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Collcetive Electron Theory of Antiferromagnetism*

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A theory of collective electron antiferromagnetism is developed on the basis of HARTREE-FOCK approximation. First, the splitting of energy band due to the presence of antiferromagnetic superstructure is examined, and antiferromagnetic energy band and eigenfunctions are determined from HARTREE-FCCK potential assumed to be different for different direction of the spin of the electron. Then the potential is determined self-consistently in terms of density matrices constructed from the antiferromagnetic energy band and eigenfunctions. The necessary and sufficient conditions for the appearance of antiferromagnetism are discussed, and the mean magnetic moment per electron of electron spin is shown to be a small fraction of a BOHR magneton owing to the fact that the electrons of both spins migrating in the whole crystal cancel most part of their moment with each other.

§ 1. Introduction

Antiferromagnetism has hitherto been studied mainly on the basis of HEITLER-LONDON approximation. This approach may be the most reasonable one for insulating antiferromagnetics which constitute the majority of existing antiferromagnetic substances. There are, however, metals and semiconductors which behave magnetically as antiferromagnetics,[1] and for these substances it might be more convenient to apply collective electron theory so as to interpret their electric as well as magnetic properties. The object of this paper is to give a quantum statistical formulation of antiferromagnetism from the view point of collective electron theory.

§ 2. Energy Band of Antiferromagnetic Metal

For the sake of bravity, we shall consider the simplest lattice, i. e., a linear chain, a 2-dimensional square net or a 3-dimensional

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simple cubic lattice, composed of N atoms. If $2z$ is the number of nearest neighbors, the above mentioned three lattices can be specified by $z=1$, 2,3 respectively. Each atom will be assumed to have one s electron outside its closed shell. The position vector of the l-th atomic nucleus is given by

$$\boldsymbol{R}_l = \sum_{i=1}^{z} l_i \boldsymbol{a}_i ,$$

where $\boldsymbol{a}_i\,(i=1, \cdots z)$ are the fundamental vectors of the lattice, and l_i's integers. The Hamiltonian for this N electron system is (using atomic unit)

$$H = -\frac{1}{2}\sum_k \nabla_k^2 + \sum_k \sum_l V(\boldsymbol{r}_k - \boldsymbol{R}_l) + \sum_{i>k}\sum \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_k|} , \qquad (2.1)$$

in which $V(\boldsymbol{r}-\boldsymbol{R}_l)$ represents the potential energy due to the nucleus and closed shell of the atom at $\boldsymbol{R}_l$. In the conventional HARTREE approximation, one seeks a proper HARTREE potential $U_0(\boldsymbol{r})$ in place of (2.1), and solves the equation

$$\left\{-\frac{1}{2}\nabla^2 + U_0(\boldsymbol{r})\right\}\phi(\boldsymbol{r}) = E\phi(\boldsymbol{r}) . \qquad (2.2)$$

Since $U_0(\boldsymbol{r})$ can be assumed to have the translational periodicity of the lattice, (2.2) has, in tight binding approximation, the following solution:

$$\psi(\boldsymbol{k};\boldsymbol{r}) = \frac{1}{\sqrt{N}}\sum_l \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_l)\,\phi(\boldsymbol{r}-\boldsymbol{R}_l) , \qquad (2.3)$$

$$E(\boldsymbol{k}) = \varepsilon - \alpha_0 - \gamma_0\xi(\boldsymbol{k}) , \qquad (2.4)$$

where $\phi(\boldsymbol{r}-\boldsymbol{R}_l)$ is the normalized wave function for an electron in an isolated atom, satisfying

$$\left\{-\frac{1}{2}\nabla^2 + V(\boldsymbol{r})\right\}\phi(\boldsymbol{r}) = \varepsilon\phi(\boldsymbol{r}) , \qquad (2.5)$$

and

$$\begin{aligned} -\alpha_0 &= \int \phi^*(\boldsymbol{r})\left\{U_0(\boldsymbol{r}) - V(\boldsymbol{r})\right\}\phi(\boldsymbol{r})\,d\boldsymbol{r} , \\ -\gamma_0 &= \int \phi^*(\boldsymbol{r}-\boldsymbol{a}_1)\left\{U_0(\boldsymbol{r}) - V(\boldsymbol{r})\right\}\phi(\boldsymbol{r})\,d\boldsymbol{r} , \qquad (2.6) \\ \xi(\boldsymbol{k}) &= 2\sum_{i=1}^{z}\cos k_i a , \end{aligned}$$

a being the lattice constant, $\boldsymbol{k}$ the wave vector of the electron.

