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EFFECT OF ELECTRON CORRELATION IN METALS ON THEIR HYBRIDIZATION AND MAGNETIC PROPERTIES

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A metal model is considered in which electrons can exist in almost free states and can also be localized at nodes in the d^1 and d^2 states of the atomic d shells. The spectrum of Fermi excitations of electrons is found, with account of the hybridization of these states and the intra-atomic interaction of the d electrons. The influence of the indicated interactions on the magnetic properties of the system is investigated; it is shown that when the number of the electrons in the atom $n \lesssim 2$, ferromagnetic ordering is possible and energetically favored.

1. As is known, in the construction of a theory of the electron gas in transition metals, it is necessary to solve two basic problems. One of these is the necessity of consideration of two sorts of electrons: the almost-free s and p electrons and the almost-localized d electrons of the existing outer shells of the atom of the transition metal. The second problem is the need of introduction of many-body effects into the theory, in particular, the electrostatic interaction of the electrons.

Considerable progress has been made in recent years toward the solution of the problem. The method of account of both types of electrons has been put forth by Ziman,[1], Heine,[2], Hubbard[3] and others, in a unified scheme in the framework of the single-electron theory. Here the single-particle wave function is assumed to consist of components corresponding to the potential motion in a weak pseudopotential (the s- and p-partial amplitude) and a resonance scattering by the quasidiscrete level formed from the existing atomic d state.

Whereas the single-electron wave function is a completely sufficient approximation in the consideration of transport phenomena, the construction of a many-particle theory is necessary for a large number of phenomena, especially magnetism, which by its very nature is associated with the collective properties of the electrons. In traditional band theory, the theory of electron interactions is considered as an addition to the single-electron energy.[4] However, there are also theories in which the correlation is assumed to be so great that it is even taken into account in the zeroth approximation. These theories are based on the works of Hubbard, Kanamori and Gutzeiller.[5] In these theories, the intra-atomic electrostatic interaction of the electrons leads to a splitting of the energy band into several subbands, corresponding to the probability of a different number of d electrons being located at the node. To impart realistic features to the correlation theory, it is necessary to include both types of electrons and their interaction in it. The first research of this type was due to Smith.[6] In it he considered a band of free electrons, hybridized with atomic d levels which were considered to be nondegenerate. The correlation of the d electrons is considered here on a single node, which is assumed to be very strong.

In the present research, the authors posed the following problem: First, to include in the theory the correlation of the d electrons, developed earlier by Hubbard[7] and the authors[8] in the approximation of overlapping Wannier functions, with the hybridization of the d-electron levels with the band of almost-free conduction electrons; second, to investigate the magnetic properties of the model, assuming that cause, defining the possibility of magnetic ordering, is the satisfaction of Hund's rule for electrons located in a single cell.

A comparison of the results of our research with the theories of Smith[6] is given in Secs. 3 and 5.

2. Thus, we consider a system of electrons in a metal. We shall assume that they can be found in almost free s states, with energy $\epsilon_k (\epsilon_k |_{k=0} = 0)$ and in almost bound states in atoms in the electronic configurations d^1 and d^2, having energies ϵ_1 and ϵ_2. In order that the s-d hybridization play an important role in the properties of the system, it is necessary that the energy of the transition $d^2 \longleftrightarrow d^1 s^1$ be comparable with the energy of the s-d interaction. For this, we shall assume that the energy $\epsilon_2 - \epsilon_1$ be positive and intersect the conduction band. We shall not consider the other configurations d^n, assuming that their energies and the corresponding differences $\epsilon_{n+1} - \epsilon_n$ lie outside the range of energy of interest to us.

Furthermore, among all the possible terms of the configuration d^2, we shall consider only the lowest. According to Hund's rule, this term is ^3F. Moreover, for simplicity, we shall assume the s band to be nondegenerate, and the atomic levels not to depend on the projections of the orbital momenta upon neglect of the effect of the crystalline field.

As has already been pointed out, the correlation theory of d electrons in a narrow energy band was formulated by Hubbard.[7] The authors[8] considered the Hubbard model with account of only one- and two-electrons states of the atoms in the approximation of a degenerate d band. Now we shall set up the problem of the account in this model of two types of electrons and their hybridization.

