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THE INDIRECT INTERACTION OF d ELECTRONS IN TRANSITION METALS. II. ANTIFERROMAGNETISM

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Antiferromagnetic substances are considered within the framework of Vonsovskiĭ's s-d-exchange model. The energy of the spin waves is determined by perturbation-theory methods. The possibility of the existence of an antiferromagnetic state in the absence of direct d-d-exchange interaction is discussed.

In their previous work[1] the authors expressed opinions regarding the necessity of studying the indirect interaction of electrons in the unfilled inner shells of the atoms of transition metals (d electrons) and rare earths (f electrons). It was shown that the indirect interaction of d electrons by means of the conduction electrons can lead to ferromagnetism. In the present paper a study of the role of the indirect interaction of d electrons is carried out for the antiferromagnetic state.

The Hamiltonian of an antiferromagnet in the s-d-exchange model has the form[2]

$$\begin{aligned}H = {} & \sum_{k\sigma} E(k)\, a^+_{k\sigma} a_{k\sigma} - J \sum_{\langle nm\rangle} S_n S_m \\ & - \frac{I}{V} \sum_{k_1 k_2 n} e^{i(k_2-k_1)n} [(S - S^z_n)\, a^+_{k_1} a_{k_2} + (S^x_n - iS^y_n)\, a^+_{k_1} a_{k_2}(-) \\ & + (S^x_n + iS^y_n)\, a^+_{k_1}(-)\, a_{k_2} + (S + S^z_n)\, a^+_{k_1}(-)\, a_{k_2}(-)] \\ & - \frac{I}{V} \sum_{k_1 k_2 m} e^{i(k_2-k_1)m} [(S - S^z_m)\, a^+_{k_1} a_{k_2} + \\ & + (S^x_m - iS^y_m)\, a^+_{k_1} a_{k_2}(-) + (S^x_m + iS^y_m)\, a^+_{k_1}(-)\, a_{k_2} \\ & + (S + S^z_m)\, a^+_{k_1}(-)\, a_{k_2}(-)],\end{aligned}$$

where a_k and $a_k(-)$ are the Fermi operators of second quantization for electrons with a momentum k and with positive and negative spins, S_n is the spin operator of the n-th lattice point, J is the d-d-exchange integral between two nearest neighbors, I is the s-d-exchange integral (independent, in our approximation, of the electron momentum), V is the volume of the system, n and m are the numbers of lattice points of two different sublattices, the sign < > denotes summation over the nearest neighbors, $E(k) = Ak^2$ is the conduction-electron energy, and A is the transport integral.

We go over from the spin operators to the Bose operators of the spin shift

$$S^z_n = 1/2 - b^+_n b_n, \quad S^x_n + iS^y_n = b_n, \quad S^x_n - iS^y_n = b^+_n,$$

$$S^z_m = -1/2 + c^+_m c_m, \quad S^x_m + iS^y_m = c^+_m, \quad S^x_m - iS^y_m = c_m$$

for the two sublattices, respectively. Then, going over to the Bose operators in wave-number space according to the formulas

$$b_n = \left(\frac{2}{V}\right)^{1/2} \sum_\lambda e^{-in\lambda} b_\lambda, \qquad c_m = \left(\frac{2}{V}\right)^{1/2} \sum_\lambda e^{im\lambda} c_\lambda,$$

we obtain the Hamiltonian in the form

$$\begin{aligned}H = {} & \sum_{k\sigma} E(k)\, a^+_{k\sigma} a_{k\sigma} - \frac{zJ}{2} \sum_\lambda [b^+_\lambda b_\lambda + c^+_\lambda c_\lambda + \gamma_\lambda (b_\lambda c_\lambda + b^+_\lambda c^+_\lambda)] \\ & - \frac{I}{V} \sum_{k\lambda} (b^+_\lambda b_\lambda - c^+_\lambda c_\lambda)(a^+_k a_k - a^+_k(-)\, a_k(-)) \\ & - \frac{I}{\sqrt{2V}} \sum_{k_1 k_2 \lambda} \delta(k_2 - k_1 + \lambda) [(c_\lambda + b^+_\lambda)\, a^+_{k_1} a_{k_2}(-) \\ & + (c^+_\lambda + b_\lambda)\, a^+_{k_2}(-)\, a_{k_1}],\end{aligned}$$

where z is the number of nearest neighbors of a given atom, $\gamma_\lambda = 1/z \sum_\rho e^{i\rho\lambda}$, and ρ is the radius vector from the given atom to its nearest neighbor. The part of the Hamiltonian quadratic with respect to the Bose operators is easily diagonalized with the aid of the linear substitution

$$b_\lambda = \alpha_{1\lambda} \xi_{1\lambda} + \alpha_{2\lambda} \xi^+_{2\lambda}, \qquad c_\lambda = \alpha_{2\lambda} \xi^+_{1\lambda} + \alpha_{1\lambda} \xi_{2\lambda}.$$

