

A Theory of Metallic Ferro- and Antiferromagnetism on Zener's Model

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The importance to the mechanism of ferromagnetism of exchange interaction between conduction electrons and unfilled inner shell electrons (called s-d interaction) has been pointed out by Zener. Especially for rare earth metals, this interaction seems to be the only mechanism which can cause ferro- and antiferromagnetism. However Zener's works are unsatisfactory because his model is phenomenological and moreover does not involve antiferromagnetism and spin wave mode.

Our paper considers this s-d interaction on a more rigorous basis. By a certain approximation, there appear long range exchange type interactions between d-electron spins and, in certain conditions both ferro- and antiferromagnetism appear. The excitations of spin wave modes are the same as those in the ordinary modes of the short range exchange force, viz, the energy of the spin wave excitations is proportional to q^2 for ferromagnetism and q for antiferromagnetism in the region of small wave vector q . The $T^{3/2}$ law for the temperature dependence of the magnetization of ferromagnetism is applicable up to very high temperatures, and this result is in good agreement with the results of experiments on metallic ferromagnetism.

§ 1. Introduction

Since Heisenberg,¹⁾ there have been many discussions on the origin of the ferro- and antiferromagnetism; however, no satisfactory theory has so far been offered. The simplest theory is that of Heisenberg using atomic wave functions, a standpoint which may be suitable for non metallic substances. Even in such a case, however, there exist certain ambiguities, as was pointed out by Slater.²⁾ It is generally accepted that Heisenberg's model can not be adopted for metallic ferromagnetism where the situation is more difficult. It is conceivable that there are two different standpoints for the origins of ferro- and antiferromagnetism. One regards the exchange interaction between the inner shell electrons as very important to the origin of ferro- and antiferromagnetism, and considers the role of conduction electron to be negligible. The other regards the exchange interaction between the conduction electron and the inner shell electron as essential. The former interaction may be essential for transition metals, e. g., Ni, Fe, Co, Cr, Mn, etc., but for rare earth metals, this interaction almost completely vanishes and the latter interaction seems to increase in importance. Even for transition metals, the latter interaction exists and plays an important role in many phenomena; for example, in the relaxation process of microwave resonance absorption,^{3,4)} in the anomalous electrical resistance of transition metals,⁵⁾ and in the temperature dependence of the anisotropy energy of Ni,⁶⁾ as was previously discussed by the author. This interaction (s-d interaction) was first discussed by Zener.⁷⁾ However his treatment is only phenomenological and on many points unsatisfactory, because his

theory does not involve antiferromagnetism or spin wave excitation. In this paper we consider this interaction on a rigorous basis, and obtain some interesting results.

§ 2. Basic Hamiltonian

The original Hamiltonian is written as follows,

$$H = \sum_i p_i^2/2m + \sum_n \sum_i v_0(|\mathbf{r}_i - \mathbf{R}_n|) + \sum_{i>j} \sum e^2/r_{ij}, \quad (1)$$

where the first term is the kinetic energy of the electrons, the second the interaction between the electrons and the ions, and the third the Coulomb interaction between the electrons. Here we consider that the positions of ions are fixed in their equilibrium positions. Now we treat Eq. (1) by the method of the second quantization and expand the quantized wave functions as follows;

$$\begin{aligned} \psi(r) &= \sum_t \sum_v a_{tv} \varphi_{tv}(r) \\ \psi^*(r) &= \sum_t \sum_v a_{tv}^* \varphi_{tv}^*(r), \end{aligned} \quad (2)$$

where t and v represent the character of orbital state and the direction of spin respectively and $\varphi_{tv}(r)$ satisfies the following equation,

$$\{p^2/2m + v(r)\} \varphi_{tv}(r) = \varepsilon_t \varphi_{tv}(r), \quad (3)$$

where the potential $v(r)$ is one to be determined later.

By using expansion (2), Hamiltonian (1) becomes

$$\begin{aligned} H = & \sum_t \sum_v \varepsilon_t a_{tv}^* a_{tv} - \sum_t \sum_{t'} \sum_v a_{tv}^* \langle t|v-v_0|t' \rangle a_{t'v} \\ & + \frac{1}{2} \sum_{t_1} \sum_{t_2} \sum_{t_3} \sum_{t_4} \sum_v \sum_\mu a_{t_1 v}^* a_{t_2 \mu}^* \langle t_1, t_2 | e^2/r | t_3, t_4 \rangle a_{t_3 \mu} a_{t_4 v}. \end{aligned} \quad (4)$$

Now $v(r)$ is determined self-consistently as follows

$$v(r) - v_0(r) = \sum_t \sum_\mu \langle t; r | e^2/|\mathbf{r} - \mathbf{r}'| | t; r' \rangle a_{t\mu}^* a_{t\mu}. \quad (5)$$

