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Electron Correlation and Ferromagnetism of Transition Metals

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The electron correlation in a narrow energy band is discussed taking into account the multiple scattering between two electrons. The discussion is an adaptation of Brueckner's theory of nuclear matter. It is assumed that electrons interact with each other only when they are at the same atom. The effect of the electron correlation depends in an intricate way on the energy spectrum of a given band. An approximate expression of the effective magnitude of the interaction is derived. The condition for the occurrence of ferromagnetism is investigated for various types of bands. The ferromagnetism of Ni and the paramagnetism of Pd can be understood reasonably through the present approach The degeneracy of the d bands is taken into account in the discussion of these metals.

§ 1. Introduction

The purpose of this paper is to present a semi-quantitative discussion of the electron correlation and its bearing on the ferromagnetism of transition metals. Although the importance of the rôle of the electron correlation in metallic ferromagnetism is emphasized by many authors,1),2) all explicit calculations have been confined to the free electron model. This model, however, is hardly justified for the d electrons. The present approach is essentially based on the contrasting *tight binding* approximation, which may be justified for metals near the end of the transition metal series. The discussion is intended to clarify the role of the intra-atomic exchange interaction of the d electrons. Ni and Pd will be the main subjects of this discussion.

In 1936 Slater3) discussed the ferromagnetism of Ni by use of the Hartree-Fock approximation in calculating the interaction energy of the d electrons, concluding that the origin of the ferromagnetism is in the intra-atomic exchange interaction. His theory has been criticized since then by several authors particularly on the fact that the electron correlation is not taken into account in the calculation. It was argued, for example by Wohlfarth2) that the electron correlation reduced the intra-atomic interaction to the extent that it was less important than the inter-atomic interaction. On the other hand, Slater showed that the necessary amount of the exchange interaction to produce the ferromagnetism is of the order of the intra-atomic exchange interaction between two d electrons in *different* atomic d orbitals, which is characterized by the exchange integral of the order of 0.6 ev. If, however, the Hartree-Fock approximation is honestly applied, the exchange interaction between two d band electrons involves the Coulomb self-energy of an atomic d orbital, which is of the order of 10 ev. This arises from the fact that two band electrons having antiparallel spins can enter into the same atomic orbital, while those with parallel spins cannot. The importance of the intra-atomic interaction, therefore, depends critically on how and to what extent this Coulomb self-energy effect is reduced by the electron correlation. We calculate this reduction by taking into account the multiple scattering between two electrons. The calculation is essentially an adaptation of Brueckner's theory of nuclear matter and He^3.[4] When the number of electrons is small, the main feature of the electron correlation is the modification of electron trajectories by the two-body collision. The present approach takes into account this effect fully, and it will serve to semi-quantitative understanding of the electron correlation effect even when the electron number is moderately high.

The s electrons, which are free electrons to good approximation, will shield the interaction between two d electrons to a considerable extent, when the d electrons are at different atoms. It is assumed in the present paper that the interaction between two d electrons vanishes unless they are at the same atom. Within the same atom the interaction will not be shielded appreciably. When the Bohm-Pines theory is applied to Ni which has 0.6 $4s$ electrons per atom, the shielded interaction changes its sign at about the distance between the nearest-neighboring lattice sites. Though this result may not be taken for a quantitative verification, the above-mentioned assumption can be regarded as a semi-quantitatively correct simplification to make the calculation feasible. In calculating the matrix elements of the interaction, we shall neglect the overlap between the atomic orbitals belonging to the neighboring atoms. In other words, the atomic orbitals are replaced by the corresponding Wannier functions. This last assumption may be justified for a nondegenerate band in the limit of tightly bound electrons. It will be re-examined later (§ 4), when the degeneracy of the d bands is taken into account.

With the above-mentioned assumptions we can show that the correlation effect reduces the intra-atomic interaction (the Coulomb self-energy) to the magnitude of the order of the band-width when the self-energy is much larger than the band width. This result may be understood physically as follows. When the intra-atomic interaction is large, electrons will avoid entering into the same atom by the sacrifice of the one electron energy of the order of the band width. Thus this increase of the one electron energy corresponds to the effective magnitude of the interaction. Since the reduction is more effective for smaller number of electrons, the paramagnetic state is stable for a sufficiently small number of electrons regardless of the energy spectrum of the band. Also the condition for the occurrence of ferromagnetism is more stringent than in the Hartree-Fock approximation. It will be shown that the occurrence of ferromagnetism for such a small number of holes as in Ni requires a special characteristic of the state-density vs energy relation.

When the electron correlation is taken into account, the definition of the one electron energy is not a simple problem. It is assumed in the present paper that one can choose an approximate one electron energy spectrum which suffices for practical purposes. This energy spectrum is assumed to be independent of spin states and to include self-consistently the effect of the interaction among electrons that does not depend on the spin states of the interacting electrons. This problem will be discussed in more detail in the following sections.

In §§ 2 and 3 we discuss the case of nondegenerate band, calculating the multiple scattering in § 2 and discussing the stability of the paramagnetic state in § 3. The possibility of other types of spin ordering than ferromagnetism is neglected in the latter discussion. Section 4 deals with the discussion of Ni and Pd. In § 5 Ni-Cu alloys and other cases will be discussed briefly.

