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Ising Spin Models of Complex Ferrimagnetism

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A simple statistical model of ferrimagnetism is investigated based upon the results of the theory of crystal statistics. It is generally composed of three kinds of Ising spins, of which one forms a plane square lattice and the other two occupy the midpoints of each of the bonds in this plane square lattice. The complete spin arrangement makes up a decorated plane square lattice, in which there exists an antiferromagnetic exchange coupling between every pair of nearest neighbouring spins. Syozi and Nakano investigated ten years ago similar kinds of Ising spin models, which were, however, simpler than the present model. The temperature dependence of the spontaneous magnetization of such a ferrimagnetic Ising model is investigated using the Onsager-Yang theory of crystal statistics. In addition to the features found by Syozi and Nakano, there appear some other features of this dependence which are not seen in the case investigated by them. The probability that two nearest neighbouring points of the lattice which consists of every midpoint are occupied by a pair of similar atoms and of dissimilar atoms is also investigated.

§ 1. Introduction

Syozi and Nakano[1] (referred to as I hereafter) calculated the temperature dependence of the spontaneous magnetization in a ferrimagnetic Ising model based upon the Onsager-Yang theory[2] and showed that the spontaneous magnetization exhibited several kinds of temperature dependence according to the assumed values of parameters. The model investigated by them was the so-called decorated lattice and the arrangement of atoms was like that in the normal spinel. The whole lattice could be divided into two sublattices, L_1 and L_2. Every point of L_1 was always occupied by an A atom and that of L_2, which was composed of one decorating point on every bond of L_1, was always occupied by a B atom. In this configuration there existed an antiferromagnetic coupling between each pair consisting of the spin of the A atom on a site of L_1 and the spin of the B atom on any site of L_2 which was a nearest neighbour to it.

In the present paper, we consider the case in which every point of L_1, which is here taken as a plane square lattice, is exclusively occupied by an A atom but any point of L_2 is occupied by either a B atom or a C atom. The total number of B atoms and that of C atoms are both definitely given. The magnetic moments of the Ising spins of A, B and C atoms are generally different from one another. We have already published a preliminary report of some parts of this article.[3]

In the case that the arrangement of B atoms and C atoms on L_1 is fixed, we can show, by calculating the partition functions of the whole systems, that the temperature dependence of the magnetization is essentially the same as that obtained in I. This is discussed in § 2. The case in which any point of L_2 is occupied by either a B atom or a C atom and their distributions are quite undetermined is also discussed by calculating the grand partition function of the system by the Onsager-Yang theory.[2] In this case we find several types of temperature dependence of the magnetization according to the relative magnitudes of the magnetic moments of the A, B and C atoms ; some of these are of a new type. The general formulation is given in § 3 and the magnetization—temperature relations are investigated in § 4. We also investigate the correlation that a B atom and a C atom come nearest to each other. We can show that the probability that two given nearest neighbouring points of L_2 are occupied by similar atoms is at most about ten percent larger than that by dissimilar atoms in the neighbourhood of the Curie temperature but, in the limits of both low and high temperatures these two probabilities are equal. An arrangement like the Verwey order is not realized by the interaction which is taken into account in the present article. These results are demonstrated in § 5.

§ 2. Ferrimagnetism of a certain fixed arrangement

The spontaneous magnetizations in the cases that all of B atoms and C atoms are distributed on the lattice L_2 in a definite way are investigated.

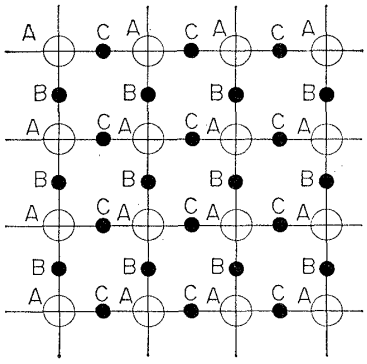

Fig. 1. An arrangement of B and C atoms (like the Verwey order).

We first investigate the magnetization in the case shown in Fig. 1 that every white point is always occupied by an A atom and the black points are occupied alternately by a B atom and a C stom. We make use of the notation μ_i, ν_j and λ_l for the spin variables of A, B and C atoms which can take values 1 and -1, γ_1 and $-\gamma_1$ and γ_2 and $-\gamma_2$ respectively. Let the spin magnetic moments of the A, B and C atoms be β, $\beta\gamma_1$ and $\beta\gamma_2$, and $-J(J>0)$ be the antiferromagnetic exchange coupling between a spin of an atom on a white point and a spin of an atom on black point which are nearest neighbouring to each other.

The partition function of the whole system exposed to an external magnetic field H is

$$Z=\sum_{\{\mu_i\}}\sum_{\{\nu_j\}}\sum_{\{\lambda_l\}}\exp[-J'\sum_{(ij)}\mu_i\nu_j-J'\sum_{(il)}\mu_i\lambda_l - H_1(\sum_i\mu_i+\sum_j\nu_j+\sum_l\lambda_l)], \qquad (2\cdot1)$$

where $J'=J/kT$ and $H_1=\beta H/kT$. $\sum_{\{\mu_i\}}$, $\sum_{\{\nu_j\}}$ and $\sum_{\{\lambda_l\}}$ indicate summations

over all the ranges of the variables, viz. all μ_i's $=\pm 1$, all ν_j's $=\pm\gamma_1$ and all λ_l's $=\pm\gamma_2$; $\sum_{(ij)}$ and $\sum_{(il)}$ are the summations over all the nearest neighbouring pairs consisting of a white point and a black point. $\sum_j$ is the summation over all white points and $\sum_j$ and $\sum_l$ over all black points occupied by B atoms and C atoms respectively. If the summations over $\{\nu_j\}$ and $\{\lambda_l\}$ are carried out first, Eq. (2·1) is reduced to the form

$$\begin{aligned} Z &= (A_1A_2)^N\sum_{\{\mu_i\}}\exp[K_1\sum_{(ic)}\mu_i\mu_c+K_2\sum_{(ir)}\mu_i\mu_r-H'\sum_i\mu_i] \\ &= (A_1A_2)^N Z_4(K_1K_2;\ H'), \end{aligned} \tag{2·2}$$