Among the remaining terms of the third term of (4), we neglect the interaction between the conduction electrons because this interaction gives the correlation and the weak exchange interaction, and is negligible compared with the exchange interaction between the conduction and the unfilled inner shell electrons. Among the remaining interactions between the unfilled shell electrons, the intra-atomic interaction gives a strong Hund coupling. On the other hand, the inter-atomic interaction is complicated for transition metals, while for rare earth metals it is negligibly small. We omit the term "inter-atomic" in this paper. The remaining interactions between the conduction electrons and the unfilled shell electrons are composed of two terms. The first term represents the transition between the conduction and the unfilled shell electrons, and this is of a higher order than the second term. We neglect the first term in this paper, but as this interaction seems to play some roles in the phenomena of rare earth metals, we will calculate it in a later papers. The

second term does not contain the transition between conduction and unfilled shell electrons and is written as follows

$$\begin{aligned} & \sum_{T_1 \neq T_2} \sum_{t_1 \neq t_2} \sum_{\nu} \sum_{\mu} A_{T_1 \nu}^* a_{t_1 \nu}^* \langle T_1, t_1 | \epsilon^2 / r | t_2, T_2 \rangle a_{t_2 \mu} A_{T_2 \nu} \\ & + \sum_{T_1} \sum_{T_2} \sum_{t_1} \sum_{t_2} \sum_{\nu} \sum_{\mu} A_{T_1 \mu}^* a_{t_1 \mu}^* \langle T_1, t_1 | \epsilon^2 / r | T_2, t_2 \rangle A_{T_2 \mu} a_{t_2 \nu} \end{aligned} \quad (6)$$

where large letters mean the operators of the unfilled shell electrons and small letters those of the conduction electrons.

The first term in (6) represents the correlation energy and does not depend on the direction of the spins; therefore we neglect this term. The second term represents the generalized exchange interaction between the conduction and the unfilled shell electrons, and depends on the direction of the spins. For rare earth metals except Gd, there remains an orbital moment and $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is a good quantum number; hence the situation is quite complicated. With this situation we shall treat in another paper. Here as our first assumption we consider only where the orbital moment vanishes. This condition is fulfilled in Gd and transition metals. Next, we assume that the wave functions of the conduction electrons are well approximated by the Bloch type wave functions and the wave functions of the unfilled shell electron are approximated by atomic wave functions neglecting the overlapping between the different atomic wave functions. Then for the creation and annihilation operators of unfilled shell electrons we can substitute the spin operators \mathbf{S}_n , and we get the following Hamiltonian

$$\begin{aligned} H_S = & \sum_t \sum_{\nu} \epsilon_t a_{t\nu}^* a_{t\nu} - N^{-1} \sum_t \sum_{t'} \sum_n J(t, t') \exp [i(\mathbf{k}_t - \mathbf{k}_{t'}) \mathbf{R}_n] \\ & \times \{ (a_{t+}^* a_{t'+} - a_{t-}^* a_{t'-}) S_n^z + a_{t+}^* a_{t'-} S_n^- + a_{t-}^* a_{t'+} S_n^+ \}, \end{aligned} \quad (7)$$

where N is the number of magnetic lattice points in a unit volume, and

$$J(t, t') = N \int \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_{dn}^*(r_1) \varphi_t^*(r_2) \epsilon^2 / r_{12} \cdot \varphi_{dn}(r_2) \varphi_{t'}(r_1) \exp [i(\mathbf{k}_{t'} - \mathbf{k}_t) \mathbf{R}_n] \quad (8)$$

does not depend on the lattice position \mathbf{R}_n . When an external field H_z is applied, we must add to (7) the Zeeman energy

$$H_{\text{Zeeman}} = -\beta H_z \{ 2 \sum_t (a_{t+}^* a_{t+} - a_{t-}^* a_{t-}) + g S_z \}. \quad (9)$$

A similar method was used first by Y. Hasegawa, which is based on atomic functions.

For simplicity, we assume in this paper that the energy spectrum of the conduction electron is free electron like, differing only in the effective mass m . Then the quantum number t in (7) is equal to the wave vector \mathbf{k} . Next, as $J(\mathbf{k}, \mathbf{k}')$ depends sensitively on $|\mathbf{k} - \mathbf{k}'|$ but on \mathbf{k} or \mathbf{k}' not sensitively, we assume that $J(\mathbf{k}, \mathbf{k}')$ depends only on $|\mathbf{k} - \mathbf{k}'|$. It is difficult to obtain the actual functional form of $J(q)$, but, it is clear that roughly it behaves as follows; as q increases from zero, $J(q)$ decreases slowly, and when q approaches the principal vector of the reciprocal lattice \mathbf{K} , $J(q)$ decreases rapidly to become very small. From this simplification, Eq. (7) can be written also in a different form. In-

roducing the well-known spin-wave operators

$$\begin{aligned} S_q &= N^{-1/2} \sum_n S_n \exp(iqR_n), \\ \sigma_q &= N^{-1/2} \sum_i \sigma_i \exp(iq\mathbf{r}_i), \end{aligned} \quad (10)$$

where \mathbf{r}_i and σ_i are the coordinate and the spin operator of i -th electron, respectively, we have

$$H_S = \sum_k \sum_v \varepsilon_k a_{kv}^* a_{kv} - \sum_q J(q) S_q \sigma_{-q}, \quad (11)$$

or in the ordinary coordinates

$$H_S = \sum_i p_i^2 / 2m - \sum_i \sum_n J(|\mathbf{r}_i - \mathbf{R}_n|) S_n \sigma_i, \quad (12)$$

where

$$J(|\mathbf{r}_i - \mathbf{R}_n|) = N^{-1} \sum_q J(q) \exp[i(\mathbf{r}_i - \mathbf{R}_n) \cdot \mathbf{q}]. \quad (13)$$

