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INTERACTION BETWEEN OUTER AND INNER ELECTRONS IN FERROMAGNETIC TRANSITION METALS

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The interaction between 4s and 3d electrons in transition metals is investigated. It is shown that the dynamical part of the interaction manifests itself in the interaction between Fermi and Bose elementary excitations. At low temperatures elastic collision between these excitations predominate, whereas at high temperatures transition processes begin to play an important part. The magnetization is calculated as a function of temperature and field strength.

1. During recent years increased interest has been shown in the transition metals, but agreement still has not been reached regarding the electron interactions that produce the ferromagnetic state of these metals. It is therefore necessary to analyze these interactions carefully in every model of the transition metals. The so-called s-d exchange model developed by Vonsovskii and his coworkers[1,2] is based on the assumption that electrons of the unfilled 3d shell play an important part in transition metals in addition to the 4s valence electrons. A strong exchange interaction with a positive exchange integral leads to complete ordering of the 3d electron spins, that is, to ferromagnetism. The 4s electrons are collectively responsible for transfer phenomena in a crystal.

This electron system has a mixed spectrum with Bose and Fermi branches. The Bose branch is associated with the 3d electrons which provide the elementary excitations called "ferromagnons" (or "spin waves") while the Fermi branch is associated with the 4s electrons which provide the elementary excitations that we call "conduction electrons."

The Hamiltonian of weakly-excited electron states in the s-d model can be represented as follows:

$$\hat{\mathscr{H}} = E_0 + \hat{H}_0 + \hat{H}_1; \tag{1}$$

$$\hat{H}_0 = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}}^{\sigma} a_{\mathbf{k}\sigma}^{+} a_{\mathbf{k}\sigma} + \sum_{\mathbf{g}} \varepsilon_{\mathbf{g}} b_{\mathbf{g}}^{+} b_{\mathbf{g}}; \tag{1a}$$

$$\hat{H}_1 = N^{-1/2} \sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{g}} J(\mathbf{k}_1\mathbf{k}_2)\, \delta(\mathbf{k}_2 - \mathbf{k}_1 + \mathbf{g})\, [a_{\mathbf{k}_1(+)} a_{\mathbf{k}_2(-)}^{+} b_{\mathbf{g}}^{+} - a_{\mathbf{k}_1(+)}^{+} a_{\mathbf{k}_2(-)} b_{\mathbf{g}}]$$

$$+ \frac{1}{N} \sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{g}_1\mathbf{g}_2} J(\mathbf{k}_1\mathbf{k}_2)\, \delta(\mathbf{k}_2 - \mathbf{k}_1 + \mathbf{g}_1 - \mathbf{g}_2)\, [a_{\mathbf{k}_1(-)}^{+} a_{\mathbf{k}_2(-)} b_{\mathbf{g}_2}^{+} b_{\mathbf{g}_1} - a_{\mathbf{k}_1(+)}^{+} a_{\mathbf{k}_2(+)} b_{\mathbf{g}_2}^{+} b_{\mathbf{g}_1}]. \tag{1b}$$

Here $a_{\mathbf{k}}$ and $a_{\mathbf{k}}^{+}$ are the Fermi second-quantization operators with the signs + and − denoting the spin projection (in the ground state of a 3d electron the spin projection is denoted by −); $b_{\mathbf{g}}$ and $b_{\mathbf{g}}^{+}$ are Bose operators; **k** and **g** are the quasi-momentum of a conduction electron and of a ferromagnon, respectively; $J(\mathbf{k}_1\mathbf{k}_2)$ is the s-d exchange integral.