where N is the total number of white points and

$$\begin{aligned} A_t &= 2[\cosh(2J'+H_1)\gamma_t\cdot\cosh(2J'-H_1)\gamma_t\cdot\cosh^2 H_1\gamma_t]^{1/4}\quad (t=1,\ 2)\ , \\ K_t &= (1/4)\ln[\cosh(2J'+H_1)\gamma_t\cdot\cosh(2J'-H_1)\gamma_t]-(1/2)\ln\cosh H_1\gamma_t, \\ H' &= H_1+(1/2)\ln[\cosh(2J'-H_1)\gamma_2\cdot\cosh(2J'-H_1)\gamma_1] \\ &\quad -(1/2)\ln[\cosh(2J'+H_1)\gamma_2\cdot\cosh(2J'+H_1)\gamma_1]. \end{aligned} \tag{2·3}$$

$\sum_{(ic)}$ and $\sum_{(ir)}$ are summations over all the nearest neighbouring pairs of white points along a column and along a row. Further,

$$Z_4(K_1K_2;H')=\sum_{\{\mu_i\}}\exp[K_1\sum_{(ic)}\mu_i\mu_c+K_2\sum_{(ir)}\mu_i\mu_r-H'\sum_i\mu_i] \tag{2·4}$$

is just the partition function of the ferromagnetic plane square lattice in a magnetic field $kT\cdot H'/\beta$ with the longitudinal exchange coupling parameter $kT\cdot K_1(>0)$ and the transverse one $kT\cdot K_2(>0)$. As shown in (2·3), A_t and K_t are even functions of H_1, and the spontaneous magnetization of the whole system,

$$\begin{aligned} M &= \beta\lim_{H_1\to 0}\partial\ln Z/\partial H_1 \\ &= \beta\lim_{H_1\to 0}\partial H'/\partial H_1\cdot\partial\ln Z_4(K_1K_2\ ;\ H')/\partial H' \end{aligned}$$

becomes accordingly

$$M=\beta f(T\ ;\ \gamma_2\gamma_1)M_4(K_1K_2), \tag{2·5}$$

where

$$f(T\ ;\ \gamma_2\gamma_1)=1-\gamma_2\tanh 2J'\gamma_2-\gamma_1\tanh 2J'\gamma_1 \tag{2·5′}$$

and

$$M_4(K_1K_2)=\lim_{H'\to 0}\partial\ln Z_4(K_1K_2\ ;\ H')/\partial H'. \tag{2·5″}$$

In the above, we have made use of the fact that H' is an odd function of H. The function $M_4(K_1K_2)$ denotes the spontaneous magnetization of the plane square lattice which has longitudinal and transversal exchange coupling parameters $kT\cdot K_1$ and $kT\cdot K_2$, when K_1 and K_2 are the values at a vanishing magnetic field. The factor $f(T\ ;\ \gamma_2\gamma_1)$ is an increasing function of temperature and its

temperature dependence is similar to that which appeared in I. The parameters $K_t(t=1, 2)$ are decreasing functions of temperature and so is $M_4(K_1K_2)$. It is expected that the variety of possibilities for the temperature dependence of the magnetization, in the case shown in Fig. 1, comes essentially from the behaviour of the function $f(T)$, and the magnetization-temperature relations are divided into typical cases which are essentially the same as those in I.

Next we consider the magnetization in the case that each white point is always surrounded by two B atoms and two C atoms on its nearest neighbouring black points. The distribution of these four atoms around a white atom may be different from that around another white atom. If the summation over the spin variables on the black points is carried out first, the partition function of this system in the presence of a magnetic field H is expressed, with the use of the functions given by $(2\cdot3)$, in the form

$$Z=(A_1A_2)^N Z_0(K_1K_2\,;\,H'),$$

where $Z_0(K_1K_2\,;\,H')$ is the partition function of the plane square lattice consisting of only white points with two kinds of coupling parameters $kT\cdot K_1$ and $kT\cdot K_2$. These parameters $kT\cdot K_1$ and $kT\cdot K_2$ appear for each bond respectively according to whether a B or C atom stands on that bond. The spontaneous magnetization is obtained in the form

$$\begin{aligned} M&=\beta \lim_{H\to 0} \frac{\partial H'}{\partial H_1}\frac{\partial}{\partial H'} \ln Z_0(K_1K_2\,;\,H') \\ &=\beta f(T\,;\,\gamma_2\gamma_1)M_0(K_1K_2), \end{aligned}$$

where

$$M_0(K_1K_2)=\lim_{H'\to 0}\frac{\partial}{\partial H'} \ln Z_0(K_1K_2\,;\,H')$$

is the spontaneous magnetization of a ferromagnetic plane square lattice in which there exist two kinds of coupling parameters $kT\cdot K_1$ and $kT\cdot K_2$ in the way mentioned above. The function $f(T\,;\,\gamma_2\gamma_1)$ is that which is given in $(2\cdot5')$. The behaviour of the temperature dependence of M_0 is supposed to be similar to the usual simple ferromagnet and therefore to that of M_4, which is given in $(2\cdot5'')$. It is therefore concluded that the spontaneous magnetization in this case also has the same features as in the model discussed in I.