The commutation relations between the operators, and the requirement that the coefficients in the nondiagonal parts of the energy operator equal zero, lead to equations for the transformation coefficients:

$$\alpha^2_{1\lambda} - \alpha^2_{2\lambda} = 1,$$

$$2\alpha_{1\lambda} \alpha_{2\lambda} + \gamma_\lambda (\alpha^2_{1\lambda} + \alpha^2_{2\lambda}) = 0.$$

Having determined these coefficients, we obtain the transformed Hamiltonian in the form

$$H = H_0 + H_{int},$$
$$H_0 = \sum_{k\sigma} E(k)\, a^+_{k\sigma} a_{k\sigma} + \sum_{\lambda} \varepsilon(\lambda)\, (\xi^+_{1\lambda}\xi_{1\lambda} + \xi^+_{2\lambda}\xi_{2\lambda}),$$
$$H_{int} = -\frac{I}{V}\sum_{k\lambda} (a^+_k a_k - a^+_k(-)\, a_k(-))\, (\xi^+_{1\lambda}\xi_{1\lambda} - \xi^+_{2\lambda}\xi_{2\lambda})$$
$$-\frac{I}{\sqrt{2V}}\sum_{k_1k_2\lambda} \delta(k_2 - k_1 + \lambda)\, g(\lambda)\, [(\xi^+_{1\lambda} + \xi_{2\lambda})\, a^+_{k_2} a_{k_1}(-)$$
$$+ (\xi_{1\lambda} + \xi^+_{2\lambda})\, a^+_{k_2}(-)\, a_{k_1}], \tag{1}$$

where $\epsilon(\lambda) = -J(z/2)^{1/2}\lambda$ is the spin-wave energy, and

$$g(\lambda) = \alpha_{1\lambda} + \alpha_{2\lambda} = (2\lambda^2/z)^{1/4}.$$

Unlike in previous work,[1] perturbation theory will be applied here not to an arbitrary spectrum but to a given unperturbed-energy level. We are interested in the correction to the elementary excitation energy of the Bose branch $\epsilon(\lambda)$ due to the interaction terms. In accordance with perturbation theory, the spin-wave energy $\tilde{\epsilon}(\lambda)$ of interest to us is equal, up to terms of the second order, to

$$\tilde{\varepsilon}(\lambda) = \varepsilon(\lambda) + \langle C_v \xi_{1\lambda} H_{int}\, \xi^+_{1\lambda} C_v\rangle$$
$$- \langle C_v \xi_{1\lambda} H_{int} (H_0 - E_0 - \varepsilon(\lambda))^{-1} H_{int}\, \xi^+_{1\lambda} C_v\rangle, \tag{2}$$

where

$$C_v = \prod_{k\leqslant k_F} \delta(N^+_k, 1)\, \delta(N^-_k, 1) \prod_{\lambda} \delta(n_{1\lambda}, 0)\, \delta(n_{2\lambda}, 0)$$

represents the unperturbed wave function of the ground state. N^+_k and N^-_k are the occupation numbers of conduction electrons with positive and negative spins, respectively, n are the occupation numbers of the spin waves, $E_0 = 2\sum_{k\leq k_F} E(k)$ is the ground-state energy of the unperturbed system, and k_F is the boundary Fermi momentum. Calculating the matrix elements in (2), we obtain

$$\tilde{\varepsilon}(\lambda) = \varepsilon(\lambda) - \frac{I^2 g^2(\lambda)}{2V} \sum_{\substack{k_1 > k_F > k_2 \\ (k_1 - k_2 = \lambda)}} \Big(\frac{1}{E(k_1) - E(k_2) + \varepsilon(\lambda)}$$
$$+ \frac{1}{E(k_1) - E(k_2) - \varepsilon(\lambda)}\Big).$$