We shall make use of "atomic" operators of second quantization, introduced in the papers[7,8]: $X_{n\Lambda}^{+}$ is the creation operator of the configuration

$$X_{n\Lambda}^{+}|n\Lambda'\rangle = \delta_{0\Lambda'}|n\Lambda\rangle;$$

$Z_n^{\Lambda_1\Lambda_2} = X^{+}_{n\Lambda_1} X_{n\Lambda_2}$ is the configurational change operator at the node n. For the operators $Z_n^{\Lambda_1\Lambda_2}$ we have the following multiplication rule:[7]

$$Z_n^{\Lambda_1\Lambda_2} Z_n^{\Lambda_3\Lambda_4} = Z_n^{\Lambda_1\Lambda_4}\delta_{\Lambda_2\Lambda_3}. \tag{2.1}$$

Any operator acting on the electrons of a given atom is expressed in terms of $Z_n^{\Lambda_1\Lambda_2}$ in the following way:

$$A_n = \sum_{\Lambda_1\Lambda_2} (n\Lambda_1|A_n|n\Lambda_2) Z_n^{\Lambda_1\Lambda_2} . \tag{2.2}$$

Our model is described by the Hamiltonian

$$H = H_d + H_s + H_{sd}. \tag{2.3}$$

In the atomic Hamiltonian H_d there enter the localized single-electron states of the atoms γ and the two-electron d^2 states Γ. Here, inasmuch as the energy level of the second electron, according to the assumed model, lies above the bottom of the conduction band, i.e., in the region of positive energy, we shall assume it to be quasidiscrete (see, for example,[9]), i.e., to have a finite width W.

Thus, in the representation of the configuration change operators,

$$H_d = \sum_n \left\{ \sum_\gamma \varepsilon_1 Z_n^{\gamma\gamma} + \sum_\Gamma \varepsilon_2 Z_n^{\Gamma\Gamma} \right\} . \tag{2.4}$$

The Hamiltonian of the conductional electrons has the usual form:

$$H_s = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^{+} c_{\mathbf{k}\sigma}. \tag{2.5}$$

The Hamiltonian of the s-d interaction in the usual form is described in the following fashion:

$$H_{sd} = \sum_{nm\mathbf{k}\sigma} \left\{ T_{\mathbf{k}\sigma}^{nm} c_{\mathbf{k}\sigma}^{+} d_{nm\sigma} + \text{c.c.} \right\}, \tag{2.6}$$

where $d_{mn\sigma}$ is the annihilation operator of the d electron on node d with the projections $m\sigma$ of orbital and spin momenta, $T_{\mathbf{k}}^{nm} = (\mathbf{k}\sigma\,|\,V\,|\,nm)$ is the matrix element of hybridization of the s and d states. The operators $d^{+}_{nm\sigma}$ and $d_{nm\sigma}$ can, according to Eq. (2.2), be expressed in terms of the atomic configuration change operator. In correspondence with the assumed model, we shall assume that only the two-electron Γ states take part in the hybridization with the s electrons, so that the expressions for d^{+} and d are described approximately in the following way:

$$d_{nm\sigma}^{+} = \sum_{\gamma\Gamma} (\Gamma|d_{nm\sigma}^{+}|\gamma) Z_n^{\Gamma\gamma}, \quad d_{nm\sigma} = \sum_{\gamma\Gamma} (\gamma|d_{nm\sigma}|\Gamma) Z_n^{\gamma\Gamma}. \tag{2.7}$$

The matrix elements $(\gamma\,|\,d\,|\,\Gamma)$ are expressed in terms of the Klebsch-Gordan coefficients.

Substituting (2.7) in (2.6), we obtain the following expression for the hybridization Hamiltonian

$$H_{sd} = \sum_{\mathbf{k}\sigma} \sum_{n\gamma\Gamma} \left\{ D_{\mathbf{k}\sigma}^{n\gamma\Gamma} c_{\mathbf{k}\sigma}^{+} Z_n^{\gamma\Gamma} + \text{c.c.} \right\}, \tag{2.8}$$

$$D_{\mathbf{k}\sigma}^{n\gamma\Gamma} = \sum_{m'\sigma'} C_{mm'}^{LM_L} C_{\sigma\sigma'}^{SM_s} T_{\mathbf{k}\sigma}^{nm'}, \tag{2.9}$$

where T contains the potential V, which is created by the nucleus, with filled inner shells and with a single d electron on the outer shell of the atom.

3. The elementary excitations are considered by means of the technique of double-time temperature Green's functions. The following Green's functions are considered (we immediately write down their Fourier transforms in the energy):

$$G_{n_1n_2}^{\gamma_1\Gamma_1\Gamma_2\gamma_2}(E) = \langle\langle Z_{n_1}^{\gamma_1\Gamma_1} | Z_{n_2}^{\Gamma_2\gamma_2} \rangle\rangle_E, \quad G_{\mathbf{k}\sigma}^{n\Gamma\gamma}(E) = \langle\langle c_{\mathbf{k}\sigma} | Z_n^{\Gamma\gamma} \rangle\rangle_E,$$
$$G_{n\gamma\Gamma}^{\mathbf{k}\sigma}(E) = \langle\langle Z_n^{\gamma\Gamma} | c_{\mathbf{k}\sigma}^{+} \rangle\rangle_E, \quad G_{\mathbf{k}\sigma}(E) = \langle\langle c_{\mathbf{k}\sigma} | c_{\mathbf{k}\sigma}^{+} \rangle\rangle_E. \tag{3.1}$$

