g-Shift and Anomalous Hall Effect in Gadolinium Metals

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It is shown that the coupling between spins of conduction and localized electrons due to a covalent mixing between them can be expressed by a usual exchange type interaction with negative (antiferromagnetic) sign.

It is proposed that the mixing effect is large in gadolinium metal under the assumption that the energy level corresponding to a trivalent gadolinium ion is very near and below the Fermi surface. Then it is shown that the mixing effect gives rise to a large negative g-shift for the localized spin, which substantially cancels the positive g-shift which comes from the exchange interaction, thus leading to a good agreement with the observation. Furthermore, by introducing a spin-orbit coupling of localized electrons, we can obtain an anisotropic interaction between conduction and localized electrons, which is found to account for a large anomalous Hall effect observed in gadolinium metal.

§ 1. Introduction

From measurements of specific heats and magnetic susceptibilities[1] and also from spin structures found at low temperatures,[2] it is clear that most of rare-earth metals consist of nearly free trivalent ions and nearly free conduction electrons which are released by the ionization of metal atoms. Then each ion has the same number of f electrons as an atom of the element does. We may assume that the Hartree-Fock solution for the free ion is a good approximation to the wave function of f electrons in the metal and plane waves for those of conduction electrons and that they are nearly independent of each other. Possible models for the interaction between them are then as follows: (1) The direct exchange coupling between spins of a conduction electron and an ion. This has been proposed by Zener[3] for transition metals and has extensively been studied by Kasuya[4] and Yosida.[5] (2) Covalent mixing between an f orbital and the conduction band. A divalent ion is formed by transferring a conduction electron to an f orbital or a tetravalent ion is formed by transferring an f electron to the conduction band. This has been proposed by Anderson and Clogston[6] for transition metals. This mechanism gives rise to an antiparallel coupling between spins of f and conduction electrons, because the orbital into which an electron is transferred must not be occupied by another electron with the same spin direction as that of the transferred electron. (3) Non-orthogonality between the wave functions of f and conduction electrons. For alkali metals, noble metals and other metals, the non-orthogonality between core wave functions

and plane waves is taken into account by the orthogonalized plane-wave method. It makes an appreciable contribution to the cohesive energy. In the present case, the wave function of a conduction electron must be orthogonalized to those of f orbitals which are occupied by the electrons with the same spin direction as that of the conduction electron. This fact also leads to a spin coupling between f and conduction electrons with the negative sign.

The purpose of this paper is to study the spin coupling arising from the effect of covalent mixing, neglecting the non-orthogonality of wave functions, and apply the results to the problems of the g-shift and the anomalous Hall effect of gadolinium metal.

According to Kasuya,[4] the anomalous electrical resistivity of rare-earth metals is due to the exchange coupling between spins of conduction and f electrons and thus depends on the magnitude of the spin of the ion. If the exchange integral involved is assumed to have the same value for all of the rare-earth elements, the magnitude of the anomalous part of the resistivity at high temperatures agrees fairly well with experiments for various elements.[7,8] On the other hand the anomalous Hall effect of a few rare-earth metals has been accounted for by that part of the exchange interaction which depends on the orbital angular momentum of the ion.[8] Thus we see that the exchange interaction may be the most dominant one of the three mechanisms mentioned above. In gadolinium, however, this is not the case, because (1) it shows the largest anomalous Hall effect of rare-earth metals whereas it has no orbital angular momentum and (2) the g-shift of the metal is much less than that calculated from the value of the exchange integral assumed above. We assume that these two facts are connected with the covalent mixing, i.e., we assume that in this metal various energy levels are so arranged that it takes only a little energy to push a conduction electron at the Fermi surface to an empty f orbital and make a divalent rare-earth ion or to push an f electron to a conduction level just above the Fermi surface and make a tetravalent rare-earth ion. We shall see, in fact, that this mechanism gives rise not only to an exchange-type coupling of spins which causes a negative g-shift of magnetization but also to an anisotropic scattering of conduction electrons which gives rise to the anomalous Hall effect. On the contrary, we shall see that its effect on the electrical resistivity is rather small, so that the conclusion drawn earlier[4,7,8] that the exchange coupling is the dominant mechanism of the anomalous electrical resistivity need not be altered.

