Dynamic mixing of localized and collectivized electron states in transition metals

E. V. Kuz'min and I. S. Sandalov

Physics Institute, Siberian Division, USSR Academy of Sciences

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A system of ineracting collectivized (*c*) and localized (*d*) electrons in a transition metal is considered. The free *c* electrons form a broad band and the *d* electrons from atomic-type states that can be described by means of Hubbard operators. It is shown that when the chemical potential is exponentially close to the difference between the $(n+1)$- and n-electron *d* terms the system is unstable with respect to mixing of *c* and *d* terms. Dynamic hybridization effects (in contrast to the usually considered hybridization due to the crystal field) are taken into account in a self-consistent manner by introducing the respective anomalous averages. The ground state of the system in the paramagnetic phase is found in the logarithmic approximation and criteria for the appearance of ferromagnetism are formulated.

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1. INTRODUCTION

It is customary in the description of the properties of transition metals to start with subdivision of the electronic states into collectivized (former valent s and p electrons) and d states. Collectivized or c electrons make up a broad conduction band which is approximately half-filled, and are described within the framework of the band theory. The states of the d electrons in transition metals, on the other hand, are intermediate between purely localized (atomic) and collectivized, so that their description entails fundamental difficulties. Although there are arguments both in favor of the band description of the d electrons and in favor of the atomic description, nevertheless the importance of the intraatomic correlations requires that preference be given to the latter, at least as the zero-order approximation. A clear example of this approach is the well-known Hubbard model[1]. If the term of the d(f) ion lies below the bottom of the conduction band and the intraatomic interactions greatly exceed all others, then it can be assumed that the d(f) electrons form a "rigid" spin. In this case the interaction of the conduction electrons with the d(f) electrons can be described within the framework of the s–d(f) exchange model as an interaction between two autonomous subsystems with a conserved number of electrons. This situation is realized in many rare-earth metals.

In transition metals of the iron group, however, and also in certain lanthanides, a situation is realized in which the atomic levels fall in the conduction band and are transformed into so-called resonance levels. The concept of d resonances is presently universally accepted, and is used to calculate the band structure of d metals with allowance for hybridization of the c and d states (for a detailed discussion see[2,3]).

Smith[4], Maksimov and Kikoin[5], and Didukh and Stasyuk[6] considered the influence of intraatomic d–d correlations on the energy spectrum and on the magnetic properties of a d metal; it was assumed that the c–d hybridization is due to the action of the crystal field, i.e., it is a one-particle effect, just as in Anderson's case[17] and in the band-structure theories[2].

It was shown in[8] that mixing of the c and d states can result from their dynamic (Coulomb) interaction. Indeed, in this case there are two channels for the scattering of the conduction electrons (e) by the d ion with n localized electrons:

1) $e + d(n) \rightarrow e' + d'(n)$,

2) $e + d(n) \rightarrow d^*(n+1) \rightarrow e' + d'(n)$.

The first channel corresponds to elastic scattering and is not accompanied by a change in the number of electrons in the c and d subsystems. The scattering in the second channel (via the compound ion), as shown in[8], can lead under certain conditions to a phase transition into the state of supermixing of c and d electrons. However, Zaslavskiĭ et al.[8] considered the simplest model of the system of two-level atoms and spinless fermions.

In this paper we consider a more realistic model of a d(f) metal which takes into account the spin states of the d and c electrons. Inclusion of the spin is fundamental for two reasons: first, it becomes possible to consider exchange effects and magnetic ordering; second, the "atomic" d subsystem becomes a p-level system ($p \geq 3$), which leads to a nonlinear connection between the c and d states even within the framework of the model Hamiltonian.

We consider below the susceptibility of a system with respect to a mixing c–d perturbation and find the conditions for the onset of instability with allowance for not only Coulomb but also (in addition to[8]) exchange interaction. Further, within the framework of the model Hamiltonian we determine in self-consistent fashion the effective parameter of the mixing interaction in the paramagnetic state and formulate criteria for the onset of ferromagnetism in the supermixing phase at T = 0.

2. THE HAMILTONIAN

We consider the model of a crystal with contact interaction between the c and d electrons. We assume for simplicity that the latter behave like s electrons, as in the Hubbard model[1], so that there are four states at the site: $|0)$—a hole, i.e., a state without a d electron, $|\sigma)$—a one-electron state with S = 1/2 and spin projection σ, and a two-electron state $|2)$ with S = 0. We represent the Hamiltonian of the model in the form

$$H=H_0+H_1, \tag{1}$$

$$H_0=\sum_{\mathbf{k}\sigma}\varepsilon_{\mathbf{k}}c_{\mathbf{k}\sigma}^{+}c_{\mathbf{k}\sigma}+\sum_{\mathbf{f}\sigma}\varepsilon_{1}d_{\mathbf{f}\sigma}^{+}d_{\mathbf{f}\sigma}+\frac{1}{2}U\sum_{\mathbf{f}\sigma}d_{\mathbf{f}\sigma}^{+}d_{\mathbf{f}\sigma}d_{\mathbf{f},-\sigma}^{+}d_{\mathbf{f},-\sigma}-\mu N_e,$$

$$H_1=\frac{1}{N}\sum_{\mathbf{k}\mathbf{k}'}\sum_{\sigma\sigma'\mathbf{f}}e^{i(\mathbf{k}-\mathbf{k}')\mathbf{f}}[Vd_{\mathbf{f}\sigma}{}^{+}d_{\mathbf{f}\sigma}\overset{+}{c}_{\mathbf{k}\sigma'}c_{\mathbf{k}'\sigma'}-Jd_{\mathbf{f}\sigma}{}^{+}d_{\mathbf{f}\sigma'}\overset{+}{c}_{\mathbf{k}\sigma'}c_{\mathbf{k}'\sigma}]$$
$$+\frac{1}{\sqrt{N}}\sum_{\mathbf{k}\mathbf{f}\sigma}[Qe^{i\mathbf{k}\mathbf{f}}c_{\mathbf{k}\sigma}{}^{+}d^{+}_{\mathbf{f},-\sigma}d_{\mathbf{f},-\sigma}d_{\mathbf{f}\sigma}+Q^{*}e^{-i\mathbf{k}\mathbf{f}}d_{\mathbf{f}\sigma}{}^{+}d^{+}_{\mathbf{f},-\sigma}d_{\mathbf{f},-\sigma}c_{\mathbf{k}\sigma}].$$