Using the commutation relations, which are easily obtained from the multiplication rule for the configuration change operators (2.1),

$$[Z_{n_1}^{\gamma_1\Gamma_1}, Z_{n_2}^{\Gamma_2\gamma_2}]_{+} = \delta_{n_1n_2}(Z_{n_1}^{\gamma_1\gamma_2}\delta_{\Gamma_1\Gamma_2} + Z_{n_1}^{\Gamma_2\Gamma_1}\delta_{\gamma_1\gamma_2}), \tag{3.2}$$

we obtain a set of equations for the Green's function, in which we perform the uncoupling

$$\langle\langle Z_n^{\gamma\gamma_1} c_{\mathbf{k}\sigma} | Z_{n_1}^{\Gamma\gamma_2} \rangle\rangle_E = \langle Z_n^{\gamma\gamma_1} \rangle G_{\mathbf{k}\sigma}^{n\Gamma\gamma_2}(E),$$
$$\langle\langle Z_n^{\Gamma_1\Gamma} c_{\mathbf{k}\sigma} | Z_n^{\Gamma\gamma} \rangle\rangle_E = \langle Z_n^{\Gamma_1\Gamma} \rangle G_{\mathbf{k}\sigma}^{n\Gamma\gamma}(E),$$
$$\langle\langle Z_n^{\gamma\gamma_1} c_{\mathbf{k}_1\sigma} | c_{\mathbf{k}\sigma}^{+} \rangle\rangle_E = \langle Z_n^{\gamma\gamma_1} \rangle G_{\mathbf{k}\sigma}(E)\delta_{\mathbf{k}\mathbf{k}_1},$$
$$\langle\langle Z_n^{\Gamma\Gamma_1} c_{\mathbf{k}_1\sigma} | c_{\mathbf{k}\sigma}^{+} \rangle\rangle_E = \langle Z_n^{\Gamma\Gamma_1} \rangle G_{\mathbf{k}\sigma}(E)\delta_{\mathbf{k}\mathbf{k}_1}. \tag{3.3}$$

Finally, we carry out averaging for those which do not depend on the number of the node and which are diagonal in the upper indices:

$$\langle Z_n^{\Lambda_1\Lambda_2} \rangle = \langle Z^{\Lambda_1} \rangle \delta_{\Lambda_1\Lambda_2} \tag{3.4}$$

and perform the Fourier transformation in k.

As a result, we obtain the set of equations for the Green's function

$$(E - \varepsilon_2 + \varepsilon_1) G_{\mathbf{k}}^{\gamma_1\Gamma_1\Gamma_2\gamma_2}(E) = \frac{K^{\gamma_1\Gamma_1}}{2\pi} \delta_{\gamma_1\gamma_2}\delta_{\Gamma_1\Gamma_2} + D_{\mathbf{k}\sigma}^{\gamma_1\Gamma_1 *} K^{\gamma_1\Gamma_1} G_{\mathbf{k}\sigma}^{\Gamma_2\gamma_2}(E),$$
$$(E - \varepsilon_{\mathbf{k}}) G_{\mathbf{k}\sigma}^{\Gamma_2\gamma_2}(E) = \sum_{\gamma\Gamma} D_{\mathbf{k}\sigma}^{\gamma\Gamma} G_{\mathbf{k}}^{\gamma\Gamma\Gamma_2\gamma_2}(E),$$
$$(E - \varepsilon_2 + \varepsilon_1) G_{\gamma_1\Gamma_1}^{\mathbf{k}\sigma}(E) = D_{\mathbf{k}\sigma}^{\gamma_1\Gamma_1 *} K^{\gamma_1\Gamma_1} G_{\mathbf{k}\sigma}(E),$$
$$(E - \varepsilon_{\mathbf{k}}) G_{\mathbf{k}\sigma}(E) = \frac{1}{2\pi} + \sum_{\gamma_1\Gamma_1} D_{\mathbf{k}\sigma}^{\gamma_1\Gamma_1} G_{\gamma_1\Gamma_1}^{\mathbf{k}\sigma}(E). \tag{3.5}$$