§ 2.   Effective Hamiltonian

We shall first consider an 8-electron problem, seven in f orbitals of an ion with the total spin quantum number $S = 7/2$ and one in the conduction band. An unperturbed state of this system is specified by the z components of the

spins of the ion and the conduction electron and by the wave vector of the conduction electron. Let two such states be Ψ_g and Ψ_g':

$$\Psi_g = (8\,!)^{-1/2} \sum_P \delta_P P \psi_k(r_0) \prod_{i=1}^7 \psi_i(r_i)\, \chi(\zeta_0)\, \Theta_{SM}(\zeta_1 \cdots \zeta_7), \tag{1}$$

$$\Psi_g' = (8\,!)^{-1/2} \sum_P \delta_P P \psi_{k'}(r_0) \prod_{i=1}^7 \psi_i(r_i)\, \chi'(\zeta_0)\, \Theta_{SM'}(\zeta_1 \cdots \zeta_7), \tag{2}$$

where $\sum_P$ is the summation over all permutations P of space and spin coordinates (r_i, ζ_i) of the eight electrons, ψ_k is a plane wave function with the wave vector k, ψ_i an atomic f function, i specifying the z component of the orbital angular momentum. χ and Θ are the spin eigenfunctions of the conduction and f electrons, respectively.

Let us consider a perturbation process in which a conduction electron with the wave number k is transferred to an empty f level ψ_m and then returns to a conduction level with another wave vector k'. Since we shall later be concerned only with the conduction electrons near the Fermi surface, their energies are assumed to be equal to the Fermi energy E_f. Then the corresponding excited state and the second-order perturbation energy are as follows:

$$\Psi_e = (8\,!)^{-1/2} \sum_P \delta_P P \psi_m(r_0) \prod_{i=1} \psi_i(r_i)\, \Theta_m(\zeta_0 \cdots \zeta_7), \tag{3}$$

$$-\langle \Psi_g' | V_{sd} | \Psi_e \rangle \langle \Psi_e | V_{sd} | \Psi_g \rangle / (E_- - E_f), \tag{4}$$

where $\Theta_m(\zeta_0 \cdots \zeta_7)$ is a spin function in which the zeroth and m-th spins are coupled antiparallel, $E_- - E_f$ the energy necessary to take an electron near the Fermi surface and place it on ψ_m, V_{sd} the perturbation which causes the electron transfer. In Eq. (4) we shall first integrate over the space coordinates and then express it in terms of a spin operator which gives the same matrix element as Eq. (4) does when integrated with the spin functions of the ground states on both sides. The part of space integral in $\langle \Psi_e | V_{sd} | \Psi_g \rangle$ is given by

$$I_m = \int \psi_m^*(r)\, V_{sd}(r)\, \psi_k(r)\, dv. \tag{5}$$

When the expansion

$$\psi_k(r) = N^{-1/2}\, e^{i k \cdot R} \sum_l (2l+1)\, i^l\, J_l(kr)\, P_l(\cos\theta_{kr}) \tag{6}$$

is inserted, this becomes

$$I_m = N^{-1/2}\, V_0\, e^{i k \cdot R}\, i^l\, (4\pi/2l+1)^{1/2}\, Y_{lm}^*(\theta_k, \varphi_k), \tag{7}$$

where R is the position vector of the ion, $l=3$ for rare-earth metals, V_0 given by

$$V_0 = \{4\pi(2l+1)\}^{1/2} \int_0^\infty P(r)\, V_{sd}(r)\, J_l(r)\, r^2 dr, \tag{8}$$

