

## A Theory of Antiferromagnetism

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A theory of antiferromagnet based on Heisenberg model is developed by a method which is much more directly the analogue of the original Bethe method than Weiss-Li's. By the present method, the calculations can be carried out over all temperatures. Especially, the situation at lower temperatures which is obscure in Weiss-Li's papers is made clear. Thus we can see that an anti-Curie point which Anderson has proposed, does not occur, if we calculate the density matrix of a cluster exactly without the perturbation method. By considering only a small cluster, being characteristic of the Bethe approximation, the long wavelength spin waves, which are important at lower temperatures, are excluded, so that the magnetization of the sublattice is completely saturated at 0°K in just the same way as in the Ising model. It is shown that, in the Bethe approximation, Curie point of antiferromagnet is higher than that of ferromagnet, for the same magnitude of  $|J|$ .

### § 1. Introduction

The results of neutron beam analysis of various antiferromagnetic substances<sup>1)</sup> seem to indicate that we can rely upon the Heisenberg model of superexchange interaction with sufficient accuracy in the theoretical treatment of antiferromagnets. Theories of antiferromagnets using Heisenberg model have been developed by Kubo *et al.*<sup>2)</sup> and Li<sup>3)</sup> respectively. The former is an expansion method of the density matrix of the entire crystal using the general expansion theorem introduced by Kubo, while the latter is the application of Weiss method<sup>4)</sup>, in which the internal field parameter is determined self-consistently. In contrast to the Bethe approximation in classical systems, in the Heisenberg model, owing to the non-commutability of the operators, there are several possibilities in introducing the internal field, besides Weiss-Li's one. Here we shall develop the theory based on another alternative of introducing the internal field. Which is the best will be made clear in future, when the rigorous solution is obtained. The present method, however, is much more directly the analogue of the original Bethe method than Weiss-Li's, since the molecular field introduced in the present method acts only on quantum mechanical averages instead of changing the eigenstates of the cluster such as in Weiss-Li's method. At present we can only remark that in every method we must make some assumption when we represent the effect of surroundings by the internal field. The accuracy of our assumption may be of the same order as that of Weiss-Li's. In practical evaluation, however, our method is far feasible to mathematical manipulation than the rests. The

calculation at lower temperatures which is unsurmountable owing to the mathematical complexity in Weiss-Li's, can be carried out in our treatment. Anderson's remarks<sup>5)</sup> on anti-Curie point, using the perturbation treatment of the Weiss model, are not appropriate for our case. Indeed, in our treatment there can be found no anti-Curie point, in fair agreement with experiments.

## § 2. The outline of the method

According to the Heisenberg model, the partition function of the antiferromagnetic crystal, with no external magnetic field, can be written ;

$$Z = \text{tr. } e^{-2|J| \beta \sum_{\langle k,l \rangle} (\mathbf{S}_k, \mathbf{S}_l)}, \quad (1)$$

where  $\mathbf{S}_k$  represents the spin operator of the  $k$ -th atom,  $|J|$  is the superexchange integral,  $\beta = 1/kT$ ,  $\sum_{\langle k,l \rangle}$  shall mean that the sum is carried out over all pairs  $(k, l)$  which are direct neighbors. The lattices to be considered in this paper are confined to those which can be divided into two sublattices  $a$  and  $b$ , in which all the nearest neighbors of any site ( $a$ - or  $b$ -site) are on the other sublattice ( $b$ - or  $a$ -site). The crystals which break these limitations cannot be ordered antiferromagnetically, and therefore will be excluded in our consideration.

If we take traces of the density matrix (1) about all the spin variables except those of the central atom on the  $a$ -site ( $\mathbf{S}_0$ ) and of  $2n$  neighboring atoms ( $\mathbf{S}_i, i=1, 2, \dots, 2n$ ), the reduced density matrix can be written in the form ;

$$e^{-2|J| \beta \sum_{i=1}^{2n} (\mathbf{S}_0, \mathbf{S}_i)} f(\mathbf{S}_0, \mathbf{S}_1, \dots, \mathbf{S}_{2n}), \quad (2)$$