The Hamiltonian (1) was obtained by Vonsovskii and Turov.[2] The following expressions were obtained for conduction electron energies:

$$\varepsilon_{\mathbf{k}}^{-} = -\alpha + \hbar^2 k^2/2m_{-}; \quad \varepsilon_{\mathbf{k}}^{+} = \alpha + \hbar^2 k^2/2m_{+}, \tag{2}$$

where m_- and m_+ are the effective electron masses with the respective spin directions and α is the coupling constant of s and d electrons, which is determined by expanding the s-d exchange integral in powers of the quasi-momenta (for a cubic crystal):

$$J(\mathbf{k}_1\mathbf{k}_2) = 2\alpha - \gamma\,[(a\mathbf{k}_1)^2 + (a\mathbf{k}_2)^2] + \ldots. \tag{3}$$

The terms in (1) have the following significance: E_0 is the constant energy of the 3d electrons with completely ordered spins; H_0 is the combined energy of all elementary excitations (conduction electrons and ferromagnons); H_1 represents the energy of interaction between the latter.

The complete Hamiltonian of the electron system must contain two more terms, one of which will describe the interaction between ferromagnons while the other describes the interaction between conduction electrons. However, as Dyson[3] has shown, the interaction between spin waves (ferromagnons) in a ferromagnet is very small and can be neglected at temperatures up to one-fourth of the Curie temperature.

Neglect of the interaction between conduction electrons does not have the same rigorous justification, but it can be assumed that the interaction between the original 4s electrons is partly taken into account self-consistently in the effective masses of the conduction electrons.

Thus the interaction between 4s and 3d electrons is manifested in two different ways. The conduction electron spectrum is altered [Eq. (2) includes the s-d interaction parameters]. This can be called the static part of the interaction, which leads to the 4s-electron magnetization noted by Vonsovskii.

Equation (1b) describes the dynamical interaction of 4s and 3d electrons by means of the interaction between conduction electrons and ferromagnons. The term of $\hat{H}_1$ which contains three operators describes transitions between these elementary excitations, while the term with four operators describes elastic collisions between these same excitations. In the present work these interactions will be taken into account in the thermodynamic function of the system.

2. We limit ourselves to low temperatures (not above one-fourth the Curie point) and use the perturbation theory of statistical mechanics with $\hat{H}_1$ as a perturbation.[4] The free energy is obtained from

$$e^{-\beta F} = \operatorname{Sp} e^{-\beta \hat{H}}, \tag{4}$$

where $\beta = 1/kT$. We obtain the following expansion of the trace in powers of $\hat{H}_1$:

$$\operatorname{Sp} e^{-\beta(\hat{H}_0+\hat{H}_1)} = \operatorname{Sp} e^{-\beta \hat{H}_0} + \beta \sum_{k=1}^{\infty} \frac{(-1)^k}{k} \times \int_0^{\beta}\int_0^{\lambda_1}\cdots\int_0^{\lambda_{k-2}} d\lambda_1 \ldots d\lambda_{k-1} \operatorname{Sp}[e^{-\beta \hat{H}_0} \hat{H}_1(\lambda_1) \ldots \hat{H}_1(\lambda_{k-1}) \hat{H}_1], \tag{5}$$

where

$$\hat{H}_1(\lambda) = e^{\lambda \hat{H}_0} \hat{H}_1 e^{-\lambda \hat{H}_0}. \tag{6}$$

When the free energy F is expanded in powers of the small parameter $\sim H_1/H_0$

$$F = F_0 + F_1 + F_2 + \ldots,$$

we obtain from (4) and (5), to second order terms,

$$F_0 = -\beta^{-1} \ln \operatorname{Sp} e^{-\beta \hat{H}_0}; \quad F_1 = \langle \hat{H}_1 \rangle_\beta; \tag{7}$$

$$F_2 = {}^1/_2 \left\{ \beta \langle \hat{H}_1 \rangle_\beta^2 - \int_0^\beta d\lambda \langle \hat{H}_1(\lambda) \hat{H}_1 \rangle_\beta \right\}, \tag{8}$$

