Electron structure and distribution function of localized states in the Anderson model. The dielectric phase

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A new approach is suggested to the problem of the localized states of ions of a transition $d(f)$-metal with strong intra-atomic interaction in a semiconductor host. Essentially, the approach consists in first constructing the correct one-electron wave function in which the d states are mixed with the host continuum states, and then taking into account the strong electrostatic interaction between the electron and the inner electrons of the d shell. The state thus obtained retains the "atomic" statistics and the nominal magnetic moment, just as in the traditional ligand field theory. The canonical-transformation method used to determine the one-electron wave functions can be employed to demonstrate the equivalence of the Anderson and Wolf Hamiltonians in the case in which a localized impurity state is present in the system, and also to analyze the problem of the dielectric-metal phase transition in variable mixed-valence compounds (in the single-site approximation) without making recourse to decoupling of the mean field. It can also be demonstrated that the transition in this model may occur only in a gradual manner.

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1. In the attempt to find the energy spectrum and the wave function of the impurity electron in the Anderson model,[1] which describes the impurity with an unfilled electron shell in a metal or dielectric, the complicated problem arises of the construction of the superposition of states obeying various statistical distributions, namely, the Fermi electrons of the continuum must be hybridized with the strongly correlating atomic states, which have the Gibbs distribution function

$$f_G(F_{p\lambda}) = \exp[-\beta(E_{p\lambda} - p\mu)] \Big/ \sum_{p\lambda} g_{p\lambda} \exp[-\beta(E_{p\lambda} - p\mu)]. \quad (1)$$

Here $E_{p\lambda}$ are the atomic terms of a shell containing p electrons, $g_{p\lambda}$ is the corresponding degeneracy factor, μ is the chemical potential, and β the inverse temperature.

This problem has been stated almost nowhere. in general form. In a number of papers, Hirst established the general principles of "intersection of configurations" and found several sum rules; however, he did not consider the problem of the construction of the superposition state (see the review[2]). In all the practical applications of the Anderson model, different variants of the molecular field approximation are used. The purpose of the present research was to demonstrate the inconsistencies that appear in the most frequently used mean-field approximations, and to suggest as an alternative a new approach, free from these inconsistencies, which we apply, at least in the semiconducting phase. It will be shown, within the framework of the suggested approach, that, in spite of the noticeable admixture of the Bloch states in the wave function of the localized electron, the localized state preserves the "atomic" quantum numbers and the distribution function of the type (1). For this reason, such thermodynamic characteristics as the impurity specific heat and paramagnetic susceptibility preserve the temperature dependence that is characteristic for an atom in the crystal field of the dielectric under conditions of the

absence of free carriers or overlap of the wave functions of the different centers.

As examples, we consider the problem of the localized moment of the impurity atom of a transition metal in a semiconductor[3-6] and the single-site variant of the theory of phase transitions semiconductor-metal in compounds of variable mixed valence.[7,8] With the help of the proposed method, these problems can be resolved without the introduction of a self-consistent field. The theory of chemisorption of hydrogen on the surface of metals and semiconductors can be one more object of its application.[9,10]

2. The Hamiltonian of an impurity atom with an incomplete shell, placed in a continuum of Bloch electrons, has the form

$$H = H_c + H_i + H_{ci} + H' \quad (2)$$

in the general case. Here H_c and H_i describe respectively the states of the electrons of the host in a periodic crystal lattice and electrons of the free atom (ion) impurity; H_{ci} is the hybridization term, and H' contains all the interactions except the intra-atomic electrostatic interaction, which enters into H_i. We shall point out the inconsistencies that arise in the use of the mean-field approximation using the example of the simplest nondegenerate Anderson Hamiltonian H_A,[1] in which

$$H_c = \sum_{k\sigma} E_{k\sigma} n_{k\sigma}, \quad H_i = E_d \sum_{\sigma} n_{d\sigma} + \frac{U}{2} \sum_{\sigma} n_{d\sigma} n_{d-\sigma},$$

$$H_{ci} = \sum_{k} g_k c_{k\sigma}^+ c_{d\sigma} + \text{H.c.} \quad (3)$$

(the notation is traditional). In this model of the Hamiltonian, the term H' is not considered, H_i describes the unperturbed atomic levels, $H_i|p\lambda\rangle = E_{p\lambda}|p\lambda\rangle$, where $|p\lambda\rangle = |0\rangle$, $|1\sigma\rangle$, $|20\rangle$ indicate the number of electrons and the spin state of the configuration d^0, d^1 and d^2 respectively.