In the Hamiltonian H_0, which describes the noninteracting c and d electrons, we have introduced the following notation: $\overset{+}{c}_{\mathbf{k}\sigma}$ and $c_{\mathbf{k}\sigma}$ are the Fermi creation and annihilation operators for conduction electrons with quasimomentum $\mathbf{k}$, spin projection σ, and dispersion law $\epsilon_{\mathbf{k}}$; $d^{+}_{\mathbf{f}\sigma}$ and $d_{\mathbf{f}\sigma}$ are the Fermi creation and annihilation operators of d electrons in the crystal-lattice site $\mathbf{R}_{\mathbf{f}}\equiv\mathbf{f}$ with spin projection σ; ϵ_1 is the energy of the one-electron state $|\sigma)$; U is the energy of the Coulomb repulsion in the two-electron state; μ is the chemical potential, and $\hat{N}_e$ is the operator of the total number of electrons (the c and d operators anticommute):

$$\hat{N}_e=\sum_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}{}^{+}c_{\mathbf{k}\sigma}+\sum_{\mathbf{f}\sigma}d_{\mathbf{f}\sigma}{}^{+}d_{\mathbf{f}\sigma}. \tag{2}$$

In the Hamiltonian H_1, which describes the interaction between the d and c electrons, N is the number of atoms in the crystal, V and J are respectively the Coulomb and exchange integrals, and Q is the integral of the dynamic "mixing" interaction:

$$Q=\int dr\,dr'\,W_{\mathbf{f}}^{*}(r)\Phi_{\mathbf{f}}^{*}(r')v(r,r')\Phi_{\mathbf{f}}(r')\Phi_{\mathbf{f}}(r),$$

where $W_{\mathbf{f}}$ is the Wannier function of the c electron, $\Phi_{\mathbf{f}}$ is the atomic function of the d electron, and v is the screened Coulomb interaction.

Since the intraatomic electron-electron interaction U is comparable in order of magnitude with the Fermi energy (or with the width of the band) of the conduction electrons, it is taken into account already in the zero-order approximation. The Hamiltonian H_0 assumes a simple form in the representation of the Hubbard operators, the properties of which are described in a number of papers[1,5]. For the considered states $|p)=|0)$, $|\sigma)$ and $|2)$ the relation between the operators $d_{\mathbf{f}\sigma}$ and the Hubbard operators $X_{\mathbf{f}}^{pq}$, which transform the ion from the state $|q)$ into the state $|p)$, takes the form

$$d_{\mathbf{f}\sigma}=X_{\mathbf{f}}{}^{0\sigma}+\eta(\sigma)X_{\mathbf{f}}{}^{-\sigma 2},\qquad d_{\mathbf{f}\sigma}{}^{+}=X_{\mathbf{f}}{}^{\sigma 0}+\eta(\sigma)X_{\mathbf{f}}{}^{2,-\sigma},$$
$$\eta(\sigma)=\begin{cases}+1, & \sigma=\uparrow(+)\\ -1, & \sigma=\downarrow(-)\end{cases}. \tag{3}$$

We shall henceforth consider only cases in which the d electrons are either in one-electron or two-electron states. This allows us to neglect transitions to the state $|0)$, so that the normalization condition for the X operators takes the form

$$\sum_{\sigma}X_{\mathbf{f}}{}^{\sigma\sigma}+X_{\mathbf{f}}{}^{22}=1. \tag{4}$$

When these circumstances are taken into account we have, apart from an inessential constant, the Hamiltonian of the system in the X representation:

$$H=H_0+H_1,$$
$$H_0=\sum_{\mathbf{k}\sigma}\xi_{\mathbf{k}}c_{\mathbf{k}\sigma}{}^{+}c_{\mathbf{k}\sigma}+\sum_{\mathbf{f}}[(\varepsilon_1-\mu)\sum_{\sigma}X_{\mathbf{f}}{}^{\sigma\sigma}+(\varepsilon_2-2\mu)X_{\mathbf{f}}{}^{22}],$$
$$H_1=-\frac{1}{N}\sum_{\mathbf{f}\mathbf{k}\mathbf{p}\sigma}e^{i(\mathbf{k}-\mathbf{p})\mathbf{f}}[VX_{\mathbf{f}}{}^{\sigma\sigma}c_{\mathbf{k}\sigma}{}^{+}c_{\mathbf{p}\sigma}+(V-J)X_{\mathbf{f}}{}^{-\sigma,-\sigma}c_{\mathbf{k}\sigma}{}^{+}c_{\mathbf{p}\sigma}+JX_{\mathbf{f}}{}^{-\sigma\sigma}c_{\mathbf{k}\sigma}{}^{+}c_{\mathbf{p},\sigma}]$$
$$+\frac{1}{\sqrt{N}}\sum_{\mathbf{k}\mathbf{f}\sigma}[Q\eta(\sigma)e^{i\mathbf{k}\mathbf{f}}c_{\mathbf{k}\sigma}{}^{+}X_{\mathbf{f}}{}^{-\sigma 2}+Q^{*}\eta(\sigma)e^{-i\mathbf{k}\mathbf{f}}X_{\mathbf{f}}{}^{2,-\sigma}c_{\mathbf{k}\sigma}], \tag{5}$$

