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Ising Lattices with Random Arrangements of Ferromagnetic and Antiferromagnetic Bonds

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A statistical model with decorated double bonds on each pair of the Ising spins is presented. The decorated Ising spin on one of the double bonds connects the neighboring Ising spins of the matrix lattice ferromagnetically and the other connects them antiferromagnetically.

The critical concentrations for the ferromagnetic or antiferromagnetic transitions are found for several types of lattices. The specific heat has a cusp at the Curie or Néel point. Dependence of Curie and Néel temperatures on the concentration ratio of ferromagnetic and antiferromagnetic components is obtained.

§ 1. Introduction

Recently, the magnetism of compounds and alloys are subjected to the experimental examinations and they are classified into several types of crystal structures, i.e. spiral-, magnetoplumbite-, perovskite-, NiAs- and corundum-type structures. We restrict ourselves to the magnetic crystals which consist of two or several kinds of magnetic materials such as MnSb-CrSb which is known as NiAs-type crystal, CoS_2-$CoSe_2$ which is the pyrite structure and Invar (which is famous for its small expansivity). The critical temperatures of them depend on the ratios of quantities of magnetic materials contained in the crystals.

Figure 1 shows the experimental results of some compounds, where T_C indicates the ferromagnetic transition temperature (Curie point) and T_N is the antiferromagnetic transition temperature (Néel point).

We must note that there are three different types of phase diagram. The first type (MnSb-CrSb) has the overlapping region between T_C and T_N curves, which shows that the compound can change the state from the ferro- to antiferro- and then to para-magnetic states as the temperature increases.[1] In the second type (Invar), T_C decreases as the concentration of Fe (f.c.c.) increases and vanishes at 65% of Fe. If we increase the concentration of Fe further, then T_N appears and increases with it.[2] The third type such as CoS_2-$CoSe_2$ shows a paramagnetic state at the intermediate concentration.[3]

Hirone, Maeda, Tsubokawa and Tsuya[1] have considered a mixed crystal of MnSb and CrSb, where the metallic ions are arranged in a form of simple hexagonal structure and non-metallic ions in a complex hexagonal structure.

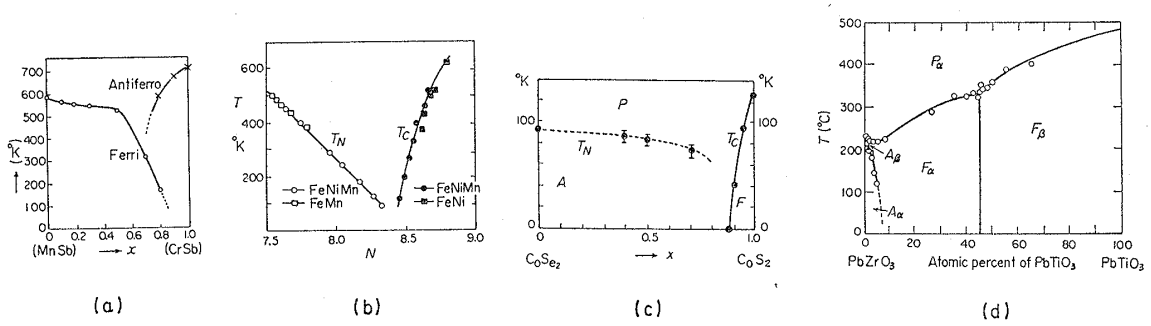

Fig. 1. Magnetic (electric) phase diagram of some compounds. (a) $(Cr_xMn_{1-x})Sb$ (after Hirone et al.[1]). (b) FeNiMn or Invar (after Shiga[2]). N; mean electron concentration. (c) $Co(S_xSe_{1-x})_2$ (after Adachi et al.[3]). (d) $Pb(TiO_3)_x(ZnO_3)_{1-x}$ (after Sawaguchi[4]).

They introduced a parameter which defines the direction of the total magnetic moment and calculated the magnetic energy of the system in the molecular field approximation. Further, they showed the occurence of complicated magnetic behavior at some fixed ratio of two magnetic ions. In this article, we consider the behavior of these compounds when the ratio of two components changes. The compound $PbZrO_3$-$PbTiO_3$[4] has also a similar property, but is more complicated than MnSb-CrSb or Invar.