A deep level can be expected to appear in the for-

bidden band of a semiconductor when the energy of the addition of a single electron (or hole) to the atomic shell amounts to a quantity of the order of the chemical potential of the host, i.e., the Hirst condition of configuration crossing is satisfied:[2]

$$E_{p\lambda} - E_{p-1,\lambda'} \cong \mu. \tag{4}$$

It is simplest to obtain the localized levels in the Hartree approximation.[3] The Green's function of the atomic electron in this case is determined by the expression:

$$G_{d\sigma}^{-1}(\omega) = \omega - E_d - U\langle n_{d-\sigma}\rangle - M(\omega), \quad M(\omega) = \sum_k g_k^2(\omega - E_k)^{-1}. \tag{5}$$

For the Green's functions of the Bloch electrons we have

$$G_{kk'}^{\sigma}(\omega) = \delta_{kk'}(\omega - E_k)^{-1}[1 + g_k g_{k'}(\omega - E_{k'})^{-1}G_{d\sigma}(\omega)]. \tag{6}$$

We find from (5) and (6) that the electrons at the impurity level obey the Fermi distribution f_F

$$\langle n_\sigma^i \rangle = \langle n_{d\sigma}^i \rangle + \langle n_{b\sigma}^i \rangle = f_F(E_{i\sigma}), \quad E_{i\sigma} = E_d + U\langle n_{d-\sigma}\rangle + M(E_{i\sigma}). \tag{7}$$

Here $\langle n_{d\sigma}^i \rangle$ and $\langle n_{b\sigma}^i \rangle$ determine the contributions from the d- and k-states to the total number of electrons with spin projection σ on the site in the localized state. It is seen that the Hartree approximation completely ignores the above-mentioned complexity of the problem of the mixing of the states, reducing H_A to a single-electron effective Hamiltonian and considering both the band and the quasi-atomic states as ordinary fermions with doubly filled levels, which contradicts the general requirement imposed on the rule for filling localized states: each level can be occupied by only one electron.

In this sense, another variant of the molecular field approximation is more reasonable, first proposed by Hewson.[11] This approach uses the atomic picture for impurities as the zeroth approximation, taking H_i into account exactly, and takes the "atomic" Green's functions

$$G_{d\sigma}^{(0)}(\omega) = \frac{1 - \langle n_{d-\sigma}\rangle}{\omega - E_d} + \frac{\langle n_{d-\sigma}\rangle}{\omega - E_d - U} \tag{8}$$

as the zero Green's functions. In the zeroth approximation, we find from (8)

$$\langle n_{d\sigma}\rangle = (1 - \langle n_{d-\sigma}\rangle)f_F(E_d) + \langle n_{d-\sigma}\rangle f_F(E_d + U),$$

which gives an atomic distribution function

$$\langle n_{d\sigma}\rangle = \frac{\exp[-\beta(E_d - \mu)] + \exp[-\beta(2E_d + U - 2\mu)]}{1 + 2\exp[-\beta(E_d - \mu)] + \exp[-\beta(2E_d + U - 2\mu)]} \rightarrow$$
$$\rightarrow \frac{1 + \exp[\beta(E_d + U - \mu)]}{1 + 2\exp[\beta(E_d + U - \mu)]} = f_\sigma(E_d + U) \tag{9}$$

that is spin-independent, if we set $p = 2$ in condition (4). Taking H_{ci} in the mean-field approximation, in accord with Hewson, we have for the impurity level[6]

$$E_{i\sigma} = E_d + U + \langle n_{d-\sigma}\rangle M(E_{i\sigma}). \tag{10}$$

The occupation numbers are determined by the expression[6]

$$\langle n_{d\sigma}^i \rangle = 1 - \langle n_{d-\sigma}\rangle + \frac{\langle n_{d-\sigma}\rangle(1 + M')}{1 + \langle n_{d-\sigma}\rangle M'} f_F(E_{i\sigma}), \quad M' = -\frac{dM(E)}{dE}\Big|_{E=E_{i\sigma}},$$
$$\langle n_{d\sigma}\rangle = \langle n_{d\sigma}^i \rangle + \langle n_{d\sigma}^b \rangle, \tag{11}$$