§ 3. Formulation in the case of variable arrangement of atoms

In this section, we investigate the model in which every white point is always occupied by an A atom but any black point is occupied not by a definite atom but by either a B atom or a C atom. The total number of black points is $2N$, $2N\cdot(1-P)$ points of which are occupied by B atoms and $2NP$ points by C atoms. We make use of the notation μ_i and ν_j for the spin variables of

atoms on white points and those on black points respectively, where the j's denote the sites of black points. The grand partition function of this system, when exposed to a magnetic field H, is written as

$$\Xi=\sum_{\{\mu_i\}}\sum_{\{\nu_j\}}\exp[-J'\sum_{(ij)}\mu_i\nu_j-H_1\cdot(\sum_i\mu_i+\sum_j\nu_j)+\xi\sum_j\nu_j^2], \tag{3·1}$$

where $\sum_{\{\nu_j\}}$ denotes summation over all range of variables on the black points, viz. $\nu_j=\gamma_1, \gamma_2, -\gamma_1$ and $-\gamma_2$; the other notation, except ξ, has the same meanings as in § 2. The parameter ξ introduced here should be determined from the equation

$$\begin{aligned}\langle\sum_j\nu_j^2\rangle&=\frac{\partial}{\partial\xi}\ln\Xi\\&=\gamma_1^2\cdot 2N(1-P)+\gamma_2^2\cdot 2NP.\end{aligned} \tag{3·2}$$

The condition (3·2) has been derived from the fact that the total number of B atoms and that of C atoms are definitely given. If the summation over $\{\nu_j\}$ is carried out first in the calculation of the grand partition function, Eq. (3·1) is reduced to the form

$$\Xi=R^{2N}\sum_{\{\mu_i\}}\exp[K\sum_{(i\rho)}\mu_i\mu_\rho-L\sum_i\mu_i]=R^{2N}Z_4(K;L), \tag{3·3}$$

where $Z_4(K;L)$ is the partition function in a magnetic field $kT\cdot L/\beta$ of the plane square lattice with the nearest neighbouring exchange coupling $kT\cdot K$, and use has been made of the abbreviations

$$R^2=4[D_1D_2D_3^2]^{1/2},$$
$$K=(1/4)\ln D_1D_2-(1/2)\ln D_3$$

and

$$L=H_1-\ln D_1+\ln D_2. \tag{3·4}$$

The new parameters introduced in (3·4) are defined by

$$D_1=\exp(\xi\gamma_2^2)\cosh(2J'+H_1)\gamma_2+\exp(\xi\gamma_1^2)\cosh(2J'+H_1)\gamma_1,$$
$$D_2=\exp(\xi\gamma_2^2)\cosh(2J'-H_1)\gamma_2+\exp(\xi\gamma_1^2)\cosh(2J'-H_1)\gamma_1$$

and

$$D_3=\exp(\xi\gamma_2^2)\cosh H_1\gamma_2+\exp(\xi\gamma_1^2)\cosh H_1\gamma_1. \tag{3·4′}$$

Ξ is an even function of H_1, as is easily seen from Eq. (3·1). On the other hand Ξ is not an odd function of ξ. Therefore $\partial\ln\Xi/\partial\xi$ is an even function of H_1, and not an even function of ξ, and it can be concluded from Eq. (3·2) that ξ should be an even function of H_1. It is then clear from Eq. (3·4) that the parameters R and K are also even functions of H_1. Making use of these

facts, we can express the spontaneous magnetization as

$$M=\beta \lim_{H\to 0} \frac{\partial L}{\partial H_1} M_4(K) , \tag{3·5}$$

where

$$M_4(K)=\lim_{H\to 0} \frac{\partial}{\partial L} \ln Z_4(K\,;\,L).$$

The parameter ξ which has appeared in (3·5) should be determined by (3·2) in which H_1 is put equal to zero. It is convenient for later discussions to introduce a variable

$$x=\exp(-2K)=(X+1)/(X\cosh 2J'\gamma_2+\cosh 2J'\gamma_1), \tag{3·6}$$

where K is the value of the expression (3·4) at $H_1=0$ and

$$X=\exp[\xi\cdot(\gamma_2{}^2-\gamma_1{}^2)]$$

in which ξ is also regarded as evaluated at $H_1=0$. After some calculation Eq. (3·2), which determines x, is reduced at $H_1=0$ to the form

$$2(1-P)/(1-x\cdot\cosh 2J'\gamma_2)+2P/(1-x\cdot\cosh 2J'\gamma_1)=1+E(x), \tag{3·7}$$

where $E(x)=(1/2N)\cdot(\partial \ln Z_4(K)/\partial K)$ is the correlation between nearest neighbouring spins of the plane square lattice with the exchange coupling parameter $(kT\cdot K)$ and has already been given by Onsager ;[2]

$$E(x)=\left(\frac{1+x^2}{1-x^2}\right)\left\{\frac{1}{2}+\frac{(1-6x^2+x^4)}{\pi(1+x^2)^2}\int_0^{\pi/2}\frac{d\varphi}{\sqrt{1-W^2\sin^2\varphi}}\right\}, \tag{3·7′}$$

where

$$W^2=\frac{16(x-x^3)^2}{(1+x^2)^4}. \tag{3·7″}$$

As X must be positive, we can see from (3·6) that x can take values between $[\cosh 2J'\gamma_2]^{-1}$ and $[\cosh 2J'\gamma_1]^{-1}$ both of which are smaller than unity, and K must be positive at $H_1=0$. Thus the $M_4(K)$ appearing in (3·5) is the spontaneous magnetization of the ferromagnetic plane square lattice with the nearest neighbouring exchange coupling $(kT\cdot K)$ and has been calculated exactly by Yang ;[2]

$$M_4(K)=N\left[\frac{(1+x^2)}{(1-x^2)^2}\cdot(1-6x^2+x^4)^{1/2}\right]^{1/4}.$$

We shall give here an explicit expression for the spontaneous magnetization given by formula (3·5). It can be rewritten as

$$M=\beta F(\gamma_1\,;\,2J'\gamma_1\,;\,\alpha)M_4(x), \tag{3·8}$$

where

$$F(\gamma_1\,;\,2J'\gamma_1\,;\,\alpha)=1-\gamma_1 D(2J'\gamma_1\,;\,\alpha) \tag{3·9}$$

and

$$\begin{aligned} D(2J'\gamma_1\,;\,\alpha)=&[\cosh 2J'\gamma_1\alpha-\cosh 2J'\gamma_1]^{-1}\cdot[2x\{\cosh 2J'\gamma_1\alpha\sinh 2J'\gamma_1\\ &-\alpha\sinh 2J'\gamma_1\alpha\cosh 2J'\gamma_1\}+2\{\alpha\sinh 2J'\gamma_1\alpha\\ &-\sinh 2J'\gamma_1\}], \end{aligned} \tag{3·10}$$

in which x is determined from (3·7) and can be proved to depend only on $2J'\gamma_1$ and the ratio γ_2/γ_1 if the parameter P is fixed. This ratio γ_2/γ_1 has been abbreviated as α.