As was pointed out by SLATER,[2] the HARTREE-FOCK potential for an electron may be different for different direction of the spin in virtue of Pauli principle, which makes two electrons with parallel spins keep apart from each other. Then if we divide the lattice into two sublattices, I and II, according to $\sum_i l_i = \text{even}$ (I-sublattice) or $\sum_i l_i = \text{odd}$ (II-sublattice), we would be able to suppose HARTREE-FOCK potentials $U_+(\boldsymbol{r})$ and $U_-(\boldsymbol{r})$ which make + and − spin electrons move preferably on I and II sublattices respectively. $U_\pm(\boldsymbol{r})$ have a periodicity twice as large as that of $U_0(\boldsymbol{r})$, i. e., they have the translational symmetry of $2\boldsymbol{a}_i\,(i=1,\cdots z)$. In the absence of external field, it can be assumed further that

$$U_+(\boldsymbol{r}+\boldsymbol{a}_i) = U_-(\boldsymbol{r})\,. \tag{2.7}$$

The energy band of electrons moving in this potential $U_\pm(\boldsymbol{r})$ is split into two bands owing to the doubled periodicity. For the + spin, for instance, the tight binding approximation gives the result

$$E(\boldsymbol{k}) = \varepsilon - \frac{\alpha_1+\alpha_2}{2} \pm \sqrt{\frac{(\alpha_1-\alpha_2)^2}{4} + \gamma^2\xi^2(\boldsymbol{k})}\,, \tag{2.8}$$

where

$$-\alpha_1 = \int \phi^*(\boldsymbol{r}-\boldsymbol{R}_I)\left\{U_+(\boldsymbol{r}) - V(\boldsymbol{r}-\boldsymbol{R}_I)\right\}\phi(\boldsymbol{r}-\boldsymbol{R}_I)\,d\boldsymbol{r} \tag{2.9}$$

$$-\alpha_2 = \int \phi^*(\boldsymbol{r}-\boldsymbol{R}_{II})\left\{U_+(\boldsymbol{r}) - V(\boldsymbol{r}-\boldsymbol{R}_{II})\right\}\phi(\boldsymbol{r}-\boldsymbol{R}_{II})\,d\boldsymbol{r} \tag{2.10}$$

$$-\gamma = \int \phi^*(\boldsymbol{r}-\boldsymbol{R}_I-\boldsymbol{a}_1)\left\{U_+(\boldsymbol{r}) - V(\boldsymbol{r}-\boldsymbol{R}_I)\right\}\phi(\boldsymbol{r}-\boldsymbol{R}_I)\,d\boldsymbol{r}\,. \tag{2.11}$$

$\boldsymbol{R}_{I,II}$ represents a lattice point of I or II sublattice. If we denote the lower energy band given by (2.8) as $E_S(\boldsymbol{k})$ and the higher one as $E_A(\boldsymbol{k})$, the corresponding eigen functions are obtained as

$$\begin{aligned}\Psi_{+S}(\boldsymbol{k};\boldsymbol{r}) &= \cos\theta_k\psi_1(\boldsymbol{k};\boldsymbol{r}) + \sin\theta_k\psi_2(\boldsymbol{k};\boldsymbol{r})\,,\\ \Psi_{+A}(\boldsymbol{k};\boldsymbol{r}) &= \sin\theta_k\psi_1(\boldsymbol{k};\boldsymbol{r}) - \cos\theta_k\psi_2(\boldsymbol{k};\boldsymbol{r})\,,\end{aligned} \tag{2.12}$$

where

$$\psi_1(\boldsymbol{k};\boldsymbol{r}) = \sqrt{\frac{2}{N}}\sum_I \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_I)\,\phi(\boldsymbol{r}-\boldsymbol{R}_I)\,, \tag{2.13}$$

$$\phi_2(\boldsymbol{k};\boldsymbol{r}) = \sqrt{\frac{2}{N}} \sum_{II} \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_{II})\,\phi(\boldsymbol{r}-\boldsymbol{R}_{II}),$$
$$\cot 2\theta_k = \frac{\alpha_2-\alpha_1}{2\gamma\xi(\boldsymbol{k})}\ . \tag{2.14}$$