$\langle n_{d\sigma}^b \rangle$ is the contribution from the states of the continuum. Here we have explicitly used the sign of the der-

ivative, since $dM/dE < 0$ in the forbidden band. In the case $M' \ll 1$, which is realized for a sufficiently deep level E_i, we find from (10) the approximate expression for $\langle n_{d\sigma}^i \rangle$. For the nonmagnetic solution

$$\langle n_d^i \rangle = f_\sigma + (2f_\sigma - 1)[\langle n_d^b \rangle + f_\sigma(1 - f_\sigma)M'] \tag{12}$$

(the spin index is omitted). Although this expression does not differ greatly from the atomic distribution function, it remains unsatisfactory for a number of reasons. In particular, it gives a non-integer number of electrons at the impurity level which, in addition, varies as a function of the position of the level relative to the edge of the forbidden band.

The reasons for the appearance of "non-integer" occupation numbers of localized states are quite evident. The atomic Green's function (8) gives the correct value $n_{d\sigma} = \frac{1}{2}$ at $\beta = \infty$ thanks to the exact account of the repulsion U, which does not permit two electrons with oppositely directed spins to be found close to the impurity atom. On the other hand, for Bloch electrons, within the framework of the Anderson Hamiltonian (3), such a prohibition is lacking, and $n_{k\sigma} = 1$ at $E_k < \mu$, $\beta = \infty$. As a result of the mixing of states, prepared "according to different recipes," we obtain a fractional occupation number for the localized level. This result does not have physical meaning, from our point of view, but is a consequence of the accepted scheme of uncoupling and the incorrect choice of the reduced Hamiltonian in the form (3) (see below). For filling the states of the continuum, which have an admixture of atomic states, we also obtain an incorrect picture. Mathematically, this is expressed by the fact that, for the density of states determined by the imaginary part of the Green's function with the components (9) and (6) it is impossible to formulate any sort of sum rule in place of the rule of Friedel for one-electron states[6] (for the Anderson model in the Hartree approximation, the sum rule of Friedel, as is well known, is satisfied automatically). Thus, in the Hewson approximation, we cannot calculate the real chemical potential of the system and, consequently, all the remaining thermodynamic and kinetic characteristics. In particular, the Anderson model cannot be used in the given form for the description of compounds with mixed valency (rare-earth chalcogenides) in the semiconducting phase.

Another source of possible ambiguities is the dependence of the energy spectrum on the average occupation numbers $\langle n_{d\sigma}\rangle$, arising in the molecular-field approximation. Thanks to its presence, we can be tempted to obtain "magnetic" solutions $\langle n_{d\sigma}\rangle \neq \langle n_{d-\sigma}\rangle$[12] or to use this molecular field for "amplification" of other phase transformations (for example, transitions of the Falicov-Kimball type[13]). Yet, it is not difficult to see that the form of the dependence of the spectrum on $\langle n_{d\sigma}\rangle$ is greatly altered in the transition from one type of mean-field approximation to another. It manifests itself in the resonance level (7) or in the hybridization term of second order (9) and can be referred to the fourth order in g_k by means of a small improvement in the procedure of decoupling of the Bogolyubov chain. In order to demonstrate this instability, we write down the

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chain of equations of motion for the operator $n_{d-\sigma}c_{d\sigma}$, which describes the configurational transition $d^2 \to d^1$:

$$(\omega - E_d - U)n_{d-\sigma}c_{d\sigma} = \sum_k g_k(n_{d-\sigma}c_{k\sigma} - c^+_{d-\sigma}c_{d\sigma}c_{k-\sigma}),$$

$$(\omega - E_k)c_{k\sigma} = g_k n_{d-\sigma}c_{d\sigma},$$

$$(\omega - E_k)c_{k\sigma}n_{d-\sigma} = g_k n_{d-\sigma}c_{d\sigma} \qquad (13)$$

$$+ \sum_{k'} g_{k'}(\langle c^+_{k'-\sigma}n_{d\sigma}c_{d-\sigma}\rangle c_{k\sigma} + \langle n_{d-\sigma}c_{d\sigma}^+ c_{k\sigma}\rangle c_{k'-\sigma}),$$

$$(\omega - E_k)c_{k-\sigma}c^+_{d-\sigma}c_{d\sigma} = \sum_{k'} g_{k'}(\langle n_{d\sigma}c^+_{d-\sigma}c_{k-\sigma}\rangle c_{k'\sigma}$$

$$- (\delta_{kk'} - \langle c^+_{k'-\sigma}c_{k-\sigma}\rangle)n_{d-\sigma}c_{d\sigma}).$$