$P(r)$ being the radial part of the atomic f function. The dependence of the matrix element on the direction of k is given by the l-th spherical harmonics

because $V_{sd}(r)$ has been assumed to be spherically symmetric. We shall see later that its axial part is important for the anomalous Hall effect. The spin part of the matrix element (4) is given by $\langle \chi' \Theta_{SM'} | \Theta_m \rangle \langle \Theta_m | \chi \Theta_{SM} \rangle$, which is identically equal to

$$\langle \chi' \Theta_{SM'} | \Gamma_m | \Theta_m \rangle \langle \Theta_m | \Gamma_m | \chi \Theta_{SM} \rangle, \tag{9}$$

where Γ_m is a projection operator which picks up those spin functions in which s_0 and s_m are antiparallel:

$$\Gamma_m = 2^{1/2} \{ (1/4) - s_0 \cdot s_m \}, \tag{10}$$

where $2^{1/2}$ is Serber's factor.[9] When summed over all excited spin functions, Eq. (9) becomes

$$\langle \chi' \Theta_{SM'} | \Gamma_m^2 | \chi \Theta_{SM} \rangle = \langle \chi' \Theta_{SM'} | \{ (1/2) - 2s_0 \cdot s_m \} | \chi \Theta_{SM} \rangle$$
$$= \langle \chi' \Theta_{SM'} | \{ (1/2) - (s_0 \cdot S/S) \} | \chi \Theta_{SM} \rangle, \tag{11}$$

where S is the total spin angular momentum of the seven f electrons. Thus we see that (4) is equivalent to

$$\{ V_0^2 / N(E_- - E_f) \} \exp[i(k - k') \cdot R] \{ (s_0 \cdot S/S) - (1/2) \}$$
$$\times \{ 4\pi/(2l+1) \} Y_{lm}^*(\theta_k, \varphi_k) Y_{lm}(\theta_{k'}, \varphi_{k'}), \tag{12}$$

when integrated over spin functions of the ground states. Summing over all excited orbital states (summation over m), neglecting the spin independent part and noting that the wave vector of the conduction electron has been changed form k to k', we see that Eq. (4) is equivalent to the following expression in our 8-electron problem;

$$N^{-1} \sum_{kk'} e^{i(k-k') \cdot R} \{ V_0^2 / (E_- - E_f) S \} P_l(\cos \theta_{kk'}) (s_0 \cdot S) a_{k'}^* a_k, \tag{13}$$

where a_k is the destruction operator of the conduction electron with the wave number k.

Let us next consider the other perturbation process in which an f electron is excited to a conduction level with the wave number k' near the Fermi surface and then another conduction electron with the wave number k near the Fermi surface is transferred to the empty f level. The excited state pertinent to this process is

$$\Psi_e = (8!)^{-1/2} \sum_P \delta_P P \psi_k(r_0) \psi_{k'}(r_m) \prod_{i \neq m} \psi_i(r_i) \chi(\zeta_0) \Theta_{SM}(\zeta_1 \cdots \zeta_7). \tag{14}$$

It is convenient in this case to rewrite Ψ_g', Eq. (2), as follows:

$$\Psi_g' = - (8!)^{-1/2} \sum_P \delta_P P \psi_m(r_0) \psi_{k'}(r_m) \prod_{i \neq m} \psi_i(r_i) \chi'(\zeta_m) \Theta_{SM'}(\zeta_1 \cdots \zeta_0 \cdots \zeta_7), \tag{15}$$

where $\Theta_{SM'}(\zeta_1 \cdots \zeta_0 \cdots \zeta_7)$ differs from $\Theta_{SM'}(\zeta_1 \cdots \zeta_7)$ in Eq. (2) in which ζ_m has been replaced by ζ_0. The corresponding perturbed Hamiltonian is given by

$$- \langle \Psi_g' | V_{sd} | \Psi_e \rangle \langle \Psi_e | V_{sd} | \Psi_g \rangle / (E_f - E_+), \tag{16}$$

where $E_f - E_+$ is the energy necessary to put an f electron on the Fermi surface. The orbital part of the integral is the same as before. The spin part is

