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Magnetization Process in an Ising Spin System

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A method of determining the state of lowest energy of an Ising spin system under an external field is proposed. The energy of a spin arrangement is expressed in terms of the total number of ***negative*** spins and the numbers of interaction lines connecting either two ***negative*** spins or ***negative*** and ***positive*** spins. It is shown by use of topological relations among these numbers that the magnetization of an Ising spin antiferromagnet increases stepwise at absolute zero with increasing field strength. The spin arrangement at each step is determined of Oguchi and Takano's model of $CoCl_2 \cdot 2H_2O$ and the simple, body-centered, face-centered cubic and MnF_2 type lattices with nearest and next-nearest neighbor interactions. Experimental results of $CoCl_2 \cdot 2H_2O$ are discussed as well.

§ 1. Introduction

The present study is motivated by Kobayashi-Haseda's[1] and Narath-Barham's[2] magnetization measurement of $CoCl_2 \cdot 2H_2O$, which is an antiferromagnet with $T_N = 17.2°K$. The crystal structure of $CoCl_2 \cdot 2H_2O$ is of monoclinic symmetry. It is inferred from a large anisotropy of the g factors ($g_b = 7.3$ and $g_c = 2.9$[2]) that a spin of Co in this substance behaves, to good approximation, like an Ising spin bound to the b axis. As is shown schematically in Fig. 1, the magnetization along the b axis measured at 4.2°K increases stepwise with increasing field strength; the discontinuities are located at 32 and 46 koe. The spins are in the ferromagnetic state with the magnetization of about $3\mu_B$ per Co above 46 koe; between 46 and 32 koe they are in an intermediate state with the magnetization of about $1\,\mu_B$ per Co. Similar phenomena are found in related substances such as $CoBr_2 \cdot 2H_2O$.[1,2] This paper proposes a general method of determining the spin structure of lowest energy of an Ising spin system under an external field. It is shown that the appearance of intermediate states in the magnetization process in an Ising spin antiferromagnet is closely related to the topology of a given lattice. The present method is applicable to three-dimensional lattices.

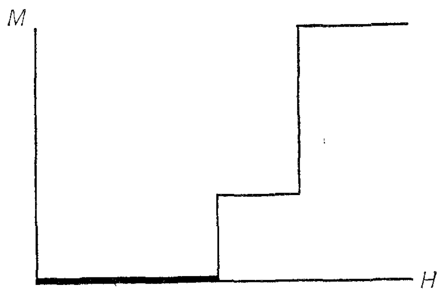


Fig. 1. A sketch of the magnetization vs. field curve of $CoCl_2 \cdot 2H_2O$.

In 1960 Domb pointed out[3] that a ferrimagnetic state is of lowest energy in a range of field strength in the case of the triangular net with the antiferromagnetic nearest neighbor interaction. The magnetization of this state is a third of that of the ferromagnetic state. Though Domb did not mention in detail his reasoning, it perhaps corresponds to a specialization of the present approach. The magnetization process in $CoCl_2 \cdot 2H_2O$ has been discussed by Oguchi and Takano[4] and Narath.[5] A crystal of $CoCl_2 \cdot 2H_2O$ may be imagined as a bundle of linear chains of -$CoCl_2$- running along the *c* axis. The interaction between two neighboring spins on a chain seems to be ferromagnetic and strong compared with inter-chain interactions.[1] Taking into account this fact, Oguchi and Takano[4] proposed a two dimensional model which corresponds to a section of the bundle of chains. They divide the lattice into four sublattices with the assumption that spins on a sublattice are kept parallel to each other throughout the magnetization process. With this approach one obtains an intermediate state whose magnetization is a half of that of the ferromagnetic state. Later Narath[5] adopted a six sublattice approach of the same model, concluding that a state with the magnetization of a third of that of the ferromagnetic state is lower in energy in a range of field strength than the ferromagnetic, antiferromagnetic and above-mentioned Oguchi-Takano states. Though the sublattice approach may yield a correct answer in some cases, it lacks the proof that the concluded state is really of lowest energy in a given field. Moreover it is difficult with this approach to gain an insight into the interrelation between the lattice topology and the magnetization process.

An outline of the present method is as follows. We assume that all spins point in positive direction in the limit of extremely strong field. A general spin arrangement is represented by a distribution of negative spins on a given lattice. A line connecting two interacting spins is called an interaction line. Interaction lines with different interaction constants are distinguished from each other. Furthermore interaction lines with the same interaction constant are divided into three categories: those connecting, 1) two negative spins, 2) negative and positive spins and 3) two positive spins. It is shown in the next section that the energy of a general spin arrangement is expressed in terms of the total number of negative spins and the numbers of interaction lines belonging to either the first or the second category. With a given number of negative spins the smallest possible numbers of interaction lines belonging to the above-mentioned categories are limited by several topological inequalities, which can be derived by an elementary analysis. By use of these inequalities we can determine the lowest value of the energy of a given system under an external field. The corresponding spin arrangement of lowest energy should satisfy several topological conditions which are, conversely, useful for the construction of such an arrangement.

We discuss the method in detail in the next section (§ 2), using the Oguchi-

Takano model as an illustrative example. In § 3 proofs are given of some topological inequalities used in the discussion of § 2. Section 4 deals with the application to three-dimensional lattices. Section 5 is devoted to supplementary discussions including the discussion of the experimental data on $CoCl_2 \cdot 2H_2O$. The appendix deals with proofs of inequalities used in the discussion of § 4.

§ 2. Principles of analyses

We express the Hamiltonian of a general Ising spin system as

$$\mathscr{H} = (1/2)\sum_{i,k,\rho} J_k\,\sigma(i)\,\sigma(i+\rho_k) - H\sum_i \sigma(i), \tag{1}$$

where σ's represent Ising sping spins, being equal to either $+1$ or -1; ρ's denote vectors connecting a spin to its interacting neighbors; the subscript k specifies a group of neighbors which interact with a given spin with an interaction contant J_k; H represents an external magnetic field measured in an appropriate unit. J_k is positive when the interaction is antiferromagnetic.

The ferromagnetic state where all spins point in positive direction is of lowest energy in the limit of extremely strong field. If we reverse a spin in that state, the associate energy change amounts to

$$\varDelta E = 2(H - \sum_k z_k J_k), \tag{2}$$

where z_k is the number of the k-th interacting neighbors. When two spins connected by a J_l interaction line are reversed in the ferromagnetic state, the energy change is given by

$$\varDelta E' = 2\varDelta E + 4J_l. \tag{3}$$

Generalizing Eqs. (2) and (3), we obtain an energy expression of a general spin arrangement given by

$$E = E_F + 2m(H - \sum_k z_k J_k) + 4\sum_k p_k J_k, \tag{4}$$

where E_F is the energy of the ferromagnetic state, m is the total number of negative spins, and p_k is the number of J_k interaction lines connecting two negative spins.