For the $-$ spin, the energy bands are the same as (2.8), and the eigenfunctions are obtained by interchanging ϕ_1 and ϕ_2:

$$\Psi_{-S}(\boldsymbol{k};\boldsymbol{r}) = \sin\theta_k\phi_1(\boldsymbol{k};\boldsymbol{r}) + \cos\theta_k\phi_2(\boldsymbol{k};\boldsymbol{r})\ ,$$
$$\Psi_{-A}(\boldsymbol{k};\boldsymbol{r}) = \cos\theta_k\phi_1(\boldsymbol{k};\boldsymbol{r}) - \sin\theta_k\phi_2(\boldsymbol{k};\boldsymbol{r})\ . \tag{2.15}$$

When $U_+(\boldsymbol{r})$ differs from $U_-(\boldsymbol{r})$, α_1 is generally different from α_2 and we have a splitting of the band. When all the electrons of $+$ and $-$ spins fill the lower bands, we get a state having magnetic superstructure. Under a certain condition discussed later, this state is proved to be more stable at 0°K than those having no magnetic superstructure. With increasing temperature, however, the thermal excitation of electrons into upper energy band will modify the electron distribution in such way as to diminish the difference between $U_+(\boldsymbol{r})$ and $U_-(\boldsymbol{r})$, which, in turn, gives rise to the decrease of the magnitude of $\alpha_2-\alpha_1$, i. e., the gap of the split bands. Thus for each temperature all the electrons will cooperate with each other in such a way as to adjust $U_\pm(\boldsymbol{r})$ and make the free energy of the total system minimum. At a certain temperature, the difference between $U_+(\boldsymbol{r})$ and $U_-(\boldsymbol{r})$, and consequently the magnetic superstructure might disappear. We shall determine such temperature-dependent potentials in the next section.

§ 3. Determination of $U_\pm(\boldsymbol{r})$

We shall take the modified form of the HARTREE-FOCK equation due to SLATER.[3] The characteristic of his modification consists in writing the HARTREE-FOCK equation in a similar form as one-particle SCHRÖDINGER equation $H_i\psi_i = E_i\psi_i$. In the original form of the HARTREE-FOCK equation, one takes

$$H_i = -\frac{1}{2}\nabla^2 + \sum_l V(\boldsymbol{r}-\boldsymbol{R}_l) + \sum_k \int \psi_k^*(\boldsymbol{r}')\psi_k(\boldsymbol{r}')\frac{d\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|}$$
$$-\sum_{\substack{k\\ /\text{spin}}} \int \psi_k^*(\boldsymbol{r}')\psi_i^*(\boldsymbol{r})\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\psi_k(\boldsymbol{r})\psi_i(\boldsymbol{r}')d\boldsymbol{r}' \Big/ \psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r})\ . \tag{3.1}$$

To make the Hamiltonian H_i independent of the electron state i, SLATER has made an approximation of modifying the fourth term of the right hand side of (3.1) by replacing it by its "weighted average"

$$\sum_{i}^{/\text{spin}} \sum_{k}^{/\text{spin}} \int \psi_k^*(\boldsymbol{r}') \psi_i^*(\boldsymbol{r}) \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \psi_k(\boldsymbol{r}) \psi_i(\boldsymbol{r}') d\boldsymbol{r}' \Big/ \sum_{i}^{/\text{spin}} \psi_i^*(\boldsymbol{r}) \psi_i(\boldsymbol{r}) . \quad (3.2)$$

In this approximation, making use of DIRAC's density matrix

$$D_{\pm}(\boldsymbol{r}\boldsymbol{r}') = \sum_{\pm\text{spin}} \psi_i^*(\boldsymbol{r}') \psi_i(\boldsymbol{r}) , \quad (3.3)$$

the HARTREE-FOCK potentials for an electron of $\pm$ spin are expressed as

$$\begin{aligned} U_+(\boldsymbol{r}) &= \sum_l V(\boldsymbol{r}-\boldsymbol{R}_l) + \int \{D_+(\boldsymbol{r}'\boldsymbol{r}') + D_-(\boldsymbol{r}'\boldsymbol{r}')\} \frac{d\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|} \\ &\quad - \int \frac{D_+(\boldsymbol{r}\boldsymbol{r}') D_+(\boldsymbol{r}'\boldsymbol{r})}{D_+(\boldsymbol{r}\boldsymbol{r})} \frac{d\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|} , \\ U_+(\boldsymbol{r}) &= \sum_l V(\boldsymbol{r}-\boldsymbol{R}_l) + \int \{D_+(\boldsymbol{r}'\boldsymbol{r}') + D_-(\boldsymbol{r}'\boldsymbol{r}')\} \frac{d\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|} \\ &\quad - \int \frac{D_-(\boldsymbol{r}\boldsymbol{r}') D_-(\boldsymbol{r}'\boldsymbol{r})}{D_-(\boldsymbol{r}\boldsymbol{r})} \frac{d\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|} . \end{aligned} \quad (3.4)$$