§ 2. Multiple scattering between two electrons in a nondegenerate band

We discuss first the multiple scattering between two electrons in the absence of other electrons. The Hamiltonian governing the motion of two electrons is represented by

$$H = H_0(1) + H_0(2) + V(1, 2), \tag{1}$$

where 1 and 2 denote the coordinates of electrons 1 and 2, respectively, H_0 is the one electron energy, $V(1, 2)$ the interaction between two electrons. The eigenvalue of H_0 associated with a given wave vector $\boldsymbol{k}$ is denoted by $\varepsilon(\boldsymbol{k})$. The corresponding wave function $\varphi(x, \boldsymbol{k})$ with $x=1$ or 2 is connected to the Wannier function associated with a given lattice site $\boldsymbol{R}$, $W(x, \boldsymbol{R})$, by the well-known relations,

$$\varphi(x, \boldsymbol{k}) = (1/N)^{1/2} \textstyle\sum_{\boldsymbol{R}} W(x, \boldsymbol{R}) \exp(i\boldsymbol{k}\cdot\boldsymbol{R}) \tag{2}$$

and

$$W(x, \boldsymbol{R}) = (1/N)^{1/2} \textstyle\sum_{\boldsymbol{k}} \varphi(x, \boldsymbol{k}) \exp(-i\boldsymbol{k}\cdot\boldsymbol{R}), \tag{3}$$

where N is the number of the lattice sites in a given volume.

As was mentioned in § 1, the matrix elements of $V(1, 2)$ referred to the Wannier functions are assumed to be

$$\begin{aligned} &\int W^*(1, \boldsymbol{R}_1)\, W^*(2, \boldsymbol{R}_2)\, V(1, 2)\, W(1, \boldsymbol{R}_3)\, W(2, \boldsymbol{R}_4)\, dv_1\, dv_2 \\ &\qquad = U \text{ if } \boldsymbol{R}_1 = \boldsymbol{R}_2 = \boldsymbol{R}_3 = \boldsymbol{R}_4, \ = 0 \text{ otherwise.} \end{aligned} \tag{4}$$

U defined by (4) will be identified with the Coulomb self-energy of the atomic orbital. The matrix elements of $V(1, 2)$ referred to φ's are easily calculated by the use of (2) and (4) to be

$$\int \varphi^*(1,\boldsymbol{k}_1)\,\varphi^*(2,\boldsymbol{k}_2)\,V(1,2)\,\varphi(1,\boldsymbol{k}_3)\,\varphi(2,\boldsymbol{k}_4)\,dv_1dv_2$$

$$=(U/N)\,\delta(\boldsymbol{k}_1,\boldsymbol{k}_2\,;\,\boldsymbol{k}_3,\boldsymbol{k}_4) \qquad (5)$$

with

$$\delta(\boldsymbol{k}_1,\boldsymbol{k}_2\,;\,\boldsymbol{k}_3,\boldsymbol{k}_4)=1 \text{ if } \boldsymbol{k}_1+\boldsymbol{k}_2=\boldsymbol{k}_3+\boldsymbol{k}_4+\boldsymbol{K}, \qquad (6)$$

$$=0 \text{ otherwise,}$$

where $\boldsymbol{K}$ represents a reciprocal lattice vector.

Let $|\boldsymbol{k}_1\sigma_1,\boldsymbol{k}_2\sigma_2\rangle$ be the antisymmetrized wave function of the state where the one electron states specified by $\boldsymbol{k}_1$ with the spin coordinate σ_1 and $\boldsymbol{k}_2$ with σ_2 are occupied. In the Hartree-Fock approximation, the interaction energy of two electrons in this state is given by

$$\varDelta E_{HF}(\boldsymbol{k}_1\sigma_1,\boldsymbol{k}_2\sigma_2)=(U/N)\,(1-\delta(\sigma_1\sigma_2)), \qquad (7)$$

where $\delta(\sigma_1\sigma_2)=1$ for parallel spins $(\sigma_1=\sigma_2)$, $\delta(\sigma_1\sigma_2)=0$ for antiparallel spins $(\sigma_1\neq\sigma_2)$. In the case of parallel spins, the wave function $|\boldsymbol{k}_1\sigma_1,\boldsymbol{k}_2\sigma_2\rangle$ is an eigenfunction of the total Hamiltonian H. In the case of antiparallel spins, however, the eigenfunction of H is of the form given by

$$\varPsi(\boldsymbol{k}_1,\boldsymbol{k}_2)=|\boldsymbol{k}_1,\boldsymbol{k}_2\rangle+(1/N)\sum_{k_3k_4}\varGamma_{k_3k_4}\delta(\boldsymbol{k}_1\,\boldsymbol{k}_2\,;\,\boldsymbol{k}_3\,\boldsymbol{k}_4)\,|\boldsymbol{k}_3\,\boldsymbol{k}_4\rangle, \qquad (8)$$

where the spin indices are omitted for simplicity. Inserting this expression into the Schroedinger equation, we can easily determine $\varGamma$ and the energy eigenvalue to be

$$\varGamma_{k_3k_4}=-\{U/(1+UG(\boldsymbol{k}_1,\boldsymbol{k}_2))\}\,\{1/(\varepsilon(\boldsymbol{k}_3)+\varepsilon(\boldsymbol{k}_4)-\varepsilon(\boldsymbol{k}_1)-\varepsilon(\boldsymbol{k}_2))\} \qquad (9)$$

and

$$E(\boldsymbol{k}_1,\boldsymbol{k}_2)=\varepsilon(\boldsymbol{k}_1)+\varepsilon(\boldsymbol{k}_2)+\varDelta E(\boldsymbol{k}_1,\boldsymbol{k}_2)$$

with

$$\varDelta E(\boldsymbol{k}_1,\boldsymbol{k}_2)=(U/N)\,\{1/(1+UG(\boldsymbol{k}_1,\boldsymbol{k}_2))\}, \qquad (10)$$

where $G(\boldsymbol{k}_1,\boldsymbol{k}_2)$ is defined by

$$G(\boldsymbol{k}_1,\boldsymbol{k}_2)=(1/N)\sum_{k_3,k_4}\delta(\boldsymbol{k}_1\,\boldsymbol{k}_2\,;\,\boldsymbol{k}_3\,\boldsymbol{k}_4)/(\varepsilon(\boldsymbol{k}_3)+\varepsilon(\boldsymbol{k}_4)-\varepsilon(\boldsymbol{k}_1)-\varepsilon(\boldsymbol{k}_2)). \qquad (11)$$