We assume for a while that all interactions are antiferromagnetic, that is, $J_k > 0$. With this assumption, the last term of the expression (4) cannot be negative. Thus the expression (4) leads to the conclusion that the ferromagnetic state is of lowest energy when $H > \sum_k z_k J_k$. At $H = H_{c1} \equiv \sum_k z_k J_k$ the states with $m > 0$ and $p_k = 0$ $(k = 1, 2, \cdots)$ are degenerate in energy with the ferromagnetic state. When H is slightly lower than H_{c1}, the state with the smallest magnetization, that is, the largest m under the conditions $p_k = 0$ $(k = 1, 2, \cdots)$ is of lowest energy. The situation is illustrated in Fig. 2.

We denote by N the total number of lattice points of a given lattice. If the above-mentioned largest possible number of m is equal to $N/2$, the cor-

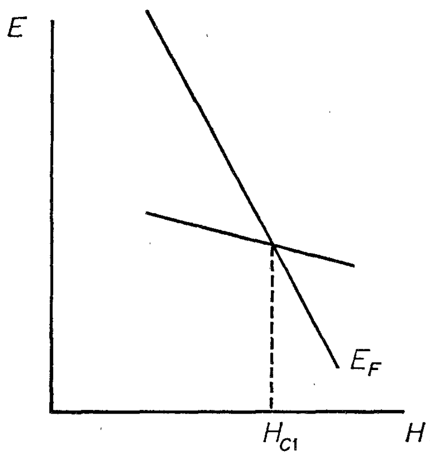


Fig. 2. The field dependence of the energy of the ferromagnetic state and the type II spin structure.

responding state is antiferromagnetic. This state should be of lowest energy until $H=0$, since its energy is independent of field strength. Thus the existence of intermediate steps in the magnetization vs. field relation of an Ising spin antiferromagnet is determined by the topological condition whether or not the largest possible number of m under the conditions $p_k=0$ $(k=1, 2, \cdots)$ is smaller than $N/2$.

We assume in the following discussion that the lattice is wrapped on a torus. If we denote by q_k the number of J_k interaction lines connecting positive and negative spins, we can easily prove the following equation:

$$2p_k+q_k=z_k m. \qquad (5)$$

When some interactions are ferromagnetic, we rewrite the expression (4) by use of Eq. (5) as

$$E=E_F+2m(H-\textstyle\sum_1 z_k J_k)+4\sum_1 p_k J_k+2\sum_2 q_l|J_l|, \qquad (6)$$

where the sum 1 is taken over the antiferromagnetic interactions and the sum 2 over the ferromagnetic interactions. Again the last two terms of the expression (6) are positive or zero. In some cases, however, the conditions $p_k=0$ and $q_l=0$ cannot be satisfied with $m>0$. Otherwise the discussion is similar to that of the preceding case where all interactions are antiferromagnetic.

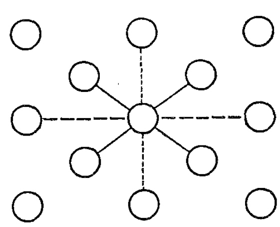


Fig. 3. Oguchi-Takano's model. The full line represents a J_1 interaction line, the dotted line a J_2 interaction line, and the broken line a J_3 interaction line.

Going back to the case where all J_k's are positive, we denote by m_I the largest possible number of m under the conditions $p_k=0$. With decreasing H a state with some p_k's>0 and $m>m_I$ may become lower in energy than the state with $m=m_I$ and $p_k=0$ when $m_I<N/2$. In order to determine the range of H in which the state with $m=m_I$ and $p_k=0$ is of lowest energy, we use several inequalities which yield the smallest possible numbers of p_k's with a given m. Since these inequalities depend on the lattice topology, we assume in the following discussion Oguchi-Takano's model of $CoCl_2 \cdot 2H_2O$ as an illustrative example. The case where some interactions are ferromagnetic is discussed also on this example.

Figure 3 illustrates Oguchi-Takano's model. The lattice is a face-centered rectangular net, in which a spin interacts with four neighbors in the directions of the face-diagonals with an interaction constant J_1, with two neighbors along the a axis with J_2, and with two neighbors along the b axis with J_3.

In the next section we shall prove the following inequalities:

$$p_1+p_2 \geqq 3m-N, \tag{7}$$

$$p_1+p_3 \geqq 3m-N, \tag{8}$$

$$2p_1+p_2+p_3 \geqq 4m-N. \tag{9}$$

It is essential that the equality in the above inequalities yields the smallest *possible* values of p's with a given m.

We discuss first that the case where all J's are positive. The ferromagnetic state is of lowest energy in the range, $H \geqq H_{c1}=4J_1+2J_2+2J_3$. The inequality (9) tells us that the largest possible value of m under the conditions $p_1=p_2=p_3=0$ is equal to $N/4$. The corresponding spin arrangement is not unique in the present case. Examples of the spin arrangements which are of lowest energy just below H_{c1} are given in Fig. 4. In these arrangements linear chains running in the direction of one of the face-diagonals are alternately ferromagnetic or antiferromagnetic. The example shown in Fig. 4a is the same as the state pointed out by Oguchi and Takano.[4] Hereafter the spin arrangements with $m=N/4$ and p's$=0$ are called type II structures. The type I stands for the ferromagnetic state.

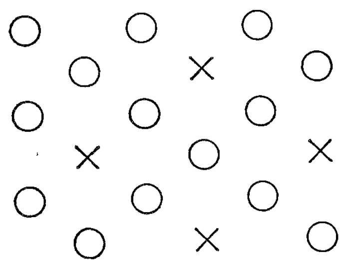
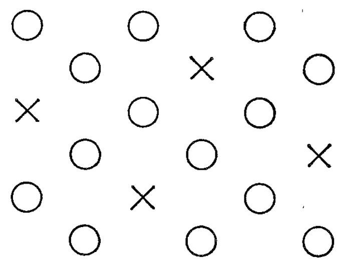
(a)  (b) 

Fig. 4. The type II structures in Oguchi-Takano's model (a and b). × represents a negative spin; ○ a positive spin.