The physical meanings of Eqs. (7), (11), (12) are quite distinct, namely, the Coulomb interaction between the conduction and the unfilled shell electron is periodic and does not scatter the conduction electron, but when the spin directions of unfilled shell electrons are disturbed, the exchange interactions are not periodic and do scatter the conduction electrons. The first order process gives rise to the resistivity, which effect has been calculated in another paper. The second order process gives rise to the effective spin-spin interaction between the unfilled shell electrons, which interaction we calculate in this work.

§ 3. The second order perturbation and the effective Hamiltonian

The Hamiltonian is

$$\begin{aligned} H_S &= \sum_k \hbar^2 k^2 / 2m (a_{k+}^* a_{k+} + a_{k-}^* a_{k-}) - \beta H_z (g S_z + \sigma_z) \\ &\quad - N^{-1} \sum_k \sum_{k'} \sum_n J(|\mathbf{k} - \mathbf{k}'|) \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_n] \\ &\quad \times \{ (a_{k+}^* a_{k'+} - a_{k-}^* a_{k'-}) S_n^z + a_{k+}^* a_{k'-} S_n^- + a_{k'-}^* a_{k+} S_n^+ \}, \end{aligned} \quad (1)$$

where

$$\begin{aligned} S_z &= \sum_n S_n^z, \\ \sigma_z &= \sum_i \sigma_i^z = \sum_k (a_{k+}^* a_{k+} - a_{k-}^* a_{k-}). \end{aligned} \quad (2)$$

The energy of the first order perturbation is

$$H^{(1)} = -N^{-1} J(0) \sigma_z S_z. \quad (3)$$

The energy of the second order perturbation is obtained as follows

$$\begin{aligned}
 H^{(2)} = & -N^{-2} \left[\sum_{\mathbf{k}}' \sum_{\mathbf{k}'} \sum_n \sum_m J^2(|\mathbf{k}-\mathbf{k}'|) \exp[i(\mathbf{k}-\mathbf{k}')\mathbf{R}_{nm}] / (\hbar^2/2m) (k^2-k'^2) \right. \\
 & \times \{f^+(\mathbf{k}') (1-f^+(\mathbf{k})) + f^-(\mathbf{k}') (1-f^+(\mathbf{k})) S_n^z S_m^z \\
 & + \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_n \sum_m J^2(|\mathbf{k}-\mathbf{k}'|) \exp[i(\mathbf{k}-\mathbf{k}')\mathbf{R}_{nm}] / (\hbar^2/2m) (k^2-k'^2) \\
 & \times \{f^-(\mathbf{k}') (1-f^+(\mathbf{k})) S_m^+ S_n^- + f^+(\mathbf{k}') (1-f^-(\mathbf{k})) S_m^- S_n^+\} \left. \right] \quad (4)
 \end{aligned}$$

or, exchanging the \mathbf{k} and \mathbf{k}' , and rearranging

$$\begin{aligned}
 H^{(2)} = & -N^{-2} \sum_{\mathbf{k}}' \sum_{\mathbf{k}'} \sum_n \sum_m J^2(|\mathbf{k}-\mathbf{k}'|) \exp[i(\mathbf{k}-\mathbf{k}')\mathbf{R}_{nm}] / (\hbar^2/2m) (k^2-k'^2) \\
 & \times \{f^+(\mathbf{k}') + f^-(\mathbf{k}')\} S_n^z S_m^z \\
 & -N^{-2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_n \sum_m J^2(|\mathbf{k}-\mathbf{k}'|) \exp[i(\mathbf{k}-\mathbf{k}')\mathbf{R}_{nm}] / (\hbar^2/2m) (k^2-k'^2) \\
 & \times \{f^-(\mathbf{k}') S_m^+ S_n^- + f^+(\mathbf{k}') S_m^- S_n^+\} \\
 & + \sum_{\mathbf{k}} \sum_{\mathbf{k}'} J^2(|\mathbf{k}-\mathbf{k}'|) / (\hbar^2/2m) (k^2-k'^2) \{f^-(\mathbf{k}') f^+(\mathbf{k}) - f^+(\mathbf{k}') f^-(\mathbf{k})\} S_z \quad (5)
 \end{aligned}$$

where $f^+(\mathbf{k})$ and $f^-(\mathbf{k})$ are the Fermi distribution function of plus and minus spin electrons, respectively, and prime in \sum' means that the summation does not include terms where $\mathbf{k}=\mathbf{k}'$, such terms having been already included in $H^{(1)}$. This calculation is similar to the nuclear $\mathbf{I}\mathbf{I}$ coupling in metals.⁸⁾ $H^{(2)}$ is now separable into two parts. One includes $\mathbf{R}_n=\mathbf{R}_m$ and is written in the form $\sigma_z S_z$ as follows

