SOVIET PHYSICS JETP VOLUME 36(9), NUMBER 3 SEPTEMBER, 1959

INDIRECT COUPLING OF d ELECTRONS IN TRANSITION METALS

I. FERROMAGNETISM

A. A. BERDYSHEV and B. V. KARPENKO

Ural' State University

Submitted to JETP editor August 3, 1958; resubmitted January 14, 1959

J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 819-822 (March, 1959)

The second-order perturbation for the s-d exchange model of transition metals yields an indirect interaction between d electrons via the conduction electrons. Consequently ferromagnetism may arise when direct d-d coupling is entirely absent or even when the d-d exchange integral is negative.

FERROMAGNETISM and antiferromagnetism in transition metals are usually accounted for by an exchange interaction between core d-electrons. A positive exchange integral between nearest neighbors makes a metal ferromagnetic, while a negative integral results in antiferromagnetism. A number of difficulties arise,[1] of which we shall mention only three: (1) Many experimental results cannot be accounted for by using the Bethe-Slater curve for the exchange integral of transition metals.[1] (2) Most theoretical evaluations of the exchange integral lead to a negative value.[2] (3) Both ferromagnetic and antiferromagnetic forms are found in dilute alloys of manganese in precious metals;[3] in these alloys transition metal atoms are separated by such large distances that any direct exchange interaction between them is entirely excluded. Similarly, ferromagnetism and antiferromagnetism in rare earths cannot be attributed to the extremely weak direct coupling between the magnetic 4f electrons.

Other possible exchange mechanisms have therefore been sought, one of which is the indirect exchange interaction suggested by Zener,[1] which he discussed from a phenomenological point of view. The present paper considers the relation of the indirect interaction to ferromagnetism.

The calculation will be based on the s-d exchange model of transition metals.[4] The energy operator of the system of s and d electrons is

$$H = H_0 + H_1 + H_2,$$

where

$$H_0 = \sum_k E_k [a_k^+ a_k + a_k^+(-) a_k(-)] + \sum_g \varepsilon_g b_g^+ b_g, \qquad H_1 = -N^{-1/2} \sum_{k,g} I(\mathbf{k}, \mathbf{k}-\mathbf{g})\, b_g a_k^+ a_{k-g}(-) + \text{compl. conj.},$$

$$H_2 = -\sum_k I(\mathbf{k},\mathbf{k})\, a_k^+(-) a_k(-) + N^{-1} \sum_{\mathbf{k}_2-\mathbf{k}_1+\mathbf{g}_2-\mathbf{g}_1=0} I(\mathbf{k},\mathbf{k}_2)\, b_{g_1}^+ b_{g_2} [a_{k_1}^+(-) a_{k_2}(-) - a_{k_1}^+ a_{k_2}],$$

where $E_k = Ak^2$ is the translational energy of a conduction electron in one-electron theory, A is the transport integral, $\epsilon_g = Jg^2$ is the energy of a spin wave with wave number **g**, J is the d-d exchange integral, $I(\mathbf{k}_1, \mathbf{k}_2)$ is the s-d exchange integral, a_k and $a_k(-)$ are Fermi operators for conduction electrons with wave number **k** and spins $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively, b_g is the Bose operator and N is the number of lattice sites.

Previous papers on the s-d exchange model of ferromagnets and antiferromagnets[4] have considered only the energy terms H_0 and H_2; this amounted to a first-order perturbation. The "ternary" terms in H_1 comprise a second-order energy correction, which can be obtained either by perturbation theory[5] or through a canonical transformation.[6] The energy then becomes

$$W = \sum_g (\varepsilon_g + g_0 \mu H) n_g + \sum_k (E_k^+ - \mu H) N_k^+ + \sum_k (E_k^- + \mu H) N_k^- - N g_0 \mu H.$$

$$E_k^+ = E_k + \frac{1}{N} \sum_g E_{kg}^+ n_g + \varepsilon_{sd}^0,$$

$$E_k^- = E_k - I(\mathbf{k},\mathbf{k}) + \frac{1}{N} \sum_g E_{kg}^- n_g,$$

$$E_{kg}^+ = -I(\mathbf{k},\mathbf{k}) + |I(\mathbf{k},\mathbf{k}-\mathbf{g})|^2 / (E_k - E_{k-g} - \varepsilon_g),$$

$$E_{kg}^- = I(\mathbf{k},\mathbf{k}) - |I(\mathbf{k},\mathbf{k}+\mathbf{g})|^2 / (E_{k+g} - E_k - \varepsilon_g)$$