Here $K^{\gamma\Gamma} = \langle Z^{\gamma} \rangle + \langle Z^{\Gamma} \rangle$. We then easily find the functions $G_{\mathbf{k}}^{\gamma\Gamma\Gamma\gamma}$ and $G_{\mathbf{k}\sigma}$ that are of interest to us:

$$G_{\mathbf{k}}^{\gamma\Gamma\Gamma\gamma}(E) = \frac{1}{2\pi} \frac{K^{\gamma\Gamma}(E - \varepsilon_{\mathbf{k}})}{(E - \varepsilon_d)(E - \varepsilon_{\mathbf{k}}) + B_\sigma(\mathbf{k})}, \tag{3.6a}$$

$$G_{\mathbf{k}\sigma}(E) = \frac{1}{2\pi} \frac{E - \varepsilon_d}{(E - \varepsilon_d)(E - \varepsilon_{\mathbf{k}}) + B_\sigma(\mathbf{k})}, \tag{3.6b}$$

$$\varepsilon_d = \varepsilon_2 - \varepsilon_1, \quad B_\sigma(\mathbf{k}) = \sum_{\gamma\Gamma} |D_{\mathbf{k}\sigma}^{\gamma\Gamma}|^2 K^{\gamma\Gamma}.$$

The poles of the Green's function (3.6) determine the energy spectrum of the elementary excitations:

$$E_{1,2}(\mathbf{k}) = {}^1/_2(\varepsilon_{\mathbf{k}} + \varepsilon_d) \mp \sqrt{{}^1/_4(\varepsilon_{\mathbf{k}} - \varepsilon_d)^2 + B_\sigma(\mathbf{k})}. \tag{3.7}$$

This is the customary expression for the two hybridized bands, formed from the broad s band and the localized d level. A formula of similar type was obtained by Smith.[6] Just as in the work of Smith, the uncoupling of our levels depends on the average number of d electrons per atom. However, in the Smith model, hybridization of the s-d type occurs, while we consider the hybridization sd – d^2. Moreover, Smith considers the d electrons to be nondegenerate, two electrons with the same projections of spin, cannot, by virtue of the Pauli principle, be found in the same node simultaneously, and the d^2 state is a singlet. We also consider the degeneracy of the d levels in the projections of the orbital momenta and, in correspondence with Hund's rule, that the ground two-electron state has the spin S = 1.

The scheme of energy bands (3.7) and density of states $\rho(E)$ are shown in Fig. 1. The numbers I and IV denote the portions of the spectrum in which the bands have an "s character" and the numbers II and III indicate the "d regions." Such a division is, of course, tentative, because, after taking hybridization into account, it makes no sense to speak of pure s- or d-electron states, and the probability of the electron's being in s or d states is determined by the shape of the entire energy spectrum. However, as will be shown below, the contribution from regions II and III to the probability of the s state, and the contribution of the regions I and IV to the probability of the d state are small.

The spectrum (3.7) generally depends on the projection of the spin σ. Therefore, the average of the number of electrons in the different states can also depend on the projections of the spin momenta:

$$\langle Z^{\gamma}\rangle = P_{\sigma}, \quad \sigma = \pm{}^1/_2, \quad \langle Z^{\Gamma}\rangle = P_{M_s}, \quad M_s = 0, \pm 1. \tag{3.8}$$

The dependence on the orbital quantum numbers is lacking, since there are none in the energy spectrum.

For the study of the properties of the considered model, we must write down the closed set of equations for the determination of the occupation numbers of the one-electron P_σ and the two-electron P_{M_S} atomic states and the conduction electron distribution function

$$n_\sigma = N^{-1}\sum_{\mathbf{k}}\langle n_{\mathbf{k}\sigma}\rangle .$$

For this purpose, we express the correlation functions $\langle Z^{\gamma}\rangle$ and $\langle Z^{\Gamma}\rangle$ in terms of the Green's functions, with the help of the Lehman-Callen formula, just as has been done previously[8] (Eqs. 35), (37) and (41)). As a result, we get the set of equations (for T = 0):

$$\begin{gathered} P_{+1} = (P_{+1} + P_{+\frac{1}{2}})J_+, \quad P_0 = (P_0 + P_{-\frac{1}{2}})J_+, \\ P_0 = (P_0 + P_{+\frac{1}{2}})J_-, \quad P_{-1} = (P_{-1} + P_{-\frac{1}{2}})J_-, \end{gathered} \tag{3.9a}$$

$$n_\sigma = N^{-1}\sum_{\mathbf{k}}\left\{\frac{\varepsilon_d - E_{1\sigma}}{E_{2\sigma} - E_{1\sigma}}\Theta(\mu - E_{1\sigma}) + \frac{E_{2\sigma} - \varepsilon_d}{E_{2\sigma} - E_{1\sigma}}\Theta(\mu - E_{2\sigma})\right\},$$