$$\begin{aligned}
 H_{S\sigma}^{(2)} = & -N^{-2} \sum_{\mathbf{k}}' \sum_{\mathbf{k}'} \sum_n J^2(|\mathbf{k}-\mathbf{k}'|) / (\hbar^2/2m) (k^2-k'^2) \{f^+(\mathbf{k}') + f^-(\mathbf{k}')\} S_n^z \\
 & -N^{-2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_n J^2(|\mathbf{k}-\mathbf{k}'|) / (\hbar^2/2m) (k^2-k'^2) \{f^+(\mathbf{k}') + f^-(\mathbf{k}')\} (S_n^{x2} + S_n^{y2}) \\
 & + N^{-2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} J^2(|\mathbf{k}-\mathbf{k}'|) / (\hbar^2/2m) (k^2-k'^2) \\
 & \times \{f^+(\mathbf{k}') (1-f^-(\mathbf{k})) - f^-(\mathbf{k}') (1-f^+(\mathbf{k}))\} S_z. \quad (6)
 \end{aligned}$$

The last term in (6) is of a higher order when compared with $H^{(1)}$ or the remaining terms of $H^{(2)}$, because the expansion parameter of this perturbation is $2mJ(0)/\hbar^2 k_f^2$ where k_f is the wave vector of the Fermi surface or σ_z/N .

The remaining terms of $H^{(2)}$ are written as a sum of the spin-spin interactions between the different lattice points :

$$\begin{aligned}
 H_{SS}^{(2)} = & -N^{-2} \sum_{\mathbf{k}}' \sum_{\mathbf{k}'} \sum_{n \neq m} J^2(|\mathbf{k}-\mathbf{k}'|) \exp[i(\mathbf{k}-\mathbf{k}')\mathbf{R}_{nm}] / (\hbar^2/2m) (k^2-k'^2) \\
 & \times \{f^+(\mathbf{k}') + f^-(\mathbf{k}')\} S_n^z S_m^z \\
 & -N^{-2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{n \neq m} J^2(|\mathbf{k}-\mathbf{k}'|) \exp[i(\mathbf{k}-\mathbf{k}')\mathbf{R}_{nm}] / (\hbar^2/2m) (k^2-k'^2) \\
 & \times \{(f^+(\mathbf{k}') + f^-(\mathbf{k}'))\} (S_n^x S_m^x + S_n^y S_m^y) \\
 & -N^{-2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{n \neq m} J^2(|\mathbf{k}-\mathbf{k}'|) \exp[i(\mathbf{k}-\mathbf{k}')\mathbf{R}_{nm}] / (\hbar^2/2m) (k^2-k'^2)
 \end{aligned}$$

$$\times \{f^+(k') - f^-(k')\} (S_m^- S_n^+ - S_m^+ S_n^-), \quad (7)$$

where the last term is the higher order term and should be omitted in our approximation.

In the first and the second terms of (6) and (7) we can replace $\{f^+(k) + f^-(k)\}/2$ with the average distribution function $f(k)$ in our approximation and performing the summation over k , $H^{(2)}$ becomes

$$H^{(2)} = - \sum_n \sum_m J'(R_{nm}) S_n^z S_m^z - \sum_n \sum_m J(R_{nm}) (S_n^x S_m^x + S_n^y S_m^y), \quad (8)$$

where

$$J'(R_{nm}) = N^{-1} \sum_q J(q) \exp(iqR_{nm}), \quad (9)$$

$$J(R_{nm}) = N^{-1} \sum_q J(q) \exp(iqR_{nm}), \quad (10)$$

$$J(q) = (1/4a) J^2(q) f(q), \quad (11)$$

$$f(q) = 1 + (4k_f^2 - q^2)/4k_f q \cdot \ln(2k_f + q)/(2k_f - q), \quad (12)$$

$$a = 1/6 \cdot \hbar^2/m \cdot q_D^3/k_f, \quad (13)$$

$$J(0) = \lim_{q \rightarrow 0} J(q) = J^2(0)/2a, \quad (14)$$

and \sum' in (9) means the summation over all q , omitting $q=0$ in the terms $S_n^z S_m^z$, q_D is Debye's cut-off wave vector.

The spin dependent Hamiltonian is now

$$H_S = \sum_k \hbar^2 k^2 / 2m \cdot (a_{k+}^* a_{k+} + a_{k-}^* a_{k-}) - \beta H_z (g S_z + \sigma_z) \\ - N^{-1} J(0) \sigma_z S_z - \sum_n \sum_m J'(R_{nm}) S_n^z S_m^z - \sum_n \sum_m J(R_{nm}) (S_n^x S_m^x + S_n^y S_m^y). \quad (15)$$

In our approximation, the first term of this can be written in σ_z , and σ_z determined by the relation $\partial H_S / \partial \sigma_z = 0$. Then, using (14), we have

$$H_S = -\beta H_z g (1 + J(0)/ga) S_z - N(\beta H_z)^2 / 2a - \sum_n \sum_m J(R_{nm}) S_n^z S_m^z \quad (16)$$

$$\sigma_z = (\beta H_z N + J(0) S_z) / a. \quad (17)$$

The relations (16), (17) are fundamental equations in the following discussions. The spin-spin interaction is thus of an exchange type.

