PHYSICS

Corresponding Member of the USSR Academy of Sciences S. V. VONSOVSKII, A. A. BERDYSHEV,

1960

SovietRxiv

Abstract

Full Text

PHYSICS

Corresponding Member of the USSR Academy of Sciences S. V. VONSOVSKII,
A. A. BERDYSHEV,
Yu. A. IZYUMOV, B. V. KARPENKO, and Yu. Ya. POLYAK

ON THE EXCHANGE INTERACTION OF INNER AND OUTER ELECTRONS IN TRANSITION METALS

1. The electronic energy spectrum of metallic crystals constructed with the participation of elements of the transition and rare-earth groups possesses specific features in comparison with crystals of elements of the main groups (alkali metals, Cu, Zn, Al, etc.). These features are due to the presence of spin-unsaturated, incomplete *d*- or *f*-shells in the electronic shell of atoms of transition elements; they are manifested primarily in the fact that, in the electronic spectrum, besides the Fermi branch with weak (Pauli) paramagnetism, there appears a spin branch responsible for ferro- or antiferromagnetism ([1]). In real crystals both branches belong to the entire system of electrons as a whole. However, our information about the behavior of this system is still insufficient, and therefore one has to use an approximate semiphenomenological treatment. The totality of experimental information on transition metals (X-ray structural, neutronographic, magnetic, etc.) makes it possible to assume that in these substances the electron density can be divided into three parts: a part localized at the nuclei, forming together with them the ionic lattice of the crystal; a delocalized part consisting of the former valence electrons of the atoms; and, finally, an intermediate part, arising mainly from electrons of the unfilled layers of the atomic shell, which become collectivized in the crystal only partially.

The nonlocalized scalar charge density $\rho(\mathbf{r})$ is associated with the first part, while the spin (vector) density $\mathbf{s}(\mathbf{r})$ describes the practically localized intermediate part. Oscillations of these densities determine the aforementioned branches of the electronic spectrum. Such a division is valid in the first approximation. Strong interactions between the densities substantially distort the Fermi branch and deprive the spin branch of exact localization. However, it is known from experiment that the energy parameter of the strongest of these interactions (electrostatic s–d exchange) $I_0 \sim 10^{-14}$—10^{-13} erg, whereas the Fermi energy of the delocalized system is $\xi \sim 10^{-12}$—10^{-11} erg. Therefore I_0/ξ can serve as a small dimensionless parameter, using which the Hamiltonian of the system may be represented in the form $H = H_s + H_d + H_{sd}$, where H_s refers to the delocalized system of conduction electrons (s-electrons), H_d to the spin system (d-electrons), and H_{sd} is the operator of the s–d exchange interaction. If we restrict ourselves to the region of low temperatures ($T < \theta/4$, where θ is the Curie point), then in H_d and H_{sd} one can pass from spin operators to the Bose operators of second quantization b_λ. Then, neglecting relativistic interactions, the Hamiltonian H takes the form*

$$H = \sum_{k\sigma} \varepsilon_k^\sigma a_{k\sigma}^+ a_{k\sigma} + \sum_\lambda \varepsilon_\lambda b_\lambda^+ b_\lambda + \left(\frac{2s}{N}\right)^{1/2} \sum_{k_1 - k_2 + \lambda = 0} J(k_1 k_2)\left[a_{k_1(+)}^+ a_{k_2(-)} b_\lambda^+ + a_{k_2(-)}^+ a_{k_1(+)} b_\lambda\right] + \frac{1}{N} \sum_{k_2 - k_1 + \lambda_2 - \lambda_1 = 0} J(k_1 k_2) b_{\lambda_1}^+ b_{\lambda_2}\left[a_{k_1(-)}^+ a_{k_2(-)} - a_{k_1(+)}^+ a_{k_2(+)}\right]; \tag{1}$$

* The Hamiltonian (1) was first obtained in work (^{2}) and, in various modifications, was used by the authors (^{3,4}).

N is the number of sites in the lattice; k and λ are the quasimomenta of the Fermi and Bose particles of the isolated systems of s- and d-electrons; $\sigma = \pm 1/2$ is the spin quantum number of the Fermi particle; $a_{k\sigma}$ are the Fermi operators of second quantization; s is the total spin of the d-shell. In the energy of the Fermi particles ε_k^σ a term is included which describes their magnetization by the vacuum of the d-electron system (^{1,2}):

$$\varepsilon_k^+ = E_k; \qquad \varepsilon_k^- = E_k - 2sJ(kk); \qquad \varepsilon_\lambda = J\lambda^2; \tag{2}$$

E_k is the ordinary translational energy of an s-electron.