In (9) and (11), $\varDelta E$ in the factor $1/[\varepsilon(\boldsymbol{k}_3)+\varepsilon(\boldsymbol{k}_4)-\varepsilon(\boldsymbol{k}_1)-\varepsilon(\boldsymbol{k}_2)-\varDelta E]$ is neglected because it is of the order of $1/N$.[*] Comparing $\varDelta E$ given by (10) with $\varDelta E_{HF}$ of (7), we can see that the reduction of the interaction energy due to the

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[*] When the energy of the initial state, $\varepsilon(\boldsymbol{k}_1)+\varepsilon(\boldsymbol{k}_2)$, is high enough to yield $1+UG(\boldsymbol{k}_1,\boldsymbol{k}_2)\leq 0$ (G becomes negative for sufficiently high initial energy), $\varDelta E$ cannot be neglected, being not of the order of $1/N$. In such a case the exact solution yields a quasi-bound state of two electrons. In the present discussion we are interested only in the low-lying initial states for which $\varDelta E$ is of the order of $1/N$.

electron correlation is indicated by the factor $1/(1+UG(\boldsymbol{k}_1, \boldsymbol{k}_2))$.

In order to take into account the presence of other electrons than the interacting pair, we make the following modification of the above calculation. In the first place, we restrict the states $\boldsymbol{k}_3$ and $\boldsymbol{k}_4$ in the sum of (8) and (11) to the unoccupied states above the Fermi level, since the occupied states below the Fermi level are not available for the scattering. In the second place, we assume that other electrons affect the motion of the interacting pair only through a self-consistently defined potential energy. This potential energy is understood to be included already in the one electron energy H_0 of (1). We may define the modified one electron energy $\varepsilon(\boldsymbol{k})$ by

$$\varepsilon(\boldsymbol{k}) = \varepsilon_0(\boldsymbol{k}) + \textstyle\sum_{k'} \Delta E(\boldsymbol{k}, \boldsymbol{k}'), \tag{12}$$

where $\varepsilon_0(\boldsymbol{k})$ is the one electron energy in the absence of other electrons, and the sum of the second term is taken over the occupied states below the Fermi level. It is $\varepsilon(\boldsymbol{k})$, not $\varepsilon_0(\boldsymbol{k})$, that should enter into the expressions of ΔE and $G(\boldsymbol{k}_1, \boldsymbol{k}_2)$, (10) and (11). One might regard (12) as the equation of self-consistency to define $\varepsilon(\boldsymbol{k})$. As was disussed by Brueckner, however, the energy of excited levels may not be determined uniquely, since it may depend on the states below the Fermi level from which the electrons are excited. To make the whole calculation self-consistently, one may follow Brueckner and Gammel's procedure faithfully, reformulating the scattering problem in terms of the reaction matrices and solving an infinite ladder of self-consistency equations. We assume in the present paper, however, that (12) defines the self-consistent one electron energy spectrum for either the occupied or the unoccupied levels.

With the above-mentioned assumptions, the effective value of U in the paramagnetic state can be defined as

$$U_{\text{eff}}(\boldsymbol{k}_1, \boldsymbol{k}_2) = U \cdot 1/(1+UG(\boldsymbol{k}_1, \boldsymbol{k}_2)), \tag{13}$$

where the sum in (11) which defines $G(\boldsymbol{k}_1, \boldsymbol{k}_2)$ is understood to be taken over the unoccupied states. Since $G(\boldsymbol{k}_1, \boldsymbol{k}_2)$ is generally of the order of $1/W$, where W is the band width, (13) yields

$$U_{\text{eff}} \approx W \text{ if } U \gg W, \tag{14}$$

whose physical meaning was discussed in § 1. If the bottom of the band corresponds to a point of high symmetry such as $\boldsymbol{k}=0$ or $\boldsymbol{k}=\boldsymbol{K}/2$, G of the pair of electrons, both of which occupy the state of lowest energy, can be written as

$$G(0,\ 0) = (1/2)\int_{\varepsilon_F}^{W} \{\eta(\varepsilon)/\varepsilon\}\, d\varepsilon, \tag{15}$$

where $\eta(\varepsilon)$ is the state density per unit energy per atom per spin, and ε_F is the Fermi energy. Except for a negligibly small number of pairs, $G(\boldsymbol{k}_1, \boldsymbol{k}_2)$ does not differ much from $G(0, 0)$. This is because the scattering process is the s wave scattering that does not depend on the relative momentum of the interacting pair, and also because the energy of low-lying excited levels involved in $G(\boldsymbol{k}_1, \boldsymbol{k}_2)$ is generally separated from the unperturbed energy by an energy of the order of ε_F by the condition of the crystal momentum conservation (6). Thus we obtain an approximate estimate of $U_{\rm eff}$,

$$U^0_{\rm dff} = U/(1+UG(0,0)). \qquad (16)$$

The difference between (16) and the average of (13) over $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ below the Fermi level is estimated by numerical calculation to be within 5 percent for the case of $\eta =$ constant. The details of the band having a constant state density will be discussed in § 4.