§ 4. Calculation

The temperature dependence of the spontaneous magnetization (3·8) is largely influenced by that of the factor $F(\gamma_1\,;\,2J'\gamma_1\,;\,\alpha)$ defined by (3·9) and (3·10). We hereafter assume, without loss of generality, that γ_2 is larger than γ_1, that is $\alpha>1$, and investigate the behaviour of the magnetization for all possible values of γ_1 and of α. We must determine x which appears in (3·10) as a function of $2J'\gamma_1$ and α from (3·7), but it is difficult to solve exactly, and we inspect the properties of the factor F in two extreme temperature regions, viz. at nearly vanishing temperatures and at the Curie temperature which is determined from (3·7) by setting $x=\sqrt{2}-1$ and $E=1/\sqrt{2}$. We hereafter assume $P=1/2$ which corresponds to the case that the total number of B atoms and that of C atoms are equal to each other and to N.

i) Near zero temperature; $x\ll 1$. Expanding $E(x)$ in terms of x, we find $E(x)=1+0(x^4)$ and $x=x_0+0(x_0^5)$ from (3·7), where

$$x_0=(\cosh 2J'\gamma_1\alpha+\cosh 2J'\gamma_1)/(2\cosh 2J'\gamma_1\alpha\cdot\cosh 2J'\gamma_1). \tag{4·1}$$

If we insert $x=x_0$ in (3·10), the factor F which is defined in (3·9) becomes

$$F=1-\gamma_1[\alpha\tanh 2J'\gamma_1\alpha+\tanh 2J'\gamma_1], \tag{4·2}$$

which is an increasing function of temperature and is the same as that in (2·5′) which corresponds to the case like the Verwey order in a real ferrimagnet shown in Fig. 1. When P is not equal to 1/2, we can easily see that the factor corresponding to (4·2) is $1-2P\gamma_2\tanh 2J'\gamma_2-2(1-P)\gamma_1\tanh 2J'\gamma_1$. In the limit of vanishing temperature, we find

$$F=1-\gamma_1(\alpha+1), \tag{4·3}$$

which shows that the spins of A atoms on white points and the spins of B and C atoms on black points are always antiparallel each other at zero temperature.

ii) At the Curie temperature: We denote the value of $2J'\gamma_1$ at the Curie temperature by $2J'_c\gamma_1$; this is determined from (3·7), in terms of α, by setting $x=\sqrt{2}-1$ and $E(x)=1/\sqrt{2}$, and we get

$$\cosh 2J_c'\gamma_1\alpha=(\cosh 2J_c'\gamma_1+1)/(\cosh 2J_c'\gamma_1-1). \tag{4·4}$$

The function D which is defined by (3·10) is therefore a function only of α at the Curie temperature and is denoted as $D_c(\alpha)$, this function can be written as

$$\begin{aligned} D_c(\alpha)=2[&\cosh 2J_c'\gamma_1\alpha-\cosh 2J_c'\gamma_1]^{-1}\cdot[\sinh 2J_c'\gamma_1 \\ &\times\{(\sqrt{2}-1)\cosh 2J_c'\gamma_1\alpha-1\}+\alpha\sinh 2J_c'\gamma_1\alpha \\ &\times\{1-(\sqrt{2}-1)\cosh 2J_c'\gamma_1\}]. \end{aligned} \tag{4·5}$$

The function $D_c(\alpha)^{-1}$ takes the value $(\sqrt{2}+1)^{1/2}/\sqrt{8}\fallingdotseq 0.55$ at the limit $\alpha\to 1$ and decreases like $(2+\sqrt{2})/4\alpha\fallingdotseq 0.85/\alpha$ as α becomes large.

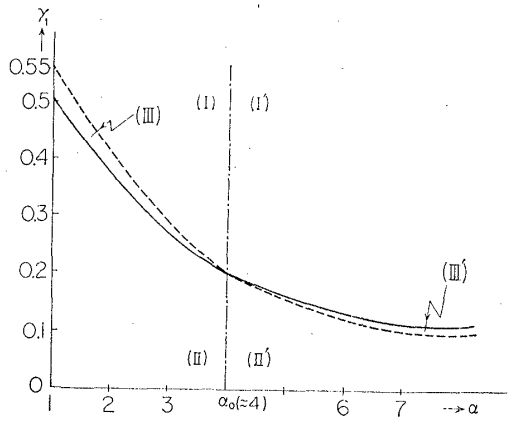

Fig. 2. Dependence of the functions $D_c(\alpha)^{-1}$ and $D_0(\alpha)^{-1}$ on α; the broken line and the solid line represent D_c^{-1} and D_0^{-1} respectively.

The value of $D_c(\alpha)^{-1}$ and the value $D_0(\alpha)^{-1}=1/(1+\alpha)$ of D at the temperature zero are calculated numerically and the curves which show the dependence of these values on α are drawn in Fig. 2. The value of D_c^{-1} and that of D_0^{-1} coincide at $\alpha=\alpha_0$ where α_0 is nearly equal to 4. We divide the $\gamma_1-\alpha$ plane into several regions shown in Fig. 2. If α is smaller than α_0, we see that D_c is always smaller than D_0 and therefore the value of F at the Curie temperature is larger than that at zero temperature. If α is larger than α_0, then the value of F at the Curie temperature is smaller than that at zero temperature.

Using these facts, and recalling that the value of F near zero temperature increases with rising temperature, we can draw schematic curves of F corresponding to the various regions in Fig. 3. The spontaneous magnetization is the absolute value of the expression (3·8) which is proportional to the product of F thus obtained with $M_4(x)$. We can easily prove, by taking derivatives with respect to temperature on both sides of (3·7), that x is an increasing function of temperature and therefore $M_4(x)$ is a decreasing function of temperatures. The spontaneous magnetization in the various regions is drawn schematically in Fig. 4. We find several types of magnetization–temperature–curves, some of which have different features from those found in I, viz. the magnetizations in the cases of (I′), (III′) and the boundary between (I′) and (III′). The types other than these are essentially the same as those which have already been found in I.