In the following discussion we assume $J_2>J_3$. Since J_2 and J_3 are interchangeable with each other, the discussion can be easily adapted to the case $J_2<J_3$. The case $J_2=J_3$ is discussed separately. We rewrite the expression corresponding to the last term of Eq. (4) as

$$4(p_1J_1+p_2J_2+p_3J_3)=4p_1(J_1-2J_3)+4p_2(J_2-J_3)+4(2p_1+p_2+p_3)J_3 \tag{10}$$

or

$$4(p_1J_1+p_2J_2+p_3J_3)=2(2p_1+p_2+p_3)J_1+2p_2(2J_2-J_1)+2p_3(2J_3-J_1). \tag{11}$$

If $J_1>2J_3$, and $J_2>J_3$, the minimum value of the expression (10) can be easily calculated by assuming the equality in the inequality (9) and $p_1=p_2=0$ as

$$4(p_1J_1+p_2J_2+p_3J_3) \geqq 16[m-(N/4)]J_3. \tag{12}$$

The expression (11) is useful in the case $2J_2>J_1$, $2J_3>J_1$. We distinguish three cases in the following discussion.

i) *Case A1*: $J_1>2J_3$, $J_1>J_2+J_3$, $(J_2>J_3)$. We denote by $E(\mathrm{II})$ the energy of the type II structures. By use of the inequality (12) we obtain

$$E-E(\mathrm{II})\geqq 2[m-(N/4)](H-4J_1-2J_2+6J_3), \tag{13}$$

where the equality holds when $p_1=p_2=0$, and $p_3=4m-N$. The inequality (13) leads to the conclusion that the type II structures are of lowest energy in the range, $H_{c1}\geqq H\geqq H_{c2}\equiv 4J_1+2J_2-6J_3$. When H is just below H_{c2}, the state whose m is maximum under the conditions $p_1=p_2=0$, and $p_3=4m-N$ is of lowest energy. This maximum value of m is equal to $N/3$ according to the inequality (7). The corresponding spin structure, which will be called type III, is shown in Fig. 5. The type III structure coincides with that pointed out by Narath.[5] Since $p_3=4(N/3)-N=N/3=m$, a negative spin should share two J_3 interaction lines with negative spins. By use of this fact we can prove the uniqueness of the type III structure.

The expression (10) can be rewritten as

$$4(p_1J_1+p_2J_2+p_3J_3)=4p_1(J_1-J_2-J_3)+4(p_1+p_2)(J_2-J_3)+4(2p_1+p_2+p_3)J_3. \tag{14}$$

By use of the above expression and the inequalities (7) and (9) we obtain

$$E-E(\mathrm{III})\geqq 2[m-(N/3)](H-4J_1+4J_2), \tag{15}$$

where $E(\mathrm{III})$ is the energy of the type III structure. The inequality (15) indicates that the type III structure is of lowest energy in the range, $H_{c2}\geqq H\geqq H_{c3}\equiv 4J_1-4J_2$. The state of lowest energy just below H_{c3} should satisfy the conditions, $p_1=0$, $p_2=3m-N$, and $p_2+p_3=4m-N$, with $m>N/3$. Figure 6 shows the type IV structure, which satisfies these conditions with $m=N/2$. Since this

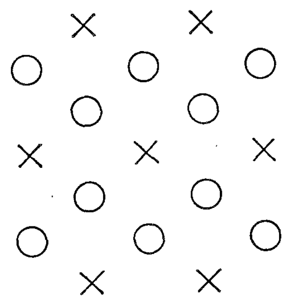


Fig. 5. The type III structure in Oguchi-Takano's model.

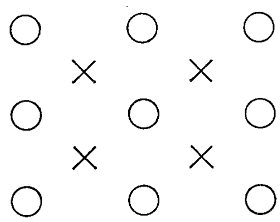


Fig. 6. The type IV structure in Oguchi-Takano's model.

state is antiferromagnetic, it is of lowest energy even at $H=0$.

ii) *Case A2*: $J_1>2J_3$, $J_1<(J_2+J_3)$, $(J_2>J_3)$. The type III structure is of lowest energy below the same H_{c2} as in the *case A1*. We rewrite the expression (10) as

$$4(p_1 J_1 + p_2 J_2 + p_3 J_3) = 4(p_1 + p_2)(J_1 - 2J_3) + 4p_2(J_2 + J_3 - J_1) + 4(2p_1 + p_2 + p_3) J_3. \tag{16}$$

By use of the above expression and the inequalities (7) and (9) we obtain

$$E - E(\mathrm{III}) \geqq 2[m - (N/3)](H + 2J_1 - 2J_2 - 6J_3), \tag{17}$$

where the equality holds when $p_2 = 0$, $p_1 = 3m - N$, and $2p_1 + p_3 = 4m - N$. Figure 7 shows the type V structure which satisfies these conditions with $m = N/2$. The transition between the type III and type V structures occurs at $H_{c3} = -2J_1 + 2J_2 + 6J_3$.

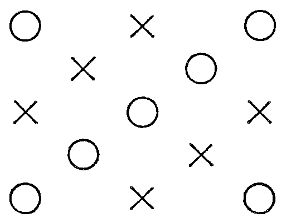


Fig. 7. The type V structure in Oguchi-Takano's model.

iii) *Case A3*: $J_1 < 2J_3$, $(J_2 > J_3)$. The expression (11) is used in the analysis of the present case. The type II structures are of lowest energy in the range, $H_{c1} \geqq H \geqq H_{c2} = 2J_2 + 2J_3$. Below H_{c2} the type V structure is of lowest energy.

As an example of the case where ferromagnetic interactions are involved, we discuss the *Case D2*: $J_1 < 0$, $J_2 > 0$, $J_3 > 0$, $|J_1| < (J_2 + J_3)$, $J_2 > J_3$. The topological inequalities used in the analysis are given by

$$q_1 + 2p_2 \geqq 2m, \tag{18}$$

$$q_1 + 2p_3 \geqq 2m. \tag{19}$$

We rewrite the last two terms of the expression (6) as

$$4(p_2 J_2 + p_3 J_3) + 2q_1|J_1| = 2(q_1 + 2p_3)|J_1| + 4p_2 J_2 + 4p_3(J_3 - |J_1|) \tag{20}$$

or

$$4(p_2 J_2 + p_3 J_3) + 2q_1|J_1| = 2(q_1 + 2p_3) J_3 + 2(q_1 + 2p_2)(|J_1| - J_3) + 4p_2(J_2 + J_3 - |J_1|), \tag{21}$$

where the expression (20) is used when $J_3 > |J_1|$, and the expression (21) is used when $|J_1| > J_3$. By use of these expressions and the inequalities (18) and (19) we obtain

$$4(p_2 J_2 + p_3 J_3) + 2q_1|J_1| \geqq 4m|J_1| \tag{22}$$

and

$$E - E_F \geqq 2m(H - 2J_2 - 2J_3 + 2|J_1|), \tag{23}$$

where the equality holds when $p_2 = p_3 = 0$, and $q_1 = 2m$. The type V structure satisfies these conditions with $m = N/2$. The transition between the ferromagnetic (type I) state and the type V structure occurs at $H_{c1} = 2J_2 + 2J_3 - 2|J_1|$.