§ 3. The stability of the paramagnetic state

In the Hartree-Fock approximation, the paramagnetic state becomes unstable if the condition,

$$U\eta(\varepsilon_F) > 1, \qquad (17)$$

is satisfied. This condition is obtained by comparing the energy of the paramagnetic state with that of the ferromagnetic state having an infinitesimal magnetization. The corresponding condition in the present approximation is given to good approximation by

$$U^0_{\rm eff}\,\eta(\varepsilon_F) > 1. \qquad (18)'$$

In order to derive this condition, we compare the energy of the paramagnetic state first with the state in which the + spin levels are occupied up to the energy $\varepsilon_F{}^+$ and the $-$ spin levels up to the energy $\varepsilon_F{}^-$. $\varepsilon_F{}^+$ and $\varepsilon_F{}^-$ satisfy the relation, $\varepsilon_F{}^+ - \varepsilon_F = \varepsilon_F - \varepsilon_F{}^- = \varDelta\varepsilon$ to the first order of $\varDelta\varepsilon$. The energy difference between the paramagnetic state and the ferromagnetic state consists of two terms,[*]

$$\varDelta E_1 = \text{the difference of } \varepsilon_0 \text{ in (12)} \qquad (19)$$

and

$$\varDelta E_2 = \int_0^{\varepsilon_F{}^+} \int_0^{\varepsilon_F{}^-} \tilde{U}_{\rm eff}(\varepsilon_1, \varepsilon_2\,;\,\varepsilon_F{}^+, \varepsilon_F{}^-)\,\eta(\varepsilon_1)\,\eta(\varepsilon_2)\,d\varepsilon_1\,d\varepsilon_2$$

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[*] In the state having infinitesimal magnetization, the one electron energy defined by (12) is shifted compared with $\varepsilon(\boldsymbol{k})$ of the paramagnetic state through the second term of (12). Since the shift may not be a constant for all states, there will be a change in the functional form of $\eta(\varepsilon)$. This change of η is neglected in deriving (19) and (20), because the shift is approximately constant for the states having the same spin (it is of opposite sign for opposite spin state). ε in (20) represents the energy measured from the bottom of the band which is different for different spin in the ferromagnetic state.

$$-\int_0^{\varepsilon_F}\int_0^{\varepsilon_F}\tilde{U}_{\mathrm{eff}}(\varepsilon_1,\varepsilon_2\,;\varepsilon_F,\varepsilon_F)\,\eta(\varepsilon_1)\,\eta(\varepsilon_2)\,d\varepsilon_1\,d\varepsilon_2, \tag{20}$$

where $\tilde{U}_{\mathrm{eff}}$ is the average of U_{eff} over the states having the energies ε_1 and ε_2; the dependence of $\tilde{U}_{\mathrm{eff}}$ on ε_F's, which arises from the dependence of G on the Fermi energies, is explicitly indicated.

ΔE_2 can be rewritten up to the second order of $\Delta\varepsilon$ as

$$\Delta E_2=\int_0^{\varepsilon_F^+}\int_0^{\varepsilon_F^-}\{\tilde{U}_{\mathrm{eff}}(\varepsilon_1,\varepsilon_2\,;\varepsilon_F^+,\varepsilon_F^-)-\tilde{U}_{\mathrm{eff}}(\varepsilon_1,\varepsilon_2\,;\varepsilon_F,\varepsilon_F)\}\,\eta(\varepsilon_1)\,\eta(\varepsilon_2)\,d\varepsilon_1\,d\varepsilon_2$$
$$-(\Delta\varepsilon)^2\eta(\varepsilon_F)^2\,\tilde{U}_{\mathrm{eff}}(\varepsilon_F,\varepsilon_F\,;\varepsilon_F,\varepsilon_F)$$
$$+(\Delta\varepsilon)^2\eta(\varepsilon_F)\int_0^{\varepsilon_F}\{\partial\tilde{U}_{\mathrm{eff}}(\varepsilon_1=\varepsilon_F,\varepsilon_2\,;\varepsilon_F,\varepsilon_F)/\partial\varepsilon_1\}\,\eta(\varepsilon_2)\,d\varepsilon_2. \tag{21}$$

The last term of (21) may be interpreted as a part of the one electron energy; adding it to ΔE_1 given by (19), we obtain $(\Delta\varepsilon)^2\eta(\varepsilon_F)$. The first term of (21) corresponds to the energy change arising from a modification of the electron correlation. Since the modification arises in the present approximation from a change in the availability of the states near the Fermi surface for the scattering, and since these states do not contribute much to the electron correlation because of the condition of the crystal momentum conservation, we may expect generally that the first term is small. It is shown in the Appendix that the first term is actually small in the case of $\eta=$constant. Neglecting thus the first term, we obtain for the condition of the occurrence of the ferromagnetism

$$\tilde{U}_{\mathrm{eff}}(\varepsilon_F,\varepsilon_F)\,\eta(\varepsilon_F)>1. \tag{22}$$

The condition (22) is too stringent, because we assumed a special type of ferromagnetism. Let $\varepsilon(\boldsymbol{k})$ be dependent on the magnitude of the wave vector only. $G(\boldsymbol{k}_1,\boldsymbol{k}_2)$ with both $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ lying at the Fermi surface diverges for $\boldsymbol{k}_1=-\boldsymbol{k}_2$ and is smallest for $\boldsymbol{k}_1=\boldsymbol{k}_2$ according to (11). Correspondingly, U_{eff} for $\boldsymbol{k}_1=-\boldsymbol{k}_2$ vanishes, and U_{eff} for $\boldsymbol{k}_1=\boldsymbol{k}_2$ will be the largest for the states at the Fermi surface. If an electron is removed from the $-$spin level with $\boldsymbol{k}$ at the Fermi surface and put in the $+$spin level with a wave vector close to $\boldsymbol{k}$, the gain of the interaction energy is specified by $U_{\mathrm{eff}}(\boldsymbol{k},\boldsymbol{k})$ which is larger than the average, $\tilde{U}_{\mathrm{eff}}(\varepsilon_F,\varepsilon_F)$. It is shown in the Appendix that $U_{\mathrm{eff}}(\boldsymbol{k},\boldsymbol{k})$ with $\boldsymbol{k}$ at the Fermi surface is equal to U_{eff}^0 given by (16) to good approximation in the case of the band having a constant state density. In this case, $\tilde{U}_{\mathrm{eff}}(\varepsilon_F,\varepsilon_F)$ is smaller by about 10 percent than $U_{\mathrm{eff}}(\boldsymbol{k},\boldsymbol{k})$. Thus U_{eff} in the condition (18) may be understood to be given by (16).