$$\langle \chi'(\zeta_m)\,\Theta_{SM'}(\zeta_1 \cdots \zeta_0 \cdots \zeta_7)\,|\,\chi(\zeta_0)\,\Theta_{SM}(\zeta_1 \cdots \zeta_7)\,\rangle \langle \chi\Theta_{SM}|\chi\Theta_{SM}\rangle$$

$$= \langle \chi'(\zeta_0)\,\Theta_{SM'}(\zeta_1 \cdots \zeta_7)\,|\,P_{0m}|\chi(\zeta_0)\,\Theta_{SM}(\zeta_1 \cdots \zeta_7)\,\rangle$$

$$= \langle \chi'\Theta_{SM'}|\,\{(1/2) + 2\boldsymbol{s}_0 \cdot \boldsymbol{s}_m\}\,|\chi\Theta_{SM}\rangle$$

$$= \langle \chi'\Theta_{SM'}|\,\{(1/2) + (\boldsymbol{s}_0 \cdot \boldsymbol{S}/S)\}\,|\chi\Theta_{SM}\rangle, \tag{17}$$

where P_{0m} is the permutation operator which interchanges ζ_0 and ζ_m. Thus in this case the equivalent Hamiltonian is expressed by

$$N^{-1}\sum_{kk'} e^{i(k-k')\cdot R}\{V_0^2/(E_f - E_+)S\}\,P_l(\cos\theta_{kk'})\,(\boldsymbol{s}_0 \cdot \boldsymbol{S})\,a_{k'}{}^* a_k. \tag{18}$$

Now considering the whole crystal, summing contributions from each ion in the crystal and adding the both processes, we have the following expression as our effective Hamiltonian:

$$H_1 = N^{-1}\sum_{nkk'} e^{i(k'-k)\cdot R_n}\,A_0 P_l(\cos\theta_{kk'})\,(2\boldsymbol{s}_0 \cdot \boldsymbol{S}_n)\,a_k{}^* a_{k'}, \tag{19}$$

where

$$A_0 = \frac{V_0^2}{2S}\left(\frac{1}{E_- - E_f} + \frac{1}{E_f - E_+}\right), \tag{20}$$

which is positive. The direct exchange interaction is expressed by

$$H_{ex} = -N^{-1}\sum_{nkk'} e^{i(k'-k)\cdot R_n}\,J_0\,(2\boldsymbol{s}_0 \cdot \boldsymbol{S}_n)\,a_k{}^* a_{k'}, \tag{21}$$

where J_0 is the exchange integral between the Bloch function and an f orbital.[*]

§ 3. *g*-shift and electrical resistivity

We shall first discuss the g-shift of a $4f$ spin due to the interactions (19) and (21). The g-shift of electron spins is like the Knight shift in NMR experiments. Averaging Eqs. (19) and (21) over the coordinates of conduction electrons which are in thermal equilibrium under the applied magnetic field H and adding both, we have

$$\left(\textstyle\sum_n S_{nz}\right) Z(A_0 - J_0)\langle 2s_{0z}\rangle,$$

where Z is the valence of the ion. Since $\langle 2s_{0z}\rangle$ is expressed in terms of the Pauli susceptibility χ of the conduction electrons from

$$\chi H = \langle 2s_{0z}\rangle\mu_B ZN,$$

this expression becomes

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[*] J_0 is the same as F_0 in reference 8) where its definition is given. In Eq. (21) we have neglected the dependence of the exchange integral over $\boldsymbol{k}$ and $\boldsymbol{k}'$.

$$(\textstyle\sum_n S_{nz})\chi(A_0 - J_0)H/\mu_B N.$$

Thus we have

$$\varDelta g = \chi(J_0 - A_0)/N\mu_B{}^2 = (J_0 - A_0)\rho(E_f)/N, \tag{22}$$

where $\rho(E_f)$ is the state density of the conduction band at the Fermi energy. This expression for the g-shift has been obtained by Yosida[5] without the mixing term. The latter term gives a negative contribution as predicted by Anderson and Clogston.[6]

The electrical resistivity due to the interactions (19) and (21) is also easily obtained[4] and is expressed in the paramagnetic region by

$$\rho_{\text{paramag}} = \frac{3\pi}{2}\frac{m}{e^2\hbar}\frac{V}{N}\frac{S(S+1)}{E_f}\left(J_0{}^2 + \frac{A_0{}^2}{2l+1}\right), \tag{23}$$

where V is the total volume of the crystal.