where  $f(\mathbf{S}_0, \mathbf{S}_1, \dots, \mathbf{S}_{2n})$  is a complicated function of the spin variables  $\mathbf{S}_0$  and  $\mathbf{S}_i$ , expressing the effect of the surrounding, and we can assume that the function can be expanded in power series in  $\mathbf{S}_0$  and  $\mathbf{S}_i$ . This function is, of course, symmetrical about the  $2n$  spin operators of the  $b$ -site atoms, but the expansion coefficients of them are, in general, different from that of the central spin. Further reducing (2) about the spin operators except those of the central atom ( $\mathbf{S}_0$ ) and of one  $b$ -site atom ( $\mathbf{S}_j$ ), we get the distribution function of one pair of spins in the following form :

$$e^{-2|J| \beta (\mathbf{S}_0, \mathbf{S}_j)} [1 + a(\mathbf{S}_0^x + \mathbf{S}_0^y + \mathbf{S}_0^z) + a'(\mathbf{S}_j^x + \mathbf{S}_j^y + \mathbf{S}_j^z) \\ + b(\mathbf{S}_0^x \mathbf{S}_j^x + \mathbf{S}_0^y \mathbf{S}_j^y + \mathbf{S}_0^z \mathbf{S}_j^z) + c(\mathbf{S}_0^x \mathbf{S}_j^y + \mathbf{S}_0^y \mathbf{S}_j^x + \dots) \\ + c'(\mathbf{S}_0^y \mathbf{S}_j^z + \mathbf{S}_0^z \mathbf{S}_j^y + \dots) + \dots].$$

From the symmetrical considerations we can conclude that  $a = a', c = c', \dots$ , but these relations are insufficient to determine all the expansion coefficients. Therefore, giving up treating this expansion faithfully, we assume that it can be written in the form  $e^{\beta \mathbf{S}^z H^b}$ . Here  $\mathbf{S}^z$  is the  $z$ -component of the resultant  $b$ -site spins, and  $H^b$  is the internal field acting on the  $b$ -site in the  $z$ -direction, which is to be determined self-

consistently. Here and henceforth, the symbol  $H$  stands for a magnetic field in gauss multiplied by  $\mu_0$  where  $\mu_0$  is the product of the Bohr magneton and the Lande  $g$ -factor. Thus the partition function of the system consisting of the central ( $a$ -site) and its nearest-neighbor spins (we shall call the system the  $a$ -cluster) is given by

$$Z_a = \text{tr. } e^{-2|J| \beta(S_0, S)} e^{\beta S^z H^b} \quad (3)$$

Thus from our standpoint, the density matrix of  $a$ -cluster in Bethe approximation consists of two factors. One is  $e^{-2|J| \beta(S_0, S)}$ , i. e. the Hamiltonian of the cluster and the other is  $e^{\beta S^z H^b}$ , the effect of the surroundings is taken as a statistical factor.

When the uniform external field  $H_0$  is acting in the  $z$ -direction, we must add  $-(S_0^z + S^z)H$  to the Hamiltonian of the cluster, and the partition function of  $a$ -cluster is

$$Z_a = \text{tr. } e^{-2|J| \beta(S_0, S) + \beta(S_0^z + S^z)H_0} e^{\beta S^z H^b} \quad (4)$$

Similarly, for the  $b$ -cluster

$$Z_b = \text{tr. } e^{-2|J| \beta(S_0, S) + \beta(S_0^z + S^z)H_0} e^{\beta S^z H^a} \quad (5)$$

These partition functions are different from Li's in that  $e^{\beta S^z H^b}$  or  $e^{\beta S^z H^a}$  is separated from the first exponential factor. Our density matrices are not hermitian, but the trace of them are equal to the hermitized operator

$$\frac{1}{2} \left( e^{-2|J| \beta(S_0, S) + \beta(S_0^z + S^z)H_0} e^{\beta S^z H^b} + e^{\beta S^z H^b} e^{-2|J| \beta(S_0, S) + \beta(S_0^z + S^z)H_0} \right)$$

Following Weiss and Li, we use the representation system in which the superexchange interaction term of the cluster is diagonalized. The basic functions of this representation are (we assume each atom has only one magnetic electron)

$$= \pm \sqrt{\frac{S \pm m + \frac{1}{2}}{2S+1}} \theta u_0 + \sqrt{\frac{S \mp m + \frac{1}{2}}{2S+1}} \theta \beta_0 \quad (6)$$

where  $u_0$  and  $\beta_0$  are the spin functions of the central atom,  $\theta_s^{m+\frac{1}{2}}$  are the spin functions of the  $2n$  resultant spins, and (6) is the recurrence formula for increasing spin one by one.  $S$  is the total spin quantum number of the outer atoms and  $m$  is the magnetic quantum number of the cluster. Using (6) as the basis of representation, we get

$$e^{-2|J| \beta(S_0, S) + \beta(S_0^z + S^z)H_0} = \begin{pmatrix} e^{-\beta(|J|S - mH_0)} & 0 \\ 0 & e^{-\beta(-|J|(S+1) - mH_0)} \end{pmatrix} \quad (7)$$