§ 4. The ground states

As it is very difficult to obtain the exact solution for the ground state of the Hamiltonian (16), we discuss here only two physically important cases, that is, ferromagnetic and antiferromagnetic ordering cases.

When the ground state is ferromagnetic, all the spins of the unfilled shell electrons are parallel. This state is the exact solution of the Hamiltonian (16) and the ground state energy is

$$E_f = -(\beta H_z)^2 / 2a \cdot N - (g + J(0)/a) \beta H_z NS - NS^2 \sum_{\mathbf{K}} J(\mathbf{K}), \quad (1)$$

where \mathbf{K} are the principal vectors of the reciprocal lattice, including $\mathbf{K}=0$.

Hereafter we do not consider the effects of the external field. The effects of the external field will be discussed separately.

For the antiferromagnetic ordering, we assume a simplified model where the crystal lattice is separable into two equivalent sublattices in each of which all the spins are parallel, the magnetization of both sublattices, however, being antiparallel. Contrary to ferromagnetism, this state is not an exact ground state. As it is difficult to obtain the exact ground state of antiferromagnetism, we calculate as usual by the method of spin-wave approximation and, in the next section, we obtain energy correction due to the quantum effect in this way. The zero order energy, namely rigid spin model, is easily obtained as follows

$$\begin{aligned} E_a^0 &= -NS^2 \left[\sum_{\mathbf{R}_n} J(\mathbf{R}_n) - \sum_{\mathbf{R}_\mu} J(\mathbf{R}_\mu) \right] \\ &= -NS^2 / 2 \left[\sum_{\mathbf{G}} J(\mathbf{G}) - \sum_{\mathbf{K}} J(\mathbf{K}) + \sum_{\mathbf{Q}} J(\mathbf{Q}) \right] \\ &= -NS^2 \sum_{\mathbf{Q}} J(\mathbf{Q}), \end{aligned} \quad (2)$$

where \mathbf{R}_n and \mathbf{R}_μ are respectively the distance between the lattice points on the same sublattice and different sublattices, \mathbf{G} the principal vector of the sublattice, and group $\{\mathbf{Q}\}$ is a part of the group $\{\mathbf{G}\}$ and equal to $\{\mathbf{G}\} - \{\mathbf{K}\}$, thus excluding $\mathbf{Q}=0$.

The difference between E_a^0 and E_f is

$$E_a^0 - E_f = NS^2 \left[\sum_{\mathbf{K}} J(\mathbf{K}) - \sum_{\mathbf{Q}} J(\mathbf{Q}) \right]. \quad (3)$$

The sign of (3) depends sensitively on the dependence of $J(q)$ on q . Ferromagnetic ordering could be established when $J(q)$ decreases rapidly with increasing q .

As it is difficult to calculate $J(q)$ exactly, we can mention in our approximation only that s-d interaction can establish both ferromagnetism and antiferromagnetism.

We must study the thermal stability of these ground states by examining the energy spectrum of the excited states. This is done in the next section.

§ 5. The excited states of ferromagnetism

In this section we calculate the energy spectrum of the excited states when the ground state is ferromagnetic.

In low temperatures, actually the spin wave method is a good approximation. Now we introduce the well-known spin-wave operator

$$\begin{aligned} S_n^+ &= (2S)^{1/2} (1 - a_n^* a_n / 2S)^{1/2} a_n, \\ S_n^- &= (2S)^{1/2} a_n^* (1 - a_n^* a_n / 2S)^{1/2}, \\ S - S_n^z &= a_n^* a_n, \end{aligned} \quad (1)$$

and

$$a_n = N^{-1/2} \sum_q \exp(-i \mathbf{q} \mathbf{R}_n) a_q, \quad (2)$$

$$a_n^* = N^{-1/2} \sum_q \exp(i \mathbf{q} \mathbf{R}_n) a_q^*,$$

then expanding with respect to the parameter $1/2S$ up to the term of the order of $(1/2S)^0$,

$$H_s = -NS^2 + 2S \sum_q \sum_K [J(K) - J(|\mathbf{K} + \mathbf{q}|)] a_q^* a_q$$

$$+ (2N^{-1}) \sum_{q_1} \sum_{q_2} \sum_{q_3} \sum_{q_4} \sum_K [J(|\mathbf{K} + \mathbf{q}_1|) + J(|\mathbf{K} + \mathbf{q}_4|) - 2J(|\mathbf{K} + \mathbf{q}_1 + \mathbf{q}_4|)]$$

$$\times \delta(\mathbf{q}_1 + \mathbf{q}_2 - \mathbf{q}_3 - \mathbf{q}_4 + \mathbf{K}) a_{q_1}^* a_{q_2}^* a_{q_3} a_{q_4}. \quad (3)$$

The first term in (3) is E_f in § 3. The second term is the excitation energy at absolute temperature zero. The third term is the first order correction at finite temperatures. In this section we consider only the second term. We are interested in the low temperature region, or in other words, in the small value region of wave vector q , and hence we can expand (3) by q .