Here

$$J_\sigma = N^{-1}\sum_{\mathbf{k}}\left\{\frac{\varepsilon_{\mathbf{k}} - E_{1\sigma}}{E_{2\sigma} - E_{1\sigma}}\Theta(\mu - E_{1\sigma}) + \frac{E_{2\sigma} - \varepsilon_{\mathbf{k}}}{E_{2\sigma} - E_{1\sigma}}\Theta(\mu - E_{2\sigma})\right\},$$

$$\Theta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases}. \tag{3.9b}$$

To these equations, we add the equation for the normalization of the probabilities

$$\sum_{\Lambda}{}' \langle Z_\Lambda\rangle = 1,$$

which has the form

$$(2l + 1)(P_{+\frac{1}{2}} + P_{-\frac{1}{2}}) + (2L + 1)(P_{+1} + P_0 + P_{-1}) = 1 \tag{3.10}$$

in terms of P_σ, P_{M_S}. We also add the equation for the total number of electrons in the cell

$$n_T = n_s + n_d, \quad n_s = n_{+\frac{1}{2}} + n_{-\frac{1}{2}}; \tag{3.11}$$

$$n_d = (2l + 1)(P_{+\frac{1}{2}} + P_{-\frac{1}{2}}) + 2(2L + 1)(P_{+1} + P_0 + P_{-1}).$$

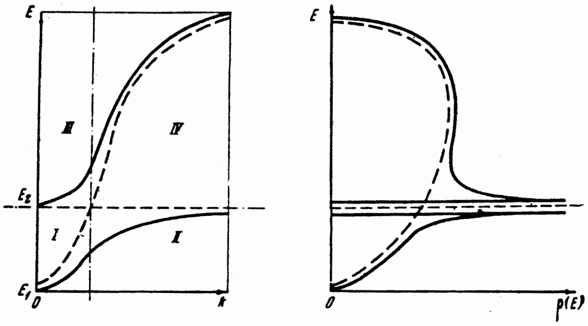

FIG. 1. Scheme of energy bands. The dashed lines indicate the energy levels ϵ_k and ϵ_d in the absence of hybridization, $\rho(E)$ is the density of states.

The eight equations (3.9a), (3.10) and (3.11) form a closed set of nonlinear equations for the eight unknowns P_σ, P_{M_S}, n_σ and n_T inasmuch as the excitation spectrum (3.7) depends in turn on the values of P_σ and P_M. Actually, by using the explicit values of the Klebsch-Gordan coefficients in Eqs. (2.9), we can show that

$$B_\pm = \xi\varepsilon_d^2(2P_{\pm 1} + P_0 + 2P_{\pm\frac{1}{2}} + P_{\mp\frac{1}{2}}). \tag{3.12}$$

The quantity ξ generally depends on k and is equal in order of magnitude to the ratio $W/(\epsilon_2 - \epsilon_1)$, where the energy W is the width of the quasidiscrete level ϵ_d.

The basis of our model is the assumption that ϵ_d is a sufficiently quasidiscrete level and, consequently, ξ is a parameter whose smallness justifies the splitting (3.3) and allows us to solve the set (3.9)–(3.11) in analytic fashion in a number of special cases. Here we shall neglect the dependence of ξ on k.

4. Thus, we must find the solutions of the set (3.9)–(3.11). In addition to the eight enumerated unknowns, there also appears the parameter μ—the chemical potential—by the variation of which we can change the total number of electrons per atom.

Generally speaking, the solution of our system is difficult without machine calculations, since the integrals J_+ and J_- are expressed in terms of elliptic functions. However, there are a number of cases in which the correlation functions are found approximately. Furthermore, the analysis of the system is materially simplified if we consider the quantities J_+, J_- and μ as independent variables. It is easy to show from the set (3.9) that

$$\begin{gathered} P_{\pm 1} = Z^{-1}J_\pm^2(1 - J_\mp)^2, \quad P_0 = Z^{-1}J_+J_-(1 - J_+)(1 - J_-), \\ P_{\pm\frac{1}{2}} = Z^{-1}J_+(1 - J_\pm)(1 - J_\mp)^2. \end{gathered} \tag{4.1}$$

The quantity Z is determined by the normalization condition (3.10):

$$\begin{aligned} Z = {} & (2l + 1)[J_+(1 - J_+)(1 - J_-)^2 + J_-(1 - J_-)(1 - J_+)^2] \\ & + (2L + 1)[J_+^2(1 - J_-)^2 + J_+J_-(1 - J_+)(1 - J_-) + J_-^2(1 - J_+)^2]. \end{aligned} \tag{4.2}$$

Substituting (4.1) in (3.12), we get

$$B_\pm = Z^{-1}\xi\varepsilon_d^2(2L + 1)(1 - J_\mp)(2J_\pm + J_\mp - 3J_+J_-), \tag{4.3}$$

and our problem reduces to the solution of two nonlinear algebraic equations:

$$J_+ = F(J_+, J_-, \mu), \quad J_- = F(J_-, J_+, \mu). \tag{4.4}$$

The function F is determined in explicit fashion by the form of the integral J_σ in (3.9b) with account of (4.3).