Since  $e^{\beta S^z H^b}$  does not commute with the expression (7), the representation of which is not diagonal, that is,

$$S^z = \begin{pmatrix} m - \frac{m}{2S+1}, & -\frac{1}{2} \sqrt{1 - \frac{4m^2}{(2S+1)^2}} \\ -\frac{1}{2} \sqrt{1 - \frac{4m^2}{(2S+1)^2}}, & m + \frac{m}{2S+1} \end{pmatrix}. \tag{8}$$

The eigenvalues of the operator (8) are, of course,  $m \pm \frac{1}{2}$ .

Now, let  $T$  be any operator having  $n$  eigenvalues  $T_i$ , that is,

$$\prod_i (T - T_i) = 0$$

and  $f(T)$  be any function of  $T$ , then  $f(T)$  can be reduced to a polynomial of  $(n-1)$ th degree as follows :

$$f(T) = \sum_{i=1}^n f(T_i) A_i \prod_{j \neq i} (T - T_j), \tag{9}$$

where  $A_i$  is defined by

$$\frac{1}{\prod_{i=1}^n (T - T_i)} = \sum_{i=1}^n \frac{A_i}{T - T_i}. \tag{10}$$

Making use of the relation (9), we get

$$\begin{aligned} e^{\beta S^z H^b} &= \left\{ e^{\beta H^b \left(m - \frac{1}{2}\right)} - e^{\beta H^b \left(m + \frac{1}{2}\right)} \right\} S^z + \left\{ e^{\beta H^b \left(m - \frac{1}{2}\right)} \left(m + \frac{1}{2}\right) \right. \\ &\quad \left. - e^{\beta H^b \left(m + \frac{1}{2}\right)} \left(m - \frac{1}{2}\right) \right\} \mathbf{1} \\ &= e^{m\beta H^b} \begin{pmatrix} -\frac{2m}{2S+1} \operatorname{sh} \frac{\beta H^b}{2} + \operatorname{ch} \frac{\beta H^b}{2}, & \dots\dots \\ \dots\dots, & \frac{2m}{2S+1} \operatorname{sh} \frac{\beta H^b}{2} + \operatorname{ch} \frac{\beta H^b}{2} \end{pmatrix}. \end{aligned} \tag{11}$$

After all,

$$\begin{aligned} &e^{-2|J|\beta(S_0, S) + \beta(S_0^z + S^z)H_0} e^{\beta S^z H^b} \\ &= e^{m\beta H^b} \begin{pmatrix} e^{-\beta(|J|S - mH_0)} \left\{ -\frac{2m}{2S+1} \operatorname{sh} \frac{\beta H^b}{2} + \operatorname{ch} \frac{\beta H^b}{2} \right\}, & \dots\dots \\ \dots\dots, & e^{-\beta(-|J|(S+1) - mH_0)} \left\{ \frac{2m}{2S+1} \operatorname{sh} \frac{\beta H^b}{2} + \operatorname{ch} \frac{\beta H^b}{2} \right\} \end{pmatrix}. \end{aligned} \tag{12}$$

The non-diagonal elements are not explicitly written down, because they are unnecessary

for our calculations. The non-diagonal element  $\sqrt{1 - \frac{4m^2}{(2S+1)^2}}$  in (8), has been quite eliminated in the expression (12), which is the reason why our calculation is far simpler than Weiss-Li's.