The states of lowest energy in other cases are listed in Table I. The

Table I. The magnetization process and the spin structure of lowest energy in Oguchi-Takano's model. Table IA deals with the definitions of various cases. The magnetization change with decreasing field and the spin structures of lowest energy are listed in Table IB I, II, etc., indicate the type of the spin structure. Table IC gives the expressions of the critical fields in terms of J's.

IA

Case	Definition ($J_2>J_3$)
$A1$	$J_1, J_2, J_3>0,\ J_1>(J_2+J_3)$
$A2$	〃 $,\ J_1<(J_2+J_3),\ J_1>2J_3$
$A3$	〃 $,\ J_1<2J_3$
$B1$	$J_1, J_2>0,\ J_3\leq 0,\ J_1>J_2$
$B2$	〃 $,\ J_1<J_2$
$C1$	$J_1>0,\ J_2, J_3<0$
$D1$	$J_1<0,\ J_2, J_3>0,\ \lvert J_1\rvert>(J_2+J_3)$
$D2$	〃 $,\ \lvert J_1\rvert<(J_2+J_3)$
$E1$	$J_1, J_3<0,\ J_2>0,\ \lvert J_1\rvert>J_2$
$E2$	〃 $,\ \lvert J_1\rvert<J_2$
$F1$	$J_1, J_2, J_3<0$

IB

$(M)\to H_{c1}\to(M/2)\to H_{c2}\to(M/3)\to H_{c3}\to(0)$				
$A1$	I	II	III	IV
$A2$	I	II	III	V
$(M)\to H_{c1}\to(M/2)\to H_{c2}\to(0)$				
$A3$	I	II	V	
$(M)\to H_{c1}\to(M/3)\to H_{c2}\to(0)$				
$B1$	I	III	IV	
$B2$	I	III	VI	
$(M)\to H_{c1}\to(0)$				
$C1$	I	IV		
$D2$	I	V		
$E2$	I	VI		
$D1$, $E1$, $E1$	always I			

IC

	H_{c1}	H_{c2}		H_{c3}
$A1$	$4J_1+2J_2+2J_3$	$4J_1+2J_2-6J_3$		$4J_1-4J_2$
$A2$				$2J_2+6J_3-2J_1$
	H_{c1}	H_{c2}		H_{c1}
$A3$	$4J_1+2J_2+2J_3$	$2J_2+2J_3$	$C1$	$4J_1$
$B1$	$4J_1+2J_2$	$4J_1-4J_2$	$D2$	$2J_2+2J_3-2\lvert J_1\rvert$
$B2$	$4J_1+2J_2$	$4J_2-4J_1$	$E2$	$2J_2-2\lvert J_1\rvert$

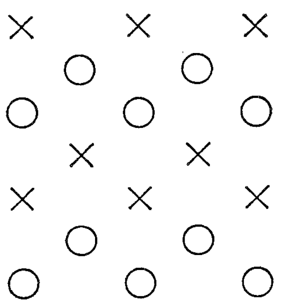


Fig. 8. The type VI structure in Oguchi-Takano's model.

magnetization of the type I (ferromagnetic) is denoted by M. The magnetization of other states are indicated by a fraction of M. The type VI structure, which is listed in Table I, is shown in Fig. 8.

When $J_2=J_3$, the type III phase disappears in the *cases A1* and *A2*. In other cases, where J_2 and J_3 are of the same sign, Table I is applicable to the case $J_2=J_3$ also.

The magnetization process in other special cases such as $J_1=J_2+J_3$ in the *cases A1* and *A2* can be easily inferred from Table I. Spin arrangements in such cases are not unique.

§ 3. Proofs of the inequalities (7), (8), (9), (18) and (19)

We divide the lattice into rhombs, as is shown in Fig. 9. The sides of a rhomb are J_1-interaction lines. The opposite vertices are connected by a J_2- or J_3-interaction line. A pair of vertices connected by a J_2-(J_3-) interaction line is called J_2-(J_3-) vertices. We divide the rhombs into nine classes according to the numbers of the J_2- and J_3-vertices occupied by negative spins. Figure 10 shows the classification. We denote by n_i the number of rhombs belonging to the i-th class. As was mentioned in the previous section, the lattice is assumed to be wrapped on a torus. We note that each vertex is shared by four rhombs, and that a J_1-interaction line is shared by two rhombs. These facts lead to the following equations:

$$N=n_1+n_2+n_3+n_4+n_5+n_6+n_7+n_8+n_9, \tag{24}$$

$$4m=4n_1+3n_2+3n_3+2n_4+2n_5+2n_6+n_7+n_8, \tag{25}$$

$$2p_1=4n_1+2n_2+2n_3+n_4, \tag{26}$$

$$2q_1=2n_2+2n_3+2n_4+4n_5+4n_6+2n_7+2n_8, \tag{27}$$

$$p_2=n_1+n_3+n_6, \tag{28}$$

$$p_3=n_1+n_2+n_5. \tag{29}$$

Expressing the both sides of the inequalities in terms of n's, we can prove easily them. For example, we obtain

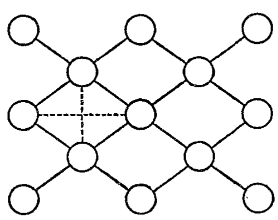


Fig. 9. Division of the face-centered rectangular lattice into rhombs.

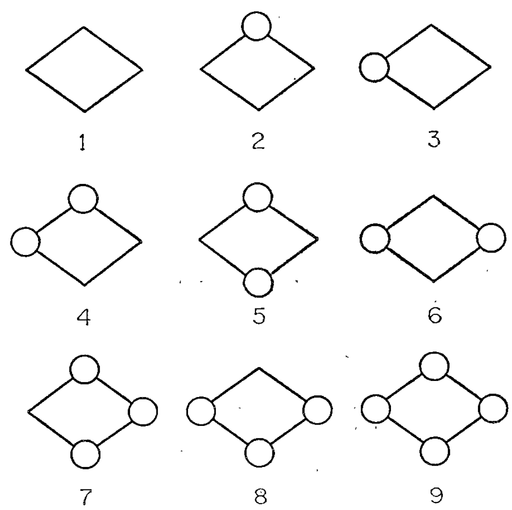


Fig. 10. Spin configurations on a rhomb. ○ represents a positive spin; a vertex without the open circle is occupied by a negative spins.

$$2p_1+p_2+p_3=6n_1+3n_2+3n_3+n_4+n_5+n_6, \tag{30}$$

$$4m-N=3n_1+2n_2+2n_3+n_4+n_5+n_6-n_9, \tag{31}$$

which lead to the inequality (9) immediately. The equality holds when n_1, n_2, n_3, n_9 are zero.