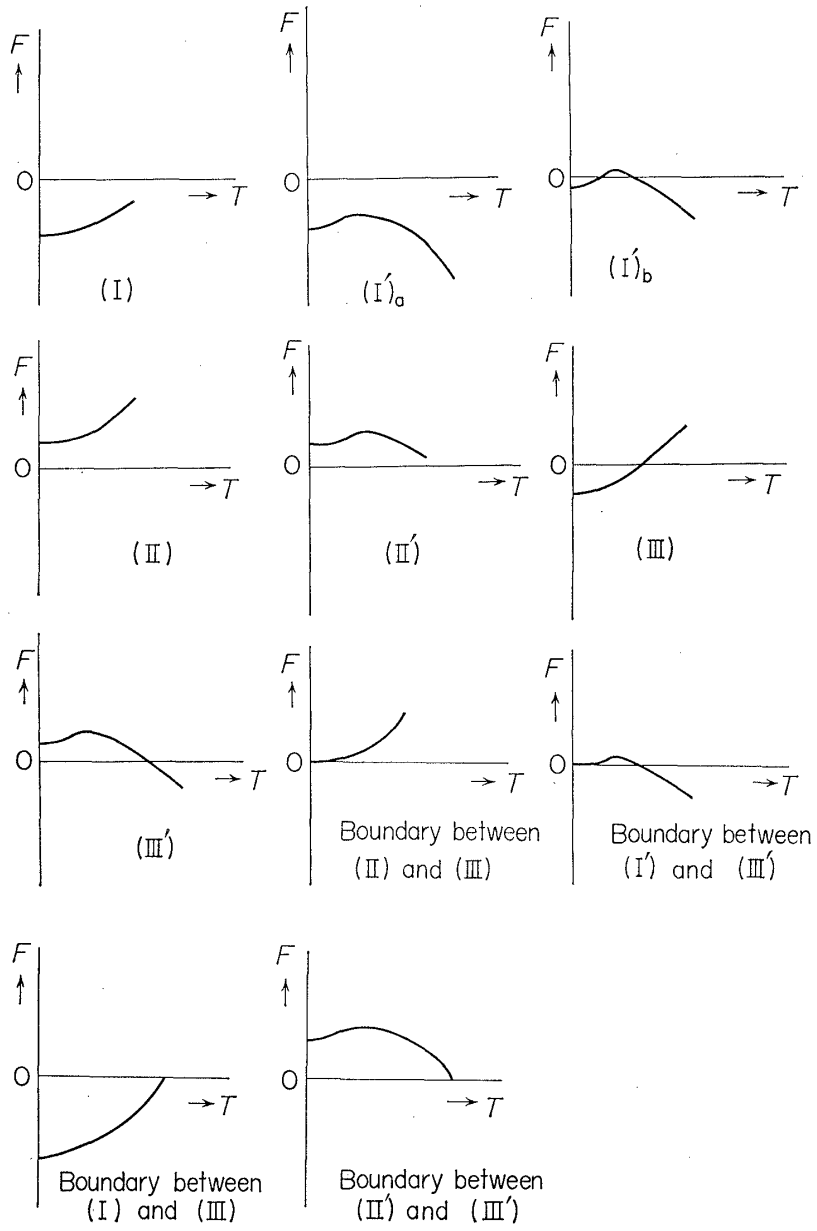

Fig. 3. Dependence of the functions F on temperature in various regions in Fig. 2.

§ 5. Ordering of B and C atoms in the sublattice L_2

The ordering of B and C atoms in the sublattice L_2 will be investigated in this section. We divide the lattice L_2 consisting of the black points in Fig. 1 into two sublattices as shown in Fig. 5, i.e. one indicated by black squares and the other by black triangles. We denote the spin variables of atoms on the white points, those on the black squares and those on the black triangles by μ_i ν_j and λ_l respectively. A white circle is always occupied by an A atom, and