The density matrix of the cluster is the direct product of the expression (12), and, taking the trace of it, we get the partition function

$$Z_a = \sum_{S=0}^n \omega(S) \left\{ \sum_{m=-(S+\frac{1}{2})}^{S+\frac{1}{2}} e^{m\beta H^b - \beta |J| S + \beta m H_0} \left( -\frac{2m}{2S+1} \operatorname{sh} \frac{\beta H^b}{2} + \operatorname{ch} \frac{\beta H^b}{2} \right) + \sum_{m=-(S-\frac{1}{2})}^{S-\frac{1}{2}} e^{m\beta H^b + \beta |J| (S+1) + \beta m H_0} \left( \frac{2m}{2S+1} \operatorname{sh} \frac{\beta H^b}{2} + \operatorname{ch} \frac{\beta H^b}{2} \right) \right\}, \quad (13)$$

$$\omega(S) = \frac{(2n)!}{(n+S)! (n-S)!} - \frac{(2n)!}{(n+S+1)! (n-S-1)!}. \quad (14)$$

(13), of course, contains a characteristic of the lattice type, but it is obtained in the closed form for any crystal.

### § 3. The transition temperature, the specific heat and the susceptibility

From now we shall confine the calculation to the case of a simple cubic lattice. The partition function of the cluster is, from (13) and (14)

$$\begin{aligned} Z_a = & 10 \operatorname{ch} \frac{\beta H_0}{2} + 18 e^{-\beta |J|} \operatorname{ch} \beta \left( H_f^b + \frac{H_0}{2} \right) + 6 \left( -e^{-\beta |J|} + e^{2\beta |J|} \right) \times \\ & \times \operatorname{sh} \frac{\beta}{2} (H_f^b - H_0) \operatorname{sh} \frac{\beta H_f^b}{2} \\ & + 18 \left( e^{-\beta |J|} + e^{2\beta |J|} \right) \operatorname{ch} \frac{\beta}{2} (H_f^b - H_0) \operatorname{ch} \frac{\beta H_f^b}{2} + 10 e^{-2\beta |J|} \operatorname{ch} \left( 2 H_f^b + \frac{H_0}{2} \right) \\ & + 4 \left( -e^{-2\beta |J|} + e^{3\beta |J|} \right) \operatorname{sh} \frac{\beta}{2} (H_f^b - H_0) \operatorname{sh} \frac{\beta H_f^b}{2} (2 + 3 \operatorname{ch} \beta H_f^b) \\ & + 20 \left( e^{-2\beta |J|} + e^{3\beta |J|} \right) \operatorname{ch} \frac{\beta}{2} (H_f^b - H_0) \operatorname{ch} \frac{\beta H_f^b}{2} \operatorname{ch} \beta H_f^b + 2 e^{-3\beta |J|} \operatorname{ch} \beta \left( 3 H_f^b + \frac{H_0}{2} \right) \\ & + \frac{2}{7} \left( -e^{-3\beta |J|} + e^{4\beta |J|} \right) \operatorname{sh} \frac{\beta}{2} (H_f^b - H_0) \operatorname{sh} \frac{\beta H_f^b}{2} (-1 + 16 \operatorname{ch} \beta H_f^b + 20 \operatorname{ch}^2 \beta H_f^b) \\ & + 2 \left( e^{-3\beta |J|} + e^{4\beta |J|} \right) \operatorname{ch} \frac{\beta}{2} (H_f^b - H_0) \operatorname{ch} \frac{\beta H_f^b}{2} (-1 + 4 \operatorname{ch}^2 \beta H_f^b), \end{aligned} \quad (15)$$

where

$$H_f^b = H^b + H_0, \quad (16)$$

and quite similar for  $Z_b$ . Though  $H_f^b$  and  $H_f^a$  have the physical meaning as the sum of the external and internal fields, here they play a role as a selector of the spin of the outer shell.  $H_0$ , also can be regarded as a selector of the central spin. Thus the magnetizations of the central and outer shell atoms are given respectively

$$m_0^a = \frac{\mu_0}{\beta} \left( \frac{\partial}{\partial H_0} \log Z_a \right)_{H_0=0}, \quad (17a)$$

$$m^b = \frac{\mu_0}{\beta} \left( \frac{\partial}{\partial H_f^b} \log Z_a \right)_{H_0=0}. \quad (17b)$$

For the  $b$ -cluster

$$m_0^b = \frac{\mu_0}{\beta} \left( \frac{\partial}{\partial H_0} \log Z_b \right)_{H_0=0}, \quad (18a)$$

$$m^a = \frac{\mu_0}{\beta} \left( \frac{\partial}{\partial H_f^a} \log Z_b \right)_{H_0=0}. \quad (18b)$$