The extension of the above results (3.4) to a finite temperature is straightforward. This can be effected by replacing the DIRAC's density matrix (3.3) by

$$\begin{aligned} D_+(\boldsymbol{r}\boldsymbol{r}') &= \sum_k W_S(\boldsymbol{k}) \Psi_{+S}^*(\boldsymbol{k};\boldsymbol{r}') \Psi_{+S}(\boldsymbol{k};\boldsymbol{r}) + \sum_k W_A(\boldsymbol{k}) \Psi_{+A}^*(\boldsymbol{k};\boldsymbol{r}') \Psi_{+A}(\boldsymbol{k};\boldsymbol{r}) , \\ D_-(\boldsymbol{r}\boldsymbol{r}') &= \sum_k W_S(\boldsymbol{k}) \Psi_{-S}^*(\boldsymbol{k};\boldsymbol{r}') \Psi_{-S}(\boldsymbol{k};\boldsymbol{r}) + \sum_k W_A(\boldsymbol{k}) \Psi_{-A}^*(\boldsymbol{k};\boldsymbol{r}') \Psi_{-A}(\boldsymbol{k};\boldsymbol{r}) , \end{aligned} \quad (3.5)$$

where

$$W_\lambda(\boldsymbol{k}) = \left[\exp\{\alpha + \beta E_\lambda(\boldsymbol{k})\} + 1\right]^{-1} , \quad (3.6)$$

with $\lambda = S$ or A, $\beta = \dfrac{1}{kT}$ and α determined from the condition

$$\frac{N}{2} = \sum_k \{W_S(\boldsymbol{k}) + W_A \boldsymbol{k})\} . \quad (3.7)$$

We can thus obtain the temperature-dependent potential $U_\pm(\boldsymbol{r})$

introduced in the preceding section.

Now, we shall calculate the quantity $\Delta=\alpha_2-\alpha_2$, which determines the magnitude of the energy gap between the lower and higher bands. In virtue of (2.7), (2.9) and (2.10), $\alpha_2-\alpha_1$ can be written as

$$\begin{aligned}\alpha_2-\alpha_1 &= \int\phi^*(\boldsymbol{r})\left\{U_+(\boldsymbol{r})-U_-(\boldsymbol{r})\right\}\phi(\boldsymbol{r})\,d\boldsymbol{r}\\ &=\iint\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\left\{\frac{D_+(\boldsymbol{r}\boldsymbol{r}')\,D_+(\boldsymbol{r}'\boldsymbol{r})}{D_+(\boldsymbol{r}\boldsymbol{r})}-\frac{D_-(\boldsymbol{r}\boldsymbol{r}')\,D_-(\boldsymbol{r}'\boldsymbol{r})}{D_-(\boldsymbol{r}\boldsymbol{r})}\right\}\phi^*(\boldsymbol{r})\phi(\boldsymbol{r})\,d\boldsymbol{r}\,d\boldsymbol{r}'\,,\end{aligned}\tag{3.8}$$

where $D_\pm(\boldsymbol{r}\boldsymbol{r}')$ are now by (2.12), (2.15) and (3.5) expressed as