where $\xi_{\mathbf{k}}=\epsilon_{\mathbf{k}}-\mu$ and $\epsilon_2=2\epsilon_1+U$ is the energy of the two-electron state. The initial energy spectrum of the considered model is shown schematically in Fig. 1: the difference between the two-electron and one-electron terms $\epsilon_2-\epsilon_1$ "intersects" a conduction band of width W. It is assumed that the chemical potential is $\mu\sim\omega\equiv\epsilon_2-\epsilon_1$, but nevertheless $V, J\ll\mu$.

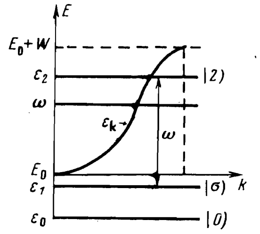


FIG. 1. The initial energy spectrum ($\epsilon_{\mathbf{k}=0}=E_0$ is the "bottom" of the c band, and the energy is reckoned from the "hole" state $|0)$).

In addition, owing to the oscillatory character of the atomic d functions, we have $Q\leq V, J$. We note that formally the Q interaction in the Hamiltonian (5) has the same structure as the hybridized Anderson interaction[7] considered in the aforementioned papers[4-6].

3. POSSIBLE INSTABILITY OF THE SYSTEM WITH RESPECT TO MIXING

In systems with localized levels "imbedded" in conduction bands, the degeneracy gives rise to competition in the filling of the electronic states. Thus, if the one-electron states ϵ_1 in Fig. 1 are completely filled and the band begins to be filled, then at $\epsilon_{\mathbf{k}}\sim\omega$ the electrons either remain in the band or fill the two-electron localized levels[1)] ϵ_2. We shall show that this degeneracy is lifted and a new hybridized ground state is produced if a dynamic interaction exists between the d and c electrons.

We introduce the retarded commutator Green's function[9]

$$\langle\langle X_{\mathbf{f}}{}^{2,-\sigma}c_{\mathbf{q}\sigma}(\tau)|\overset{+}{c}_{\mathbf{q}'\sigma'}X_{\mathbf{f}'}^{-\sigma'2}(0)\rangle\rangle\equiv G_{\mathbf{f}\mathbf{q}\sigma}^{\mathbf{f}'\mathbf{q}'\sigma'} \tag{6}$$

(the time τ pertains to the entire operator $X_{\mathbf{f}}^{2,-\sigma}c_{\mathbf{q}\sigma}$), which is proportional to the susceptibility of the system relative to the mixing Q interaction in the Hamiltonian H_1. The equation of motion for the Fourier transform of (6) is

$$[E-(\xi_{\mathbf{q}}-\Delta)]G_{\mathbf{f}\mathbf{q}\sigma}^{\mathbf{f}'\mathbf{q}'\sigma'}(E)=\frac{i}{2\pi}K_{\mathbf{f}\mathbf{q}\sigma}^{\mathbf{f}'\mathbf{q}'\sigma'}-\frac{1}{N}\sum_{\mathbf{k}\mathbf{p}}e^{i(\mathbf{k}-\mathbf{p})\mathbf{f}}\langle\langle VX_{\mathbf{f}}^{2,-\sigma}\overset{+}{c}_{\mathbf{k},-\sigma}c_{\mathbf{p},-\sigma}c_{\mathbf{q}\sigma}$$
$$+(V-J)X_{\mathbf{f}}{}^{2,-\sigma}c_{\mathbf{k}\sigma}{}^{+}c_{\mathbf{p}\sigma}c_{\mathbf{q}\sigma}+JX_{\mathbf{f}}^{2,\sigma}c_{\mathbf{k}\sigma}{}^{+}c_{\mathbf{p},-\sigma}c_{\mathbf{q}\sigma}|A'\rangle\rangle_E$$
$$-\frac{1}{N}\sum_{\mathbf{p}\mathbf{j}}e^{i(\mathbf{q}-\mathbf{p})\mathbf{j}}\langle\langle VX_{\mathbf{f}}^{2,-\sigma}X_{\mathbf{j}}^{\sigma\sigma}c_{\mathbf{p}\sigma}+(V-J)X_{\mathbf{f}}^{2,-\sigma}X_{\mathbf{j}}^{-\sigma,-\sigma}c_{\mathbf{p}\sigma}$$
$$+JX_{\mathbf{f}}^{2,-\sigma}X_{\mathbf{j}}^{-\sigma,\sigma}c_{\mathbf{p},-\sigma}|A'\rangle\rangle_E, \tag{7}$$

where

$$A'\equiv\overset{+}{c}_{\mathbf{q}'\sigma'}X_{\mathbf{f}'}^{-\sigma',2};\quad\Delta=\omega-\mu,\qquad K_{\mathbf{f}\mathbf{q}\sigma}^{\mathbf{f}'\mathbf{q}'\sigma'}\equiv\langle[X_{\mathbf{f}}{}^{2,-\sigma}c_{\mathbf{q}\sigma},\overset{+}{c}_{\mathbf{q}'\sigma'}X_{\mathbf{f}'}{}^{-\sigma',2}]\rangle.$$