Or, one can get the magnetization directly, without evaluating the partition function

$$m_0^a = \mu_0 \bar{S}_0^z = \mu_0 \frac{\text{tr. } \mathbf{S}_0^z e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S}) + \beta \mathbf{S}_0^z H_0} \cdot e^{\beta \mathbf{S}^z H^b}}{\text{tr. } e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S}) + \beta \mathbf{S}_0^z H_0} \cdot e^{\beta \mathbf{S}^z H^b}}, \quad (19a)$$

$$m^b = \mu_0 \bar{S}^z = \mu_0 \frac{\text{tr. } \mathbf{S}^z e^{-|J|\beta(\mathbf{S}_0, \mathbf{S}) + \beta \mathbf{S}_0^z H_0} \cdot e^{\beta \mathbf{S}^z H^b}}{\text{tr. } e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S}) + \beta \mathbf{S}_0^z H_0} \cdot e^{\beta \mathbf{S}^z H^b}}. \quad (19b)$$

If the density matrix commutes with  $\mathbf{S}_0^z$  and  $\mathbf{S}^z$ , the expressions (17), of course, give the same result as (19). But even if it does not commute with  $\mathbf{S}_0^z$  and  $\mathbf{S}^z$ , both expressions give the same results. The proof will be given in the Appendix.

The requirements of self-consistency are expressed as,

$$m_0^a = \frac{1}{2n} m^a, \quad m_0^b = \frac{1}{2n} m^b. \quad (20)$$

These equations have two solutions  $H^a = H^b$ , and  $H^a = -H^b$ , and the latter is the stable one. From now we shall write  $H^a = -H^b = H$ . For the simple cubic lattice, the equation (20) is rewritten explicitly

$$\begin{aligned} \text{sh } \beta H [(15 e^{-\beta|J|} - 6 e^{2\beta|J|}) + (1 + 4 \text{ch } \beta H) (6 e^{-2\beta|J|} - e^{3\beta|J|}) \\ + (-2 + 4 \text{ch } \beta H + 12 \text{ch}^2 \beta H) e^{-3\beta|J|}] = 0. \end{aligned} \quad (21)$$

At higher temperatures (21) has only one real root  $H=0$ , but when the temperature is lowered below certain point, there appears non-trivial root  $H \neq 0$ , which makes the free energy minimum. This temperature is interpreted as the Curie point. Therefore the Curie point is determined by

$$15 e^{-\beta|J|} + 30 e^{-2\beta|J|} + 14 e^{-3\beta|J|} - 6 e^{2\beta|J|} - 5 e^{3\beta|J|} = 0. \quad (22)$$

In Table I, the Curie temperatures of various lattices are listed. For comparison the results of Li and Kubo *et al.* and Opechowski are shown. According to our results the two and three-dimensional lattices can become antiferromagnetic.

Table I. The Curie point of different lattices. The numerical values are those of  $kT_c/|J|$ .

	present authors	Li	Kubo (The fourth approximation)	Opechowski
Linear chain	—	—	1.387	0.313
Quadratic layer	1.582	—	2.073	0.439
Simple cubic	2.618	2.004	2.710	0.654
Body-centered cubic	3.636	3.18	3.278	0.613

If we treat the ferromagnet by our model, every lattice has no Curie point. It is concluded quite generally that in treating both ferromagnet and antiferromagnet by the models of Weiss-Li's and ours, the antiferromagnet always has a higher Curie point than the ferromagnet, for the same magnitude of  $|J|$ . For, in ferromagnet the lowest energy of the cluster is  $-JS$ , while in antiferromagnet it is  $-|J|(S+1)$ . For the first, second, ....., excited states antiferromagnet has lower energies than ferromagnet. This is the reason why antiferromagnet has a higher Curie point. In this point, the quantum-mechanical Bethe's method gives quite different results from those of the Ising model. As will be discussed later, at extremely lower temperatures antiferromagnet has larger zero-point energy, and the treatment of only one cluster becomes very poor approximation. For the discussion of the Curie temperatures, however this zero-point energy matters little, i. e. treating one cluster becomes a good approximation, the above conclusion that antiferromagnet has a higher Curie point seems to be correct. In most real substances, the magnitude of  $|J|$  is much smaller for antiferromagnet, so the Curie temperatures of which lie lower than that of ferromagnet.