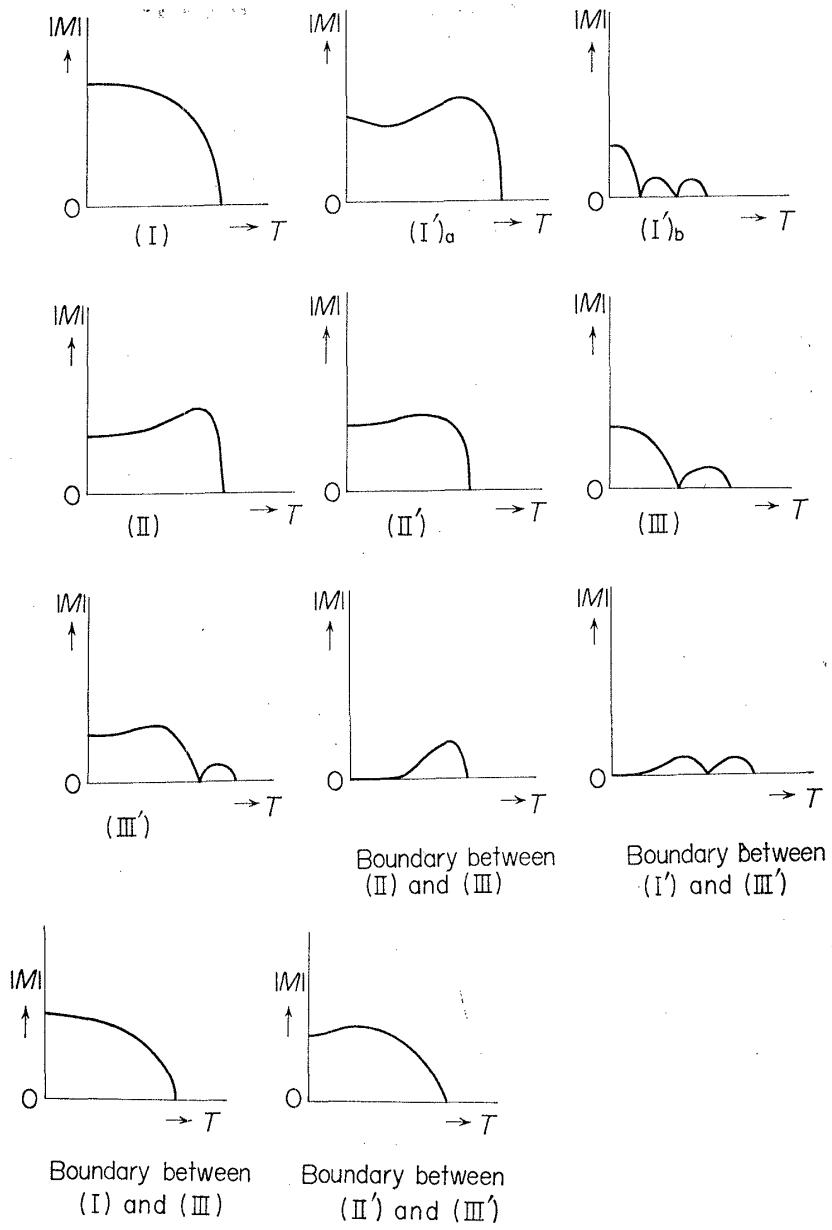

Fig. 4. Dependence of the magnetizations on temperature in respective regions in Fig. 2.

the black squares and black triangles are each occupied by either a B or a C atom.

If we assume by the use of a sort of long range order parameter s that the black squares are occupied by $N\cdot(1+s)/2$ B atoms and $N\cdot(1-s)/2$ C atoms in all, and all the black triangles by $N\cdot(1-s)/2$ B atoms and $N\cdot(1+s)/2$ C atoms, the average value $\langle s^2\rangle$ of s^2 is calculated first. It can be calculated using the equation

$$\frac{1}{N^2}\langle\sum_j \nu_j^2\cdot\sum_l \lambda_l^2\rangle=\frac{1}{N^2}\lim_{\substack{\eta_1\to 0\\ \eta_2\to 0}}\frac{\partial^2\Xi'}{\partial\eta_1\partial\eta_2}\Big/\Xi', \tag{5·1}$$

where

$$\Xi'=\sum_{\{\mu_i\}}\sum_{\{\nu_j\}}\sum_{\{\lambda_l\}}\exp[-J'\sum_{(ij)}\mu_i\nu_j-J'\sum_{(il)}\mu_i\lambda_l$$
$$+\eta_1\sum_j\nu_j^2+\eta_2\sum_l\lambda_l^2+\xi\cdot\{\sum_j\nu_j^2+\sum_l\lambda_l^2\}]. \tag{5·2}$$

The parameter ξ is determined from (3·2) or (3·7), that is to say, from the condition that the total number of B atoms and that of C atoms are both equal to N. The summations $\sum_{\{\nu_j\}}$ and $\sum_{\{\lambda_l\}}$ imply respectively summation over all ranges of variables on the black squares and on the black triangles, and therefore each of the ν_j's and λ_l's can take four values $\pm\gamma_1$ and $\pm\gamma_2$. The other notation means the same as before. By making use of the identity

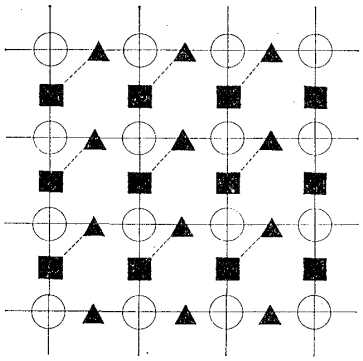

Fig. 5. Sublattice with the black squares and that with the black triangles.

$$\frac{1}{N^2}\frac{\partial^2\Xi'}{\partial\eta_1\partial\eta_2}\Big/\Xi'$$
$$=\left(\frac{1}{N}\frac{\partial\ln\Xi'}{\partial\eta_1}\right)\cdot\left(\frac{1}{N}\frac{\partial\ln\Xi'}{\partial\eta_2}\right)$$
$$+\frac{1}{N^2}\frac{\partial^2}{\partial\eta_1\partial\eta_2}\ln\Xi',$$

we can obtain, for an infinitely large N, the equation

$$\lim_{\substack{\eta_1\to 0\\ \eta_2\to 0}}\frac{1}{N^2}\frac{\partial^2\Xi'}{\partial\eta_1\partial\eta_2}\Big/\Xi'=\lim_{\substack{\eta_1\to 0\\ \eta_2\to 0}}\left(\frac{1}{N}\frac{\partial\ln\Xi'}{\partial\eta_1}\right)\cdot\left(\frac{1}{N}\frac{\partial\ln\Xi'}{\partial\eta_2}\right)$$

in which the right-hand side expression is nothing but $\langle(1/N)\cdot\sum_j\nu_j^2\rangle\cdot\langle(1/N)\cdot\sum_l\lambda_l^2\rangle$, and Eq. (5·1) can therefore be rewritten as follows:

$$\langle\frac{1}{N}\sum_j\nu_j^2\cdot\frac{1}{N}\sum_l\lambda_l^2\rangle=\langle\frac{1}{N}\sum_j\nu_j^2\rangle\cdot\langle\frac{1}{N}\sum_l\lambda_l^2\rangle. \tag{5·3}$$

Equation (5·3) is always valid whatever couplings exist between any pair of spins, because in the proof of (5·3) use has not been made of any special form of coupling. Equation (5·3) is reduced to the form $\langle s^2\rangle=\langle s\rangle^2$ where s is the long range order parameter introduced above. It is required that $\langle s\rangle$ should vanish in the present model because the sublattice composed of black squares and that of black triangles are equivalent. This fact is based upon quite the same state of affairs as in the theory of a diatomic alloy. On the basis of the equation $\langle s^2\rangle=\langle s\rangle^2$, $\langle s^2\rangle$ equals zero, too. Accordingly an arrangement shown in Fig. 1

like the Verwey order cannot be realized in the present model.