Introducing the following variables

$$\mathbf{x} = \mathbf{q}/2k_f, \quad \mathbf{p} = \mathbf{K}/2k_f, \quad X = p^2,$$

$$\delta = \{(\mathbf{K} + \mathbf{q})^2 - K^2\} / 4k_f^2 = 2\mathbf{p}\mathbf{x} + x^2, \quad (4)$$

the energy of the excited states of the spin wave of wave vector \mathbf{q} is

$$\varepsilon_q^0 = 2S \sum_K [J(K) - J(|\mathbf{K} + \mathbf{q}|)]$$

$$= -2S \sum_p \left\{ \delta \frac{d}{dX} + \frac{1}{2} \delta^2 \frac{d^2}{dX^2} + \frac{1}{6} \delta^3 \frac{d^3}{dX^3} + \dots \right\} J(X). \quad (5)$$

Considering the crystal is to be cubic, and taking terms up to q^4 , we have

$$\varepsilon_q^0 = -2S \sum_p \left\{ x^2 \left(\frac{d}{dX} + \frac{2}{3} X \frac{d^2}{dX^2} \right) + \frac{1}{2} x^4 \left(\frac{d^2}{dX^2} + \frac{4}{3} X \frac{d^3}{dX^3} \right) \right\} J(X). \quad (6)$$

To perform further calculations, we neglect the derivative of $J(q)$. This neglect may be a fairly good approximation when $\mathbf{K} = 0$, but not so good when $\mathbf{K} \neq 0$. Therefore this approximation may be justified when the contribution to ε_q^0 is mainly from the part $\mathbf{K} = 0$. Then

$$\varepsilon_q^0 = A_2^0 (q/q_D)^2 + A_4^0 (q/q_D)^4 \quad (7)$$

$$A_2^0 = \frac{S}{8a} \left(\frac{q_D}{k_f} \right)^2 \sum_p J^2(X) \left(\frac{1}{6X^{1/2}} \right) \ln \frac{X^{1/2} + 1}{X^{1/2} - 1} - \frac{1}{3} \frac{1}{X - 1}$$

$$= \frac{S}{12a} \left(\frac{q_D}{k_f} \right)^2 \left[\sum_{X < 1} J^2(X) \left(1 + \frac{2}{3} X + \dots \right) \right.$$

$$\left. - \frac{1}{3} \sum_{X > 1} J^2(X) \frac{1}{X^2} \left(1 + \frac{6}{5X} + \dots \right) \right] \quad (8)$$

$$\begin{aligned}
 A_4^0 &= \frac{S}{64a} \left(\frac{q_D}{k_f} \right)^4 \sum_p J^2(X) \left(\frac{1}{8} \frac{X+7}{X^{3/2}} \ln \frac{X^{1/2}+1}{X^{1/2}-1} - \frac{1}{4} \frac{1}{X^2} \frac{X-7}{X-1} + \frac{2}{3} \frac{1}{X} \frac{1}{(X-1)^2} \right) \\
 &= (S/240a) (q_D/k_f)^4 \left[\sum_{X<1} J^2(X) (1+X+\dots) \right. \\
 &\quad \left. + 5/2 \sum_{X>1} J^2(X) X^{-1} (1+2X^{-1}+\dots) \right]. \quad (9)
 \end{aligned}$$

The condition of thermal stability of ferromagnetism is $\varepsilon_q^0 > 0$, or $A_2^0 > 0$. If the part $\mathbf{K} \neq 0$ were to make a larger contribution than that of $\mathbf{K} = 0$, the condition of the thermal stability would be $X < 1$, or in other words, $q_D/k_f < 1$, i. e., that the valency of the conduction electron must be larger than 2. In thermal stability, the part $X > 1$ contributes only almost zero and we can neglect this part.

Considering only the first term of the expansion of part $X < 1$,

$$A_4^0/A_2^0 = (1/20) (q_D/k_f)^2. \quad (10)$$

For comparison, we give the result of the ordinary nearest neighbors interaction. In this case

$$A_4^0/A_2^0 = -(1/20) (q_D R_0)^2 \quad (11)$$

where R_0 is the distance between the nearest neighbouring spins.

For simplicity, we put R_0 as a diameter of the sphere having the same volume as the specific volume per magnetic lattice point. Then

$$(q_D R_0)^2 = 23. \quad (12)$$

Therefore (11) is considerably larger than (10), i. e., the $T^{3/2}$ law of temperature dependence of the magnetization may hold very well. We have calculated this phenomenon in the next section.

§ 6. Temperature dependence of the magnetization

Recently Schafroth⁹⁾ calculated the temperature dependence of magnetization by the variational method based on Kubo's method.¹⁰⁾ According to Schafroth the $T^{3/2}$ law does not hold except at very near zero.