Brout[5] proposed a statistical model of random ferromagnetic system with paramagnetic impurities and explained the qualitative property of the random system. In 1966, Syozi[6] proposed a model of the dilute ferromagnetism and calculated the critical concentration of non-magnetic impurities for the occurence of the phase transition. In the case of a square lattice, the system does not exhibit any cooperative phenomena if it contains the impurities more than 0.5 in concentration. In §§ 2~4 new models are proposed and their thermal properties are discussed. The Curie temperature of the ferromagnetic substance decreases as the antiferromagnetic component increases and at last it vanishes at the first critical concentration. Futhermore as the antiferromagnetic component increases, the Néel temperature appears at the second critical concentration and increases gradually. In § 5, a model with the anisotropic chemical potentials is presented.

§ 2. Ising lattice with double bonds

We should like to propose an Ising model with decorated double bonds between the nearest neighbor lattice sites of the matrix lattice (see Fig. 2). A decorated lattice point on one bond is called the A site and the other is called the B site. If an Ising spin is placed on the A site, it interacts with neighboring spins on the matrix lattice points with the same interaction parameters J and $J(J>0)$. If an Ising spin is set on the B site the interaction parameter with the spins of the both sides have opposite sign, i.e. J and $-J$. An occupation of A site by an Ising spin corresponds to the ferromagnetic coupling with respect to a pair of the neighboring spins of the matrix lattice and an occupation of

the B site corresponds to the antiferromagnetic coupling for the neighboring spins of the matrix lattice.

To every site of the matrix lattice, we attribute an Ising spin variable $\mu_i(=\pm 1)$, and to A and B sites, we attribute spin variables σ_{ij} and σ'_{ij} respectively which can take three values ± 1 or 0, where 0 corresponds to the absence of an Ising spin on the decorated site.

The grand partition function $\Xi(L;\xi,\xi')$ for this model will be reduced to the partition function $Z_0(K)$ of the ordinary Ising model for the matrix lattice.

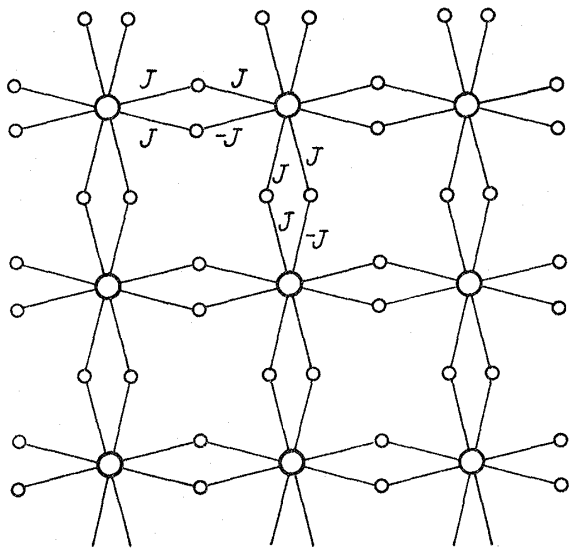

Fig. 2. The double bond model for the square lattice.

$$\Xi(L;\xi,\xi')=\sum_{\{\mu_i\}}\sum_{\{\sigma_{ij},\sigma_{ij'}\}}\exp[L\sum_{(i,j)}\{\sigma_{ij}(\mu_i+\mu_j)+\sigma'_{ij}(\mu_i-\mu_j)\}+\xi\sum_{(i,j)}\sigma^2_{ij}+\xi'\sum_{(i,j)}\sigma'^2_{ij}]$$
$$=A^{zN/2}\sum_{\{\mu_i\}}\exp(K\sum_{(i,j)}\mu_i\mu_j)\equiv A^{zN/2}Z_0(K), \tag{1}$$

where $L=J/kT$, the parameters ξ and ξ' are chemical potentials for the spins on A and B sites respectively dievided by $-kT$, N denotes the number of lattice points for the matrix lattice, and z the coordination number for the matrix lattice. The expressions for A and K are given as functions of L, ξ and ξ' corresponding to the following two cases: the independent double bond model, i.e. the spin variables of the double bonds, are independent and the exclusive double bond model, i.e. A and B sites can be occupied exclusively.