Rather than following Hewson[11] and decoupling the first of these equations, we break the chain at the second step. Then, in first order in g_k, we have, in place of (9), $E_i = E_d + U + M(E_i)$. The corrections of fourth order arise from the mean values

$$\sum_k \langle c^+_{k-\sigma}c_{k-\sigma}\rangle, \quad \langle c^+_{d-\sigma}n_{d\sigma}c_{k\sigma}\rangle,$$

the basic contribution to which is made by the residues of the corresponding Green's functions at the pole E_i. These corrections have the form $\langle n_{d-\sigma}\rangle M(E_i)M'(E_i)$.

3. In view of the ambiguity of the results obtained by the method of introduction of molecular fields into the Hamiltonian H_A(3), it is necessary to find more realistic grounds for the construction of the localized states in the forbidden band. In this section, such grounds are proposed within the framework of the Hamiltonian of general form (2). We assume that in those cases in which there is a localized level in the spectrum, the use of the impurity Hamiltonian in the reduced form (3) is generally not entirely correct (although one can obtain the correct distribution function for the localized state, as will be shown below, even within the framework of the Anderson Hamiltonian). Actually, the wave function of the localized electron, corresponding to the representation (5), (6) for the Green's function, has the form[6]

$$\varphi(r) = \varphi_1(r) + \varphi_2(r), \quad \varphi_1(r) = (1+M')^{-1/2}\psi_d(r),$$

$$\varphi_2(r) = (1+M')^{-1/2}\sum_k \frac{g_k}{E_i - E_k}\psi_k(r). \qquad (14)$$

Here ψ_d and ψ_k are the atomic and Bloch wave functions, respectively of the electron. The well arguments of Anderson[1] on the importance of taking into account the intra-atomic Coulomb interaction refer to a strongly localized function $\varphi_1(r)$. However, the function $\varphi_2(r)$ also falls off exponentially at distances of several lattice constants: $\varphi_2(r) \sim r^{-1}e^{-\varkappa r}$, $\varkappa = (2m^*E_i)^{1/2}$ (E_i is measured from the edge of the nearest allowed band).[6] This means that the Coulomb interaction corresponding to this part of the wave function also plays an important role in the formation of many-electron states. It should be taken into account in the construction of the impurity wave function. The first step in this direction was made in Ref. 6, in which, by solving the problem of multiple-charge impurity states, we have taken the dd interaction into account exactly and, the ss and sd interactions in the molecular-field approximation. Such an inconsistent approach has led to the result that

all the disparities of the model considered in the previous section of the present paper were preserved. Here we set forward a new approach, in which the entire Coulomb interaction of the states localized on the impurity site is taken into account exactly.

We first consider the nondegenerate variant of the Hamiltonian (2), in which, the electrostatic interaction of valence electrons with one another and with the electrons of the unfilled shell of the impurity is taken into account along with the intra-atomic interaction of Anderson-Hubbard:

$$H = H_i + \sum_{\alpha\beta\gamma\delta}\sum_{\sigma_1\sigma_2}(\alpha\beta|W|\gamma\delta)c^+_{\alpha\sigma_1}c^+_{\beta\sigma_2}c_{\delta\sigma_2}c_{\gamma\sigma_1},$$

$$W = |r - r'|^{-1},$$

$$H_i = H_c + E_d\sum_\sigma n_{d\sigma} + H_{ci}, \quad \alpha, \beta, \gamma, \delta = k, d. \qquad (15)$$