$\langle \ldots \rangle$ denotes averaging over the statistical assembly with the Hamiltonian $\hat{H}_0$. A direct calculation by means of (6) shows that the $\hat{H}_1 \to \hat{H}_1(\lambda)$ transition corresponds to the following substitution of operators:

$$a_{\mathbf{k}} \to a_{\mathbf{k}} e^{-\lambda \varepsilon_{\mathbf{k}}}, \quad a_{\mathbf{k}}^{+} \to a_{\mathbf{k}}^{+} e^{\lambda \varepsilon_{\mathbf{k}}}, \quad b_{\mathbf{g}} \to b_{\mathbf{g}} e^{-\lambda \varepsilon_{\mathbf{g}}}, \quad b_{\mathbf{g}}^{+} \to b_{\mathbf{g}}^{+} e^{\lambda \varepsilon_{\mathbf{g}}}.$$

In calculating various average values we use the following expressions, which can also be derived by direct calculation:

$$\langle b_{\mathbf{g}_1}^{+} b_{\mathbf{g}_2} \rangle_\beta = \delta(\mathbf{g}_1 - \mathbf{g}_2) f_{\mathbf{f}}(\mathbf{g}_1) = \delta(\mathbf{g}_1 - \mathbf{g}_2)[\exp\{\beta \varepsilon_{\mathbf{g}_1}\} - 1]^{-1}; \tag{9}$$

$$\langle a_{\mathbf{k}_1(+)}^{+} a_{\mathbf{k}_2(+)} \rangle_\beta = \delta(\mathbf{k}_1 - \mathbf{k}_2) f_e^{+}(\mathbf{k}_1) = \delta(\mathbf{k}_1 - \mathbf{k}_2)[\exp\{\beta(\varepsilon_{\mathbf{k}_1}^{+} - \xi)\} + 1]^{-1}, \tag{10}$$

where ξ denotes the chemical potential of the electrons and is determined from the conservation of the number of 4s electrons:

$$\sum_{\mathbf{k}} [f_e^{+}(\mathbf{k}) + f_e^{-}(\mathbf{k})] = N_s. \tag{11}$$

The following results are now obtained from a calculation of (7) and (8):

$$F_0 = N_s \xi - \beta^{-1} \sum_{\mathbf{k}} [\ln(1 + \exp\{-\beta(\varepsilon_{\mathbf{k}}^{+} - \xi)\}) + \ln(1 + \exp\{-\beta(\varepsilon_{\mathbf{k}}^{-} - \xi)\})] + \beta^{-1} \sum_{\mathbf{g}} \ln(1 - \exp\{-\beta \varepsilon_{\mathbf{g}}\}); \tag{12}$$

$$F_1 = \frac{1}{N} \sum_{\mathbf{g}} f_{\mathbf{f}}(\mathbf{g}) \sum_{\mathbf{k}} J(\mathbf{k}\mathbf{k}) [f_e^{-}(\mathbf{k}) - f_e^{+}(\mathbf{k})]; \tag{13}$$

$$F_2^{(3)} = \frac{1}{2N} \sum_{\mathbf{k}\mathbf{g}} J^2(\mathbf{k}, \mathbf{k} - \mathbf{g}) \left\{ \frac{\exp\{-\beta(\varepsilon_{\mathbf{k}-\mathbf{g}}^{-} - \varepsilon_{\mathbf{k}}^{+} + \varepsilon_{\mathbf{g}})\} - 1}{\varepsilon_{\mathbf{k}-\mathbf{g}}^{-} - \varepsilon_{\mathbf{k}}^{+} + \varepsilon_{\mathbf{g}}} f_e^{+} \times (\mathbf{k})(1 - f_e^{-}(\mathbf{k} - \mathbf{g}))(1 + f_{\mathbf{f}}(\mathbf{g})) - \frac{\exp\{\beta(\varepsilon_{\mathbf{k}-\mathbf{g}}^{-} - \varepsilon_{\mathbf{k}}^{+} + \varepsilon_{\mathbf{g}})\} - 1}{\varepsilon_{\mathbf{k}-\mathbf{g}}^{-} - \varepsilon_{\mathbf{k}}^{+} + \varepsilon_{\mathbf{g}}} f_e^{-}(\mathbf{k} - \mathbf{g})(1 - f_e^{+}(\mathbf{k})) f_{\mathbf{f}}(\mathbf{g}) \right\}. \tag{14}$$

We note that the first approximation of the three-operator terms vanishes in virtue of the properties of the operators b_g and b_g^{+}, so that $F_2^{(3)}$ is the first nonvanishing correction from the three-operator terms in $\hat{H}_1$ which describe transitions. This corresponds formally to the second approximation in the perturbation theory. F_1 is the first approximation correction from the four-operator terms in $\hat{H}_1$.