In the following we assume the condition (18) with U^0_{eff} defined by (16). From (15) and (16) we can see that G increases and U^0_{eff} decreases with decreasing number of electrons. Thus there is a lower limit for the number of electrons to satisfy the condition (18) even when $U=\infty$. Of various state density functions, this critical number of electrons is calculated for the cases of $U=\infty$ and $U=2W$. The result is summarized in Table I, where n is defined to be the total number of electrons of both spins per atom and $\eta(\varepsilon)$ is normalized to satisfy $\int_0^W \eta(\varepsilon)d\varepsilon=1$. Also the minimum value of U required to satisfy the condition (18) for the optimum number of electrons ($n=1$) is listed in the Table. Though the present approximation is not valid for $n\sim1$, the result may be useful for semi-quantitative discussions.

Table I.

$\eta(\varepsilon)$	$WG(0,\ 0)$, $x=\varepsilon_F/W$	$n_{\mathrm{cr}}(U=\infty)$	$n_{\mathrm{cr}}(U=2W)$	U_{cr}/W
$1/W$	$(1/2)\log(1/x)$	0.271	0.446(0.000)	1.53
$2\varepsilon/W^2$	$1-x$	0.222	0.500(0.125)	0.89
$2(W-\varepsilon)/W^2$	$x-\log x-1$	0.233	0.440(0.000)	1.12
$4\varepsilon/W^2(\varepsilon<W/2)$ $4(\varepsilon-W/2)/W^2(\varepsilon>W/2)$	$2\log 2-2x$	0.214	0.395(0.063)	0.62
$6\varepsilon(W-\varepsilon)/W^3$	$(3/2)(1-x)^2$	0.208	0.367(0.047)	0.89

η is the state density per atom per unit energy per spin, W the band width, ε_F the Fermi energy. n_{cr} is the minimum number of electrons per atom required for obtaining ferromagnetism, U_{cr} is the minimum of U required to produce ferromagnetism for the optimum number of electrons ($n=1$), the figures in parenthesis are the corresponding values obtained in the Hartree-Fock approximation.

§ 4. Ferromagnetism of Ni and Pd

In Ni and Pd, the d bands are occupied by about 0.6 holes per atom. The calculations of the $3d$ bands made by Fletcher,[5] Segall,[6] and Yamashita et al.[7] indicate that these holes are distributed mostly among the three d bands whose atomic orbitals correspond to the $d\varepsilon$ orbitals, i.e. $d(xy)$, $d(yz)$, and $d(zx)$ orbitals, where xy, etc. denote the angular part of the d orbitals. These three bands are degenerate by cubic symmetry. The states of highest energy (the bottom of the band for holes) of the $d(xy)$ band are specified by the $\boldsymbol{k}$ vectors, $(2\pi/a)$ $(\pm1, 0, 0)$ and $(2\pi/a)$ $(0, \pm1, 0)$, where a is the lattice parameter of the cubic unit cell, those of the $d(yz)$ band by $(2\pi/a)$ $(0, \pm1, 0)$ and $(2\pi/a)$ $(0, 0, \pm1)$, and those of the $d(zx)$ band by $(2\pi/a)$ $(0, 0, \pm1)$ and $(2\pi/a)$ $(\pm1, 0, 0)$, two of the three bands being degenerate at each of these points. At a general point in the $\boldsymbol{k}$ space, these degenerate bands are mixed with each other by the periodic potential. We shall neglect this band mixing in the following discussion, primarily because the mixing is small in the vicinity of the top of the bands and will not be essential for the intended semi-quantitative discussion. It might be worth while, however, to discuss briefly the definition of the Wannier function in degenerate bands.

If the band mixing is taken into account, the eigenfunction is generally a linear combination of the Bloch orbitals, each of which is constructed with a given atomic d orbital. Correspondingly, the degenerate energy eigenvalues are split by the mixing. When an energy band is defined by the requirement that the energy is a continuous function within a band, the level of the highest energy at each point in the $\boldsymbol{k}$ space belongs always to the first band, the second highest to the second band, and so on. With the energy band thus defined, it is impossible to assign a unique atomic orbital to each band and accordingly the Wannier function does not correspond to any atomic orbital. The energy band is invariant with respect to the transformation of the coordinate axes belonging to the cubic group in the sense that the operation transforms a given wave function into another wave function of the same band. Thus the Wannier function, which is a sum of all wave functions belonging to the band, is invariant under the operation, while the atomic d orbitals are not invariant. The Wannier function associated with a given lattice point consists of the d orbitals of surrounding atoms; the envelope of their amplitudes is zero at the central atom, perhaps having a maximum at the nearest neighbors, then decreasing with increasing distance from the central atom. On the other hand, if the band mixing is neglected, the $d(xy)$ band, etc. are not invariant with respect to the coordinate transformation, and the Wannier functions correspond to the atomic orbitals.