§ 3. Independent double bond model

By an extended iteration process, we have

$$A^2=(2\,\mathrm{ch}\,2Le^{\xi}+1)\,(2e^{\xi}+1)\,(2\,\mathrm{ch}\,2Le^{\xi'}+1)\,(2e^{\xi'}+1), \tag{2}$$

$$e^{2K}=(2\,\mathrm{ch}\,2Le^{\xi}+1)\,(2e^{\xi'}+1)/(2\,\mathrm{ch}\,2Le^{\xi'}+1)\,(2e^{\xi}+1). \tag{3}$$

Easily we can get the concentrations p_1 and p_2 for the spins on A and B sites.

$$p_1=(1/2N)\,\partial\ln\Xi/\partial\xi$$
$$=\mathrm{ch}\,2Le^{\xi}(1+\varepsilon)/(2\,\mathrm{ch}2Le^{\xi}+1)+e^{\xi}(1-\varepsilon)/(2e^{\xi}+1), \tag{4}$$

$$p_2=(1/2N)\,\partial\ln\Xi/\partial\xi'$$
$$=e^{\xi'}(1+\varepsilon)/(2e^{\xi'}+1)+\mathrm{ch}\,2Le^{\xi'}(1-\varepsilon)/(2\,\mathrm{ch}\,2Le^{\xi'}+1), \tag{5}$$

where $\varepsilon=(1/2N)\,\partial\ln Z_0/\partial K$ is the correlation of a pair of the nearest neighboring

Ising spins on the matrix lattice point. When $K=K_C$, the Ising system shows a phase transition as is well known. With the critical values, we can calculate the phase transition temperature by Eqs. (3), (4) and (5) for the fixed concentrations p_1 and p_2. When $p_2=0$, the model is reduced to Syozi's model and the critical concentration $p_C=0.5$ is obtained. The phase diagram has two parameters p_1 and p_2 and the critical surfaces are shown in Fig. 3 for the square lattice.

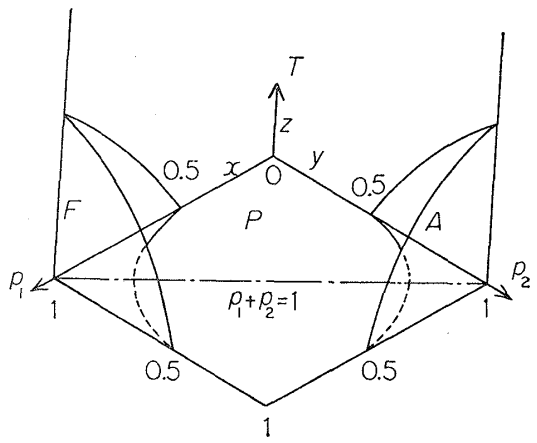

Fig. 3. The phase diagram of the independent double bond model. Two surfaces show the Curie temperature and the Néel temperature respectively. Here ferro-, antiferro- and paramagnetic regions are abbreviated to F, A and P respectively.

§ 4. Exclusive double bond model

In this model a pair of spin variables on the double bonds $(\sigma_{ij};\sigma'_{ij})$ can take four pairs of values $(0;\pm 1)$ and $(\pm 1;0)$. Thus A and K in (1) are given by

$$A^2=4\,(e^{\xi'}+e^{\xi}\,\mathrm{ch}\,2L)\,(e^{\xi}+e^{\xi'}\,\mathrm{ch}\,2L)\,, \tag{6}$$

$$e^{2K}=(e^{\xi'-\xi}+\mathrm{ch}\,2L)\,/\,(1+e^{\xi'-\xi}\,\mathrm{ch}\,2L)\,. \tag{7}$$

The mean concentration p of the Ising spins on A sites is given by

$$p=\mathrm{ch}\,2L\,(1+\varepsilon)\,/2\,(e^{\xi'-\xi}+\mathrm{ch}\,2L)+(1-\varepsilon)\,/2\,(e^{\xi'-\xi}\,\mathrm{ch}\,2L+1)\,. \tag{8}$$

As the occupation of A and B sites on each double bonds is exclusive, it is evident that we have the relation $p+p'=1$, where p' denotes the concentration of the Ising spins on B sites.

From Eqs. (7) and (8), we obtain

$$(2p-1-\varepsilon)\,\mathrm{ch}^2\,2L-2\,(\mathrm{sh}\,2K-\varepsilon\,\mathrm{ch}\,2K)\,\mathrm{ch}\,2L-2p+1-\varepsilon=0\,, \tag{9}$$

which connects L with K for a given p (see Fig. 4).