According to the observation by Elliott, Legvold and Spedding,[10] an extrapolated value of magnetization to absolute zero is $7.12\,\mu_B$ per ion, which corresponds to $\varDelta g = 0.034$,[*] whereas ρ_{paramag} is $106\,\mu\Omega\,\text{cm}$ as measured by Colvin, Legvold and Spedding.[11] Then assuming the free-electron value of $\rho/N = 0.61$ $(\text{ev})^{-1}$, we have from these values of $\varDelta g$ and ρ_{paramag}

$$J_0 = 0.230\ \text{ev}, \quad A_0 = 0.174\ \text{ev}. \tag{24}$$

The value of J_0 is in reasonable agreement with the previous estimate,[8] $0.25\,\text{ev}$, which was determined to agree with measurements of resistivities of more than half-filled rare-earth metals assuming $A_0 = 0$. As will be seen later from the sign of the anomalous Hall effect, we have $E_f - E_+ \ll E_- - E_f$, i.e., the level corresponding to a trivalent gadolinium ion is very near and below the Fermi surface. Then from (24) and (20) we have

$$V_0{}^2/(E_f - E_+) = 1.2\ \text{ev}. \tag{25}$$

As can be seen from (23), the effect of covalent mixing on resistivity is greatly reduced as compared with the exchange term due to the factor $1/(2l+1)$, whereas it makes a comparable and negative contribution to the g-shift. (This would be 0.14 with the exchange term only.)

§ 4. The anomalous Hall effect

In this section we shall calculate the anomalous Hall effect by putting forward the perturbation calculation to the third-order, taking the spin-orbit coupling of f electrons as an additive perturbation. The third-order perturbed Hamiltonian is expressed by

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[*] Kip, Kittel, Portis, Barton and Spedding[10a] have measured ESR of gadolinium metal; their result gives $\varDelta g = -0.05$.

$$\langle \Psi_g{}' | V_{sd} | \Psi_e{}' \rangle \langle \Psi_e{}' | \lambda \sum_{i=0}^{7} \boldsymbol{l}_i \cdot \boldsymbol{s}_i | \Psi_e \rangle \langle \Psi_e | V_{sd} | \Psi_g \rangle / (\varDelta E)^2, \qquad (26)$$

where $\boldsymbol{l}_i$ is the operator representing the orbital angular momentum of the i-th electron, taking the nucleus of the ion as the origin of the position vector, λ the constant of spin-orbit coupling, which has the value 0.2 ev for a trivalent ion.[12] $\varDelta E$ is the difference in energies of Ψ_g and Ψ_e, which is assumed to be equal to that between $\Psi_g{}'$ and $\Psi_e{}'$. $\Psi_e{}'$ may or may not be different from Ψ_e in the assignment of the f orbital which is doubly occupied or wholly empty. Thus it is given by Eq. (3) or (14) with m replaced by m'.

Carrying a similar calculation to the previous section, we obtain an equivalent operator, which gives the same matrix element as Eq. (26) does when integrated with the spin functions of Ψ_g and $\Psi_g{}'$ on both sides. Adding contributions of two processes and summing over the whole ions in the crystal, we find that the operator is expressed by

$$N^{-1} \sum_{nkk'} e^{i(k'-k)\cdot R_n} \, iP_l{}' (\cos \theta_{kk'})$$

$$\times [B_1 (\boldsymbol{\kappa}' \times \boldsymbol{\kappa}) \cdot \boldsymbol{S}_n + B_2 \{ (\boldsymbol{\kappa}' \times \boldsymbol{\kappa}) \cdot \boldsymbol{S}_n (\boldsymbol{S}_n \cdot \boldsymbol{s}_0) + (\boldsymbol{S}_n \cdot \boldsymbol{s}_0)(\boldsymbol{\kappa}' \times \boldsymbol{\kappa}) \cdot \boldsymbol{S}_n \}] a_k{}^* \, a_{k'}, \qquad (27)$$