For the right-hand side we can substitute the integral

$$\frac{V}{(2\pi)^3}\int \Big(\frac{1}{E(k_1) - E(k_2) + \varepsilon(\lambda)}$$
$$+ \frac{1}{E(k_1) - E(k_2) - \varepsilon(\lambda)}\Big)\, \delta(k_1 - k_2 - \lambda)\, d^3k_1\, d^3k_2,$$

which can be easily calculated in the approximation $\lambda/k_F \ll 1$.[3] Substituting $k_2 + \lambda$ for k_1, discarding in the denominator terms with λ/k_F to a power greater than 1, and taking into account that $k_2 + \lambda > k_F$, we obtain for the integral

$$\frac{V}{(2\pi)^3}\int_0^{2\pi} d\varphi \int_0^1 d\mu \int_{k'_F}^{k_F} k_2^2\, dk_2 \Big(\frac{1}{2Ak_F\lambda\mu + \varepsilon(\lambda)} - \frac{1}{2Ak_F\lambda\mu - \varepsilon(\lambda)}\Big),$$

where μ is the cosine of the angle between k_2 and λ, and $k'_F = k_F(1 - 2\mu q/k_F)^{1/2}$.

Finally we find that

$$\tilde{\varepsilon}(\lambda) = \varepsilon(\lambda) - \frac{I^2 g^2(\lambda)\, k_F}{(4\pi)^2 A}\Big[2 + \frac{\varepsilon(\lambda)}{2A\lambda k_F} \ln \frac{1 - 2A\lambda k_F/\varepsilon(\lambda)}{1 + 2A\lambda k_F/\varepsilon(\lambda)}\Big]. \tag{3}$$

To analyze this expression formally, we can consider the two limiting cases: a) $2A\lambda k_F/\epsilon(\lambda) \ll 1$, and b) $2A\lambda k_F/\epsilon(\lambda) \gg 1$. The first case corresponds to the approximation in which the energy of the virtual electron transitions is assumed to be considerably smaller than the energy of the corresponding spin wave. Expanding the expression in square brackets in (3) into a series in $2A\lambda k_F/\epsilon(\lambda)$ and limiting ourselves to the first nonvanishing terms of the third order, we obtain

$$\tilde{\varepsilon}(\lambda) = J_{\text{eff}}\lambda, \quad J_{\text{eff}} = -J\sqrt{\frac{z}{2} + \frac{\sqrt{2}}{3\pi^2 z^{3/2}} k_F^3 A \frac{I^2}{J^2}}.$$

Thus, in our case the indirect interaction favors antiferromagnetic ordering, increasing the effective exchange integral.

The second case corresponds to the approximation for which the energy of virtual electron transitions is considerably larger than the spin-wave energy. In this case we obtain from (3)

$$\tilde{\varepsilon}(\lambda) = \varepsilon(\lambda) - I^2 g^2(\lambda)\, k_F/8\pi^2 A$$

or

$$\tilde{\varepsilon}(\lambda) = J_{\text{eff}}\lambda, \qquad J_{\text{eff}} = -J\sqrt{\frac{z}{2}} - \frac{I^2 k_F}{8\pi^2 A}\sqrt{\frac{2}{z}}.$$

The effective integral in this case, as in case a), consists of two terms corresponding to direct and indirect exchange. However, in this case the indirect exchange decreases the effective exchange integral, and in the absence of direct d-d-exchange coupling $(J = 0)$ the effective integral becomes negative. Consequently, the energies of the elementary excitations and of the spin waves become negative, which means that the antiferromagnetic state becomes energetically unfavorable and, therefore, does not come into being.

Case a), although it offers the possibility that indirect exchange favors antiferromagnetic ordering, is nevertheless of no physical significance, since the inequality $2A\lambda k_F/\epsilon(\lambda) \ll 1$ is not fulfilled in any of the known estimates. Therefore, this case need be considered only as a purely formal possibility.

Thus, the general conclusion is that indirect interaction of d electrons through conduction electrons in transition metals decreases the antiferromagnetic exchange coupling, preventing the formation of antiferromagnetic ordering and, consequently, cannot lead, in the absence of direct d-d-exchange interaction or of some other ordering mechanism, to antiferromagnetism.

The calculations in the present paper are exact up to second-order terms of perturbation theory. The calculation of higher-order corrections, beginning with the third, require that account be taken of Hamiltonian terms which contain products of four or more Bose operators, and which were left out in the derivation of (1). Thus, the precision of the calculations increases when the system is considered at low temperatures.

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