Treating the three d bands separately, we assign 0.2 holes to each band. The intra-band interaction, which is defined as the interaction between two holes belonging to the same band, is characterized by the Coulomb self-energy U as in the case of a single band. On the other hand, the inter-band interaction may be divided into three scattering processes; the process in which the interacting electrons (holes) remain in the original bands after scattering is characterized by the Coulomb integral defined by

$$U' = \int W^*(1)\, W'^*(2)\, V(1, 2)\, W(1)\, W'(2)\, dv_1 dv_2 ; \tag{23}$$

the process in which the electrons are exchanged between two bands is characterized by the exchange integral defined by

$$J = \int W^*(1)\, W'^*(2)\, V(1, 2)\, W'(1)\, W(2)\, dv_1\, dv_2 ; \tag{24}$$

the process which corresponds to the transfer of a pair of electrons from one band to another is characterized by the integral,

$$J' = \int W^*(1)\, W^*(2)\, V(1, 2)\, W'(1)\, W'(2)\, dv_1\, dv_2 . \tag{25}$$

In (23), (24), and (25), W and W' represent the Wannier functions of two different bands associated with the same atom. If W and W' are identified with the corresponding atomic d orbitals, integrals other than those mentioned above vanish by symmetry. U' is of the same order of magnitude as U. J and J', which are equal to each other within the present approximation, are much smaller than U or U', since they correspond to the exchange integral between different atomic d orbitals of the order of 0.6 ev.

The inter-band interactions will be reduced by the electron correlation to roughly the same extent as the intra-band interaction. This reduction can be discussed by adapting the theory developed in § 2. If only the scattering process characterized by (23) is considered, the effective value of U' is obtained by replacing in (13) U by U' and G by G' defined by

$$G'(\boldsymbol{k}_1, \boldsymbol{k}_2) = (1/N)\sum\delta(\boldsymbol{k}_1\boldsymbol{k}_2\,;\,\boldsymbol{k}_3\boldsymbol{k}_4)/(\varepsilon(\boldsymbol{k}_3)+\varepsilon'(\boldsymbol{k}_4)-\varepsilon(\boldsymbol{k}_1)-\varepsilon'(\boldsymbol{k}_2)), \tag{26}$$

where $\varepsilon(\boldsymbol{k})$ and $\varepsilon'(\boldsymbol{k})$ represent the one electron energies of a given pair of the bands. Since the interaction is independent of the spin states of interacting electrons, we may suppose that its effect is self-consistently incorporated in the one electron energy.

The effect of other scattering processes is negligibly small. If the exchange scattering is taken into account, the interaction energy of a pair of electrons with parallel spins, which belong to different bands, is modified to be given by

$$\begin{aligned}\Delta E &= (1/N)\{(U'-J)/[1+(U'-J)G']\}\\ &\cong (1/N)\{U'/(1+U'G')-J/(1+U'G')^2\},\end{aligned} \tag{27}$$

and ΔE of antiparallel spins by

$$\begin{aligned}\Delta E &= (1/2N)\{(U'+J)/[1+(U'+J)G']\\ &\qquad +(U'-J)/[1+(U'-J)G']\},\\ &\cong (1/N)\{U'/(1+U'G')-J^2G'/(1+U'G')^3\}.\end{aligned} \tag{28}$$

Comparing (27) and (28) with corresponding expressions in the Hartree-Fock approximation, we can see that the difference of the inter-band interaction between the case of parallel spins and that of antiparallel spins is reduced approximately by the factor $1/(1+U'G')^2$ which is estimated to be less than 0.1. Also the transfer process given by (25), which is effective only for antiparallel spins, modifies the intra-band interaction only slightly.*) The smallness of the above-mentioned effects may be understood qualitatively from the argument that the effective magnitude of the inter-band exchange interaction is reduced by the electron correlation to the same extent as the intra-band interaction is reduced, since the reduction arises in both cases from the decrease of the probability of finding two holes at the same atom.

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*) The effect of the transfer process can be taken into account approximately by replacing U by $U(1-2J^2/U)$ in (10).

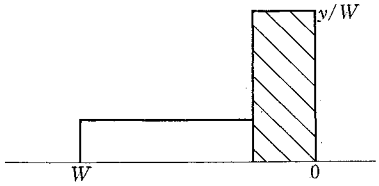

Fig. 1. A state density vs energy curve which favors the ferromagnetic state. The hatched region (the high density region) contains x states per atom per spin in total. The state density of the high density region is defined to be y/W; the state density of the low density region can be expressed in terms of x and y.

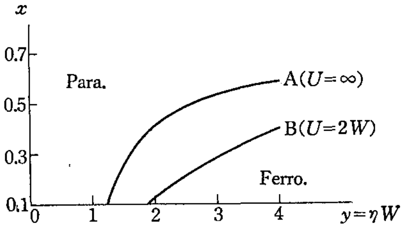

Fig. 2. The region in the x-y plane (x and y are defined in Fig. 1.) in which the ferromagnetic state is favored energetically for $n=0.2$. The condition $U^0{}_{\rm eff}\eta=1$ is satisfied on curve A for $U=\infty$ and on curve B for $U=2$W.

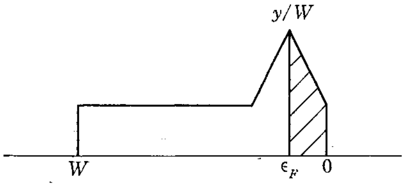

Fig. 3. A state density curve assumed for Pd. The hatched region is assumed to be occupied by holes of 0.2 per atom. The state density at the Fermi level is assumed to be $2.4/W$.

With the considerations so far discussed, the problem is now reduced to that of a single band. According to the available calculations of the *d* bands in Ni, the band width W is 3 to 4 ev. U of Ni is estimated by Van Vleck[1] to be about 7.6 ev. Thus we may assume $U\cong 2W$ for Ni. Table I shows that simple state density functions such as those listed in the Table do not yield ferromagnetism for $n=0.2$. To satisfy the condition (18), we must have a high state density at the Fermi level, and furthermore, a relatively low average state density, $1/W$. Without the latter condition the reduction of $U_{\rm eff}$ by the electron correlation is too large to produce ferromagnetism. A simplified state density vs energy curve which satisfies the requirements is shown in Fig. 1.