In the Hamiltonian (15), we transform from the representation of non-interacting states $|k\sigma\rangle$, $|d\sigma\rangle$, to the representation of hybridized states $|\tilde{k}\sigma\rangle$, $|\tilde{d}\sigma\rangle$:

$$c_{\alpha\sigma} = e^S \tilde{c}_{\alpha\sigma}e^{-S}, \quad S = \sum_{k\sigma}u_k \tilde{c}^+_{k\sigma}\tilde{c}_{d\sigma} - \text{H.c.} \qquad (16)$$

The coefficients u_k are determined from the condition of vanishing of the matrix element of hybridization in the effective Hamiltonian $H(\tilde{c})$ (see the Appendix):

$$u_k = \frac{\text{arctg}(M')^{1/2}}{(M')^{1/2}}\frac{g_k}{E_k - E_i}. \qquad (17)$$

The one-electron Hamiltonian H_i takes in this case the form

$$H_i(\tilde{c}) = \sum_\sigma E_i\tilde{c}^+_{d\sigma}\tilde{c}_{d\sigma} + \sum_{kk'\sigma}(E_k\delta_{kk'} + W_{kk'})\tilde{c}^+_{k\sigma}\tilde{c}_{k'\sigma}, \quad E_i = E_d + M(E_i); \qquad (18)$$

$$\tilde{c}_{d\sigma} = (1+M')^{-1/2}\left(c_{d\sigma} - \sum_k \frac{g_k}{E_k - E_i}c_{k\sigma}\right), \qquad (19)$$

$$\tilde{c}_{k\sigma} = c_{k\sigma} + (1+M')^{-1/2}\frac{g_k}{E_k - E_i}\left(\frac{1 - (1+M')^{1/2}}{M'}\sum_{k'}\frac{g_{k'}}{E_{k'} - E_i}c_{k'\sigma} - d_\sigma\right). \qquad (19b)$$

The operator $\tilde{d}_\sigma$ describes the state of the electron at the impurity level E_i in the forbidden band [cf. (14)], while $\tilde{c}_{k\sigma}$ corresponds to the Bloch wave distorted by resonance scattering.[1] As a result of the canonical transformation (16), a part of the Hamiltonian, corresponding to states of the continuum, became nondiagonal, since k is not a better quantum number. We shall not write down the explicit form of the matrix element W_{kk} here, since the diagonalization of the states of the continuum, described by the Hamiltonian $H_c(c)$, does not enter into the problem of the present paper. Returning to Eq. (19) and substituting $c_{\alpha\sigma}(\tilde{c}_{\beta\sigma})$ in the Hamiltonian (15), (18), we find that it is transformed to

$$H = H_i + H_c + H', \quad H_i = \sum_\sigma E_i\tilde{n}_{i\sigma} + \frac{U}{2}\sum_\sigma \tilde{n}_{i\sigma}\tilde{n}_{i-\sigma},$$

$$H' = \sum'(\bar{\alpha}\bar{\beta}|W|\bar{\gamma}\bar{d})\tilde{c}^+_{\alpha\sigma_1}\tilde{c}^+_{\beta\sigma_2}\tilde{c}_{\delta\sigma_2}\tilde{c}_{\gamma\sigma_1}. \qquad (20)$$

The prime on the sum indicates the absence in it of the term with $\alpha = \beta = \gamma = d$, which is associated with H_i.

From the point of view of the statistics of impurity levels, which is of interest to us, the transformed Hamiltonian (20) possesses advantages in comparison

with (2) and is free of the inadequacies inherent in the effective Hamiltonian which uses the mean-field approximation.[3,6,9] The entire interaction of electrons localized on the impurity site is taken into account in (20), in contrast with H_A in (2.3). The "basis" states, described by the term H_i, have the correct atomic statistics in that the mixing of waves functions of the electrons of the unfilled shell with the continuum are taken into account in them. The distribution function

$$f_\sigma(E_i) = [2 + \exp(\beta(E_i - \mu))]^{-1} \qquad (21)$$

gives the correct occupation number $\bar{n}_{i\sigma} \to \frac{1}{2}$ as $\beta \to \infty$.