We next consider the correlation between a black square and a black triangle which are connected with broken lines in Fig. 5. We compare the probability that such pair is occupied by similar atoms with the probability that it is occupied by dissimilar atoms. Let the symbols [BB], [CC], [BC] and [CB] denote the total numbers of the above mentioned pairs, which are occupied by two B atoms, two C atoms, a B and a C atoms and a C and a B atoms respectively. As already shown in this section, all the black squares are always occupied by $N/2$ B atoms and $N/2$ C atoms and also all the black triangles by $N/2$ B atoms and $N/2$ C atoms. There are the following relations among the numbers [BB], [CC], [BC] and [CB]:

$$\frac{N}{2} = [\mathrm{BB}] + [\mathrm{BC}],$$

$$\frac{N}{2} = [\mathrm{CB}] + [\mathrm{CC}],$$

$$\frac{N}{2} = [\mathrm{BB}] + [\mathrm{CB}]$$

and

$$\frac{N}{2} = [\mathrm{BC}] + [\mathrm{CC}].$$

These relations are reduced to the following:

$$[\mathrm{BB}] = [\mathrm{CC}],\ [\mathrm{BC}] = [\mathrm{CB}],$$

$$\mathrm{N} = [\mathrm{BB}] + [\mathrm{CC}] + [\mathrm{BC}] + [\mathrm{CB}]. \tag{5·4}$$

We see from (5·4) that if $2\langle[\mathrm{BB}]\rangle/N$ is lager than 1/2, the probability that a pair of sites connected by an oblique broken line in Fig. 5, of which one is a black square and the other is a black triangle, is occupied by similar atoms is larger than the probability that this pair is occupied by dissimilar atoms, and if $2\langle[\mathrm{BB}]\rangle/N$ is smaller than 1/2, then the state of affairs is reversed. To see whether $2\langle[\mathrm{BB}]\rangle/N$ is larger or smaller than 1/2, it is useful to consider the average value $\langle\sum_{(jl)}\nu_j^2\lambda_l^2\rangle$ of $\sum_{(jl)}\nu_j^2\lambda_l^2$ in which $\sum_{(jl)}$ denotes the summation over all the above mentioned pairs, because we have the relation

$$\frac{1}{N}\langle\sum_{(jl)}\nu_j^2\lambda_l^2\rangle = \left(\frac{1}{N}\langle[\mathrm{BB}]\rangle - \frac{1}{4}\right)(\gamma_2^2-\gamma_1^2)^2 + \frac{1}{4}(\gamma_2^2+\gamma_1^2)^2.$$

This average value can be calculated from the equation

$$\frac{1}{N}\langle\sum_{(jl)}\nu_j^2\lambda_l^2\rangle = \frac{1}{N}\lim_{\eta\to 0}\left(\frac{\partial}{\partial\eta}\right)\ln\Xi, \tag{5·5}$$

where

$$\Xi=\sum_{\{\mu_i\}}\sum_{\{\nu_j\}}\sum_{\{\lambda_l\}}\exp\left[-J'\sum_{(ij)}\mu_i\nu_j-J'\sum_{(il)}\mu_i\lambda_l\right.$$
$$\left.+\eta\sum_{(jl)}\nu_j^2\lambda_l^2+\xi\cdot\{\sum_j\nu_j^2+\sum_l\lambda_l^2\}\right]. \qquad (5\cdot6)$$

The parameter ξ is similar to the one introduced in § 3, which is determined from the condition that the total number of B atoms and that of C atoms are both equal to N. If the summations over $\sum_{\{\nu_j\}}$ and $\sum_{\{\lambda_l\}}$ are carried out first in the calculation of the right-hand side of Eq. (5·6), the grand partition function Ξ is reduced to the following form:

$$\Xi=A^N\sum_{\{\mu_i\}}\exp[K_1\sum_{(in)}\mu_i\mu_n+K_2\sum_{(is)}\mu_i\mu_s]$$
$$=A^N Z_t(K_1K_2),$$

where

$$Z_t(K_1K_2)=\sum_{\{\mu_i\}}\exp[K_1\sum_{(in)}\mu_i\mu_n+K_2\sum_{(is)}\mu_i\mu_s]$$

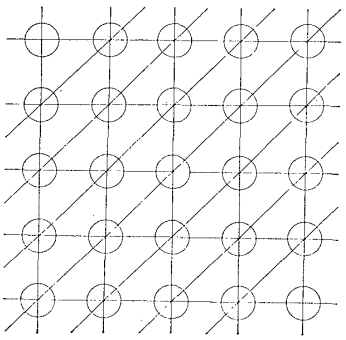

Fig. 6. The triangular lattice with the coupling parameters $kT\cdot K_1$ on the vertical and horizontal bonds, and $kT\cdot K_2$ on the oblique bond.

is the partition function of the triangular lattice with the coupling parameters $kT\cdot K_1$ on both the vertical and horizontal bonds, and $kT\cdot K_2$ on the oblique bond as shown in Fig. 6. It can also be regarded as the partition function of the plane square lattice with a second nearest neighbour coupling parameter $kT\cdot K_2$ as well as the nearest-neighbour coupling parameter $kT\cdot K_1$. Use has been made of the abbreviations

$$A^2=\sqrt{P_1P_2}\cdot P_3,$$
$$K_1=\frac{1}{4}\ln P_1-\frac{1}{4}\ln P_2$$

and

$$K_2=-\frac{1}{4}\ln P_1+\frac{1}{4}\ln P_2-\frac{1}{2}\ln P_3,$$

where

$$P_1=4\{\exp[\eta\gamma_2^4+2\xi\gamma_2^2]\cdot\cosh^2 2J'\gamma_2$$
$$+2\exp[\eta\gamma_2^2\gamma_1^2+\xi\cdot(\gamma_2^2+\gamma_1^2)]\cdot\cosh 2J'\gamma_2\cosh 2J'\gamma_1$$
$$+\exp[\eta\gamma_1^4+2\xi\gamma_1^2]\cdot\cosh^2 2J'\gamma_1\},$$
$$P_2=4\{\exp[\eta\gamma_2^4+2\xi\gamma_2^2]+2\exp[\eta\gamma_2^2\gamma_1^2+\xi\cdot(\gamma_2^2+\gamma_1^2)]$$
$$+\exp[\eta\gamma_1^4+2\xi\gamma_1^2]\}$$