§ 4. Three-dimensional lattices

The method developed in the previous sections is applicable to three-dimensional lattices. We describe below the results of the analysis of the simple, body-centered, face-centered cubic and MnF_2 type lattices with the nearest and next nearest neighbor interactions. Detailed discussions are given on some representative cases only. Proofs of the inequalities are given in the Appendix.

We denote by J_1 the interaction constant of the nearest neighbor interaction, by J_2 that of the next nearest neighbor interaction.

A. *Simple cubic lattice*

The following inequalities exist among p's and q's:

$$4p_1+p_2\geqq 12m-3N, \tag{32}$$

$$p_2\geqq 4m-N, \tag{33}$$

$$2q_1+p_2\geqq 6m, \tag{34}$$

$$q_1+p_2\geqq 4m. \tag{35}$$

We discuss the case, $J_1<0$ and $J_2>0$. We rewrite the last two terms of the expression (6) adapted to the present case as

$$4p_2 J_2+2q_1|J_1|=2p_2(2J_2-|J_1|)+2(q_1+p_2)|J_1| \tag{36}$$

$$4p_2 J_2+2q_1|J_1|=2(2q_1+p_2)(|J_1|-2J_2)+2(q_1+p_2)(4J_2-|J_1|) \tag{37}$$

or

$$4p_2 J_2+2q_1|J_1|=4(2q_1+p_2)J_2+2q_1(|J_1|-4J_2). \tag{38}$$

i) $2J_2>|J_1|$. Assuming $p_2=0$ and the equality in the inequality (35), we obtain by use of the expression (36)

$$E-E_F\geqq 2m(H-12J_2+4|J_1|), \tag{39}$$

which determines H_{c1} as $H_{c1}=12J_2-4|J_1|$. The inequality (33) tells us that the largest possible value of m under the condition $p_2=0$ is equal to $N/4$. Thus the spin structure with $m=N/4$, $p_2=0$, and $q_1=4m=N$ becomes of lowest energy when the field H decreases through H_{c1}. This spin structure, which is called type V, is shown in Fig. 11. Subtracting E(V) from the energy of a general state with $m>N/4$ and assuming the equality in the inequalities (33) and (35), we obtain

$$E-E(\mathrm{V}) \geqq 2[m-(N/4)](H-4J_2), \tag{40}$$

which determines the range of the type V phase as $H_{c1} \geqq H \geqq H_{c2} = 4J_2$. The type VI structure, which is explained in Table II, satisfies the equality conditions of the inequalities (33) and (35) with $m = N/2$.

ii) $4J_2 > |J_1| > 2J_2$. Assuming the equality in the inequalities (34) and (35) we obtain from the expression (37)

$$E-E_F \geqq 2m(H-8J_2+2|J_1|). \tag{41}$$

The type VI structure satisfies the equality conditions with $m = N/2$. H_{c1} is given by $H_{c1} = 8J_2 - 2|J_1|$.

iii) $|J_1| > 4J_2$. The ferromagnetic state is always of lowest energy in this case.

Table II and Fig. 11 summarize the results of the analysis of other cases.

Table II. The magnetization process in the simple cubic lattice with the nearest and next nearest neighbor interactions.

IIA

Cases	Definition
*A*1	$J_1>0,\ J_2>0,\ J_1>4J_2$
*A*2	$J_1>0,\ J_2>0,\ J_1<4J_2$
*B*1	$J_1<0,\ J_2>0,\ \lvert J_1\rvert<2J_2$
*B*2	$J_1<0,\ J_2>0,\ 2J_2<\lvert J_1\rvert<4J_2$
*B*3	$J_1<0,\ J_2>0,\ \lvert J_1\rvert>4J_2$
*C*1	$J_1>0,\ J_2<0$
*D*1	$J_1<0,\ J_2<0$

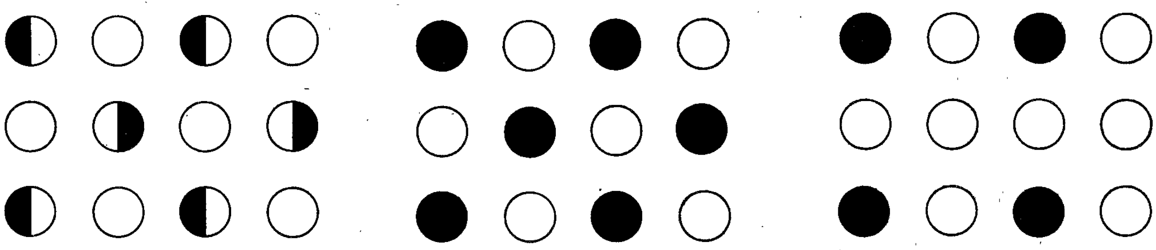
IIB

	$(M) \to H_{c1} \to (M/2) \to H_{c2} \to (0)$		
*A*1	I	II	III
*A*2	I	II	IV
*B*1	I	V	VI
	$(M) \to H_{c1} \to (0)$		
B2	I		VI
*C*1	I		III

The type III denotes the structure in which nearest neighboring spins are antiparallel to each other. The type VI is a layer structure in which (001) planes are occupied by negative and positive spins alternately. The type II, IV and V structures are shown in Fig. 11. The *Cases B*3 and *D*1 are ferromagnetic in the whole range of *H*.

IIC

	H_{c1}	H_{c2}
*A*1	$6J_1+12J_2$	$6J_1-12J_2$
*A*2	"	$2J_1+4J_2$
*B*1	$12J_2-4\lvert J_1\rvert$	$4J_2$
*B*2	$8J_2-2\lvert J_1\rvert$	
*C*1	$6J_1$	



a b c

Fig. 11. Spin structures in the simple cubic lattice. Figures a, b and c represent the projections of spin structures on a (001) plane; black and open circles represent the sequence of negative and positive spins in the direction [001], respectively. A half-open half-black circle corresponds to a linear chain in the direction [001] on which negative and positive spins alternate; the black (open) right half circle represents a negative (positive) spin on a (001) plane, and the left half a positive (negative) spin on its adjacent planes. Figure 11a represents the type II′ structure; Fig. 11b the type IV structure; Fig. 11c the type V structure.

B. *Body-centered cubic lattice*

The inequalities in the present case are given by

$$3p_1+2p_2 \geqq 12m-3N, \tag{42}$$

$$3q_1+4p_2 \geqq 12m. \tag{43}$$

Table III summarizes the results of the analysis.

Table III. The magnetization process in the body-centered cubic lattice with the nearest and next nearest neighbor interactions.