$$\begin{aligned}D_+(\boldsymbol{r}\boldsymbol{r}') &= \sum_{\boldsymbol{k}}\Big[A(\boldsymbol{k})\psi_1^*(\boldsymbol{k};\boldsymbol{r}')\psi_1(\boldsymbol{k};\boldsymbol{r})+B(\boldsymbol{k})\psi_2^*(\boldsymbol{k};\boldsymbol{r}')\psi_2(\boldsymbol{k};\boldsymbol{r})\\ &\quad+C(\boldsymbol{k})\left\{\psi_1^*(\boldsymbol{k};\boldsymbol{r}')\psi_2(\boldsymbol{k};\boldsymbol{r})+\psi_2^*(\boldsymbol{k};\boldsymbol{r}')\psi_1(\boldsymbol{k};\boldsymbol{r})\right\}\Big]\,,\\ D_-(\boldsymbol{r}\boldsymbol{r}') &= \sum_{\boldsymbol{k}}\Big[B(\boldsymbol{k})\psi_1^*(\boldsymbol{k};\boldsymbol{r}')\psi_1(\boldsymbol{k};\boldsymbol{r})+A(\boldsymbol{k})\psi_2^*(\boldsymbol{k};\boldsymbol{r}')\psi_2(\boldsymbol{k};\boldsymbol{r})\\ &\quad+C(\boldsymbol{k})\left\{\psi_1^*(\boldsymbol{k};\boldsymbol{r}')\psi_2(\boldsymbol{k};\boldsymbol{r})+\psi_2^*(\boldsymbol{k};\boldsymbol{r}')\psi_1(\boldsymbol{k};\boldsymbol{r})\right\}\Big]\,,\end{aligned}\tag{3.9}$$

with

$$\begin{aligned}A(\boldsymbol{k}) &= \cos^2\theta_{\boldsymbol{k}}W_S(\boldsymbol{k})+\sin^2\theta_{\boldsymbol{k}}W_A(\boldsymbol{k})\,,\\ B(\boldsymbol{k}) &= \sin^2\theta_{\boldsymbol{k}}W_S(\boldsymbol{k})+\cos^2\theta_{\boldsymbol{k}}W_A(\boldsymbol{k})\,,\\ C(\boldsymbol{k}) &= \sin\theta_{\boldsymbol{k}}\cos\theta_{\boldsymbol{k}}\left\{W_S(\boldsymbol{k})-W_A(\boldsymbol{k})\right\}\,.\end{aligned}\tag{3.10}$$

If we neglect entirely the overlapping between two atomic wave functions with different centers $\phi(\boldsymbol{r}-\boldsymbol{R})$ and $\phi(\boldsymbol{r}-\boldsymbol{R}')(\boldsymbol{R}\neq\boldsymbol{R}')$, then

$$\begin{aligned}D_+(\boldsymbol{r}\boldsymbol{r}') &\simeq A\sum_I\phi^*(\boldsymbol{r}'-\boldsymbol{R}_I)\phi(\boldsymbol{r}-\boldsymbol{R}_I)+B\sum_{II}\phi^*(\boldsymbol{r}'-\boldsymbol{R}_{II})\phi(\boldsymbol{r}-\boldsymbol{R}_{II})\,,\\ D_-(\boldsymbol{r}\boldsymbol{r}') &\simeq B\sum_I\phi^*(\boldsymbol{r}'-\boldsymbol{R}_I)\phi(\boldsymbol{r}-\boldsymbol{R}_I)+A\sum_{II}\phi^*(\boldsymbol{r}'-\boldsymbol{R}_{II})\phi(\boldsymbol{r}-\boldsymbol{R}_{II})\,,\end{aligned}\tag{3.11}$$

where

$$A=\frac{2}{N}\sum_{\boldsymbol{k}}A(\boldsymbol{k})\,,\qquad B=\frac{2}{N}\sum_{\boldsymbol{k}}B(\boldsymbol{k})\,,\tag{3.12}$$

and thereby $\alpha_2-\alpha_1$ reduces to

$$\Delta=\alpha_2-\alpha_1=(A-B)J\tag{3.13}$$

in which J is defined by

$$J = I_0 - 2zI_1 ,$$
$$I_0 = \iint \phi^*(\boldsymbol{r})\phi^*(\boldsymbol{r}')\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\phi(\boldsymbol{r})\phi(\boldsymbol{r}')d\boldsymbol{r}d\boldsymbol{r}' , \tag{3.14}$$
$$I_1 = \iint \phi^*(\boldsymbol{r})\phi^*(\boldsymbol{r}'-\boldsymbol{a}_1)\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\phi(\boldsymbol{r}')\phi(\boldsymbol{r}-\boldsymbol{a}_1)d\boldsymbol{r}d\boldsymbol{r}' .$$