Such an implausible result is owing to the variational method, because by this method the treatment of the diagonal and non-diagonal parts is quite at disparity and thus the character of the exchange interaction is disregarded. Therefore an effective anisotropic field appears and the excitation of the spin-waves is unnaturally depressed. This is the reason for such an implausible result. To obtain reasonable results we must recognize that the non-diagonal terms are important and that in the approximation of spin wave method we must use an expansion with respect to the parameter $1/2S$. A detailed discussion was given in a previous paper.¹¹⁾

Here we calculate the departure of the temperature dependence of the magnetization from the $T^{3/2}$ law caused by the following three mechanisms, each up to the first order; (i) the existence of the terms proportional to q^4 in the excitation energy ε_q ; (ii) the

higher order terms in the expansion of the spin wave method, namely, the third term in eq. (3) of § 4; (iii) the restriction that the degree of freedom of motion of the spin system is finite.

Now we consider the third term in eq. (3) of § 4.

The excitation energy of the spin wave of wave vector q contributed by the third term in (3) of § 4 is

$$A_q = 2 \sum_{q'} n_{q'}/N \cdot \sum_K [J(|K+q|) + J(|K+q'|) - J(K) - J(|K+q+q'|)]. \quad (1)$$

Expanding in q and using the same method as in § 4, we have

$$A_q = -\frac{10}{3} S \sum_{x'} \frac{n_{q'}}{NS} x'^2 x^2 \sum_p \left(\frac{d^2}{dX^2} + \frac{4}{3} X \frac{d^3}{dX^3} \right) J(X), \quad (2)$$

where

$$x' = q'/2k_f \quad (3)$$

and the others have the same meaning as in § 4.

The form (2) is the same as the second term in (6), § 4, and written with A_4^0 as

$$A_q = \frac{10}{3} A_4^0 \left(\frac{q}{q_D} \right)^2 \sum_{q'} \left(\frac{q'}{q} \right)^2 \frac{n_{q'}}{NS}. \quad (4)$$

Adding this term, the excitation energy of the spin wave of wave vector q becomes

$$\epsilon_q = A_2 (q/q_D)^2 + A_4^0 (q/q_D)^4, \quad (5)$$

where

$$\begin{aligned} A_2 &= A_2^0 \left\{ 1 + \frac{10}{3} \frac{A_4^0}{A_2^0} \sum_{q'} \left(\frac{q'}{q_D} \right)^2 \frac{n_{q'}}{NS} \right\} \\ &\doteq A_2^0 \left\{ 1 + \frac{1}{6} \sum_{q'} \left(\frac{q'}{q_D} \right)^2 \frac{n_{q'}}{NS} \right\} \end{aligned} \quad (6)$$

$$A_4^0 \doteq (1/20) (q_D/k_f)^2 A_2^0 \quad (7)$$

$$A_2^0 \doteq (S/12a) (q_D/k_f)^2 \sum_K J^2(K) \quad (8)$$

and the magnetization in finite temperature T is

$$NS - S_z = \sum_{q=0}^{q_D} [\exp(\epsilon_q/\kappa T) - 1]^{-1}. \quad (9)$$

Replacing summation by the integration, and confining us only to the first order for the deviation of each of the three causes, we get

$$NS - S_z = 3.5 \left(\frac{\kappa T}{A_2^0} \right)^{3/2} \left[1 - 1.9 \frac{\kappa T}{A_2^0} \frac{A_4^0}{A_2^0} + 1.5 \frac{A_2^0 - A_2}{A_2^0} \right]$$

$$-0.43 \left(\frac{A_2^0}{\kappa T} \right)^{1/2} \exp(-A_2^0/\kappa T) \Big]. \quad (10)$$

Putting the values of (6) and (7), we have

$$NS - S_z = 3.5 \left(\frac{\kappa T}{A_2^0} \right)^{3/2} \left[1 - 0.095 \left(\frac{q_D}{k_f} \right)^2 \frac{\kappa T}{A_2^0} - \frac{0.67}{S} \left(\frac{q_D}{k_f} \right)^2 \left(\frac{\kappa T}{A_2^0} \right)^{5/2} - 0.43 \left(\frac{A_2^0}{\kappa T} \right)^{1/2} \exp(-A_2^0/\kappa T) \right]. \quad (11)$$

For example, taking $\kappa T/A_2^0 = 1/2$, the bracket in (11) is

$$[1 - 0.05 (q_D/k_f)^2 - (0.21/S) (q_D/k_f)^2 - 0.08] \quad (12)$$

and the deviation is less than 15% for the usual metal. The result that the $T^{3/2}$ law holds very well is in good agreement with the experimental results for rare earth metals, especially for Gd.¹²⁾

Contrary to the above result, the $T^{3/2}$ law does not hold so well when we use the ordinary nearest neighbors interaction method. In that case

$$A_4^0/A_2^0 = -(1/20) (q_D R_0)^2, \quad (13)$$

$$A_2 = A_2^0 \{1 - (0.45/S) (q_D R_0)^2 (\kappa T/A_2^0)^{5/2}\}, \quad (14)$$

and, as mentioned in § 4, by approximating

$$(q_D R_0)^2 = 23, \quad (15)$$

the bracket in (10) becomes

$$\left[1 + 2.2 \left(\frac{\kappa T}{A_2^0} \right) + \frac{15}{S} \left(\frac{\kappa T}{A_2^0} \right)^{5/2} - 0.43 \left(\frac{A_2^0}{\kappa T} \right)^{1/2} \exp(-A_2^0/\kappa T) \right]. \quad (16)$$

The deviation is very much larger than that in (11) and the $T^{3/2}$ law holds only in low temperatures. The peculiar term which appeared in Schafroth's method does not appear in ours.