and

$$P_3=4\{\exp[\eta\gamma_2^4+2\xi\gamma_2^2]\cdot\cosh 2J'\gamma_2+\exp[\eta\gamma_2^2\gamma_1^2+\xi\cdot(\gamma_2^2+\gamma_1^2)]$$
$$\times(\cosh 2J'\gamma_2+\cosh 2J'\gamma_1)+\exp[\eta\gamma_1^4+2\xi\gamma_1^2]\cdot\cosh 2J'\gamma_1\}.$$

By using the fact that the parameter K_2 tends to zero as $\eta\to 0$, we can rewrite, without knowledge of the explicit expression for the partition function $Z_t(K_1K_2)$, Eq. (5·5) as follows:

$$\frac{2\langle[\mathrm{BB}]\rangle}{N}-\frac{1}{2}=\frac{[(1-x\cosh 2J'\gamma_2)(1-x\cosh 2J'\gamma_1)]^2}{2x^2\cdot[\cosh 2J'\gamma_2-\cosh 2J'\gamma_1]^2}$$
$$\times[\langle\mu\mu''\rangle-\langle\mu\mu'\rangle^2], \tag{5·7}$$

where $\langle\mu\mu''\rangle$ denotes the correlation between a pair of second nearest neighbouring spins in the plane square lattice L_1 which interacts with the coupling parameter $(kT\cdot K)$ expressed in terms of K given in (3·4), and $\langle\mu\mu'\rangle$ is equal to the $E(x)$ which appears in (3·7), that is to say, it is the correlation between a pair of nearest neighbouring spins in the lattice L_1. For $\langle\mu\mu''\rangle$ and $\langle\mu\mu'\rangle$ Kaufman and Onsager found the expressions

$$\langle\mu\mu''\rangle=\left(\frac{1+x^2}{1-x^2}\right)\langle\mu\mu'\rangle-\left(\frac{1+x^2}{1-x^2}\right)^2\cdot\left[\frac{1}{2}-\frac{1}{\pi}\int_0^{\pi/2}\sqrt{1-W^2\sin^2\varphi}\,d\varphi\right]$$

and

$$\langle\mu\mu'\rangle=E(x),$$

where $E(x)$ and W^2 were given respectively in (3·7′) and (3·7″). The parameter x is determined from Eq. (3·7) at $P=1/2$. It is seen that at low temeratures, the right-hand side of (5·7) is positive and tends to zero at vanishing temperatures. At high temperatures, the right-hand side of (5·7) is also positive and tends to zero as the temperature rises. At the Curie temperature, by setting $x=\sqrt{2}-1$, $\langle\mu\mu'\rangle=1/\sqrt{2}$ and $\langle\mu\mu''\rangle=2/\pi$ and using Eq. (4·4), we obtain from (5·7) the following equation:

$$\frac{2}{N}\langle[\mathrm{BB}]\rangle_{T=T_c}-\frac{1}{2}=\frac{[(\sqrt{2}-1)\cosh 2J_c'\gamma_1-1)^2]}{2(\cosh 2J_c'\gamma_1+\sqrt{2}-1)^2}\cdot\left[\frac{4}{\pi}-1\right]. \tag{5·8}$$

The right-hand side of (5·8) is an increasing function of α and it can be shown that

$$0<\frac{2}{N}\langle[\mathrm{BB}]\rangle_{T=T_c}-\frac{1}{2}<\frac{1}{2}(3-2\sqrt{2})\cdot\left(\frac{4}{\pi}-1\right)\fallingdotseq\frac{0.047}{2}.$$

The probability that a pair of sites connected with a broken line in Fig. 5 is occupied by similar atoms is at most about ten percent larger than the probability that it is occupied by dissimilar atoms:

$$0<\frac{2}{N}\langle[\mathrm{BB}]\rangle_{T=T_c}-\frac{2}{N}\langle[\mathrm{BC}]\rangle_{T=T_c}<\frac{0.094}{2}\fallingdotseq 0.094\cdot\frac{2}{N}\langle[\mathrm{BB}]\rangle_{T=T_c}.$$

§ 6. Conclusion

The spontaneous magnetization and the ordering of atoms in the decorated plane square lattice have been investigated. In the case that an arrangement of atoms is fixed like the perfect Verwey ordering in a real ferrimagnet, which is shown in Fig. 1, and in some rather more general cases which have been investigated in § 2, the types of magnetization—temperature—curve are essentially the same as those found in I where all sites of the decoration lattice L_2 were exclusively occupied by a single sort of atom. When a decoration point indicated by a black circle in Fig. 1 is occupied by either a B atom or a C stom, and the total number of B atoms and that of C atoms are respectively given, there appears several types of temperature dependence of the magnetization according to the relative magnitudes of the magnetic moments of the three kinds of atoms, some of which are new types, as shown in Fig. 4; the new types correspond to the cases that the numerical relation between γ_1 and α is represented by the regions (I′), (III′) and the boundary between (I′) and (III′).

Dividing the lattice L_2 into two sublattices as shown in Fig. 5, we can conclude, in the present model, that all the black squares are occupied by B atoms and C atoms whose numbers are equal to each other, and that also in the sublattice of black triangles, the total number of B atoms and that of C atoms are equal to each other. The probabilities that a pair of sites connected with a oblique broken line in Fig. 5 is occupied respectively by similar atoms and by dissimilar atoms are nearly equal to each other both near zero temperature and at high temperatures. At the Curie temperature, the probability of occupation by similar atoms is at most about ten percent larger than that of occupation by dissimilar atoms. The explicit expression in this case is given in (5·7).

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