where B_1 and B_2 are defined by

$$B_1 = (\lambda V_0{}^2 / 2S) \left[\{ 1/2 (E_f - E_+)^2 \} - \{ 1/(E_- - E_f)^2 \} \right], \qquad (28)$$

$$B_2 = \{ \lambda V_0{}^2 / S(2S-1) \} \left[\{ 1/2 (E_f - E_+)^2 \} + \{ 1/(E_- - E_f)^2 \} \right], \qquad (29)$$

$\boldsymbol{\kappa}$ and $\boldsymbol{\kappa}'$ are unit vectors in the directions of $\boldsymbol{k}$ and $\boldsymbol{k}'$. The prime on the Legendre function P_l denotes differentiation with respect to the argument. Since the matrix element of (27) between ψ_k and $\psi_{k'}$ changes its sign, when $\boldsymbol{k}$ and $\boldsymbol{k}'$ are interchanged, one might expect that it might give rise to the anomalous Hall effect when the transition probability of scattering of conduction electrons is calculated to the second Born approximation, using (27) and (21) as perturbations causing scattering.[8] It is found, however, that this is not the case unless $l=1$. This is because the above mentioned transition probability gives rise to a deviation from spherical symmetry of the distribution function of conduction electrons, which is represented by the l-th spherical harmonics and thus gives nothing to the total current density unless $l=1$.

This conclusion is connected with the assumption that $V_{sd}(\boldsymbol{r})$ is spherically symmetric. There must be, however, an axially symmetric part of $V_{sd}(\boldsymbol{r})$, because gadolinium metal has a hexagonal structure, although this may be much smaller than the spherical part. Then let $V_2(r) P_2(\cos \theta)$ be the axial part of $V_{sd}(\boldsymbol{r})$, where θ is the angle between the position vector and the crystallographic c axis, which we shall call the z axis. When this is substituted, Eq. (5) is expressed by a sum of spherical harmonics of $\boldsymbol{k}$ with $l=1\cdots5$, of which we take only the term of $l=1$. Then we find from (5)

$$I_m = (4\pi/3)^{1/2} (V_1/N^{1/2}) \, e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \begin{cases} 2^{1/2} \, iY_{1\pm1}^*(\theta_k, \varphi_k) & m = \pm 1 \\ 3^{1/2} iY_{10}^*(\theta_k, \varphi_k) & m = 0 \\ 0 & \text{otherwise,} \end{cases} \qquad (30)$$

where

$$V_1 = (12\pi/7)^{1/2}(3/5)\int_0^\infty R(r)\,V_2(r)\,J_1(kr)\,r^2\,dr.^{*)} \qquad (31)$$

Carrying a similar perturbation calculation, adding contributions of two processes and summing over the whole ions in the crystal, we find that the equivalent operator is expressed by

$$H_2 = N^{-1} \sum_{nkk'} e^{i(k'-k)\cdot R_n} \, iA_1\{3\boldsymbol{S}_n \cdot (\boldsymbol{\kappa}' \times \boldsymbol{\kappa}) - 2S_{nz}(\boldsymbol{\kappa}' \times \boldsymbol{\kappa})_z\} a_k^* a_{k'} \qquad (32)$$

plus a term involving $\{(\boldsymbol{S}_n \cdot \boldsymbol{s}_0)\boldsymbol{S}_n \cdot (\boldsymbol{\kappa}' \times \boldsymbol{\kappa}) + \boldsymbol{S}_n \cdot (\boldsymbol{\kappa}' \times \boldsymbol{\kappa})(\boldsymbol{S}_n \cdot \boldsymbol{s}_0)\}$ as a factor, which we shall neglect, because it contributes nothing to the anomalous Hall effect as we have already seen in reference 8). A_1 is defined by

$$A_1 = \frac{\lambda V_1^2}{S}\left\{\frac{1}{(E_- - E_f)^2} - \frac{1}{2(E_f - E_+)^2}\right\}. \qquad (33)$$