Let us consider the nonmagnetic solution. Then $J_+ = J_- = J$, and the set (4.4) reduces to a single equation

$$J = \int d\varepsilon S(\varepsilon)\left\{\frac{\varepsilon - E_1}{E_2 - E_1}\Theta(\mu - \mathrm{E}_1) + \frac{E_2 - \varepsilon}{E_2 - E_1}\Theta(\mu - E_2)\right\}. \quad (4.5)$$

Here

$$S(\varepsilon) = \frac{dN(\varepsilon)}{d\varepsilon} \qquad N(\varepsilon) = N^{-1}\sum_{\mathbf{k}}\Theta(\varepsilon - \varepsilon_k). \quad (4.6)$$

Let the chemical potential be found in region I (Fig. 1), i.e., $\Delta \gg \xi^{1/2}\epsilon_d$, where $\Delta = \epsilon_d - \mu$. Then we have, in first order in ξ (assuming $\epsilon_k = k^2$),

$$J = \frac{B}{2\pi^2}\int_0^\mu \frac{\varepsilon^{1/2} d\varepsilon}{(\varepsilon_d - \varepsilon)^2}, \qquad B = \xi\varepsilon_d^2\frac{3}{2}\,\frac{2L+1}{2l+1}, \quad (4.7)$$

$$P_{\pm 1/2} = \frac{1}{2(2l+1)}\left[1 - \frac{3}{2}\,\frac{2L+1}{2l+1}J\right], \quad P_{+1} = P_0 = P_{-1} = \frac{J}{2(2l+1)},$$

$$n_+ = n_- = N(\mu)(1 - 3B/2\mu\Delta) - J.$$

In the case considered, the effective mass on the Fermi surface is equal to

$$m^* = \left(\frac{d^2E_1}{dk^2}\right)^{-1}\bigg|_\mu = m_0(1 - B\Delta^{-2} - 4B\mu\Delta^{-3}), \quad m_0 = \left(\frac{d^2\varepsilon_k}{dk^2}\right)^{-1}\bigg|_\mu \quad (4.8)$$

i.e., the effective mass of the hybridized state only slightly exceeds the mass of the bare conduction electron and, consequently, the spectrum in region I has an "s character."

If the chemical potential intersects the level E_1 in region II, i.e., $0 < \Delta \ll \xi^{1/2}\epsilon_d$, it is sufficient to compute the integral (4.5) in the zeroth approximation in ξ:

$$J = N(\varepsilon_F) - N(\varepsilon_d), \qquad \varepsilon_F = \varepsilon_d + B\Delta^{-1},$$
$$B = \xi\varepsilon_d^2 3(2L+1)Q(J), \quad (4.9)$$

$$P_{\pm 1/2} = (1 - J)Q(J), \quad P_1 = P_0 = P_{-1} = JQ(J),$$

$$Q^{-1}(J) = 2(2l+1)(1-J) + 3(2L+1)J, \quad n_+ = n_- = N(\varepsilon_d),$$

$$(m^*)^{-1} = m_0^{-1}\left[\Delta^2B^{-1} - 2m_0\Delta^3B^{-2}\left(\frac{d\varepsilon_k}{dk}\right)^2_{\varepsilon_F}\right], \quad m_0^{-1} = \frac{d^2\varepsilon_k}{dk^2}\bigg|_{\varepsilon_F}. \quad (4.10)$$

We see that the effective mass is very large (and negative) in this case. This gives us reason for saying that the spectrum has a "d character."

The equations (4.9) determine the occupation number in implicit fashion, and we see that with increase in μ (i.e., as $\Delta \to 0$), the quantity J increases and so does n_{d^2}—the number of electrons in the d^2 states:

$$n_{d^2} = 2(2L+1)(P_{+1} + P_0 + P_{-1}).$$

The number of electrons in d^1 states decreases here, and the number of s electrons remains approximately at a constant level.

We now investigate the possibility of a magnetic solution of the set (4.4), when $J_+ \neq J_-$. In the general case, the set is not given to analytic investigation. However, in the case $\epsilon_d \ll \epsilon_c$, $N(\epsilon_c) = 1$ (ϵ_c is the width of the conduction band), Eqs. (4.4) are rather easily solved if it is assumed that the chemical potential is such that the subband E_1^+ is completely filled and the subband E_1^- intersects the chemical potential in region II, and

$$\Delta^2 \ll B_-, \quad B_- \ll \varepsilon_d\Delta. \quad (4.11)$$

In this case, the integrals $J_\pm$ can be computed from Eq. (4.9)

$$J_\pm = N(\varepsilon_F^\pm) - N(\varepsilon_d), \qquad \varepsilon_F^\pm = \varepsilon_d + B_\pm\Delta^{-1}.$$

Under our assumptions, $\epsilon_F^+ = \epsilon_c$ and therefore

$$J_+ = 1 - N(\varepsilon_d).$$

Using the second condition of (4.11), we find

$$J_- = (\varepsilon_F^- - \varepsilon_d)\frac{dN(\varepsilon)}{d\varepsilon}\bigg|_{\varepsilon_d} = B_-\Delta^{-1}S(\varepsilon_d). \quad (4.12)$$