We now consider the correlation terms that enter into H'. First of all we call attention to the fact that H' contains the effective hybridization interaction

$$\sum_{k\sigma} (d\tilde{d}|W|d\tilde{k}) \bar{n}_{d\sigma} \tilde{c}_{d-\sigma}^+ \tilde{c}_{k-\sigma} + \text{H.c.}$$

$$+ \sum_{k_1 k_2 k_3} \sum_{\sigma\sigma'} (d\tilde{k}_1|W|\tilde{k}_3\tilde{k}_2) \tilde{c}_{d\sigma}^+ \tilde{c}_{k_1\sigma'}^+ \tilde{c}_{k_2\sigma'} \tilde{c}_{k_3\sigma}. \qquad (22)$$

These terms require discussion, since, along with the discarded integrals of the type $(dd|W|dk)$ and $(dk_1|W|k_3k_2)$, they contain a contribution from the strong Coulomb interaction U, which transforms into H' as a result of the canonical transformation (16) and at sufficiently large U the resulting hybridization can turn out to be comparable with the initial mixing, which we sought to eliminate by means of the transformation (16). The contribution of this can be estimated by transforming to the Wannier representation for the states of the continuum. We see from (19) that the d component of the functions $\tilde{\psi}_{k\sigma}$ transforms into

$$\tilde{\psi}_k(r, R_i) = (1+M')^{-1/2} \psi_d(r) \sum_k g_k \frac{\exp(ikR_i)}{E_k - E_i} \qquad (23)$$

(the impurity site is located at the origin). It is then seen that the maximum contribution to the effective hybridization gives $R_i = 0$. Estimate of the Coulomb integrals in (22) gives

$$(d\tilde{d}|W|d\tilde{k}) \approx Ug^{-1}M(1+M')^{-1/2} \sim Ug/D, \qquad (d\tilde{k}_1|W|\tilde{k}_3\tilde{k}_3) \sim U(g/D)^3.$$

All the remaining integrals in H' can be estimated in similar fashion.

We first note that the first of the hybridization terms in (22) basically affects the states of the continuum and the states with two localized electrons at the site,[2,6] which we shall not consider and, in the renormalization of the level E_i it can give only a constant contribution, which does not violate the atomic statistics (21) [the latter can be shown by writing, for example, the chain of equations of motion of the type (13) for the operator $c_{d\sigma}^+(1 - n_{d-\sigma})$]. In the same way we can establish the fact that the hybridization corrections from the second term in (22) arise only in very high orders in $g(\sim g^8)$ and can be discarded, in any case in those situations in which $U \lesssim D$. If $U > D$, the proposed method becomes ineffective. In this limit, along with the Coulomb hybridization, it is necessary to take into account also the strong interaction between states of the continuum, since the d-component of the scattered wave (23), localized near the impurity site, no longer can be regarded

in the one-electron approximation, so that the d-component of the two-electron states, determined by the operator $\tilde{c}_{d\sigma}^+ \tilde{c}_{k\sigma}$ will be suppressed in the same measure as the state $\tilde{c}_{d\sigma}^+ \tilde{c}_{d-\sigma}^+$ with two electrons, localized near the impurity site.[2]

Thus the effective Hamiltonian with account of the most important interactions between the continuum and the localized states has the form

$$H = E_i \sum_\sigma \tilde{N}_\sigma + (2E_i + U) \tilde{N}_2 + \sum_{kk'\sigma} (E_k \delta_{kk'} + W_{kk'}) \tilde{c}_{k\sigma}^+ \tilde{c}_{k'\sigma}$$

$$+ \sum_{k\sigma} (g_{ik} \tilde{c}_{d\sigma}^+ \tilde{n}_{d-\sigma} \tilde{c}_{k\sigma} + \text{H.c.}) + \sum_{kk'} \sum_{\sigma\sigma'} (U_i^{kk'} \tilde{n}_{d\sigma} \tilde{c}_{k\sigma}^+ \tilde{c}_{k'\sigma'} - J_i^{kk'} \tilde{c}_{d\sigma}^+ \tilde{c}_{d\sigma'} \tilde{c}_{k\sigma'}^+ \tilde{c}_{k'\sigma}),$$

$$(24)$$

$$g_{ik} = (d\tilde{d}|W|d\tilde{k}), \quad U_i^{kk'} = (d\tilde{k}|W|d\tilde{k}'), \quad J_i^{kk'} = (d\tilde{k}|W|\tilde{k}'d),$$
$$\tilde{N}_\sigma = \tilde{n}_{d\sigma}(1 - \tilde{n}_{d-\sigma}), \quad \tilde{N}_2 = \tilde{n}_{d\sigma}\tilde{n}_{d-\sigma}.$$

