 31 points, the distribution of which is taken to be symmetric with respect to  $x$  and to be dense near  $x = -1, 1$  and rough near  $x = 0$ , the integral equation is solved by iteration method, the error is estimated as smaller than 1%, i.e., the convergence of the functions is judged by  $\int |g_{\alpha}^{i+1}(x) - g_{\alpha}^i(x)| dx \leq 0.002$  for all  $\alpha$ . Owing to complexity of the calculation we could not determine the fine behavior of the order parameter (sublattice magnetization) near the critical field. This may be important to study more detailed mechanism of the phase transition in the random mixture.

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### Appendix

The framework of the formulation of the Bethe approximation is given. We consider a cluster of  $\alpha$  atom and surrounding  $\beta_1, \beta_2, \dots, \beta_z$  atoms. The spins of  $\beta_1, \beta_2, \dots, \beta_z$  atoms take molecular fields  $H_1^*, H_2^*, \dots, H_z^*$  in addition to the external magnetic field  $H$ . Then the Hamiltonian of the cluster is given by

$$H = -2 \sum_{i=1}^z J_{\alpha\beta_i} S_0^z S_i^z - 2m_{\alpha} H S_0^z - \sum_{i=1}^z (2m_{\beta_i} H + H_i^*) S_i^z. \quad (\text{A}\cdot 1)$$

The expected values of each spin is given as

$$\sigma_0 = f_{\alpha}^0(C_{\alpha}, C_{\beta_1}, \dots, C_{\beta_z}, K_{\alpha\beta_1}, \dots, K_{\alpha\beta_z}, H_1^*, \dots, H_z^*), \quad (\text{A}\cdot 2)$$

$$\sigma_i = f_{\beta_i}^i(C_{\alpha}, C_{\beta_1}, \dots, C_{\beta_z}, K_{\alpha\beta_1}, \dots, K_{\alpha\beta_z}, H_1^*, \dots, H_z^*), \quad (\text{A}\cdot 3)$$

where  $\sigma_i = 2\langle S_i^z \rangle$ . Then eliminating  $H_1^*, H_2^*, \dots, H_z^*$ , we obtain

$$\sigma_0 = f(C_{\alpha}, C_{\beta_1}, \dots, C_{\beta_z}, K_{\alpha\beta_1}, \dots, K_{\alpha\beta_z}, \sigma_1, \dots, \sigma_z). \quad (\text{A}\cdot 4)$$

This corresponds to Eq. (2.1). Hence, we obtain the formulation of the Bethe approximation theory as Eq. (A.4) and Eqs. (2.2) ~ (2.5).

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