It then follows that $J_- \ll \epsilon_d S(\epsilon_d) \sim N(\epsilon_d) \ll 1$. Thus J_+ is close to unity and J_- is close to zero. In this case, Eq. (4.3) gives

$$B_+ \approx 2\xi\varepsilon_d^2, \quad B_- \approx \xi\varepsilon_d^2 N(\varepsilon_d). \quad (4.13)$$

Substituting B_+ in the equation $\epsilon_F^+ = \epsilon_c$, we find

$$\Delta \equiv \Delta_c = \frac{B_+}{\varepsilon_c - \varepsilon_d} \approx \frac{2\xi\varepsilon_d^2}{\varepsilon_c}. \quad (4.14)$$

Hence, and also from (4.12) and (4.13), we get

$$J_- = \varepsilon_c S(\varepsilon_d)N(\varepsilon_d). \quad (4.15)$$

Using this expression, we can easily see that the inequalities (4.11) are equivalent to the inequalities

$$\xi\left(\frac{\varepsilon_d}{\varepsilon_c}\right) \ll \left(\frac{\varepsilon_d}{\varepsilon_c}\right)^{1/2} \ll 1, \quad (4.16)$$

which are satisfied automatically whenever $\epsilon_d \ll \epsilon_c$. From (4.1), we find

$$P_{+1} = (2L+1)^{-1}\left[1 - \frac{2l+1}{2L+1}N(\varepsilon_d)\right], \quad P_{+1/2} = (2L+1)^{-1}N(\varepsilon_d),$$

$$n_\pm = N(\varepsilon_d), \quad P_0 \approx 0, \quad P_{-1} \approx 0, \quad P_{-1/2} \approx 0, \quad (4.17a)$$

$$n_T = 2 + \left(2 - \frac{2l+1}{2L+1}\right)N(\varepsilon_d). \quad (4.17b)$$

Here the magnetic moment, in units of μ_B, is equal to

$$s = n_+ - n_- + (2l+1)(P_{+1/2} - P_{-1/2}) + 2(2L+1)(P_{+1} - P_{-1})$$
$$= n_T - 2N(\varepsilon_d). \quad (4.18)$$

Thus, we have found the solution of the set (3.9)–(3.11) for which the d electrons are virtually completely polarized, while the superimposed magnetization of the s electrons is negligibly small (see Fig. 2). In order to prove that the magnetic solution thus found is more advantageous energetically than the nonmagnetic solution with the same number of electrons (4.17b), we show that the chemical potential of the nonmagnetic solution is higher. It is easy to see that upon satisfaction of the inequality $\epsilon_d \ll \epsilon_c$ the total number of electrons in the nonmagnetic case is equal

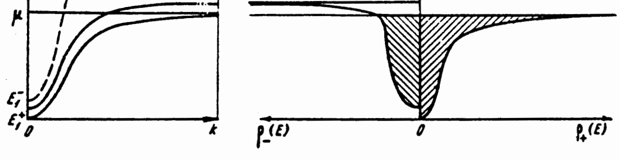

FIG. 2. Scheme of filling of the energy levels in the case of almost complete magnetic ordering.

to the quantity (4.17b) if

$$J = 1 - {}^3\!/_2 N(\varepsilon_d). \tag{4.19}$$

Here $N(\epsilon_F) = 1 - \frac{1}{2}N(\epsilon_d)$, $\epsilon_F = \epsilon_d + \xi\epsilon_d^2\Delta_{\text{nonmag}}^{-1}$. It then follows that $\epsilon_F \sim \epsilon_c$ and

$$\Delta_{\text{nonmag}} \approx \xi\varepsilon_d^2/\varepsilon_c = {}^1\!/_2\Delta_c. \tag{4.20}$$

We thus see that the magnetic solution (4.17) is energetically more profitable (see (4.14)).

It is easy to show that the nonmagnetic solution (4.7) is the only solution of the set (3.9)–(3.11) for the condition $\Delta \gg \xi^{1/2}\epsilon_d$. Inasmuch as we have just now found the magnetic solution for the case $\Delta \approx \xi\epsilon_d^2/\epsilon_c$ with almost complete polarization, it is clear that a critical value Δ_{cr} should exist, such that only for $\Delta < \Delta_{cr}$ is there a second, magnetic solution along with the nonmagnetic.