Recognizing that V/μ, $J/\mu\ll 1$, we can confine ourselves to the simplest splittings. In terms containing summation over the sites, we separate the term with $\mathbf{f}=\mathbf{j}$ and use the rule for the multiplication of Hubbard operators, while the correlation between the different sites $\mathbf{f}\neq\mathbf{j}$ will be taken into account in the self-consistent-field approximation

$$\langle\langle X_{\mathbf{j}}^{2,-s}X_{\mathbf{f}}{}^{\sigma\sigma}c_{\mathbf{p}s}|\rangle\rangle\to N_\sigma\langle\langle X_{\mathbf{j}}^{2,-s}c_{\mathbf{p}s}|\rangle\rangle,\quad N_\sigma\equiv\langle X_{\mathbf{f}}{}^{\sigma\sigma}\rangle,$$
$$\langle\langle X_{\mathbf{j}}^{2,-s}X_{\mathbf{f}}{}^{-s,s}c_{\mathbf{p},-s}|\rangle\rangle\to 0.$$

We confine ourselves to searches for solutions that are homogeneous over the crystal, so that $\langle X_{\mathbf{f}}^{\sigma\sigma}\rangle$ is assumed to be independent of the number of the site. The Green's functions that contain three c operators in the left-hand bracket will be replaced by functions corresponding to the random-phase approximation, for example

$$\langle\langle X_j^{2,-s}c_{ks}^+c_{ps}c_{qs}|\rangle\rangle\to\delta_{kp}G_{jqs}^{j'q's'}(E)n_k^s-\delta_{kq}G_{jps}^{j'q's'}(E)n_k^s,$$
$$n_k^s\equiv\langle c_{ks}^+c_{ks}\rangle.$$

The function $G_{fq\sigma}^{f'q'\sigma'}$ is now connected with itself and with the function $G_{fq,-\sigma}^{f'q'\sigma'}$. Thus, we have the system of equations

$$G_{fq\sigma}^{f'q'\sigma'}(E)=\frac{i}{2\pi}K_{fq\sigma}^{f'q'\sigma'}\frac{1}{E-B_q^\sigma}-\frac{(V-J)(1-n_q^\sigma)-JN_{-\sigma}}{E-B_q^\sigma}e^{iqf}G_{f\sigma}^{f'q'\sigma'}(E)$$
$$-\frac{J(1-n_q^\sigma)}{E-B_q^\sigma}e^{iqf}G_{f,-\sigma}^{f'q'\sigma'}(E),\tag{8}$$

where, in the assumed approximation,

$$K_{fq\sigma}^{f'q'\sigma'}=\delta_{qq'}\delta_{\sigma\sigma'}\delta_{ff'}[N_2(1-n_q^\sigma)-n_q^\sigma N_{-\sigma}]-\delta_{ff'}\delta_{-\sigma,\sigma'}\langle c_{q',-\sigma}^+c_{q\sigma}X_f^{\sigma,-\sigma}\rangle,$$
$$B_q^\sigma=\xi_q-\Delta-V(1-N_2)-Vn_c+JN_{-\sigma},$$
$$n_c=N^{-1}\sum_{k\sigma}n_k^\sigma,\quad N_2=\langle X_f^{22}\rangle.$$

It follows from the system (8) that the poles of the susceptibility of interest to us (with the exception of the trivial case $E=B_q^\sigma$) are determined by the poles of the function

$$G_{f\sigma}^{f'q'\sigma'}(E)=\frac{1}{N}\sum_q e^{-iqf}G_{fq\sigma}^{f'q'\sigma'}(E).$$

Neglecting the transverse spin correlations in the expression for $K_{fq\sigma}^{f'q'\sigma'}$ (they are vanishingly small in the ground state at T = 0), we obtain from the system (8)

$$G_{f\sigma}^{f'q\sigma}(E)={}^1/_2i\pi^{-1}\delta_{ff'}e^{-iqf}[N_2(1-n_q^\sigma)-n_q^\sigma N_{-\sigma}][1+(V-J)L_{-\sigma}-JN_\sigma B^{-\sigma}]$$
$$\times\{(E-B_q^\sigma)[[1+(V-J)L_{-\sigma}-JN_{-\sigma}B^\sigma][1+(V-J)L_\sigma-JN_\sigma B^{-\sigma}]-J^2L_\sigma L_{-\sigma}]\}^{-1}.\tag{9}$$

Here

$$L_\sigma(E)=\frac{1}{N}\sum_k\frac{1-n_k^\sigma}{E-B_k^\sigma},\qquad B^\sigma(E)=\frac{1}{N}\sum_k\frac{1}{E-B_k^\sigma}.$$

In the paramagnetic state, the occupation numbers and the coefficients B^σ etc. do not depend on the spin. Putting $N_\sigma=N_1/2$ and $B_q^\sigma=B_q$, we obtain from (9) an equation for determination of the poles of interest to us:

$$[1+(V-J)L(E)-{}^1/_2JN_1B(E)]^2-J^2L^2(E)=0.\tag{10}$$

It follows from (10) that in order for the system to become unstable with respect to the mixing interaction it is necessary in the static case (E = 0) to satisfy at least one of the conditions:

$$L_1(0)=-(V-2J)^{-1}[1-{}^1/_2JN_1B(0)]\ \text{or}\ L_2(0)=-V^{-1}[1-{}^1/_2JN_1B(0)].\tag{11}$$

To explain the physical meaning of these conditions, we obtain B(0) and $L_{1,2}(0)$ in the rectangular-band model for collectivized electrons. In this case their density for one spin direction is given in the form

$$g(E)=\begin{cases}g_0, & E\in[E_0,E_0+W]\\ 0, & \text{outside of this interval,}\end{cases}\tag{12}$$

Integrating the conditions (11) at T = 0 and omitting the insignificant addition $JB\ll1$, we obtain

$$\Delta_v\approx W\exp\left[-\frac{1}{vg_0}\right],\quad\Delta=\omega-\mu,\quad v=V,V-2J.\tag{13}$$

The conditions (13) denote that for stability with respect to mixing to set in it is necessary that the chemical potential be exponentially close to the transition energy.