The internal energy  $E$  is given by

$$\begin{aligned}
 E &= \frac{N|J|}{Z_a} [ 6(1 + 2 \operatorname{ch} \beta H) (e^{-8|\beta J|} - e^{2\beta|\beta J|}) \\
 &\quad + 6(-1 + 2 \operatorname{ch} \beta H + 4 \operatorname{ch}^2 \beta H) (e^{-2\beta|\beta J|} - e^{3\beta|\beta J|}) \\
 &\quad + \frac{12}{7} (-1 - 4 \operatorname{ch} \beta H + 4 \operatorname{ch}^2 \beta H + 8 \operatorname{ch}^3 \beta H) (e^{-3\beta|\beta J|} - e^{4\beta|\beta J|}) ] \\
 &\equiv \frac{N|J|}{Z_a} f(H, \beta), \tag{23}
 \end{aligned}$$

and the specific heat is

$$C_v = -k\beta^2 N|J| \frac{1}{Z_a^2} \left\{ \left( \frac{\partial f}{\partial \beta} + \frac{\partial f}{\partial H} \frac{\partial H}{\partial \beta} \right) Z_a - f \left( \frac{\partial Z_a}{\partial \beta} + \frac{\partial Z_a}{\partial H} \frac{\partial H}{\partial \beta} \right) \right\}. \tag{24}$$

The Curie point is the branching point of the partition function so that the phase change is of second order. The discontinuity of the specific heat is

$$\Delta C_v = \left| \frac{k\beta^2 N |J|}{Z_a^2} f \frac{\partial Z_a}{\partial H} \frac{\partial H}{\partial \beta} \right|_{\substack{H=0 \\ \beta=\beta_0}} = 3.56 kN. \quad (25)$$

This is larger than Li's value  $1.0 kN$ .

If we expand the susceptibility above the transition point in terms of  $\beta$ , it coincides with the result of Weiss-Li's. This fact is derived from the general theorem of the density matrix<sup>6)</sup>. Consequently the paramagnetic Curie point  $\theta$ , which is defined as the crossing point of the asymptote of inverse susceptibility at  $T \rightarrow \infty$  and of the abscissa in the  $1/\chi - T$  diagram, coincides in both methods. On the other hand, as can be seen from the Table I, the Curie point is higher in our model, so  $\theta/T_c$  is 1.15 which is less than 1.50 of Li's. The experimental values are often larger than these. But taking into account of the fact that the experimental values are derived from the inclination of the susceptibility little higher than  $T_c$  and that almost all the antiferromagnetic atoms have larger spin values than  $S=1/2$ , this disagreement is not unsatisfactory.

#### § 4. Considerations at lower temperatures

Using our model, the calculations can be carried out exactly to the lower temperatures. The internal field is given by

$$\begin{aligned} \text{ch } \beta H = & \frac{1}{6} e^{3\beta |J|} \left[ - (6e^{-2\beta |J|} + e^{-3\beta |J|} - e^{3\beta |J|}) \right. \\ & + (7e^{-6\beta |J|} - 6e^{-5\beta |J|} - 9e^{-4\beta |J|} + 18e^{-3\beta |J|} \\ & \left. + 1 - 12e^{\beta |J|} + 6e^{6\beta |J|})^{\frac{1}{2}} \right]. \end{aligned} \quad (26)$$

In Fig. 1 the temperature variation of the internal field is shown. The field increases monotonically as the temperature is lowered. This implies that the magnetization of the sublattice increases monotonically, and there are no anti-Curie points.

At very lower temperatures the susceptibility in the  $z$ -direction varies as

$$\chi_{11} \propto e^{-\text{const}/kT}. \quad (27)$$

This temperature dependence is different from the results of spin wave theory,  $\chi_{11} \propto T^2$  and of the classical theory,  $\chi_{11} \propto T$ .

Near the 0°K, the magnetization of each sublattice is given by

$$m_0 \sim \frac{\mu_0}{2} (1 - \text{const } e^{\beta |J|}). \quad (28)$$

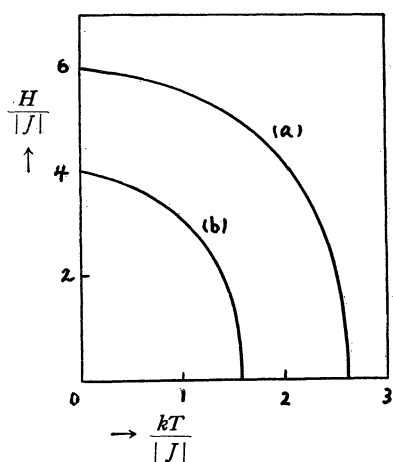


Fig. 1.  $H/|J|$  vs.  $kT/|J|$  diagram. Curve (a) simple cubic lattice, (b) body centered cubic lattice.