Although the state density function $\eta(\varepsilon)$ defined implicitly by (12) is not necessarily equivalent to that obtained in the usual band calculation in which the charge neutrality of an atom is assumed, the difference will be small when the number of electrons is small. The state density of the *d* bands calculated by Fletcher is actually characterized by the region of high state density at the top of the bands. A simplified model of the *d* bands was proposed by Gautier.[8] If the $d(xy)$ band is taken as the representative band, the energy of this band is nearly independent of $\boldsymbol{k}_z$ in the vicinity of the top specified by $(2\pi/a)$ $(\pm 1, 0, 0)$ and $(2\pi/a)$ $(0, \pm 1, 0)$, since the overlap of the atomic $d(xy)$ orbitals of neighboring atoms in the z direction is small there.[8] Thus the energy is approximately represented by the kinetic energy of a two-dimensional gas. The constancy of the state density near the top of the band can be easily verified with this simplified model. Since the correlation reduction of U does not depend much on the details of a given band, the state density curve shown in Fig. 1 can be regarded as an approximation which has the essential feature of the $d\varepsilon$ bands in Ni.

According to the specific heat measurement at low temperatures, the state density of ferromagnetic Ni at the Fermi level is about 3.1 states per atom per ev. Subtracting the contribution of the s band of about 0.3 states per atom per ev and dividing by 3, we obtain an approximate estimate of $\eta(\varepsilon)$ to be about 0.9 per atom per ev per spin. Since there will be a small contribution by other $(d\gamma)$ bands and also since the state density seems to be at maximum at the Fermi level of ferromagnetic Ni, the averaged η to be used for the state density curve of Fig. 1 will be around 0.75 states per atom per ev per spin. This corresponds to $y=\eta W=3$ if W is taken to be 4 ev.

With the state density curve of Fig. 1 and by the use of (16), the condition for the occurrence of ferromagnetism, (18), is investigated for various pairs of x and y which are defined in Fig. 1. The curve in the x-y plane on which the condition $U^0_{\text{eff}}\eta=1$ is satisfied is shown in Fig. 2. We can see from the figure that the ferromagnetic state is favored energetically for $y=3$ and $U=2W$ if x is smaller than 0.28. According to Fletcher's calculation x seems to be smaller than 0.25. Thus we may conclude that the ferromagnetic state has lower energy than the paramagnetic state in Ni. This conclusion does not depend on our choice of the band width. The magnitude of U^0_{eff} is mainly determined by U and y/W besides x, but only slightly dependent on W.*)

The specific heat measurement[9] indicates that the state density at the Fermi level of paramagnetic Pd is about 4 states per atom per ev (including both spin states). Subtracting again 0.3 states per atom of the s band, and dividing by 6, we obtain $\eta(\varepsilon_F)\cong 0.6$ per atom per ev per spin. U of Pd will be about the same as that of Ni. If we assume $W=4$ ev and the state density curve of Fig. 1, we obtain $y=2.4$. The corresponding x which favors the ferromagnetic state is less than 0.19 states per atom per spin. This seems to indicate that the paramagnetic state is very likely lower in energy than the ferromagnetic state within the present approximation. This conclusion does not depend on the assumed shape of the state density curve. If the state density curve shown in Fig. 3 is taken, the paramagnetic state is still found to be stable. This state density curve resembles more closely the one which is suggested by the specific heat measurement of Pd-Rh and Pd-Ag alloys.[9]

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*) If a larger W is assumed, y becomes larger since $\eta=y/W$ is fixed. Then, however, U/W should be smaller, which cancels the effect of larger y.

§ 5. Supplementary discussions

The ferromagnetism of Ni-Cu alloys with Cu concentration less than 60 percent was regarded as a support for the simple theory of band electron ferromagnetism. Since the present theory denies the occurrence of ferromagnetism for such a small number of *d* holes as in the case of 50 percent Ni-50 percent Cu, the observed ferromagnetism might look a contradiction with the theory. However, the repulsive interaction between the *d* holes and the Cu atoms reduces the effective volume available for the *d* hole correlation and thereby the effectiveness of the hole correlation. Thus U_{eff} in Ni-Cu alloys will remain about the same as in Ni in spite of the smallness of the number of *d* holes.

In Co and Fe, where more than one *d* holes per atom are present, the exchange interaction between different atomic *d* orbitals will make some contribution to the energy difference between the ferromagnetic state and the paramagnetic state. The discussion of these metals, however, requires both detailed knowledge of the *d* band and a more refined treatment of the electron correlation. The discussion of light transition metals such as V and Ti will be also not feasible, since a simple tight binding approximation such as that employed in the present paper will not be justified in these metals, and the inter-atomic interaction neglected in the present paper might play an important role.

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Appendix

As was mentioned in the text, the energy spectrum of a two-dimensional gas given by

$$\varepsilon=\alpha(k_x^2+k_y^2) \tag{A1}$$

yields the constant state density per unit energy. We define vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ (two-dimensional) by

$$\begin{aligned} \boldsymbol{k}_1&=\boldsymbol{u}_1+\boldsymbol{v}_1, & \boldsymbol{k}_3&=\boldsymbol{u}_2+\boldsymbol{v}_2, \\ \boldsymbol{k}_2&=\boldsymbol{u}_1-\boldsymbol{v}_1, & \boldsymbol{k}_4&=\boldsymbol{u}_2-\boldsymbol{v}_2. \end{aligned} \tag{A2}$$