4. MODEL HAMILTONIAN AND EQUATIONS FOR THE GREEN'S FUNCTIONS

The effects of interest to us, those of dynamic mixing of c and d states, can be obtained from a certain model Hamiltonian. It follows from the preceding section that in the description of systems in which the condition (13) is satisfied, it is necessary to take into account the resonant scattering of the conduction electrons by a localized level or, in other words, to take into account the second channel of scattering via the stage of the composite atom. To this end, we introduce the anomalous mean values $\langle c_{p\sigma}^+X_f^{-\sigma2}\rangle$. We make the following change of operators in the Hamiltonian (5):

$$X_f^{\sigma\sigma}c_{k\sigma}^+c_{p\sigma}\to N_\sigma c_{k\sigma}^+c_{p\sigma}+\delta_{kp}n_k^\sigma X_f^{\sigma\sigma},$$
$$X_f^{-\sigma,-\sigma}c_{k\sigma}^+c_{p\sigma}\to N_{-\sigma}c_{k\sigma}^+c_{p\sigma}+\delta_{kp}n_k^\sigma X_f^{-\sigma,-\sigma}+\langle c_{k\sigma}^+X_f^{-\sigma2}\rangle X_f^{2,-\sigma}c_{p\sigma}$$
$$+\langle X_f^{2,-\sigma}c_{p\sigma}\rangle c_{k\sigma}^+X_f^{-\sigma2},$$
$$X_f^{-\sigma,\sigma}c_{k\sigma}^+c_{p,-\sigma}\to\langle c_{k\sigma}^+X_f^{-\sigma2}\rangle X_f^{02}c_{p,-\sigma}+c_{k\sigma}^+X_f^{-\sigma,2}\langle X_f^{2,\sigma}c_{p,-\sigma}\rangle,\tag{14}$$

where we have used the rule for multiplying the X operators: $X_f^{\sigma\sigma'}=X_f^{\sigma q}X_f^{q\sigma'}$. After making the substitution (14), we obtain in place of the Hamiltonian (5) the model Hamiltonian

$$\tilde{H}=\tilde{H}_0+\tilde{H}_1,$$
$$\tilde{H}_0=\sum_{k\sigma}\xi_kc_{k\sigma}^+c_{k\sigma}+\Delta\sum_fX_f^{22},$$
$$\tilde{H}_1=\sum_{kf\sigma}\left[A_\sigma\frac{e^{ikf}}{\sqrt{N}}c_{k\sigma}^+X_f^{-\sigma2}+A_\sigma^*\frac{e^{-ikf}}{\sqrt{N}}X_f^{2,-\sigma}c_{k\sigma}\right],\tag{15}$$

where

$$A_\sigma=\eta(\sigma)Q-(V-J)\gamma_\sigma-J\gamma_{-\sigma},\quad\gamma_\sigma=\frac{1}{N}\sum_k\langle c_{k\sigma}^+X_k^{-\sigma,2}\rangle\tag{16}$$

and where we have left out for simplicity the renormalizations of ξ_k and ω, which are connected with the normal mean values of N_σ and n_k^σ. The model Hamiltonian (15) now contains the thermodynamic mean values γ_σ, which should be obtained in a self-consistent manner.

To find the mean values of n_k^σ, N_σ, and γ_σ, we set up a system of equations for Fourier transforms of the anticommutator Green's functions:

$$(E-\xi_k)\langle\langle c_{k\sigma}|c_{k'\sigma'}^+\rangle\rangle_E=\frac{i}{2\pi}\delta_{kk'}\delta_{\sigma\sigma'}+\sum_f\frac{e^{ikf}}{\sqrt{N}}A_\sigma\langle\langle X_f^{-\sigma2}|c_{k'\sigma'}^+\rangle\rangle_E,$$
$$(E-\Delta)\langle\langle X_f^{-\sigma,2}|c_{k'\sigma'}^+\rangle\rangle_E=\sum_p\frac{e^{-ipf}}{\sqrt{N}}A_\sigma^*(1-N_\sigma)\langle\langle c_{p\sigma}|c_{k'\sigma'}^+\rangle\rangle_E,$$
$$(E-\Delta)\langle\langle X_f^{-\sigma2}|X_{f'}^{2,-\sigma}\rangle\rangle_E=\frac{i}{2\pi}\delta_{ff'}(1-N_\sigma)+\sum_p\frac{e^{-ipf}}{\sqrt{N}}A_\sigma^*(1-N_\sigma)\langle\langle c_{p\sigma}|X_{f'}^{2,-\sigma}\rangle\rangle_E,$$
$$(E-\xi_p)\langle\langle c_{p\sigma}|X_{f'}^{2,-\sigma}\rangle\rangle_E=\sum_f\frac{e^{ipf}}{\sqrt{N}}A_\sigma\langle\langle X_f^{-\sigma2}|X_{f'}^{2,-\sigma}\rangle\rangle_E.\tag{17}$$

We note that, owing to the properties of the Hubbard operators, the model Hamiltonian (15) does not lead to a closed system of equations for the introduced Green's functions. Therefore the function $\langle\langle(X_f^{-\sigma,-\sigma}+X_f^{22})c_{p\sigma}|\rangle\rangle$ that arises in the equations is replaced by $(1-N_\sigma)\langle\langle c_{p\sigma}|\rangle\rangle$, and the function $\langle\langle X_f^{-\sigma\sigma}c_{p,-\sigma}|\rangle\rangle$ is discarded (allowance for the latter leads to an exaggeration of the accuracy assumed in (12)).