2. In earlier works on the s—d model (^{2,3}), the off-diagonal terms in (1) (the operator H_{sd}) were regarded as the cause of transitions between the zero levels of the system. In the present work we pose a more general problem —to determine the influence of these terms on the genesis of the exchange bond in the system of d-electrons, i.e., on the spectrum of this system and on the spectrum of the s-electrons. The idea that s—d exchange affects the genesis of the d—d bond was first expressed by Zener (^{5}). Later Kasuya (^{4}) gave a microscopic interpretation of Zener' s idea. A somewhat different formulation was proposed by two of us (^{6}), and it was shown that an error had crept into Kasuya' s reasoning*. It seems expedient to us to apply, to the study of the properties of the electron system of a transition metal, the method of retarded and advanced statistical Green functions developed by N. N. Bogolyubov and S. V. Tyablikov (^{7})**.

First of all it is necessary to calculate the distribution functions of the Bose and Fermi particles of the system under study:

$$n_\lambda = \langle b_\lambda^+ b_\lambda \rangle; \qquad n_k^\sigma = \langle a_{k\sigma}^+ a_{k\sigma} \rangle, \tag{3}$$

where $\langle ... \rangle$ denotes statistical averaging over the canonical ensemble with Hamiltonian (1). We introduce the Green functions for the Bose and Fermi particles:

$$D_\lambda(t-t') = \langle\langle b_\lambda(t) \mid b_\lambda^+(t') \rangle\rangle; \qquad G_k^\sigma = \langle\langle a_{k\sigma}(t) \mid a_{k\sigma}^+(t') \rangle\rangle, \tag{4}$$

where $b_\lambda(t)$ and $a_{k\sigma}(t)$ are the operators from (1) in the Heisenberg representation. In the chain of coupled equations for determining (4), higher-order Green functions appear:

$$T_{k,k-\lambda,\lambda}(t-t') = \langle\langle a_{k(+)}(t) a_{k-\lambda(-)}^+(t) \mid b_\lambda^+(t') \rangle\rangle; ... \tag{5}$$

Using the small parameter I_0/ξ, one may introduce an approximation of the type

$$\langle\langle b_{\lambda_1} a_{k_1(-)}^+ a_{k_2(--)} \mid b_{\lambda_2}^+ \rangle\rangle = n_{k_1}^- \, \delta(k_1-k_2) \, \langle\langle b_{\lambda_1} \mid b_{\lambda_2}^+ \rangle\rangle; ...$$

Then the infinite chain of equations can be reduced to the finite system

$$i\frac{d}{dt} D_\lambda = \delta(t-t') + (\varepsilon_\lambda + \Delta_0) D_\lambda + \left(\frac{2s}{N}\right)^{1/2} \sum_k J(k,k-\lambda) \, T_{k,k-\lambda,\lambda},$$

$$i\frac{d}{dt} T_{k,k-\lambda,\lambda} = \{\varepsilon_k^+ - \varepsilon_{k-\lambda}^- + (\mu-1)(J(k-\lambda,k-\lambda) - J(kk))\} T_{k,k-\lambda,\lambda} +$$

$$+ \left(\frac{2s}{N}\right)^{1/2} J(k,k-\lambda)(n_{k-\lambda}^- - n_k^+) D_\lambda, \tag{6}$$

$$i\frac{d}{dt} G_k^\sigma = \delta(t-t') + [\varepsilon_k^\sigma - 2\mu\sigma J(kk) - \xi] G_k^\sigma.$$

We solve system (6) by an integral Fourier transform; this gives

$$D_\lambda(E) = \frac{1}{2\pi}[E - \varepsilon_\lambda - \Delta_0 - P_\lambda(E)]^{-1}; \qquad G_k^\sigma(E) = \frac{1}{2\pi}[E - \tilde{\varepsilon}_k^\sigma + \xi]^{-1}, \tag{7}$$

* These arguments led Kasuya to the incorrect conclusion that the indirect interaction can lead to the appearance of antiferromagnetism. In fact, it always favors ferromagnetism (see below).