3. We shall now calculate the magnetization $M = \partial F/\partial H$. In a magnetic field directed along the axis of spontaneous magnetization the energy is

changed by the amount

$$\Delta H = -N\mu_0 H + 2\mu_0 H \sum_{\mathbf{g}} n_{\mathbf{g}} + \mu_0 H \sum_{\mathbf{k}} (n_{\mathbf{k}}^{+} - n_{\mathbf{k}}^{-}),$$

after which the distribution functions $f_e(\mathbf{k})$ and $f_f(\mathbf{g})$ will depend on the magnetic field. For the zero approximation of the magnetization we obtain

$$M_d^0 = N\mu_0 \left\{1 - \frac{2}{N} \sum_{\mathbf{g}} f_f(\mathbf{g})\right\}; \tag{15}$$

$$M_s^0 = \mu_0 \sum_{\mathbf{k}} [f_e^{-}(\mathbf{k}) - f_e^{+}(\mathbf{k})]. \tag{16}$$

Instead of immediately calculating the next approximation of the magnetization we shall first calculate the free energy corrections F_1 and $F_2^{(3)}$. We note that (11), (13), and (16) possess the same structure and can be calculated by the same method. In these expressions we pass from summation over k to integration. Integrating by parts, we distinguish the derivative of the distribution function in the integrand and regard it as the nucleus of an integral operator which is approximated by

$$-\frac{d}{dx}(e^{x-\beta\xi}+1)^{-1} = \delta(x-\beta\xi)\left(1+\frac{\pi^2}{6}\frac{d^2}{dx^2}+\ldots\right), \tag{17}$$

since $\beta\xi$ is much larger than unity. After calculation of the integrals the results can be represented conveniently by means of the notation

$$X_{s,p}^{\pm} = \left(\frac{m_-}{m}\right)^p \left(1+\frac{\alpha+\mu_0 H}{\xi}\right)^s \pm \left(\frac{m_+}{m}\right)^p \left(1-\frac{\alpha+\mu_0 H}{\xi}\right)^s, \tag{18}$$

where m is the electron mass. From (11) we obtain the chemical potential of the conduction electrons in the magnetic field:

$$\xi = \xi_0 \left[\frac{1}{2} X_{3/2,3/2}^{+} + \frac{\pi^2}{16}\left(\frac{kT}{\xi_0}\right)^2 X_{-1/2,3/2}^{\pm}\right]^{-2/3}; \quad \xi_0 = \frac{\hbar^2}{2m}(3\pi^2 n_s^0)^{2/3}. \tag{19}$$

n_s^0 is the number of 4s electrons per unit volume. Since $(kT/\xi_0)^2 < 10^{-4}$ we can neglect the dependence of ξ on temperature. In the same approximation we obtain for (16) and (13):

$$M_s^0 = N_s \mu_0 X_{3/2,3/2}^{-} (X_{3/2,3/2}^{+})^{-1}; \tag{20}$$

$$F_1 = \frac{1}{N}\sum_{\mathbf{g}} f_f(\mathbf{g}) \cdot 2N_s \left\{\alpha X_{3/2,3/2}^{-}(X_{3/2,3/2}^{+})^{-1} - \gamma\left(\frac{2ma^2\xi_0}{\hbar^2}\right)\frac{3}{10} X_{5/2,5/2}^{-}\left(\frac{1}{2}X_{3/2,3/2}^{+}\right)^{-5/3}\right\}. \tag{21}$$