The solution of the system (17) takes the form

$$\langle\langle c_{k\sigma}|c_{k'\sigma'}\rangle\rangle_E=\frac{i}{2\pi}\delta_{kk'}\delta_{\sigma\sigma'}\frac{E-\Delta}{D_k^\sigma(E)},$$
$$\langle\langle X_f^{-\sigma,2}|X_{f'}^{2,-\sigma}\rangle\rangle_E=\frac{i}{2\pi}\sum_k\frac{e^{ik(f-f')}}{N}\frac{(1-N_\sigma)(E-\xi_k)}{D_k^\sigma(E)}$$
$$\langle\langle X_f^{-\sigma,2}|c_{k\sigma}^+\rangle\rangle_E=\frac{i}{2\pi}A_\sigma^*\frac{e^{-ikf}}{\sqrt{N}}\frac{1-N_\sigma}{D_k^\sigma(E)}$$

$$\langle\langle c_{\mathbf{k}\sigma}|X_{\mathbf{f}}^{2,-\sigma}\rangle\rangle_E=\frac{i}{2\pi}A_\sigma\frac{e^{i\mathbf{k}\mathbf{f}}}{\sqrt{N}}\frac{1-N_\sigma}{D_{\mathbf{k}}^\sigma(E)}$$

where

$$D_{\mathbf{k}}^\sigma(E)=(E-\xi_{\mathbf{k}})(E-\Lambda)-|A_\sigma|^2(1-N_\sigma).$$

The poles of the Green's functions yield the spectrum of the system with mixing of states

$$\Xi_{\mathbf{k}\sigma}^{(\pm)}=E_{\mathbf{k}\sigma}^{(\pm)}-\mu,\quad E_{\mathbf{k}\sigma}^{(\pm)}={}^1/_2(\varepsilon_{\mathbf{k}}+\omega\pm\nu_{\mathbf{k}\sigma}),$$
$$\nu_{\mathbf{k}\sigma}=\sqrt{(\varepsilon_{\mathbf{k}}-\omega)^2+4|A_\sigma|^2(1-N_\sigma)}. \tag{18}$$

Using the solution of the system (18) and the spectral theorem [9], we obtain a system of equations for the determination of the mean values of γ_σ, N_σ, N_2, and n_σ:

$$\frac{N_2}{1-N_\sigma}=\frac{1}{N}\sum_{\mathbf{k}}\nu_{\mathbf{k}\sigma}^{-1}[(E_{\mathbf{k}\sigma}^{(+)}-\varepsilon_{\mathbf{k}})f(E_{\mathbf{k}\sigma}^{(+)}-\mu)-(E_{\mathbf{k}\sigma}^{(-)}-\varepsilon_{\mathbf{k}})f(E_{\mathbf{k}\sigma}^{(-)}-\mu)], \tag{19}$$

$$n_\sigma=\frac{1}{N}\sum_{\mathbf{k}}\nu_{\mathbf{k}\sigma}^{-1}[(E_{\mathbf{k}\sigma}^{(+)}-\omega)f(E_{\mathbf{k}\sigma}^{(+)}-\mu)-(E_{\mathbf{k}\sigma}^{(-)}-\omega)f(E_{\mathbf{k}\sigma}^{-)}-\mu)], \tag{20}$$

$$\gamma_\sigma=A_\sigma(1-N_\sigma)\frac{1}{N}\sum_{\mathbf{k}}\nu_{\mathbf{k}\sigma}^{-1}[f(E_{\mathbf{k}\sigma}^{(+)}-\mu)-f(E_{\mathbf{k}\sigma}^{(-)}-\mu)], \tag{21}$$

$$N_1+N_2=1,\quad N_1=N_++N_-, \tag{22}$$

$$N_1+2N_2+n_c=\rho. \tag{23}$$

Here (22) is the averaged normalization condition (4), while (23) gives the relation between the electron density $\rho=\langle\hat{N}_e\rangle/N$ and the chemical potential; $f(x)\equiv[e^{\beta x}+1]^{-1}$.

5. SUPERMIXING STATE AND FERROMAGNETISM CRITERIA

The most interesting situation from the point of view of magnetism and mixing arises at $\mu \lesssim \omega$, for in this case a contribution to the magnetic moment of the crystal can come not only from the conduction electrons but also from ions that are in a one-electron state. Figure 2 shows schematically the spectrum (18) and the position of the chemical potential. It is obvious that at T = 0°K a contribution to (19)–(23) is made only by the lower band $E_{\mathbf{k}\sigma}^{(-)}$. An investigation of the system of equations (19)–(23) will be carried out in the model of the rectangular band (12).