$$\varepsilon_{sd}^0 = \frac{1}{N} \sum_{kg} |I(\mathbf{k},\mathbf{k}-\mathbf{g})|^2 / (E_k - E_{k-g} - \varepsilon_g),$$

where g_0 is the Landé factor, μ is the Bohr magneton, n_g and $N_k^{\pm}$ are the occupation numbers of ferromagnons and conduction electrons. We assume for simplicity that $I(\mathbf{k}_1, \mathbf{k}_2) = I_0 = \text{const}$. The state sum and the free energy are calculated by the method of steepest descent;[7] the free energy of the system is given by

$$F = F_s + F_{sd} + F_d,$$

$$F_s = \zeta N - kT \sum_k \left[\ln \left\{ 1 + \exp\left(-\frac{E_k - \zeta - \mu H}{kT} \right) \right\} + \ln \left\{ 1 + \exp\left(-\frac{E_k - I_0 - \zeta + \mu H}{kT} \right) \right\} \right],$$

$$F_{sd} = \frac{I_0^2}{N} \sum_{k,g} f(E_k - \mu H) / (E_k - E_{k-g} - \varepsilon_g),$$

$$F_d = -N g_0 \mu H + kT \sum_g \ln(1 + \exp) - \mathscr{E}_g / kT)),$$

$$\mathscr{E}_g = \varepsilon_g + g_0 \mu H + \Delta_1 + \Delta_2,$$

$$\Delta_1 = \frac{I_0}{N} \sum_k [f(E_k - I_0 + \mu H) - f(E_k - \mu H)],$$

$$\Delta_2 = \frac{I_0^2}{N} \sum_k \left[\frac{f(E_k - \mu H)}{2Akg\cos\vartheta - (A + J)g^2} - \frac{f(E_k - I_0 + \mu H)}{2Akg\cos\vartheta + (A - J)g^2} \right],$$

where $f(E)$ is the Fermi distribution function; the chemical potential ζ of conduction electrons (the Fermi energy) is given by

$$\sum_k [f(E_k - \mu H) + f(E_k - I_0 + \mu H)] = N - \frac{1}{N_k T} \sum_{kg} N(\mathscr{E}_g) \times \left[E_{kg}^{+} \frac{\partial f(E_k - \mu H)}{\partial \zeta} + E_{kg}^{-} \frac{\partial f(E_k - I_0 + \mu H)}{\partial \zeta} \right] - \frac{I_0^2}{N} \sum_{kg} \frac{\partial f(E_k - \mu H) / \partial \zeta}{E_k - E_{k-g} - \varepsilon_g}.$$

The magnetic moment of the electron system is determined by

$M = -\partial F / \partial H$ and is equal to $M = M_s + M_{sd} + M_d$, where

$$M_d = N g_0 \mu \left\{ 1 - \frac{1}{N} \left[1 + \frac{1}{g_0} (\Delta_1^1 + \Delta_2^1) \right] \sum_g N(\mathscr{E}_g) \right\},$$

$N(\mathscr{E}_g)$ being the Bose distribution function. For $g \ll 1$ we obtain approximately

$$\Delta_1 = \Delta_0 + \Delta_1^1 \mu H,$$

$$\Delta_0 = \frac{I_0^2}{4\pi^2 A} \sqrt{\frac{\zeta}{A}} \left[1 - \frac{\pi^2}{24} \left(\frac{kT}{\zeta} \right)^2 \right], \quad \Delta_1^1 = \frac{I_0}{2\pi^2 A} \sqrt{\frac{\zeta}{A}},$$

$$\Delta_2 = \Delta_2^0 + \Delta_2^1 \mu H,$$

$$\Delta_2^0 = -\Delta_0 + \frac{I_0^2 (A^2 + 3J^2)}{48\pi^2 A^2 \sqrt{\zeta A}} \left[1 - \frac{\pi^2}{16} \left(\frac{kT}{\zeta} \right)^2 \right], \quad \Delta_2^1 = 0.$$

Then $\mathscr{E}_g = J_{\text{eff}} g^2 + g_0 \mu H$,

$$J_{\text{eff}} = J + J^{(s)} = J + \frac{I_0^2 (A^2 + 3J^2)}{48\pi^2 A^2 \sqrt{\zeta A}} \left[1 - \frac{\pi^2}{16} \left(\frac{kT}{\zeta} \right)^2 \right].$$