On the other hand, using (2.14), (3.10) and (3.12), $A-B$ can be put into the form

$$A-B = \frac{2}{N}\sum_{\boldsymbol{k}} \frac{\Delta}{\sqrt{\Delta^2+4\gamma^2\xi^2(\boldsymbol{k})}}\left[W_S(\boldsymbol{k})-W_A(\boldsymbol{k})\right] ,$$

and equating this with (3.13) divided by J, we find an equation which determines the temperature variation of the energy gap. The final result is as follows:

$$\Delta = J\left(\frac{a}{\pi}\right)^z \int\cdots\int \frac{\Delta}{\sqrt{\Delta^2+4\gamma^2\xi^2(\boldsymbol{k})}} \tanh\left\{\frac{\beta}{4}\sqrt{\Delta^2+4\gamma^2\xi^2(\boldsymbol{k})}\right\} dk_1\cdots dk_z . \tag{3.15}$$

In deriving (3.15), we have eliminated α using the condition (3.7) and replaced the summation $\frac{2}{N}\sum_{\boldsymbol{k}}\cdots$ by the integration $\left(\frac{a}{\pi}\right)^z\int\cdots\int\cdots d\boldsymbol{k}$. It is not difficult to show that at sufficiently low temperatures equation (3.15) has a solution $\Delta\neq 0$ in addition to a trivial solution $\Delta=0$, the necessary condition for this being provided by

$$J = I_0 - 2zI_1 > 0 . \tag{3.16}$$

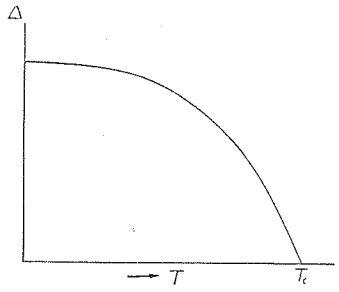

Fig. 1.
Temperature variation of Δ.

In Fig. 1 the temperature variation of Δ expected from (3.15) has been sketched. It must be noted that (3.16) is not a sufficient condition for antiferromagnetism to occur, as will be discussed in the next section.

§ 4. The Condition for Antiferromagnetism

One might fail to conclude from $J>0$ that a metal is antiferromagnetic at sufficiently low temperatures, because the ferromagnetic or paramagnetic state might have lower energy at 0°K

than the antiferromagnetic state. Therefore, let us calculate the energy of the system at 0°K for para-, ferro- and antiferromagnetic states and compare them with each other in order to decide what is the true condition for the appearance of antiferromagnetism.

In the HARTREE-FOCK approximation, the energy of the system at 0°K will be generally given by the following expression:

$$\begin{aligned} E = &(\text{the sum of HARTREE-FOCK eigenenergy over occupied states}) \\ &-1/2\times(\text{the sum of coulomb integrals}) \\ &+1/2\times(\text{the sum of exchange integrals})\,. \end{aligned} \tag{4.1}$$

For the antiferromagnetic state, after some manipulation, (4.1) yields the result

$$E_A = N\varepsilon + \frac{N}{4}J\left\{1-\frac{4}{N}\sum_{k}{}'\sqrt{x^2+b^2\xi^2(\boldsymbol{k})}+x^2\right\} \tag{4.2}$$

where $b=\dfrac{2\gamma_0}{J}$ and $x=\dfrac{\Delta}{J}$, the latter being determined from

$$\frac{2}{N}\sum_{k}{}'\frac{1}{\sqrt{x^2+b^2\xi^2(\boldsymbol{k})}}=1\,. \tag{4.3}$$

$\sum_{k}{}'$ means the summation over the lower $\dfrac{1}{2}N$ values of $\boldsymbol{k}$ in the Brillouin zone. For the paramagnetic state, the wave functions are given by (2.4) and the energy band by (2.3), which is half-filled by $\dfrac{1}{2}N$ electrons of both spins. In the same approximation as that used in §3, we can easily show that

$$\alpha_0 \simeq \frac{1}{2}(I_0-2zI_1) = J/2\,,$$

and thus we get the energy of the paramagnetic state as

$$E_P = N\varepsilon + \frac{N}{4}J-\gamma_0\sum_{k}{}'\xi(\boldsymbol{k})\,. \tag{4.4}$$

For the ferromagnetic state, we shall consider a state in which all the electrons have + spins. A similar calculation gives the energy band of these electrons

$$E(\boldsymbol{k}) = \varepsilon - zI_1 - \gamma_0\xi(\boldsymbol{k})\,. \tag{4.5}$$