Using the relation $dE_{\mathbf{k}\sigma}^{(-)}/d\epsilon_{\mathbf{k}}=\frac{1}{2}[1-(\epsilon_{\mathbf{k}}-\omega)/v_{\mathbf{k}\sigma}]$ and carrying out the integration in (19)–(21) with allowance for (12), we obtain

$$\frac{N_2}{1-N_\sigma}=2g_0|A_\sigma|^2(1-N_\sigma)\left[\frac{1}{E_\sigma^{(-)}(E_0)-\omega}+\frac{1}{\Delta}\right], \tag{24}$$

$$n_\sigma=g_0[\mu-E_\sigma^{(-)}(E_0)],\quad \gamma_\sigma=(1-N_\sigma)A_\sigma g_0\ln\frac{\Delta}{\omega-E_\sigma^{(-)}(E_0)}. \tag{25}$$

Using the definition (16) of A_σ, we obtain γ_σ. Then

$$A_\sigma=\eta(\sigma)Q-(\bar{V}_\sigma-\bar{J}_\sigma)A_\sigma-\bar{J}_{-\sigma}A_{-\sigma}\equiv\Phi(N_\sigma, N_{-\sigma}; A_\sigma, A_{-\sigma}), \tag{26}$$

where $\bar{V}_\sigma$ and $\bar{J}_\sigma$ are the renormalized dimensionless interaction constants:

$$\bar{V}_\sigma\equiv Vg_0(1-N_\sigma)\ln\frac{\Delta}{\omega-E_\sigma^{(-)}(E_0)}.$$

Equations (24) and (25) contain $|A_\sigma|$, so that the phase can be obtained only from (26). We consider the solution (26) in the paramagnetic state of the metal. We seek A_σ in the form

$$A_+=A,\quad A_-=Ae^{i\varphi}. \tag{27}$$

For the nonmagnetic solution, $N_\sigma=N_{-\sigma}=N_1/2$ and the renormalized interaction constants are also independent of the spin, since the logarithm depends only on $|A_\sigma|$. Adding Eqs. (26), we obtain

$$A(1+e^{i\varphi})(1+\bar{V})=0. \tag{26a}$$

Equation (26a) has solutions either at $\varphi=\pi$ or at $1+\bar{V}=0$ (there is no solution A = 0 at $Q\neq 0$).

We consider first the case $\varphi=\pi$. Then (26) leads to the following equation for A:

$$1+\bar{V}-2\bar{J}=Q/A, \tag{28}$$

which has two solutions, A_1 and A_2. The solution $A_1\sim Q$ lies in the region $\bar{V}\sim 2\bar{J}$. The last equation can be satisfied either at $V\sim 2J$ or at large Δ. We note that at V, J → 0 there remains in (26) only the "direct" mixing Q, which can exist off resonance. It is precisely this nonresonant mixing which was investigated in [4–6]. However, Eq. (28) also has another solution, $A_2\gg Q$. It is obtained from (24)–(26) and from the equation $1+\bar{V}-2\bar{J}\approx 0$. We shall find this solution in the case when the crystal has two electrons per atom. At T = 0°K and without the c–d interaction, we have in this case $n_c^0=1$, $N_2^0=0$, $N_1^0=1$ (the band is half-filled; all the one-electron levels are occupied). When the interaction is turned on, δn_c electrons are "pumped over" to the two-electron level

$$\delta N_2=N_2-N_2^0\approx 2g_0\omega z,$$
$$\delta n_c=n_c-n_c^0\approx -2g_0\omega z. \tag{29}$$

In this case

$$\mu\approx\omega-W_-z,\quad A_2\approx 2\omega z,$$

$$z=\exp\left[-\frac{2}{(V-2J)g_0(1+N_2)}\right],\quad W_-=\omega-E_0. \tag{30}$$

We now consider the solution A_3, which corresponds to the case $1+\bar{V}=0$. From (26) we obtain an equation for the phase shift

$$e^{i\varphi}=1+Q/A_3\bar{J}(A_3),\quad \bar{J}<0,$$

which has a solution $\varphi\approx 0$ at $Q/A_3\ll 1$. In this case the values of μ, δN_2, δn_c, and A_3 can be obtained by replacing $V-2J$ in (29) and (30) by V. Thus, under certain conditions there exists, in addition to the usual mixing ~Q, also a much stronger mixing A_2 and $A_3\gg Q$ (called supermixing in [8]); it does not vanish as Q → 0.

Figure 3 shows the regions of existence of the solution A_2 ($\varphi=\pi$) in region II, the solution A_3 ($\varphi\approx 0$) in region III, and the solutions A_2 and A_3 simultaneously in region I. V_{cr} stands for the minimum value of the inter-

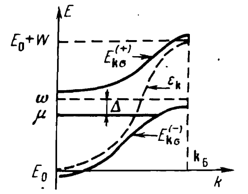
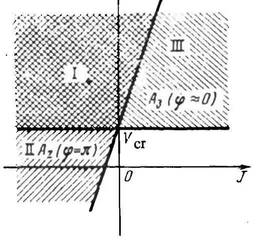


FIG. 2. Quasiparticle spectrum (18).

FIG. 3



action at which the nontrivial solution appears for the first time for the mixing constant:

$$g_0V_{cr}={}^1/_2(1+N_2)\ln(\omega/\Delta). \tag{31}$$

It is seen from the first equation of (30) that the chemical potential depends on the value of A. In region I, both processes are resonant, the liquid becomes two-component, and on the average ρ_1 electrons per atom are scattered "with a phase shift $\varphi = \pi$," while ρ_2 electrons are scattered with $\varphi = 0$, with $\rho_1 + \rho_2 = \rho$.

Thus, moving along any line in the (V, J) plane through the regions 0—II—I—III, we obtain a cascade of "phase transitions" in the interaction constants: on going from region 0 to II we get supermixing, from II to I a jumpwise change takes place in the derivative of A along the line of motion, a second jump occurs from I to III, and finally from III to 0 the supermixing vanishes. Usually $V > |J|$, which also limits the regions where the solutions exist.