The condition of the momentum conservation requires $\boldsymbol{u}_1=\boldsymbol{u}_2$. In terms of $\boldsymbol{u}$ and $\boldsymbol{v}$, $G(\boldsymbol{k}_1, \boldsymbol{k}_2)$ is expressed as

$$G(\boldsymbol{k}_1, \boldsymbol{k}_2) = (\eta_0/2\pi)\int dv_2\{v_2/(v_2^2-v_1^2)\}\cdot f(v_2\,;\,u, k_F), \tag{A3}$$

where η_0 is the state density per unit energy per atom per spin, and $f(v_2\,;\,u, k_F)$ is the weight function that is obtained by the integration of the angular part of v_2. From the conditions, $k_3^2>k_F^2$ and $k_4^2>k_F^2$, we obtain

$$
\begin{aligned}
f(v_2\,;\,u,\,k_F) &= 0 \quad \text{for } v_2 \leq (k_F^2-u^2)^{1/2},\\
&= 4\sin^{-1}\{(u^2+v_2^2-k_F^2)/2v_2u\}\\
&\qquad \text{for } (k_F^2-u^2)^{1/2} \leq v_2 \leq k_F+u,\\
&= 2\pi \quad \text{for } k_F+u \leq v_2.
\end{aligned}
\tag{A4}
$$

Putting $u=0$ and $v_1=0$, we obtain from (A3)

$$
G(0,\,0) = \eta_0\int_{k_F} dv_2/v_2. \tag{A5}
$$

The difference between (A3) and (A5) is given by

$$
\begin{aligned}
\Delta G(\boldsymbol{k}_1,\,\boldsymbol{k}_2) &= \eta_0\int_{k_F+u} v_1^2/v_2(v_2^2-v_1^2)\cdot dv_2\\
&\quad + (2\eta_0/\pi)\int_{(k_F^2-u^2)^{1/2}}^{k_F+u} \{v_2\,dv_2/(v_2^2-v_1^2)\}\sin^{-1}\{(u^2+v_2^2-k_F^2)/2uv_2\}\\
&\quad - \eta_0\int_{k_F}^{k_F+u} dv_2/v_2.
\end{aligned}
\tag{A6}
$$

The upper limit of the integral of the first term in (A6) will be assumed to be independent of u. The resulting error is negligible for small k_F. Putting $u=k_F$ and $v_1=0$, we obtain $G(\boldsymbol{k},\,\boldsymbol{k})$ with $\boldsymbol{k}$ lying at the Fermi surface to be

$$
\Delta G(\boldsymbol{k},\,\boldsymbol{k}) = (2\eta_0/\pi)\int_0^{2k_F} (dv_2/v_2)\sin^{-1}(v_2/2k_F) - \eta_0\int_{k_F}^{2k_F} (dv_2/v_2). \tag{A7}
$$

It can be shown easily that (A7) vanishes.

In order to estimate the first term of (21) of the text, we expand U_{eff} in powers of ΔG to obtain

$$
U_{\text{eff}}(\boldsymbol{k}_1,\,\boldsymbol{k}_2) = U/(1+UG(0,\,0)) - \{U^2/(1+UG(0,\,0))^2\}\,\Delta G(\boldsymbol{k}_1,\,\boldsymbol{k}_2). \tag{A8}
$$

The first term of (21) is now expressed to the first order of ΔG by

$$
\Delta E_2' = -U_{\text{eff}}^{0\,2}\,\Delta I_{\text{av}} \tag{A9}
$$

with U_{eff}^0 defined by (16) and ΔI_{av} defined by

$$
\Delta I_{\text{bv}} = \left\langle \int_{(k_F^2-u^2)^{1/2}}^{k_F^{+}+u} (\eta_0/2\pi)\,(v_2\,dv_2/(v_2^2-v_1^2))\,(f(v_2\,;\,u,\,k_F^{+},\,k_F^{-}) - f(v_2\,;\,u,\,k_F)) \right\rangle_{\text{av}}, \tag{A10}
$$

where the average is taken over v_1 and u of occupied states; k_F^{+} and k_F^{-} satisfy the relation $k_F^2 - k_F^{-2} = k_F^{+2} - k_F^2 \equiv \Delta$; $f(v_2\,;\,u,\,k_F^{+},\,k_F^{-})$ is given by

$$\begin{aligned} f(v_2\,;\, u,\, k_F{}^+,\, k_F{}^-) &= 2[\sin^{-1}\{(u^2+v_2{}^2-k_F{}^2-\Delta)/2uv_2\} \\ &\quad +\sin^{-1}\{(u^2+v_2{}^2-k_F{}^2+\Delta)/2uv_2\}] \\ &\quad \text{for } (k_F{}^2-u^2)^{1/2}\leq v_2\leq k_F{}^-+u, \\ &= \pi+2\sin^{-1}\{(u^2+v_2{}^2-k_F{}^2-\Delta)/2uv_2\} \\ &\qquad \text{for } k_F{}^-+u\leq v_2\leq k_F{}^++u. \end{aligned} \tag{A11}$$

The contribution to the integral (A10) is made mainly by the region $v_2\sim k_F+u$. Defining $g(x)$ by

$$\begin{aligned} g(x) &= \sin^{-1}x \quad \text{for} \quad x\leq 1, \\ &= \pi/2 \qquad \text{for} \quad x\geq 1, \end{aligned}$$

we can easily show that

$$\int_0^{1+\delta} dx\{(1/2)\,(g(x+\delta)+g(x-\delta))-g(x)\} = -\delta^2/2+0(\delta^4). \tag{A12}$$

In (A12) the region $x<1$ makes a positive contribution which is overcome by the contribution from $x\sim 1$. Thus taking the contribution from $v_2\sim k_F+u$ in (A10), we obtain a rough estimate of (A9) given by

$$\Delta E_2{}' = (1/8\pi)\, U_{\mathrm{eff}}^{0\;2}\, \eta_0{}^2\cdot\eta_0(\alpha\Delta)^2. \tag{A13}$$

Comparing with the corresponding increase of the one electron energy given by $\eta_0(\alpha\Delta)^2$, we can see that (A13) amounts to only 4 percent of the one electron energy increase for $U_{\mathrm{eff}}^0\eta_0=1$. A more exact estimate shows that $\Delta E_2{}'$ is even smaller than the above estimate.

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