Since $\sum_k \xi(k)$ is to vanish, the energy for the ferromagnetic state becomes

$$E_F = N\varepsilon - NzI_1 \tag{4.6}$$

Now if we put down the formulae (4.2), (4.4) and (4.6) in a single form

$$E_\lambda = N\varepsilon + \frac{N}{4} J[1-\eta_\lambda(b)], \quad \lambda = A, P, F, \tag{4.7}$$

then $\eta_\lambda(b)$ is given by

$$\begin{aligned} \eta_A(b) &= \frac{4}{N} \sum_k{}' \sqrt{x^2+b^2\xi^2(k)} - x^2 , \\ \eta_P(b) &= \frac{4b}{N} \sum_k{}' \xi(k) , \\ \eta_F(b) &= \frac{I_0+2zI_1}{I_0-2zI_1} \end{aligned} \tag{4.8}$$

and the most stable state will correspond to that which has the largest of η_λ. In Fig. 2 η_λ's are plotted as functions of b. From this figure we can see that, for a sufficiently narrow band (i.e. small b), the ferromagnetic state is the most stable, while for a broad band the antiferromagnetic state is the most stable, the paramagnetic state being always intermediate. Therefore, the

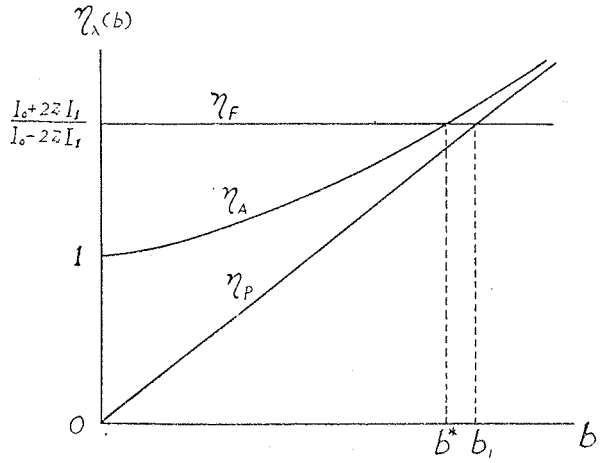

Fig. 2.

condition for antiferromagnetism is, in addition to $J>0$, that the band width b should exceed a certain value b^*, which is determined from

$$\eta_A(b^*) = \eta_F(b^*) \ .$$

The conclusion derived here may not of course be applicable directly to real substances, because we have so far confined ourselves to a too-simplified model on one hand, and also made somewhat rough approximations of calculations on the other hand. In fact, the weak point of the collective electron theory manifests itself in our theory in that the paramagnetic state is always intermediate and that the necessary condition for antiferromagnetism (3.16) contains the 'intra-atomic' exchange integral I_0 as its major part. As was discussed by many authors,[4] if we take account of the inter-electron correlation, the paramagnetic state has to become most stable when the band width decreases below a certain value. Furthermore, the intra-atomic exchange integral is to be diminished significantly in a correct theory. In particular, for the case of s band I_0 should drop out entirely, and therefore the condition (3.16) will not be fulfilled for this case, because I_1 is definitely positive. For the case of degenerate bands, for instance the case of d bands, our theory would be required some modification. But if we content ourselves with the first approximation, the necessary condition for the appearance of antiferromagnetism for degenerate bands will be given by

$$\bar{I}_0 - 2z\bar{I}_1 > 0 \ , \qquad (4.9)$$

where $\bar{I}_0$ and $\bar{I}_1$ represent respectively the 'intra-' and 'inter-atomic' exchange integrals suitably averaged over the degenerate orbitals. And under certain limited circumstances some part of $\bar{I}_0$ may remain, even if we take account of the inter-electron correlation, in such an extent that (4.9) is fulfilled. This might be the case of Cr and Mn.[1]

§ 5. Mean Magnetic Moment

According to Shull and Wilkinson,[1] Cr and Mn seem to be antiferromagnetic metals, having magnetic moment of 0.4 Bohr magnetons per atom for Cr and possibly 0.5 Bohr magnetons per

atom for Mn. These observed values of magnetic moments are surprisingly small in view of their electronic configurations, i. e., $(3d)^5$, $(4s)^1$ of Cr and $(3d)^5$ $(4s)^2$ of Mn. An explanation for this fact has been given based upon tne ZENER's idea that each magnetic moment of localized 3d shell is fluctuating with respect to its direction so frequently that, in the time average, the magnetic moment is considerably diminished to such an extent as it was actually observed. Another and probably more natural interpretation can be provided by our collective electron theory. Namely, from our point of view, electrons of both spins can migrate on the I-sublattice points as well as on the II-sublattice points, though there exists a slight difference in the probability of finding an electron on each of two sublattice points, and therefore both spins cancel with each other on each lattice point, leaving but a small fractional net moment per atom.