Integration over **g** (neglecting the correction $\Delta_1^1 \ll 1$) gives

$$M_d = N g_0 \mu \left\{ 1 - \gamma \left(\frac{T}{\Theta_c} \right)^{3/2} \right\}, \quad \gamma = 0.1174, \quad 2k\Theta = J_{\text{eff}}$$

which is the familiar $T^{3/2}$ law for low-temperature magnetization. It thus results from the second-order correction that the free energy and magnetic moment contain, instead of the direct coupling $J \equiv J_{dd}$, the effective exchange integral J_{eff} consisting of a direct d-d exchange integral and an "integral" $J^{(s)}$ of indirect interaction. The latter is always positive, so that the existence of ferromagnetism does not require that J_{dd} be necessarily positive. Ferromagnetism also may exist when $J_{dd} = 0$ (in rare earths and dilute alloys of manganese) and even with a negative d-d exchange integral. The more general criterion for ferromagnetism is now $J_{\text{eff}} = J + J^{(s)} > 0$.

In addition, the second-order correction completely nullifies the first-order magnetization correction. It has previously been shown[8] that the existence of a "zero-point" energy Δ_0 of a spin wave leads either to the exponential dependence of M_d on T when Δ_0 is large, or to a small departure from the $T^{3/2}$ law when Δ_0 is small. In the second approximation the correction Δ_0 drops out of $\mathscr{E}_g$ completely, so that there is no departure from the $T^{3/2}$ law.

The still unconsidered last two components of the total magnetic moment of the s and d electron system are easily calculated, giving

$$M_s + M_{sd} = \left[\frac{N\mu I_0}{4\pi^2 A} \sqrt{\frac{\zeta}{A}} + \mu^2 N \frac{H}{\pi^2 A} \sqrt{\frac{\zeta}{A}} \right] + \frac{3N\mu}{64\pi^2} \frac{I_0^2}{\zeta A} \sqrt{\frac{\zeta}{A}}.$$

The first and third terms of this sum describe the "magnetization" of conduction electrons by the "field" of core electrons and the spontaneous magnetic moment of conduction electrons. This moment depends on the magnitude and sign of the s-d exchange integral I_0. The second term describes the usual Pauli paramagnetic susceptibility of conduction electrons.

We note in conclusion that the effective exchange integral J_{eff} is slightly reduced as the temperature rises. However, this dependence is too weak to account for the transition from ferromagnetism to antiferromagnetism at a high temperature, which is observed in some alloys and rare earths.[3,5] Also, the entire calculation is based on the approximating assumption that the magnetization of the system is close to its maximum value, so that we cannot draw conclusions that will be valid for high temperatures. The different methods required at high temperatures will be discussed in another paper.

We have also considered the case of a negative effective exchange integral. The indirect interaction "integral" $J^{(s)}$ now differs somewhat because of the different dispersion laws for spin waves in ferromagnets and antiferromagnets. This case will be discussed in the next paper.

The authors are grateful to S. V. Vonsovskiĭ and E. A. Turov for discussions and a number of valuable comments.

---

[1] C. Zener and R.R. Heikes, Revs. Modern Phys. **25**, 191 (1953); [cf. also C. Zener, Пробл. совр. физ. (Problems of Contemporary Physics) No. 5, (1952)].

[2] H. Kaplan, Phys. Rev. **85**, 1038 (1952); E. P. Wohlfarth, Nature **163**, 57 (1949).

[3] J. Owen and M. E. Browne, Phys. Chem. Solids **2**, 85 (1957); F. A. Otter, J. Franklin Inst. **260**, 75 (1955).

[4] S. V. Vonsovskiĭ and E. A. Turov, J. Exptl. Theoret. Phys. (U.S.S.R.) **24**, 419 (1953); S. V. Vonsovskiĭ and A. A. Berdyshev, Izv. Akad. Nauk SSSR, Ser. Fiz. **18**, 328 (1954).

[5] T. Kasuya, Progr. Theoret. Phys. **16**, 45 (1956); K. Yosida, Phys. Rev. **106**, 893 (1957), **107**, 396 (1957).

[6] Y. Kitano and H. Nakano, Progr. Theoret. Phys. **9**, 370 (1953).

[7] M. A. Leontovich, Статистическая физика (Statistical Physics), Gostekhizdat, 1944, Ch. 5.

[8] A. A. Berdyshev and Yu. A. Izyumov, Физика металлов и металловедение (Physics of Metals and Metal Research) **5**, 552 (1957); E. A. Turov, J. Exptl. Theoret. Phys. (U.S.S.R.) **25**, 352 (1953).

Translated by I. Emin
147