This shows that the magnetization of each sublattices saturates completely. The situation is similar to the case of the Ising model. But in the quantum-mechanical antiferromagnetic system, the state in which the each sublattice is completely saturated is not the eigenstate of the Hamiltonian and the above result is incorrect. As Anderson pointed out, the reason for this is that in considering one cluster only, we omit the effect of the long wavelength spin waves, which plays a dominant role at lower temperatures. The action of this long wave is to decrease the magnetization of the sublattice. As we exclude this long waves, we get the saturated magnetization at 0°K. This is the weak point of our model.

Anderson's remarks on the Weiss method, saying that the exclusion of the long wavelength spinwaves is the cause of the appearance of the anti-Curie point, are difficult to understand. His reasoning is the following<sup>7)</sup>: It is only through the medium of thermal excitation overcoming the tendency towards preferential alignment by  $H^b$  of the outer atoms of the cluster that the Curie point occurs. As the cluster size increase the states become more closely spaced and thermal effects become more important relative to the perturbation by  $H^b$ . Thus the anti-Curie point tends to disappear. On the other hand, our opinion is that the long waves oppose to the tendencies towards preferential alignment of outer atoms and also center atom of the cluster, so the solution of  $m_0^a = \frac{1}{2n} m^a$  always exists below the Curie point, that is, an anti-Curie point does not occur, and the exclusion of the long waves works so as to make the sublattice magnetization greater than the real case as shown above.

To the authors the derivation of the anti-Curie point by Anderson seems to be questionable. As shown in Fig. 1, the energy due to the internal field becomes comparable with the exchange interaction energy at the immediately lower temperature than the Curie point. Probably this is also true for Weiss-Li's method. So Anderson's method treating the internal field as the second order perturbation will not give a correct result. In our case, the off-diagonal elements of  $S^z$  do not cause the effect, so we cannot discuss the perturbation treatment in the same way as Anderson does. His perturbation treatment, however, utilizes the Weiss' formulae which are the power series of the molecular field divided by the exchange integral. In our case, if we do not calculate density matrix of the cluster exactly, but expand it in the power series of the molecular field, we can follow the same procedure as Anderson's, and obtain an anti-Curie point. This shows that the perturbation treatment is not allowed for.

In conclusion the authors wish to express their gratitude to Dr. R. Kubo who has kindly criticized the work in letters, and also to Dr. P. W. Anderson who communicated his opinion in detail and commented on our work.

### Appendix

Since  $\beta(S_0^z + S^z)H_0$  commutes with  $2|J|\beta(S_0, S)$  and  $\beta S^z H^b$ , we can write the density matrix (4) as

$$\begin{aligned} & e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \cdot e^{\beta(\mathbf{S}_0^z, \mathbf{S}^z)H_0 + \beta\mathbf{S}^z H_f^b} \\ &= e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \cdot e^{\beta\mathbf{S}_0^z H_0 + \beta\mathbf{S}^z H_f^b}. \end{aligned}$$

Further we hermitize it as following :

$$\frac{1}{2} \left\{ e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \cdot e^{\beta\mathbf{S}_0^z H_0 + \beta\mathbf{S}^z H_f^b} + e^{\beta\mathbf{S}_0^z H_0 + \beta\mathbf{S}^z H_f^b} \cdot e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \right\}. \quad (\text{A.1})$$

If we regard (A.1) as the density matrix, no changes occur in the results of this paper, because the trace of (A.1) is the same as that of (4).