IIIA

Cases	Definition
$A1$	$J_1>0,\ J_2>0,\ 2J_1>3J_2$
$A2$	$J_1>0,\ J_2>0,\ 2J_1<3J_2$
$B1$	$J_1<0,\ J_2>0,\ 3J_2>2\|J_1\|$
$B2$	$J_1<0,\ J_2>0,\ 3J_2<2\|J_1\|$
$C1$	$J_1>0,\ J_2<0$
$D1$	$J_1<0,\ J_2<0$

IIIB

	$(M)\to H_{c1}\to(M/2)\to H_{c2}\to(0)$		
$A1$	I	II	III
$A2$	I	II	IV
	$(M)\to H_{c1}\to(0)$		
$B1$	I	IV	
$C1$	I	III	

IIIC

	H_{c1}	H_{c2}
$A1$	$8J_1+6J_2$	$8J_1-6J_2$
$A2$		$6J_2$
$B1$	$6J_2-4\|J_1\|$	
$C1$	$8J_1$	

The body-centered cubic lattice can be decomposed into two simple cubic sublattices. The type II structure is such that one sublattice is antiferromagnetic and the other is occupied by positive spins. In the type III one sublattice is occupied by negative spins and the other by positive spins. Each sublattice is antiferromagnetic in the type IV structure. The *Cases* $B2$ and $D1$ are ferromagnetic in the whole range H.

C. *Face-centered cubic lattice*

The inequalities are given by

$$2p_1+p_2 \geqq 6m-N, \tag{44}$$

$$2p_1+p_2 \geqq 12m-3N, \tag{45}$$

$$p_1 \geqq 4m-N, \tag{46}$$

$$q_1+2p_2 \geqq 6m, \tag{47}$$

where the inequality (44) applies to the case $m \leqq N/3$, the inequality (45) to the case $m \geqq N/3$. We discuss the case $J_1>0$, $J_2>0$ as an example of the analysis. From the general discussion given in § 2, we obtain $H_{c1}=12J_1+6J_2$. According to the inequality (44) the largest possible value of m under the conditions $p_1=p_2=0$ is equal to $N/6$. The corresponding spin structure, which will be called type II, is shown in Fig. 12. We rewrite the last term of the expression (4) adapted to the present case as

$$4p_1 J_1+4p_2 J_2=4p_1(J_1-2J_2)+4(2p_1+p_2)J_2, \tag{48}$$

or

$$4p_1 J_1+4p_2 J_2=2(2p_1+p_2)J_1+2p_2(2J_2-J_1). \tag{49}$$

i) $J_1>2J_2$. Assuming $p_1=0$ and the equality in the inequality (44), we obtain by use of the expression (48)

$$E-E(\mathrm{II}) \geqq 2[m-(N/6)](H-12J_1+6J_2), \tag{50}$$

which determines the range of the type II phase as $H_{c1} \geqq H \geqq H_{c2}=12J_1-6J_2$. It is seen from the inequality (46) that the largest possible value of m under the condition $p_1=0$ is equal to $N/4$. The type III structure, which satisfies $p_1=0$ and the equality condition of the inequality (44) with $m=N/4$, is shown in Fig. 12.

In order to determine the range of the type III phase, we assume the equality in the inequalities (44) and (46). By use of the expression (48) and these equalities we obtain

$$E-E(\mathrm{III}) \geqq 2[m-(N/4)](H-4J_1-10J_2), \tag{51}$$

which determines the range as $H_{c2} \geqq H \geqq H_{c3}=4J_1+10J_2$. The largest possible value of m under the equality condition $2p_1+p_2=6m-N$ is equal to $m=N/3$, since the inequality (45) replaces (44) when $m>N/3$. The type IV structure, which satisfies the equality conditions of the inequalities (44) and (46), is shown in Fig. 12.

Assuming the equality in the inequalities (45) and (46) and using the expression (48) we obtain

$$E-E(\mathrm{IV}) \geqq 2[m-(N/3)](H-4J_1+2J_2), \tag{52}$$

which determines the lower limit of the type IV range as $H_{c4}=4J_1-2J_2$. Below H_{c4} the type V structure, which is shown also in Fig. 12, is of lowest energy. It satisfies the equality conditions of the inequalities (45) and (46) with $m=N/2$.

ii) $J_1<2J_2$. The analysis of this case is based on the expression (49). The results are listed in Table IV and Fig. 13.

The results of the analysis of other cases are also listed in Table IV. The spin arrangement on the face-centered cubic lattice in the absence of external field was discussed by Anderson.[6] The type V structure corresponds to the pattern of the third kind in his notation, the type VII to that of the second kind, and the type IX to that of the first kind. There are two different spin structures belonging to the second kind of ordering. One is of trigonal sym-

Table IV. The magnetization process in the face-centered cubic lattice with the nearest and next nearest neighbor interactions.

IVA

Cases	Definition
*A*1	$J_1>0,\ J_2>0,\ J_1>2J_2$
*A*2	$J_1>0,\ J_2>0,\ J_1<2J_2$
*B*1	$J_1<0,\ J_2>0,\ J_2>\lvert J_1\rvert$
*B*2	$J_1<0,\ J_2>0,\ J_2<\lvert J_1\rvert$
*C*1	$J_1>0, J_2<0$
*D*1	$J_1<0,\ J_2<0$

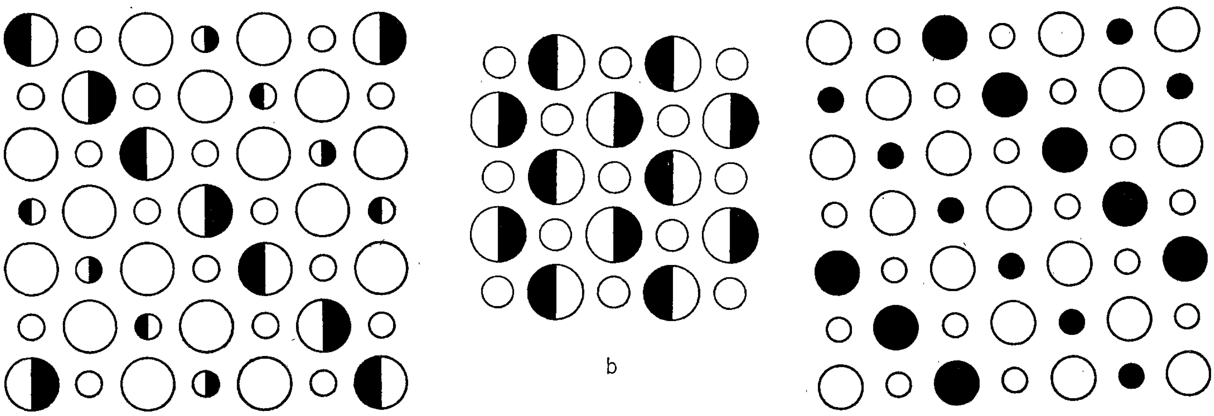
IVB

	$(M)\to H_{c1}\to(2M/3)\to H_{c2}\to(M/2)\to H_{c3}\to(M/3)\to H_{c4}\to(0)$					
*A*1	I	II	III	IV	V	
	$(M)\to H_{c1}\to(2M/3)\to H_{c2}\to(M/3)\to H_{c3}\to(0)$					
*A*2	I	II	VI	VII		
	$(M)\to H_{c1}\to(0)$		$(M)\to H_{c1}\to(M/2)\to H_{c2}\to(0)$			
*B*1	I	VII	*C*1	I	VIII	IX