When $p=1$ or 0, Eq. (9) is reduced to the formula for the ordinary decorated Ising model (iteration process); $\mathrm{ch}\,(2L)=e^{2K}$ or e^{-2K} respectively. Inserting the critical value K_C for the parameter K and ε_C for the correlation ε of the matrix lattice to Eq. (9), we can get the critical point L_C for the present model as a function of the concentration p, i.e.

$$\mathrm{ch}\,2L_C=[\mathrm{sh}\,2K_C-\varepsilon_C\,\mathrm{ch}\,2K_C\pm\{(\mathrm{sh}\,2K_C-\varepsilon_C\,\mathrm{ch}\,2K_C)^2+(2p-1)^2-\varepsilon_C^2\}^{1/2}]$$
$$\times\,(2p-1-\varepsilon_C)^{-1}. \tag{10}$$

The solutions for L_C which are given by taking $\pm$ signs respectively in (10)

correspond to the positive values of ε_C and K_C (the ferromagnetic critical values) and the negative value of ε_C and K_C (the antiferromagnetic critical values) respectively for the matrix lattice, whose sites can be divided into two equivalent sublattices. These two branches are drawn symmetrically with respect to the line $p=1/2$ (see Fig. 5). If we put

$$p=1-p', \qquad K_C=-K_N, \qquad \varepsilon_C=-\varepsilon_N, \tag{11}$$

in Eq. (10), then we can obtain a formula for the Néel point, which have the same form as Eq. (10).

As the concentration p decreases from 1, L_C increases ($T_C=J/kL_C$ decreases), until L_C becomes infinite (T_C becomes zero), when $p_C=(1+\varepsilon_C)/2$. From the symmetry with respect to the Curie point and the Néel point for the present model, we can easily get the critical concentration p_N for the antiferromagnetic ordering as $p_N=(1+\varepsilon_N)/2$. These relations for the critical concentrations can be applied to several types of matrix lattices and the results are tabulated in Table I.

For the specific heat C_p at a fixed concentration p for this model whose matrix lattice is a square lattice, we have

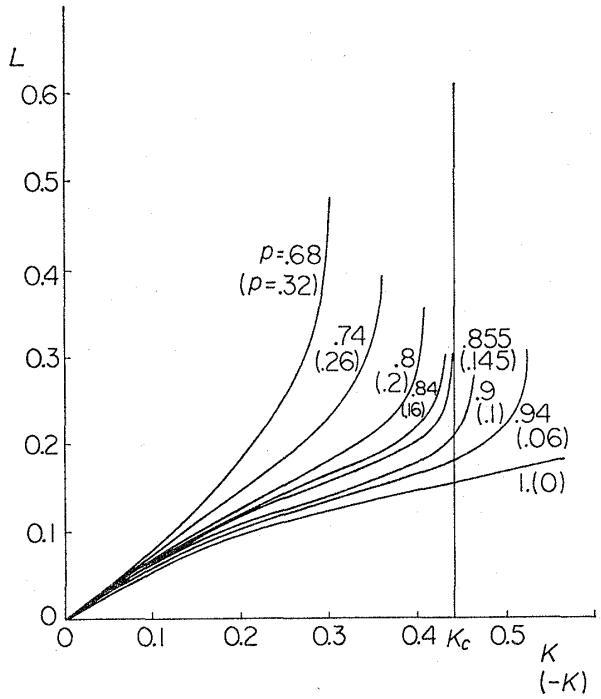

Fig. 4. Parameter L as a function of K at a constant p. The parameter p in the parentheses corresponds to the case of antiferromagnetic ordering.

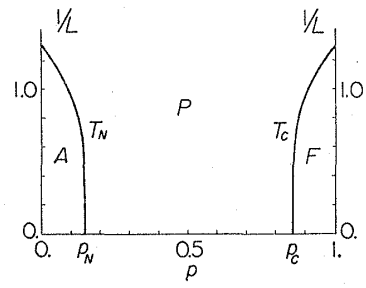

Fig. 5. The phase diagram of the exclusive double bond model for the lattice shown by Fig. 2.

Table 1. The critical concentrations and the critical data for matrix lattices.