§ 7. The excited states of antiferromagnetism

For antiferromagnetism, we also introduce the spin wave operators a_q^* , a_q and b_q^* , b_q , which are the creation and annihilation operators, respectively, at A and B sites. Then taking terms up to the two spin wave process, in the expansion, we have

$$\begin{aligned} H_s = & -NS^2 \sum_Q J(Q) \\ & + 2S \sum_q \left[\sum_G \{J(G) - J(|G+q|)\} - \sum_Q J(Q) - \sum_K J(K) \right] (a_q^* a_q + b_q^* b_q) \\ & - 2S \sum_q \left[\sum_Q J(Q+q) - \sum_K J(K+q) \right] a_q b_{-q} + \text{c. c.} \end{aligned} \quad (1)$$

We easily diagonalize (1) by the well-known transformation, and (1) is written in

the new operators α_q^* , α_q , β_q^* and β_q , as

$$H_s = E_a + \sum_q \varepsilon_q (\alpha_q^* \alpha_q + \beta_q^* \beta_q), \quad (2)$$

where

$$E_a = -NS^2 \sum_Q J(Q) - 2S \sum_q [\sum_G \{J(G) - J(|G+q|)\} + \sum_Q J(Q) - \sum_K J(K)] - \sum_q \varepsilon_q \quad (3)$$

$$\varepsilon_q = 4S [\{\sum_Q (J(Q) - J(|Q+q|))\} \{\sum_Q J(Q) - \sum_K J(K) + \sum_K \{J(K) - J(|K+q|)\}\}]^{1/2}. \quad (4)$$

To perform this transformation, it is required that (i) the coefficient of the second term of (1) be positive, and (ii) ε_q in (4) be real.

From § 3 and § 4, it is easily seen that

$$2S \sum_K \{J(K) - J(|K+q|)\} = A_2^0 (q/q_D)^2, \quad (5)$$

$$2S \sum_Q \{J(Q) - J(|Q+q|)\} = B_2^0 (q/q_D)^2, \quad (6)$$

$$2S \{\sum_Q J(Q) - \sum_K J(K)\} = (2/NS) (E_f - E_a^0) \equiv \Delta E, \quad (7)$$

where B_2^0 is obtained from A_2^0 by replacing K with Q .

By using (5), (6) and (7)

$$E_a = E_a^0 - \sum_q [\{\Delta E + A_2^0 (q/q_D)^2\}^{1/2} - (B_2^0)^{1/2} q/q_D]^2, \quad (8)$$

$$\varepsilon_q = 2 [B_2^0 \{\Delta E + A_2^0 (q/q_D)^2\}]^{1/2} q/q_D, \quad (9)$$

and the restrictions (i) and (ii) become

$$\begin{aligned} \text{(I)} \quad & \Delta E > 0, \\ \text{(II)} \quad & A_2^0 > 0, \\ \text{(III)} \quad & B_2^0 > 0. \end{aligned} \quad (10)$$

(I) is fulfilled when antiferromagnetic state is more stable than ferromagnetic in the ground state energy. (II) is the same as in § 4. (III) is usually fulfilled when (II) is fulfilled or, strictly speaking, when the valency of the conduction electron is larger than unity. These three restrictions are the same as of thermal stability of antiferromagnetism.

§ 8. Conclusion

Here we summarize the above calculations.

(i) We assume that the conduction electron is nearly free electron like and that the unfilled inner shell electron is localized and the interaction between the unfilled shell electrons in the different lattice points is small.

(ii) We assume that the orbital moment of the unfilled shell electrons is quenched.

This assumption is true for transition metals because in these metals the crystalline field is very strong. In rare earth metals, however, l-s coupling is more important than the crystalline field and j is a good quantum number and hence the above assumption holds only for Gd. We will treat in another paper the case in which j is a well considered quantum number.

(iii) We assume the orbital configuration of the unfilled inner shell electrons to be fixed. This is related to (ii). The effects of the excited configuration seem to be small.

(iv) Under the above assumptions, the exchange interaction between the conduction and the unfilled inner shell electrons is written as a form of exchange type interaction as in Eqs. (7), (11) and (12) in § 2. The second order perturbation gives rise to the effective exchange-like interaction between the spins in the different lattice points. The character of this exchange-like interaction is a long range force and hence it is difficult to obtain the real ground state. The ordering of the ground state depends sensitively on the functional form of the generalized exchange integral $J(q)$.

(v) When the ground state is ferromagnetic, the excited state is written by spin wave mode, and the excited energy is proportional to the square of the wave vector. The $T^{3/2}$ law of temperature dependence of the magnetization holds very well, which is satisfactory to the experimental fact of Gd.

(vi) The excitation energy in the antiferromagnetic ordering is proportional to the absolute value of the wave vector.

(vii) For the thermal stability, it is required that the valence of the conduction electron be larger than 2.

The phenomena in fairly high temperatures and in the paramagnetic region will be treated in a following paper.

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