We cannot calculate (14) to the same order of approximation; a number of supplementary approximations are required. We neglect the energy and momentum of the ferromagnons if they are of the same order as the energy and momentum of electrons, since the principal contribution to the sums comes from terms with small ferromagnon momenta and large electron momenta (on the order of the Fermi momentum). Separating the summations over **k** and **g**, we integrate over **k** using the approximation (17) and obtain

$$F_2 = -\frac{1}{N}\sum_{\mathbf{g}} f_f(\mathbf{g}) \cdot 3N_s \frac{\alpha^2}{\xi_0}\frac{kT}{\alpha} \tanh\frac{\alpha}{kT}\left(1-\frac{\mu_0 H}{kT}\right). \tag{22}$$

In order to make the meaning of the final result clearer we neglect the difference between the effective electron masses in (19), (20) and (21), letting $m_- = m_+ = m$, $\gamma = 0$. Since α and $\mu_0 H \ll \xi$, we assume

$$X_{s,p}^{+} \approx 2; \quad X_{s,p}^{-} \approx 2s(\alpha+\mu_0 H)/\xi_0; \quad \xi = \xi_0.$$

The total correction to the free energy due to the interaction between conduction electrons and ferromagnons is given by

$$F_1 + F_2 = \frac{1}{N}\sum_{\mathbf{g}} f_f(\mathbf{g}) \cdot 3N_s \frac{\alpha^2}{\xi_0} D(H),$$
$$D(H) = 1 + \frac{\mu_0 H}{\alpha} - \frac{kT}{\alpha}\tanh\frac{\alpha}{kT}\left(1-\frac{\mu_0 H}{kT}\right). \tag{23}$$

We shall now calculate the magnetization. In the given approximations the magnetization of s electrons is, according to (20),

$$M_s^0 = 3N_s\mu_0\alpha/2\xi_0 + 3N_s\mu_0^2 H/2\xi_0 \tag{24}$$

where the second term is the paramagnetic (Pauli) magnetization of the electron gas, while the first (constant) term results from magnetization of the 4s-electron gas by 3d electrons, the s-d exchange field being the equivalent of an effective magnetic field $H_{\mathrm{eff}} = \alpha/\mu_0$. If we assume that α is of the order of 5×10^{-15} erg, then H_{eff} is of the order of 10^6 oersteds, so that the 4s electrons will contribute considerably to the spontaneous magnetization of metals. Using (15), (23), and (24) we obtain an expression for the total magnetization in terms of the 3d-electron magnetization:

$$M = \left(1+\frac{3}{2}\frac{N_s}{N}\frac{\alpha}{\xi_0}\right)M_d^0 + \frac{3}{2}N_s\mu_0\frac{\alpha}{\xi_0}\left\{\frac{\mu_0 H}{\alpha} - \left(1-\frac{M_d^0}{N\mu_0}\right)\tanh\frac{\alpha}{kT} + D(H)\frac{\alpha}{\mu_0}\frac{\partial}{\partial H}\left(\frac{M_d^0}{N\mu_0}\right)\right\}. \tag{25}$$

Since M_d^0 is the magnetization of 3d electrons in the absence of an s-d interaction, the first term in this expression represents the usual spontaneous magnetization of ferromagnetic 3d electrons and of the fraction of the 4s electrons which is magnetized by the s-d exchange field. Thus this term describes ideal ferromagnetism with the average number of electrons per lattice site given by $1 + (3N_s/2N)\alpha/\xi_0$. The second term in (25) provides a correction to the magnetization resulting from the dynamical interaction of 4s electrons and ferromagnons.