For the determination of the critical value of the parameter μ for which the number of real solutions changes in the set of algebraic equations (4.4), it is necessary and sufficient to find the solution $\mu = \mu_c$ for which the directions of the tangents coincide at the point of intersection of the curves (4.4a) and (4.4b). This requirement leads to the equation (see[10])

$$\left.\frac{dF(J_+, J_-)}{dJ_+}\right|_{J_+=J_-} - \left.\frac{dF(J_+, J_-)}{dJ_-}\right|_{J_+=J_-} = 1. \tag{4.21}$$

For $\epsilon_d \ll \epsilon_c$ this equation has the form

$$\xi\frac{\varepsilon_d^2}{\Delta_{cr}}S(\varepsilon_F)(2L+1)\frac{1+3J}{J(1-J)[2(2l+1)(1-J)+3(2L+1)J]} = 1. \tag{4.22}$$

The solutions of this equation depend on the ratio ϵ_d/ϵ_c. In particular, by taking $N(\epsilon_d) = 10^{-1}$, we find, numerically, $\Delta_c = 0.3\,\xi\epsilon_d^2$, $n_T = 1.73$. Comparison of this value of n_T with the expression (4.17b) shows that for $\epsilon_d \ll \epsilon_c$, there is a comparatively broad region of values in which there exists a state of the system with spontaneous magnetization (and which is energetically profitable). The increase in the chemical potential from the value $\mu = \epsilon_d - \Delta_c$ to $\mu = \epsilon_d - \frac{1}{2}\Delta_c$ leads to a gradual decrease in the spontaneous moment from its maximum value to zero. Thanks to the modeling assumption ξ = const, there is a gap in the spectrum, and for

$$n_T{}^c = 2 + N(\varepsilon_d)\left(2 - \frac{2}{3}\frac{2l+1}{2L+1}\right)$$

our system takes on the character of a semiconductor.1) However, too great a value should not be given to this conclusion, inasmuch as first, in the more realistic model, one should expect that the level ϵ_d intersect several conduction bands and, second, the quantity ξ can generally vanish on the boundaries of the Brillouin zone. It is clear that the region of existence of a magnetic solution here becomes smaller than when ξ = const, because in this case there is a second solution ($\Delta = \Delta'_{cr}$) ($\Delta_c < \Delta'_{cr} < \Delta_{cr}$) for which the magnetic solution of the set (3.9)–(3.11) again vanishes. When the total number of particles exceeds the value n_T^c, filling of the band $E_2(k)$ begins (see (3.7)). It is easy to show that the magnetic solution of the system is lacking in this case.

5. In conclusion, it is useful again to compare the principles involved in the work of Smith[6] and in our model. Essentially, there is an alternative in these two works relative to the mutual position of the s and d levels in the crystal (see Fig. 3). Smith assumed that filling of the energy levels takes place in the following order: first, the lowest level of the s band is filled, then the localized d level. The third electron, because of the strong intra-atomic correlations, is practically never localized at a node and is also in the broad conduction band. It is assumed in our model that the single-electron level is filled first. To the second and third electrons on the node there is the "choice" of being in the collectivized s state or in the quasilocalized d state in a cell where there is already one electron.

A different form of energy spectra leads to different reasons for magnetic ordering and to different regions of existence of magnetism. In the Smith model, as has already been mentioned, two electrons can be found at a single node, having opposite spin directions but such a situation almost never occurs, because of the electrostatic repulsion. The possibility of ferromagnetism in this model is due to the fact that the energy of the subband with given spin is lowered in hybridization by an amount that is the larger the smaller the number of electrons in the system with opposing spins. Here, such a lowering takes place only for $\mu < \epsilon$, i.e., when the mean number of electrons per atom is not greater than unity.

In our model, the d level is assumed to be degenerate, the magnetic electrons, in contrast with the Smith model, spend a larger portion of time in the two-electron atomic states, where Hund's rule is satisfied. Although the mechanism for the appearance of magnetism in our case is the same as Smith's (lowering of the band energy in hybridization), the region of existence of the ferromagnetic phase is different: that situation is most favorable for magnetic ordering in which about two electrons come to the atom. It can be shown that the Smith model corresponds to the assumption that atomic states of the type $3d^{10}4s$, $3d^94s^2$ are realized in a crystal of a transition metal, while in our model, the states $3d^84s^2$, $3d^94s$ are considered to be the most important, as was formerly proposed by Van Vleck.[11]

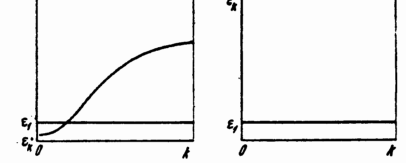

FIG. 3. Position of the electron levels in the Smith model (a) and in the present research (b).

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1) At first glance, it seems odd that the band E_1 is filled for a non-integer value of n_T. This is connected with the fact that, in contrast with the usual band theory, we have here a hybridization between states with different statistical weights ($g_s = 2$, $g_d = 1$). For example, the effective statistical weight g_{eff} of the hybridized band E_1, defined as $g_{\text{eff}} = (n_T - 1)/N(\epsilon_F)$, changes from 2 to 1 in the change of ϵ_F from 0 to ϵ_c.

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265