Equation (32) is anisotropic in the sense that the z axis is distinguished from the x and y axes. The Hall effect resulting from it is anisotropic, too. However, we shall not be concerned with the anisotropy here, firstly, because an experiment has been made only on a polycrystal and secondly, because it is when we know about the anisotropies of band structure and scattering mechanism that we can make any accurate prediction of the anisotropy of the anomalous Hall effect. Thus we consider in the following discussion the Hamiltonian of the form

$$H_2' = N^{-1} \sum_{nkk'} e^{i(k'-k)\cdot R_n} 3iA_1 \, \boldsymbol{S}_n \cdot (\boldsymbol{\kappa}' \times \boldsymbol{\kappa}) a_k^* a_{k'} \qquad (32')$$

instead of (32). This may amount to an overestimation of the effect, because the real matrix element is one-third of (32') when $\boldsymbol{S}_n$ is in the z direction. But a qualitative result may be correct.

A calculation of the anomalous Hall effect has been made in reference 8) with the exchange interaction (21) and a Hamiltonian which has the same form as (32') as interactions causing scattering of conduction electrons. The result for the Hall resistivity is expressed by

$$\rho_H = \frac{27\pi^4}{24}\frac{3A_1 J_0^2}{E_0^3}\,r(T)\frac{\hbar}{e^2 k_F}, \qquad (34)$$

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*) It is possible that the Bloch function is modulated from the plane wave by a function u_k with the periodicity of the lattice, which might contain a d component. Then I_m can contain a component of $l=1$, even when $V_{sd}(r)$ is spherically symmetric, and can be expressed by the same expression as Eq. (30), though the definition of V_1 may be different from Eq. (31).

where k_F is the magnitude of the wave vector at the Fermi surface, E_0 and $r(T)$ are defined by

$$E_0 = (\hbar^2/2m)\,(3\pi^2 N/V)^{2/3}, \tag{35}$$

$$r(T) = \langle (M - \langle M \rangle)^3 \rangle, \tag{36}$$

M denoting the component of a spin S in the direction of the effective field. The average is taken over thermal equilibrium. In the paramagnetic region $r(T)$ becomes

$$r(T) = -\mu_B H 2S(S+1)(2S^2+2S+1)/15k(T-\theta_p), \tag{37}$$

where H is the applied field, θ_p the asymptotic Curie temperature.

The Hall coefficient, which is ρ_H devided by H, has been determined experimentally by Kevane, Legvold and Spedding[13] (Fig. 1) and is represented quite well by

$$R = \left(0.95 + \frac{1400}{T-290} \right) \times 10^{-12} \ \text{volt} \cdot \text{cm/amp} \cdot \text{oersted} \tag{38}$$

above $T = 300°\text{K}$. The constant term represents the usual Hall effect and corresponds to 2 negative carriers per atom in the free-electron approximation.[13] The second term is an anomalous one, which may correspond to that calculated in this section. Taking $E_0 = 3.5$ ev (free-electron value), $J_0 = 0.23$ ev and $A_1 = -0.022$ ev, we find that the agreement with the experiment is satisfactory as shown in Fig. 1.[*] The value of A_1 may be reasonable, because it is smaller than A_0. The negative sign of A_1 indicates that $1/(E_f - E_+)^2$ dominates over
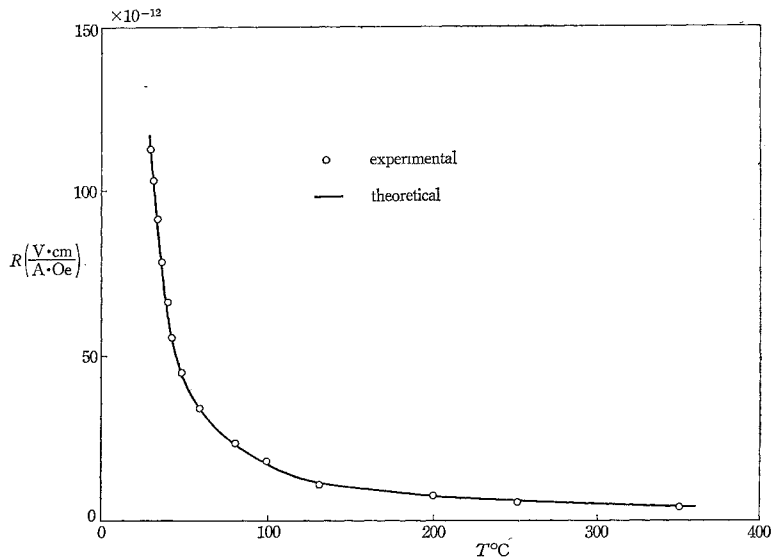