Without the last three terms, the form of (24) actually represents the Hamiltonian of Wolf,[16] in which the rearrangement of the continuum under the effect of resonance scattering is additionally taken into account. This property is not accidental: the central point of the Wolf, model, as in our case, was the requirement that the Coulomb interaction between electrons in the localized states, produced by the impurity scattering, be taken into account. The difference is that in the Wolf model, this state was created by the short-range Slater-Koster potential, while in our case, by the resonance Friedel scattering.

Before going on to the consideration of the thermodynamic and magnetic properties of the system described by the Hamiltonian (24), we generalize the proposed approach to the case of real, polyelectronic atoms with an unfilled shell, when, along with the interactions included in (24), there is also an interaction with the core states of the impurity. For definiteness, we shall have in mind the $3d$-shell of a transition metal of the iron group and assume that the orbital momentum $l = 2$ and the addition of the momenta is carried out according to the Russel-Saunders scheme. Generalization to another case does not represent any difficulty in principle. In the traditional theory of transition metals, the core states are those of the inner, filled shells. However, in recent years, an approach has been intensively developed, first clearly formulated by Hubbard,[17] which considers the elementary excitations in the $d(f)$ shells as a change in the atomic configurations. Taking this approach, we must re-examine the concept of core states.

The method developed in the present paper, as in the conceptually similar approach of Hirst,[2,18] essentially revives, on a new basis, the idea expressed in their time by Pauling and Goodenough, who proposed to separate the electrons of the unfilled shell into a localized core which determines the magnetic moment of the atom, and the collectivized electrons which are hybridized in our case with the valence electrons of the semiconductor host. As a criterion for such a separation, we use here the relation (4), i.e., the core electrons are those whose binding energy in the shell is much greater than the chemical potential of the system, and the valence electrons are the last one or two electrons in the shell. Thus, the mechanism that governs

the possibility of division of the electrons of the unfilled shell into two groups is in our case the intra-atomic Coulomb interaction of van-Vleck–Anderson–Hubbard.

The proposed approach reduces to the following. In contrast to schemes based on a purely atomic, zeroth approximation for all the configurations of the d electrons,[6,11] we shall first separate the valence electrons and construct for them a correct wave function that possesses the point symmetry of the crystal and is hybridized with the Bloch electrons of the host, and then pair this superposition state with the many-electron core according to the usual scheme of addition of momenta. Thus, let E_γ be the energy of the p-th electron of the d shell in the self-consistent Hartree field of the core d^{p-1}, and ψ_γ be the corresponding wave function. For semiconducting systems $A_{II}B_{VI}$ and $A_{III}B_V$ of $V, Cr, \ldots$, Ni alloys, $p = 1, 2, \ldots, 7$: correspondingly for SmS we have $p = 6$ and so on. It is convenient from the first to take into account the splitting of the d levels of the impurity in the crystal field, so that the ground state of the ion d^{p-1} is characterized by the term $E_{\Gamma_{p-1}}$, Γ_{p-1} contains the indices of the irreducible representation of the point group of the crystal and the total spin of the shell. Then $E_\gamma = E_{\Gamma_p} - E_{\Gamma_{p-1}}$, $\gamma = t_2$ or e. The wave function of the p-th electron and the energy and the energy of the deep level are determined by the expressions[6]

$$\varphi_\gamma \sim \psi_\gamma + \sum_k \frac{(k|V|\gamma)}{E_{i\gamma} - E_k} \psi_k, \quad E_{i\gamma} = E_\gamma + \sum_k \frac{|(\gamma|V|k)|^2}{E_{i\gamma} - E_k}, \quad (25)$$