From the density matrix (3.11), we know that the probability of finding out a + spin electron on one of I-sublattice points is equal to A and that for $-$ spin electron on the same point it is B, so that the mean magnetic moment per electron, μ, becomes

$$\mu = (A-B)\mu_0 = \frac{\Delta}{J}\mu_0 \tag{5.1}$$

where μ_0 is the Bohr magneton. Thus μ/μ_0 decreases with increasing temperatures just as sketched in Fig. 1, qualitatively in agreement with the experimental results observed for Cr and Mn. The magnitude of μ/μ_0 at 0°K can be calculated from (3.15) and (4.3) as

$$m_0 \equiv \left(\frac{\mu}{\mu_0}\right)_{T=0} = \left(\frac{a}{\pi}\right)^z \int\cdots\int \frac{m_0}{\sqrt{m_0^2 + \frac{4\gamma_0^2}{J^2}\xi^2(k)}}\, dk_1 \cdots dk_z \,. \tag{5.2}$$

In the case of linear chain, the above integration is easily performed, the result being

$$m_0 = \frac{2}{\pi}\sqrt{1-y^2}\; K(y) \tag{5.3}$$

where $K(y)$ is the complete elliptic integral of the first kind, and

$$y = \frac{b}{\sqrt{m_0^2+b^2}}\,, \qquad b = \frac{4\gamma_0}{J} \tag{5.4}$$

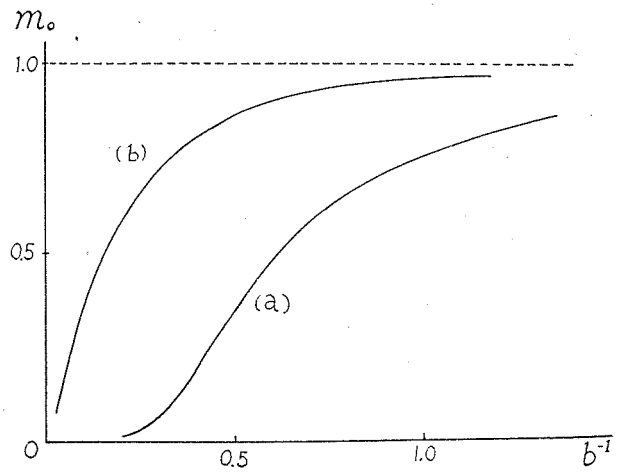

Fig. 3. m_0 as functions of b^{-1}.
(a): linear chain.
(b): body-centered cubic lattice.

In Fig. 3 the calculated values of m_0 for the linear chain and body-centered cubic lattice are shown as functions of b^{-1}. As is evident from this figures, the magnitude of m_0 depends solely on b, the ratio of the band width to the exchange integral, and the larger is b, the smaller m_0 becomes compared with unity. If we assume that this result obtained for s band can be also applied to d bands and if we take for Mn

$$4\gamma_0 \sim 2.7 \text{ e. v.}^{5)}, \qquad J/2k \sim T_c = 100^\circ\text{K}^{1)},$$

then we get from the curve (b) of Fig. 3 $m_0 \simeq 0.05$, which is to be compared with the experimental value 0.1 for Mn estimated by SHULL and WILKINSON.

§ 6. Conclusions

The calculations above suggest that the antiferromagnetic superstructures with the extraordinary small average magnetic moments of atoms discovered in the metals Cr and Mn are well explained by our collective electron theory. The absence of the anomalies of magnetic susceptibility and specific heat for these metals will be also expected from our theory. For instance, the transition energy of our antiferromagnetic metal is estimated as

$$\Delta E \sim J\left(\frac{\Delta}{J}\right)^2 \sim J m_0^2 \qquad \text{per atom ,}$$

and since $T_c \sim J/k$, the specific heat anomaly at the critical temperature T_c will be approximately given by

$$\Delta C/k \sim \Delta E/kT_c \sim m_0^2 ,$$

which is too small to be observed when $m_0 \lesssim 0.1$.

References

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