We now ascertain the conditions for the onset of ferromagnetic order near the obtained paramagnetic solutions. In the assumed approximation, n_σ does not enter in expressions (24) and (26) and depends on N_σ and A_σ. We shall therefore obtain the ferromagnetism criterion from expressions (24) and (26). Using the normalization relation for the occupation numbers per site, we rewrite (24) in the form

$$N_{-\sigma}=1-N_\sigma-2g_0|A_\sigma|^2(1-N_\sigma)^2\left[\frac{1}{\Delta}-\frac{2}{W_-+\sqrt{W_-^2+4|A_\sigma|^2(1-N_\sigma)}}\right]\equiv\Psi(N_\sigma,A_\sigma). \tag{32}$$

From (32) and (26) we obtain the condition for the onset of spontaneous magnetization:

$$\left[1+\left(\frac{\partial\Psi}{\partial N_\sigma}\right)_0\right]\left[\left(\frac{\partial\Phi}{\partial A_\sigma}\right)_0-\left(\frac{\partial\Phi}{\partial A_{-\sigma}}\right)_0-1\right]$$
$$=\left(\frac{\partial\Psi}{\partial A_\sigma}\right)_0\left[\left(\frac{\partial\Phi}{\partial N_\sigma}\right)_0-\left(\frac{\partial\Phi}{\partial N_{-\sigma}}\right)_0\right]. \tag{33}$$

All the derivatives are calculated here at the point of one of the paramagnetic solutions. In the calculation of the criteria we neglect throughout the derivatives $A(\partial\ln.../\partial A)_0$ and $(\partial\ln.../\partial N_\sigma)_0$ in comparison with unity. Near A_2, the condition (33) is not satisfied. Near $A_1 \sim Q$ we obtain

$$\left(\frac{3}{2}V-2J\right)g_0\left(1-\frac{1}{2}N_1\right)\ln\frac{\omega}{\Delta}\geqslant 1. \tag{34}$$

Finally, near $A_3 \gg Q$ we have

$$6\bar{J}(A_3)+Q/A_3=-1. \tag{35}$$

Let us briefly discuss the obtained criteria. Equation (34) contains the constant for the Coulomb interaction of an electron with a c electron. At first glance this may seem unusual, since the initial Hamiltonian contains one and the same constant V both at the term $d^+_\uparrow d_\uparrow c^+_\downarrow c_\downarrow$, and $d^+_\uparrow d_\uparrow c^+_\uparrow c_\uparrow$. In addition, as seen from (34), it is easier to satisfy the criterion at $J < 0$, although usually the ferromagnetic state sets in only at $J > 0$. The reason is that in the chosen model the resonant interaction of the conduction electron with the d electron via the stage of the compound ion occurs only when their spins are antiparallel. For conduction electrons with spin σ scattered by an ion with spin σ, there is no second scattering channel. The criterion (35) is easier to understand in the limit as $Q \to 0$ (this limit can be considered, since the solution A_3 does not vanish as $Q \to 0$). In this case we have

$$Jg_0\left[3(1+N_2)\ln\frac{\omega}{\Delta}\right]\equiv J\tilde{g}=1. \tag{36}$$

We see that the criterion (36) differs from the usual Stoner criterion in the presence of a factor in the square brackets. The presence of the quasilevel ϵ_2 and the proximity of the chemical potential to the transition energy $\omega = \epsilon_2 - \epsilon_1$ leads to a logarithmic growth of the density of states of the electron system at this place, and this indeed explains the possibility of satisfying the ferromagnetism criterion.

Thus, in addition to mixing (hybridization) of the c and d electronic states due to the action of the crystal field, an additional mixing occurs if the chemical potential is exponentially close to the energy of the transition between (n + 1)-electron and n-electron terms; this additional mixing is due to the dynamic interaction of the electrons. The resultant supermixing state is characterized primarily by the fact that the c—d interaction proceeds via a compound-ion stage, and can be described in terms of anomalous mean values of the type $\langle c^+_\lambda X^{pq}_{\mathbf{f}}\rangle$. The final delocalization of the d states and the growth of the density of states near the transition energies facilitate the satisfaction of the ferromagnetic criterion of the Stoner type and increase the role of the d states in the formation of the interatomic-cohesion forces. In addition, the supermixing state, as follows from our preceding paper[8], is characterized by a unique superstructure of the type of the "reduced" metal of Abrikosov[10].

Attention should be paid to the fact that the proposed model is a development of the ideas of Goodenough and Wollan[11] concerning the simultaneous existence, in 3d metals, of localized (e_g) and collectivized (t_{2g}) d electrons. It is therefore assumed that the states of the collectivized part of the d electrons are included in the c-electron band (these arguments were already used in[12]), while only the fraction e_g of the total number of the d electrons is in the supermixing state. We note that in x-ray absorption spectra the states of the electrons that are in the supermixing phase should become manifest in the form of sharp peaks of width $\sim A^2/\mu$ in the vicinity of the Fermi energy against a background of much broader (~2—5 eV) bands of the collectivized part of the d electrons.

The results of the present analysis are also valid in those cases when the e_g electrons form bands of width $W_e < \Delta$; on the other hand, when the inverse inequality is satisfied, only a fraction of these electrons is in the supermixing phase, but this question calls for a special investigation.

We note also that inclusion of the magnetic field h leads to a replacement of Δ under the logarithm side by $\Delta_\sigma = \Delta + (1/2)\mu_B h\eta(\sigma)$, and that the value of Δ_σ decreases for electrons with spin ↓. Therefore in those systems in which the resonance condition (13) is not satisfied we can attempt to "make them resonant" by turning on a magnetic field and thereby produce a supermixing state for electrons with one of the spin projections.

In conclusion, the authors are grateful to G. M. Zaslavskiĭ for useful discussions.

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