	Sq.	Hon.	Tri.	Kag.	Dice	Diam.	S.C.	B.C.	F.C.
$\exp(-2K_c)$	$\sqrt{2}-1$	$2-\sqrt{3}$	$1/\sqrt{3}$	0.393	0.435	0.477	0.641	0.727	0.815
ε_C	$\sqrt{2}/2$	$4\sqrt{3}/9$	2/3	0.744	0.668	0.57	0.357	0.268	0.244
p_C	0.854	0.885	0.833	0.872	0.834	0.78	0.678	0.634	0.622
p_N	0.146	0.115	None	None	0.166	0.22	0.322	0.366	None

$$C_p = (kL^2/\mathrm{sh}^2 2L)\,[\mathrm{sh}\,2L\{(d\varepsilon/dK-2)\,\mathrm{sh}\,2K+2\varepsilon\,\mathrm{ch}\,2K\}\,dK/dL + \mathrm{ch}\,2L(\mathrm{ch}\,2K-\varepsilon\,\mathrm{sh}\,2K)-1], \tag{12}$$

where

$$dK/dL = 4\,\mathrm{sh}\,2L\{\mathrm{ch}\,2L(2p-\varepsilon-1)-(\mathrm{sh}\,2K-\varepsilon\,\mathrm{ch}\,2K)\} \times\{(\mathrm{ch}^2 2L-2\,\mathrm{ch}\,2L\mathrm{ch}\,2K+1)\,d\varepsilon/dK + 4\,\mathrm{ch}\,2L(\mathrm{ch}\,2K-\varepsilon\,\mathrm{sh}\,2K)\}^{-1}, \tag{13}$$

which has a symmetry with respect to the concentration $p=1/2$, i.e. $C_p=C_{p'}=C_{1-p}$. When $p>p_C$ or $p<p_N$, C_p has a cusp at the critical point L_C where it is equal to

$$C_{pC} = \{2p(1-p)\}^{-1}k[\{(2p-1)\sqrt{2}-1\}(6p^2-6p+1/2) + \{2p^2-(2+\sqrt{2})p+(2+\sqrt{2})/2\}(4p^2-4p+1/2)^{1/2}] \tag{14}$$

and the tangent tends to be vertical on both sides of the cusp. When p is slightly greater than p_C, the other broad peak appears. When $p=1/2$, C_p is reduced to the specific heat of a linear chain, i.e. $C_{1/2}=kL^2\,\mathrm{ch}^{-2}L$ (see Fig. 6).

In this exclusive double bond model we introduce a factor α by which the antiferromagnetic coupling J is multiplied, i.e. the antiferromagnetic couplings with neighboring spins are αJ and $-\alpha J$. Then the case $\alpha=1$ corresponds to the above mentioned model and the case $\alpha=0$ to Syozi's model of dilute ferromagnetism.[6] For this generalized exclusive double bond model, the critical points L_C are determined as functions of the concentration p of the spins on A sites from the equation

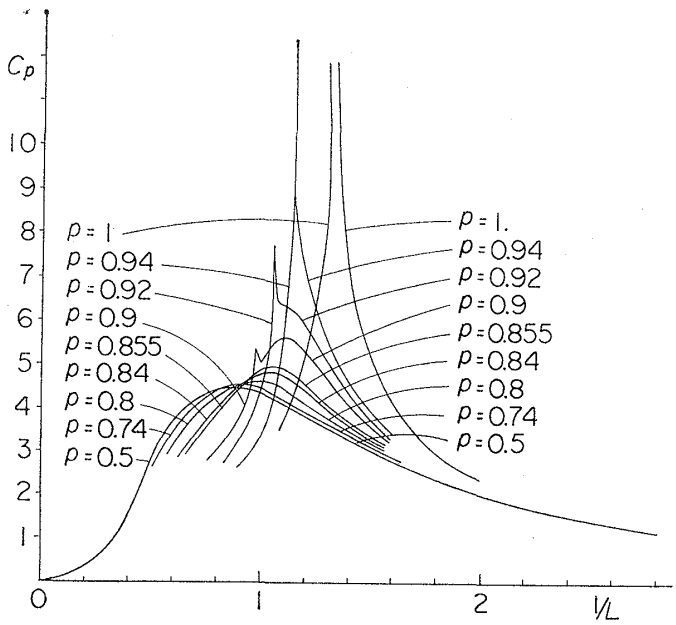

Fig. 6. Specific heat C_p of the exclusive double bond model at p ($\geq 1/2$) versus $1/L$. For $p<1/2$, curves for C_p are obtained by the equation $C_p=C_{1-p}$.