** We are grateful to Tu Fu-chao, S. V. Tyablikov, T. Shiklosh, and also D. N. Zubarev for kindly sending preprints of their works.

where

$$\tilde{\varepsilon}_k^\sigma = E,-s(1-2\mu\sigma)J(kk); \qquad \mu = 1 - \frac{1}{N}\sum_\lambda n_\lambda; \tag{8}$$

$$\Delta_0 = \frac{1}{N}\sum_k J(kk)(n_k^- - n_k^+); \tag{9}$$

$$P_\lambda(E) = \frac{2s}{N}\sum_k \frac{|J(k,k-\lambda)|^2(n_{k-\lambda}^- - n_k^+)}{E - \tilde{\varepsilon}_k^+ + \tilde{\varepsilon}_{k-\lambda}^- + 2s(\mu-1)J(k-\lambda,k-\lambda)}; \tag{10}$$

μ is the relative magnetization of the d-electrons. According to (7), the functions (3) are calculated by means of the spectral representation

$$n_\lambda = \int_{-\infty}^{+\infty} J_\lambda(E)\,dE; \qquad n_k^\sigma = \int_{-\infty}^{+\infty} J_{k\sigma}(E)\,dE,$$

where the spectral densities are determined by the relations ($\varepsilon \to 0$)

$$D_\lambda(E+i\varepsilon) - D_\lambda(E-i\varepsilon) = -i(e^{E/kT}-1)J_\lambda(E),$$

$$G_k^\sigma(E+i\varepsilon) - G_k^\sigma(E-i\varepsilon) = -i(e^{(E-\xi)/kT}+1)J_{k\sigma}(E).$$

Using this, we find

$$n_k^\sigma = \left[\exp\frac{\tilde{\varepsilon}_k^\sigma - \xi}{kT} + 1\right]^{-1}, \tag{11}$$

$$n_\lambda = \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{dE}{e^{E/kT}-1}\,\frac{\gamma_\lambda(E)}{[E-\varepsilon_\lambda-\Delta_0-P_\lambda(E)]^2+\gamma_\lambda^2(E)}, \tag{12}$$

where $P(E)$ is the principal value of the integral (10), and

$$\gamma_\lambda(E) = 2\pi s\frac{1}{N}\sum_k |J(k,k-\lambda)|^2(n_{k-\lambda}^- - n_k^+)\delta\{E - \tilde{\varepsilon}_k^+ + \tilde{\varepsilon}_{k-\lambda}^-$$

$$+2s(\mu-1)J(k-\lambda,k-\lambda)\}. \tag{13}$$

In the approximation under consideration, n_k^σ is the Fermi distribution function for the s-electrons, whose energy is changed under the influence of the s–d coupling; n_λ is a superposition of Bose excitations with a "resonance" intensity and damping frequency $\gamma_\lambda(E)$, coinciding with the expression obtained by Turov $^{(8)}$. As $\gamma_\lambda \to 0$, the resonance function of E in (12) has a sharp maximum at $E = \tilde{\varepsilon}_\lambda$, where

$$\tilde{\varepsilon}_\lambda - \varepsilon_\lambda - P_\lambda(\tilde{\varepsilon}_\lambda) - \Delta_0 = 0, \tag{14}$$

and it may approximately be replaced by a δ-function. Then, instead of (12), we obtain the usual Bose distribution function with energy $\tilde{\varepsilon}_\lambda$.

3. Equation (14) for $\lambda = 0$ gives two roots for the spin-wave energy

$$\tilde{\varepsilon}_k^{(1)} = 0; \qquad \tilde{\varepsilon}_0^{(2)} = 2s(1+\mu)I_0, \tag{15}$$

where

$$\mu_s = \frac{1}{2sN} \sum_k (n_k^- - n_k^+)$$

is the relative magnetization of the s-electrons;

I_0 is the parameter of the s—d exchange coupling, approximately taken as constant. Thus, one of the branches of the spectrum at $\lambda = 0$ has zero energy; the second has a gap of order I_0, as do the analogous branches in ferrites with two magnetic sublattices. These results have already been obtained by one of us $^{(9)}$ from the solution of the equations of motion of the magnetization.