M_d^0 can be calculated from (15) if the dispersion law for ferromagnons is known. If we assume the usual result of spin-wave theory, which gives $\epsilon_g \sim Jg^2$, the derivative, with respect to the field, of the resulting expression for M_d^0 will diverge at $H = 0$, and we obtain a diverging expression for the magnetization (25). The reason for such singularities in the theory of magnetism has frequently been discussed (see reference 5, for example), and evidently lies in the fact that in such instances a decisive part is played by magnetic interactions which are not taken into account by the Bloch spin-wave theory. We shall assume that as a result of the magnetic interaction there is required a certain activation energy ΔE of a spin-wave with zero quasi-momentum, so that

$$\varepsilon_g = \Delta E + J(ag)^2.$$

The calculation of ΔE does not enter into our problem, but we can state immediately that it must be small, being of the order of the anisotropy energy. It is easily found that

$$\frac{1}{N}\sum_g f_f(g) = \frac{1}{(2\sqrt{\pi})^3}\left(\frac{kT}{J}\right)^{3/2} Z_{3/2}\left(\frac{\Delta E + 2\mu_0 H}{kT}\right),$$

where

$$Z_{3/2}(x) = \sum_{n=1}^{\infty} n^{-3/2}\, e^{-xn}$$

$$= 2.61 - 3.54x^{1/2} + 1.46x - 0.104x^2 + \ldots$$

This last expression was obtained by Robinson[6] and converges rapidly for $x \leq 1$. Keeping only the first two terms in the expansion, we obtain

$$M_d^0 = N_{\mu_0}\left\{1 - 0.1174\left(\frac{kT}{J}\right)^{3/2}\left[1 - 1.36\left(\frac{\Delta E + 2\mu_0 H}{kT}\right)^{1/2} + 0.56\left(\frac{\Delta E + 2\mu_0 H}{kT}\right) - \ldots\right]\right\}, \tag{26}$$

which is applicable to not too low temperatures, where $(\Delta E + 2\mu_0 H) < kT$. Eqs. (25) and (26) give the dependence of the magnetization on temperature and field. Let us consider two limiting cases:

(a) $\alpha \ll kT$, weak s-d coupling, high temperature; $D(H) \approx \mu_0 H/\alpha \ll 1$. We see that the first and second approximation corrections to the free energy cancel each other to a considerable extent and disappear entirely in the absence of a magnetic field. We obtain for the spontaneous magnetization:

$$M = \left(1 + \frac{3}{2}\frac{N_s}{N}\frac{\alpha}{\xi_0}\right)M_d^0 - 0.1174\frac{3N_s\mu_0\alpha^2}{2\xi_0 J^{3/2}}(kT)^{1/2}. \tag{27}$$

(b) $\alpha \gg kT$, strong s-d coupling, low temperature; $D(H) \approx 1 + 2\mu_0 H/\alpha$. In this case the first and second approximation corrections to the free energy, which depend on the field, are equal, but the first approximation correction, which corresponds to elastic collisions, is predominant in their constant parts. The spontaneous magnetization is given by

$$M = \left(1 + \frac{3}{2}\frac{N_s}{N}\frac{\alpha}{\xi_0}\right)M_d^0 + 0.159\frac{3N_s\mu_0\alpha^2}{2\xi_0 J^{3/2}(\Delta E)^{1/2}}kT. \tag{28}$$

Except for the notation this agrees with the expression obtained in references 7 and 8, where only elastic collisions were taken into account. We have now determined the range of applicability of this result.

Despite the fact that the correction terms in (27) and (28) contain the factors $(kT/J)^{1/2}$ and (kT/J), which at low temperatures decrease more slowly than the term containing $(kT/J)^{3/2}$ in M_d^0, they remain smaller than the latter in the given temperature range because of their small coefficients. By means of the values given above it can easily be shown that the second term in (28) does not exceed 10% of the first term.

Thus of the two types of dynamic interaction between 3d and 4s electrons elastic collisions between ferromagnons and conduction electrons dominate at low temperatures, while at higher temperatures transition processes begin to play a part. These two temperature regions are separated by the temperature $\theta = \alpha/k$. Since our calculation is valid in the temperature range from a few degrees to ~ 200° the possibility of including transition processes in this region depends on the magnitude of the s-d exchange integral.

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