Let the eigenvalue and the normalized eigenfunction of the density matrix (A.1) be denoted by  $e^{-\beta E_n}$  and  $\psi_n$  respectively. Then (17a) is given by

$$m_0^a = \frac{\mu_0}{\beta} \frac{\partial}{\partial H_0} \log \sum_n e^{-\beta E_n} = \mu_0 \frac{\sum_n \left( -\frac{\partial E_n}{\partial H_0} \right) e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}. \quad (\text{A.2})$$

While, (19a) can be written as

$$m_0^a = \mu_0 \frac{\sum_n (\psi_n, \mathbf{S}_0^z \psi_n) e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}, \quad (\text{A.2})$$

where

$$\begin{aligned} \sum_n e^{-\beta E_n} &= \text{tr} \cdot \frac{1}{2} \left\{ e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \cdot e^{\beta\mathbf{S}_0^z H_0 + \beta\mathbf{S}^z H_f^b} + e^{\beta\mathbf{S}_0^z H_0 + \beta\mathbf{S}^z H_f^b} \cdot e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \right\} \\ &= \sum_n \left( \psi_n, \frac{1}{2} \left\{ \quad \right\} \psi_n \right), \end{aligned} \quad (\text{A.4})$$

and we have used an abbreviation  $\frac{1}{2} \left\{ \quad \right\}$ . If we differentiate the both sides of (A.4) with  $H_0$ ,

$$\begin{aligned} \sum_n \left( -\beta \frac{\partial E_n}{\partial H_0} \right) e^{-\beta E_n} &= \sum_n \left( \frac{\partial \psi_n}{\partial H_0}, \frac{1}{2} \left\{ \quad \right\} \psi_n \right) + \sum_n \left( \psi_n, \frac{1}{2} \left\{ \quad \right\} \frac{\partial \psi_n}{\partial H_0} \right) \\ &+ \sum_n \left( \psi_n, \frac{1}{2} \left\{ e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \beta\mathbf{S}_0^z e^{\beta\mathbf{S}_0^z H_0 + \beta\mathbf{S}^z H_f^b} \right. \right. \\ &\left. \left. + \beta\mathbf{S}_0^z e^{\beta\mathbf{S}_0^z H_0 + \beta\mathbf{S}^z H_f^b} \cdot e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \right\} \psi_n \right). \end{aligned} \quad (\text{A.5})$$

$\frac{1}{2} \left\{ \quad \right\}$  is hermitic so that the second term of (A.5) is equal to  $\sum_n \left( \frac{1}{2} \left\{ \quad \right\} \psi_n, \frac{\partial \psi_n}{\partial H_0} \right)$  and cancels out with the first term as follows ;

$$\begin{aligned} & \sum_n e^{-\beta E_n} \left\{ \left( \frac{\partial \psi_n}{\partial H_0}, \psi_n \right) + \left( \psi_n, \frac{\partial \psi_n}{\partial H_0} \right) \right\} \\ &= \sum_n e^{-\beta E_n} \frac{\partial}{\partial H_0} (\psi_n, \psi_n) = 0. \end{aligned} \tag{A.6}$$

The third term of (A.5) is

$$\begin{aligned} & \text{tr.} \frac{1}{2} \left\{ e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \beta \mathbf{S}_0^z e^{\beta \mathbf{S}_0^z H_0 + \beta \mathbf{S}_z H_f^b} + \beta \mathbf{S}_0^z e^{\beta \mathbf{S}_0^z H_0 + \beta \mathbf{S}^z H_f^b} \cdot e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \right\} \\ &= \text{tr.} \left[ \beta \mathbf{S}_0^z \frac{1}{2} \left\{ e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \cdot e^{\beta \mathbf{S}_0^z H_0 + \beta \mathbf{S}^z H_f^b} + e^{\beta \mathbf{S}_0^z H_0 + \beta \mathbf{S}_z H_f^b} \cdot e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \right\} \right. \\ & \quad \left. - \beta \mathbf{S}_0^z \frac{1}{2} e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \cdot e^{\beta \mathbf{S}_0^z H_0 + \beta \mathbf{S}^z H_f^b} \right. \\ & \quad \left. + \frac{1}{2} e^{-2|J|\beta(\mathbf{S}_0, \mathbf{S})} \beta \mathbf{S}_0^z e^{\beta \mathbf{S}_0^z H_0 + \beta \mathbf{S}_z H_f^b} \right] \\ &= \sum_n \beta (\psi_n, \mathbf{S}_0^z \psi_n) e^{-\beta E_n}. \end{aligned} \tag{A.7}$$

After all, from (A.5), (A.6) and (A.7), we get

$$\sum_n \left( -\frac{\partial E_n}{\partial H_0} \right) e^{-\beta E_n} = \sum (\psi_n, \mathbf{S}_0^z \psi_n) e^{-\beta E_n}. \tag{A.8}$$

This shows the identities of (17) and (19).

Similar proof can be obtained using the perturbation method.

### References

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