Fig. 1. The Hall effect in gadolinium metal above the Curie temperature.

[*] See notes added in proof, 1).

$1/(E_- - E_f)^2$, so that the level corresponding to a trivalent gadolinium ion is very near and below the Fermi surface. Then we have from $A_1 = -0.022$ ev

$$\lambda V_1^2 / (E_f - E_+)^2 = 0.15 \text{ ev}.$$

§ 5. Discussion

We have shown in this paper that the coupling between spins of conduction and localized electrons due to a covalent mixing between them is expressed by a usual exchange-type interaction. We have also found that the coupling is negative (antiferromagnetic). We can expect that this interaction between conduction and localized electrons can have an appreciable effect on various phenomena of transition metals, rare-earth metals and dilute alloys.

Thus we have calculated its contributions to the *g*-shift and the electrical resistivity of gadolinium metal, which are found to consistently account for the experimental observations of both phenomena, if compounded with the direct exchange interaction. Moreover it is quite possible that a part of the anomalous electrical resistivity of ferromagnetic transition metals is caused by the mixing effect.

An indirect coupling between localized spins can also arise from this interaction through the second-order perturbation process. Its magnitude may be of the order of $V_{sd}^4 / (\varDelta E)^2 E_f$. It should be noted, however, that other terms of the same order may result from many other processes which are not included in the above-mentioned second-order process. Thus it may be an interesting subject to investigate this point.

The spin polarization of conduction electrons due to mixing is interesting, too. It should be noted that its spatial distribution may be quite different from that due to the usual exchange interaction, especially near the localized spins, because the k- and k'-dependence of the interaction is expressed by a Legendre function of the cosine of the angle between k and k'. If the scattered waves are analysed in terms of the partial waves, only the l-th wave is modified. This means that the spin polarization at the center of the localized spin vanishes[*]. This point and a similar problem arising from the non-orthogonality of the wave functions will be a subject of further publication.

Acknowledgements

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[*] See notes added in proof, 2).

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Notes added in proof : 1) Recently K. J. Tauer measured the anomalous Hall effect of gadolinium below the Curie temperature. The temperature dependence has a close resemblance to that calculated from Eq. (36) (see Fig. 1 of reference 8)). However, its magnitude is about three times as large as Eq. (34) with the values of parameters determined in the text. In our opinion the discrepancy may be due to our neglect of the inelastic scattering,[8] whose contribution relative to that of the elastic scattering should be different below and above the Curie temperature. We thank Dr. K. J. Tauer for showing us his result before publication.

2) Recently J. Ehara measured ESR of manganese in palladium. (We thank him for showing us his results before publication.) According to his result Δg is negative and large (~ -0.02). He also observed a hyperfine splitting which is about 60% of that in ionic crystals. Since the hyperfine field in ionic crystals is negative, this result indicates that the contribution from conduction electrons to the internal field is positive if $S=5/2$ is assumed. These apparently contradictory results (the negative g-shift and the positive polarization) can be reconciled in the light of the present theory, if $A_0 > J_0 > 0$ is assumed. Then the g-shift is negative, while the internal field at the nucleus, which is caused solely by J_0, is positive.