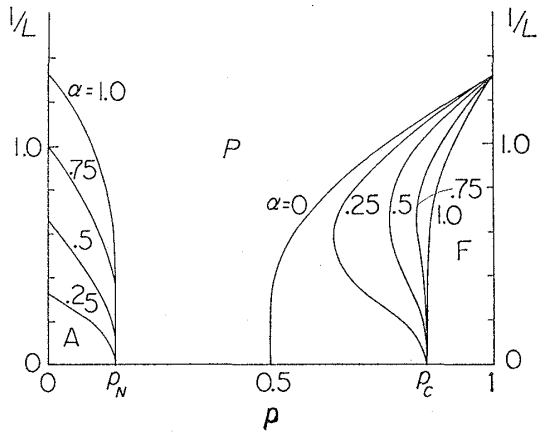

Fig. 7. The phase diagram of the exclusive double bond model with factor α. Each pair of curves corresponding to a value of α separates different magnetic regions, i. e. F and P or A and P. The notations F, A and P are the same as those in Fig. 3.

$$p=\frac{\{\mathrm{ch}\,2\alpha L_C-\exp(\mp 2K_C)\}\{(1\pm\varepsilon_C)\,\mathrm{ch}\,2L_C+(1\mp\varepsilon_C)\exp(\pm 2K_C)\}}{2(\mathrm{ch}\,2L_C\,\mathrm{ch}\,2\alpha L_C-1)}\,, \tag{15}$$

where each of the double signs corresponds to ferro- and antiferro-magnetic regions respectively. This result for the square lattice is represented in Fig. 7, where ferromagnetic region corresponding to each value of α except $\alpha=0$ or 1 has two critical points[7] within the appropriate limits of concentration p below p_C. In Fig. 7 we omit the curves for $\alpha>1$, for no new feature appeares except that the shape of curve limiting ferromagnetic region is exchanged with that limiting antiferromagnetic region.

§ 5. Anisotropic model

In the exclusive double bond model, it is interesting to count the number of spins on A sites separately according to their bond directions. We attribute different parameters for the chemical potential according to their bond directions. For simplicity, we confine ourselves to the case of a square lattice. In this case, we have two partial concentrations p_1 and p_2, which correspond to the spins on the horizontal and vertical bonds respectively. By the same consideration as in the former model, we obtain a pair of equations which determine the critical partial concentrations p_{1C} and p_{2C} given by

$$p_{1C}=(1+\varepsilon_{1C})/2\,,\qquad p_{2C}=(1+\varepsilon_{2C})/2\,, \tag{16}$$

where ε_{1C} and ε_{2C} are the critical values of the correlation functions for the anisotropic Ising model given by

$$\varepsilon_{iC}=\mathrm{sign}\,(K_{iC})\,(2/\pi)\,\mathrm{cth}\,(2K_{iC})\tan^{-1}(\mathrm{sh}\,2K_{iC})\qquad (i=1,2) \tag{17}$$

and

$$\mathrm{sh}\,2|K_{1C}|\cdot\mathrm{sh}\,2|K_{2C}|=1\,, \tag{18}$$

where K_{1C} and K_{2C} are the critical values of the interaction parameters for the horizontal and vertical bonds of the matrix lattice.

The curves of the critical concentration on the p_1 versus p_2 plane are shown in Fig. 8 where F, A and P denote the ferro-, antiferro- and para-magnetic regions respectively.

When two partial critical concentrations are equal, i.e. $p_{1C}=p_{2C}$, their numerical values are equivalent to the critical concentration for the former case, i.e. $p_{1C}=p_{2C}=(2+\sqrt{2})/4=0.8535\cdots$ and $p_{1N}=p_{2N}=(2-\sqrt{2})/4=0.1416\cdots$.

It is easily calculated that if p_{1C} is increased to 1, p_{2C} decreases to $(2+\pi)/2\pi=0.8183\cdots$, where we have used the relations

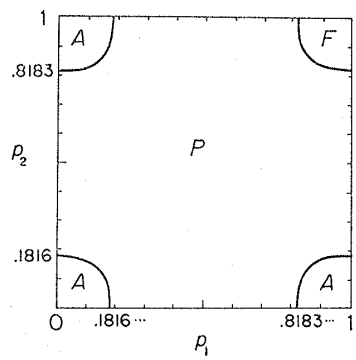

Fig. 8. The phase diagram of the exclusive double bond model with the anisotropic chemical potentials. p_1; concentration of Ising spins on horizontal bonds. p_2; concentration of Ising spins on vertical bonds.

$$\varepsilon_{1C} \to 1\,, \quad \varepsilon_{2C} \to (2/\pi) \quad \text{as} \quad K_{1C} \to \infty\,, \quad K_{2C} \to 0\,. \tag{19}$$

It is interesting to note that ε_{2C} does not tend to zero as $K_{2C} \to 0$ ($K_{1C} \to \infty$ by (17)).

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