Let us consider the solution of (14) for $\lambda \neq 0$. Taking into account that $E_k = E_{-k}$ for an arbitrary dispersion law, it is not difficult to see that $\tilde{\varepsilon}_\lambda$ is an even

function λ. Then, for the branch of the spectrum without a gap, one may use a solution of the form $\tilde{\varepsilon}_\lambda = J^*\lambda^2$. Carrying out the integration over k in (9) and (10), we find, in the approximation of a quadratic dispersion law for (8), which is inessential for the qualitative result,

$$\Delta_0 = 3sI_0^2 n_s / 2\xi;$$

$$P_\lambda(\tilde{\varepsilon}_\lambda) = \frac{sI_0^2}{8\pi^2 A\lambda} \left\{ \frac{J^*\lambda^2 - 2sI_0}{A\lambda}(k_- - k_+) - \lambda(k_- + k_+) + f_-(\lambda) + f_+(\lambda) \right\}; \tag{16}$$

$$f_\pm(\lambda) = \left\{ k_\pm^2 - \frac{\left[(J^* - A)\lambda^2 - 2sI_0\right]^2}{4A^2\lambda^2} \right\} \ln \frac{2sI_0 - 2Ak_\pm\lambda - (J^* \pm A)\lambda^2}{2sI_0 + 2Ak_\pm\lambda - (J^* \pm A)\lambda^2}.$$

Here $A = \hbar^2/2m$, and the limiting momenta of the "right" and "left" s-electrons are determined from the equalities $Ak_-^2 - 2sI_0 = Ak_+^2 = \xi$; n_s is the number of s-electrons per atom. Restricting ourselves to the quadratic approximation in I_0/ξ, we obtain, using the relation $\xi = \frac{\hbar^2}{2m}(3\pi^2 n_s)^{2/3}$,

$$P_\lambda(\tilde{\varepsilon}_\lambda) = -\Delta_0 + \frac{sI_0^2(A^2 + 3J^{*2})}{24\pi^2 A^2\sqrt{\xi A}}\lambda^2. \tag{17}$$

Substituting (18) into (14) and (10), we finally find

$$\tilde{\varepsilon}_\lambda = J^*\lambda^2 = \left[J + \frac{sI_0^2(A^2 + 3J^2)}{24\pi^2 A^2\sqrt{\xi A}}\right]\lambda^2. \tag{18}$$

The present calculation can without difficulty be generalized also to the case when Bose operators are not introduced in (1), while the spin operators are retained. In this case, as before, the lowest branch of the spectrum contains no gap, i.e., this conclusion is valid for the entire temperature range down to θ.

Calculations were also carried out for the case of an antiferromagnetic metal. For the lowest branch of the spectrum, a linear dispersion law $\tilde{\varepsilon}_\lambda = J^*\lambda$ was obtained with an effective exchange integral

$$J^* = J - \frac{3s}{8}\frac{I_0^2}{\xi}n_s^{1/3}\sqrt{\frac{2}{z}}, \tag{19}$$

where z is the number of nearest neighbors in the lattice. Expressions (18) and (19) coincide with analogous formulas obtained in [6] by another method.

4. The results of the present calculation make it possible to draw the general conclusion that the exchange interaction between the external and internal electrons of transition metals leads to the appearance of an effective (indirect) exchange coupling between the internal electrons. As is seen from (18) and (19), this interaction has the character of a ferromagnetic coupling and therefore, in the absence of direct d–d exchange of the internal electrons, can lead only to ferromagnetism. In general, the indirect interaction through the conduction electrons leads only to a renormalization of the exchange integral and does not qualitatively change the energy spectrum of spin waves. In particular, no energy gap appears in this spectrum.

Institute of Metal Physics
Academy of Sciences of the USSR

Ural State University
named after A. M. Gorky

Received
8 February 1960

CITED LITERATURE

[1] S. V. Vonsovskii, ZhETF, **16**, 981 (1946).
[2] S. V. Vonsovskii, E. A. Turov, ZhETF, **24**, 419 (1953).
[3] S. Kittel, E. Abrahams, Rev. Mod. Phys., **25**, 233 (1953); E. Abrahams, Phys. Rev., **98**, 387 (1954); A. H. Mitchell, Phys. Rev., **105**, 439 (1957); K. Yosida, Phys. Rev., **106**, 893 (1957); **107**, 396 (1957).
[4] T. Kasuya, Progr. Theor. Phys., **16**, 45 (1956).
[5] C. Zener, Phys. Rev., **81**, 440; **82**, 403; **83**, 299 (1951).
[6] A. A. Berdyshev, B. V. Karpenko, ZhETF, **36**, 819 (1959).
[7] N. N. Bogolyubov, S. V. Tyablikov, DAN **126**, 53 (1959).
[8] E. A. Turov, Izv. AN SSSR, ser. fiz., **19**, 462 (1955).
[9] Yu. A. Izyumov, Fiz. met. i metalloved., **9**, No. 5 (1960).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.