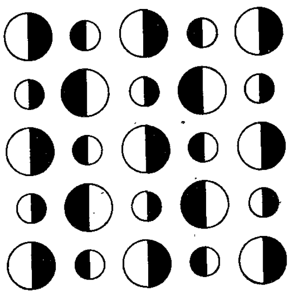
One of the four simple sublattices is occupied by negative spins in the type VIII structure. The type IX denotes the structure in which two simple cubic sublattices are occupied by negative spins. Other types are shown in Figs. 12 and 13. The *Cases B*2 and *D*1 are ferromagnetic in the whole range of *H*.

IVC

	H_{c1}	H_{c2}	H_{c3}	H_{c4}
$A1$	$12J_1+6J_2$	$12J_1-6J_2$	$4J_1+10J_2$	$4J_1-2J_2$
$A2$		$6J_1+6J_2$	$6J_2$	
$B1$	$6J_2-6\|J_1\|$			
$C1$	$12J_1$	$4J_1$		

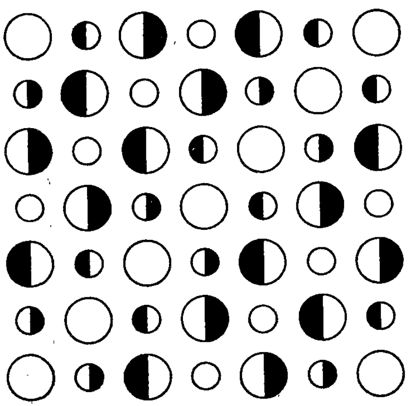


a b c

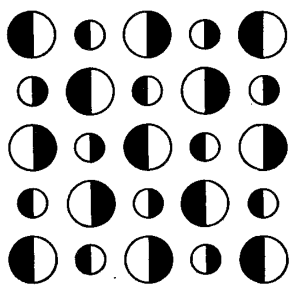


d

Fig. 12. Spin structures in the face-centered cubic lattice (*Case A*1). A large circle represents a spin on a (001) plane; a small circle a spin on an adjacent (00 1/2) plane. The definition of black, open, and half-open circles is the same as in Fig. 11. Figure 12a represents the type II structure; Fig. 12b the type III; Fig. 12c the type IV; Fig. 12d the type V.



a



b

Fig. 13. Spin structures in the face-centered cubic lattice. Fig.13a. represents the type VI structure; Fig. 13b the type VII structure.

metry, being called the Néel structure. The other is of cubic symmetry. Figure 13 shows the former only.

D. *MnF_2 (rutile) type lattice*

Mn in MnF_2 is on a body-centered tetragonal lattice with the c axis shorter than the a axis. We assume two kinds of interactions: the body-center to corner interaction specified by J_1 and the interaction between the nearest neighbors on the c axis specified by J_2.

The inequalities are given by

$$p_1+2p_2 \geqq 6m-2N, \tag{53}$$

$$q_1+4p_2 \geqq 4m. \tag{54}$$

Table V. The magnetization process in the MnF_2 type lattice.

VA

Cases	Definition
$A1$	$J_1>0,\ J_2>0,\ 2J_1>J_2$
$A2$	$J_1>0,\ J_2>0,\ 2J_1<J_2$
$B1$	$J_1<0,\ J_2>0,\ J_2>2\|J_1\|$
$B2$	$J_1<0,\ J_2>0,\ J_2<2\|J_1\|$
$C1$	$J_1>0,\ J_2<0$
$D1$	$J_1<0,\ J_2<0$

VB

	$(M)\to H_{c1}\to(M/3)\to H_{c2}\to(0)$		
$A1$	I	II	III
$A2$	I	II	IV

	$(M)\to H_{c1}\to(0)$	
$B1$	I	IV
$C1$	I	III

The types of structure are explained in the text.
The *Cases* $B2$ and $D1$ are ferromagnetic in the whole range of H.

VC

	H_{c1}	H_{c2}
$A1$	$8J_1+2J_2$	$8J_1-4J_2$
$A2$	$8J_1+2J_2$	$2J_2-4J_1$
$B1$	$2J_2-4\|J_1\|$	
$C1$	$8J_1$	

The results of the analysis are listed in Table V. Definitions of the spin structures are as follows. The type II structure is such that every three c plane is occupied by negative spins; the type III structure is an antiferromagnetic arrangement in which spins at the body-centered sites are antiparallel to those at the corner sites; the type V structure is a bundle of antiferromagnetic linear chains running along the c axis.

§ 5. Discussions

The gist of the present method is the use of the topological inequalities. It is essential that the equality holds in these inequalities for several special spin arrangements. The inequalities are derived by 1) finding an elementary figure formed by interaction lines, 2) enumerating different spin configurations on the figure, and 3) expressing N, m, p's, and q's in terms of the number of the figures of each class of a spin arrangement. With these inequalities the determination of the magnetization process at absolute zero can be carried out rigorously.

One might question that inequalities other than those mentioned in the preceding sections would exist. The condition that the equality should be satisfied by at least several spin structures, however, excludes such a possibility. Of course less restrictive inequalities in which the equality is never satisfied by any spin structure are out of the question. For example, the equality in the inequality (7) is satisfied by the type III structure with $m=N/3$ and $p_1=p_2=0$, the type IV structure with $m=N/2$, $p_1=0$ and $p_2=N/2$, and the type V or VI structure with $m=N/2$, $p_1=N/2$ and $p_2=0$. It should be emphasized that the inequality (7) is derived and proved by an argument which does not presuppose these structures. The inequality (7) and the existence of the type IV, V and VI structures guarantee that the minimum value of p_1 with $m=N/2$ and $p_2=0$ or the minimum value of p_2 with $m=N/2$ and $p_1=0$ is equal to $N/2$. Suppose we have an inequality

$$\alpha_1 p_1+\alpha_2 p_2 \geqq N/2, \tag{55}$$

where m is assumed to be equal to $N/2$. If the equality in the inequality (55) is satisfied by the type IV and V structures, α's are concluded to be equal to one; in this case the inequality (55) coincides with the inequality (7). Suppose the equality is not satisfied by the type IV structure. Then α_2 should be larger than one, since the minimum value of p_2 with $p_1=0$ is equal to $N/2$. In this case we can show that the equality in (55) is never satisfied by any spin structure with $p_2>0$. Assuming the equality in (55) and replacing $N/2$ by $\alpha_1 p_1+\alpha_2 p_2$ in the inequality (7), we obtain

$$(1-\alpha_1)p_1+(1-\alpha_2)p_2 \geqq 0. \tag{56}$$

The inequality can be right only when $p_2=0$ and $\alpha_1=1$, since α_2 is larger than one and α_1 cannot be smaller than one. Thus we can conclude that the inequality (7) is the only one whose equality is satisfied by at least two spin structures with $m=N/2$, and that the inequality (55) is essentially the same as the inequality (7) whenever the equality is satisfied.

One might question further that there might be a more restrictive inequality in an intermediate range of m, for example, between $m=N/3$ and $m=N/2$ in the case of the inequality (7). Such an inequality, however, is of no interest in the present analysis, because we always look for a spin structure which satisfies the equality with the largest possible m.

The spin structure of $CoCl_2 \cdot 2H_2O$ at $H=0$ has been determined by Narath[2] by use of proton resonance to be of type IV. It is seen from Table I that *Case B*1 fits in with the experimental results. *Case A*1, however, cannot be excluded completely, since the type II phase might be masked by experimental uncertainty.

Recently Date and Motokawa[7] have measured the magnetization and microwave absorption of this substance. They have found a large hysteresis at the transition between the type IV and III structures, while practically no hysteresis has been observed at the transition between the type III and I (ferromagnetic) structures. This can be understood qualitatively if J_3 is assumed to be small. Assuming $J_3=0$ (*Case B*1), we note that the local effective field at negative spins in the type IV structure or that at positive spins in the type III structure does not vanish at the transition field. In other words, the structures are locally stable at H_{c2}. On the other hand, the corresponding field vanishes at $H=H_{c1}$. This discussion is based on the assumption that a spin in the two-dimensional model, that is, the total spin of a linear chain can change its direction in short time in the absence of local field.

The microwave absorption is observed to occur at the transition fields only, irrespective of the microwave frequency. This is probably related to the appearance of transient spin structures at the transitions.

An approximate calculation of the magnetization vs. field relation at finite temperature will be reported in future.

Acknowledgements

I shoule like to express my thanks to Professor T. Nakamura and Professor M. Date for valuable discussions on both theoretical and experimental points. Thanks are due also to Mr. M. Motokawa for discussions on the experimental data.

Appendix

The inequalities in the three-dimensional cases can be derived by the same procedure as in the two-dimensional case.

A. *Simple cubic lattice*

We divide the lattice into squares whose sides and diagonals are J_1 and J_2 interaction lines, respectively. The squares are classified in six categories according to the configurations of negative and positive spins at four vertices. Noting that a vertex is shared by twelve squares and a J_1 interaction line is shared by four squares, we can easily prove the inequalities (32) and (34).

In order to prove the inequality (33) we adopt as a counting unit the tetrahedron shown in Fig. 14. The sides of the tetrahedron are J_2 interaction

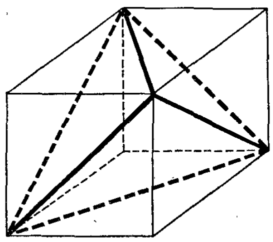


Fig. 14. The tetrahedron formed by J_2-interaction lines in the simple cubic lattice.

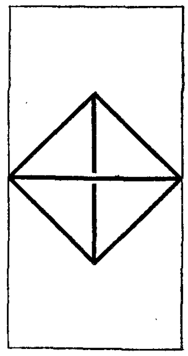


Fig. 15. The projection of the tetrahedron on a (001) plane in the body-centered cubic lattice.

lines. A tetrahedron is topologically equivalent to a rhomb with two diagonals connecting opposite vertices. Since all interaction lines are equivalent in the present case, we do not distinguish between the categories 2 and 3, 7 and 8, and among the categories 4, 5 and 6 in Fig. 10. Noting that a vertex is shared by eight tetrahedrons and a J_2 interaction line is shared by two tetrahedrons, we can prove easily the inequality (33). The inequality (35) can be proved if the cubic unit cell is adopted as a unit. There are twenty-two different spin configurations on a unit cell. Though the enumeration is tedious, the expressions of p_2, q_1, and m in terms of the number of the cubes of each category lead to the inequality immediately.

B. *Body-centered cubic lattice*

The terahedron shown in Fig. 15 serves to prove the inequalities (42) and (43). One of the pairs of opposite sides of the tetrahedron is J_2 interaction lines, and the other two pairs are J_1 interaction lines. Transformed into a rhomb, the sides correspond to J_1 interaction lines, and the diagonals to J_2 interaction lines. Taking into the equivalence between the J_2 and J_3 vertices in Fig. 10, we do not distinguish between the categories 2 and 3, 5 and 6, and 7 and 8. Expressing p's, q_1, m and N in terms of n's, we can prove the inequalities.

C. *Face-centered cubic lattice*

We divide the lattice into the octahedrons shown in Fig. 16. The sides of the octahedron are J_1 interaction lines, and the diagonals J_2 interaction lines. According to the spin configurations the octahedrons are divided into ten classes.

The total number of the octahedrons is given by N. Each vertex is shared by six octahedrons, and a J_1 interaction line is shared by two octahedrons. By use of these facts we can prove the inequalities (44), (45), and (47).

The inequality (46) is proved by use of the tetrahedron which is shown also in Fig. 16. This inequality is of the same topological character as the inequality (33) in the simple cubic lattice.

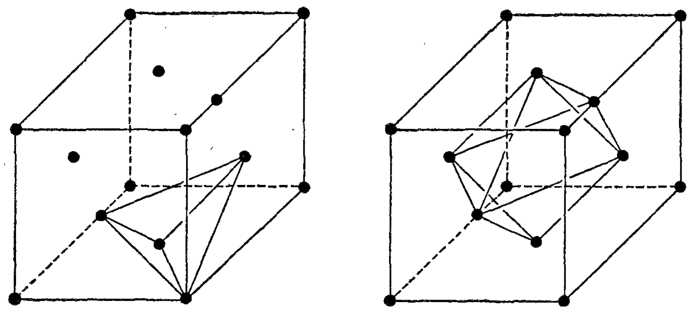


Fig. 16. The tetrahedron (Fig. 16a) and the octahedron (Fig. 16b) in the face-centered cubic lattice.

D. *MnF_2 type lattice*

We divide the lattice into triangles whose sides are two J_1 and a J_2 interaction lines. The inequalities (53) and (54) can be derived by the same procedure as in the previous cases.

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