V is the crystal field of the host. Than, taking into account the intra-atomic exchange interaction, we add together the momenta of the p-th electron and the ion d^{p-1} according to the scheme of the mean crystal field. This scheme can be applied to our "quasi atom" without any changes, since the hybridization (or covalent chemical bond) of the d electron of the impurity with the electrons of the semiconductor host does not change its point symmetry.[5] As a result, we obtain the level energy and the wave function of the impurity quasi atom, in which all the covalent (hybridization) effects are taken into account, but the atomic classification of the levels is maintained:

$$\psi_{\Gamma_p} = \sum_{\gamma \Gamma_{p-1}} C^\Gamma_{\gamma, \Gamma_{p-1}} \psi_{\Gamma_{p-1}} \varphi_{\gamma}, \quad E_{i\Gamma_p} = E_{i\gamma} + (\Gamma_p|W|\Gamma_p)_{ex}. \quad (26)$$

Here $(\Gamma_p|W|\Gamma_p)_{ex}$ is the matrix element of the exchange interaction, $C^\Gamma_\gamma {}^p \Gamma_{p-1}$ is a coefficient determining the scheme of vector addition.

The effective impurity Hamiltonian can be written down with the help of the operators of change of the atomic configurations, introduced in Ref. 17:

$$H_i = \sum_{\Gamma_n} E_{\Gamma_n} |\Gamma_n)(\Gamma_n|, \quad n = p-2, p-1, p, p+1 \ldots) . \quad (27)$$

In contrast to Refs. 17 and 4, the effect of the crystal field in the Hamiltonian (27) was taken into account from the very beginning. In the language of crystal field theory, the results obtained in this section mean that, in contrast with the states of the core, which are determined by the ordinary electrostatic field of the

ligands, for the "valence configurations," p, $p+1$ the resonance component of this field (25) is also important,[5] and, furthermore, the effect of hybridization of the valence states with the continuum reduces completely to the formation of the crystal field. The Hamiltonian (27) corresponds to the Gibbs distribution function (1).

4. In this section, we consider as the proposed method of canonical transformation two physical problems which can be solved with its help, without the introduction of self-consistent molecular fields.

A. Localized momenta and the paramagnetic susceptibility of impurities of transition metals in semiconductors

It is not difficult to see that in a system described by the Hamiltonian (24),(27), in the absence of free carriers, there is always a magnetic moment and it preserves its nominal value, corresponding to the free state of the paramagnetic ion of configuration d^p in the ligand field. In this sense, our model is greatly different from the approximate mean-field scheme,[11] in which, as is well known, the conditions of the existence of a localized moment are very stringent.[3] We then immediately obtain the Curie law for the paramagnetic susceptibility in the case of an impurity in the S state

$$\chi = \frac{1}{3} g^2 \mu_B^2 S(S+1)\beta, \quad (28)$$

and for the multiplet, split by the crystal field and the spin-orbit interaction–the formula of Van Vleck:

$$\chi^{(p)} = Z^{-1} \sum_{\Gamma_p} \exp(-\beta E_{\Gamma_p}) [\beta a_1^{\Gamma_p} + 2a_2^{\Gamma_p}]. \quad (29)$$

Here $a_1^{\Gamma_p}$ and $a_2^{\Gamma_p}$ are the coefficients in the case of H and H^2 in the effective spin Hamiltonian for the ion d^p, and Z is the statistical sum in the distribution on (1).

The measurements of the paramagnetic susceptibility in the semiconducting alloys $A_{II}B_{VI}$ and $A_{III}B_V$ doped with transition metals give satisfactory agreement with the formulas (28) and (29) (see, for example, Refs. 19, 20). The departure from the Van Vleck curve obtained by the method of effective spin Hamiltonian is brought about, in our view, by the effect of the resonance covalent part of the crystal field,[5] which distorts the structure of the levels, split by the electrostatic ligand field; this can change the value of the g factor and even lead to inversion of the terms.

B. Semiconductor-metal phase transition with change in valence

The so called "single-site approximation" is frequently used for the description of phase transitions will change in valence.

Here the real periodic structure of atoms with unfilled f shells is approximated by a set of noninteracting "impurity" atoms (see, for example, Refs. 8, 13, and 14). The system is described by the Anderson Hamiltonian, while the phase transition is assured by the Coulomb interaction between the conduction electrons and the f electrons (the Falicov mechanism). If in the descrip-

tion of the metallic phase of variable mixed-valence compounds (VMC), the single-site approximation can be used only as a rough qualitative estimate of the thermodynamic and kinetic characteristics of the system, then this approximation should, at first glance, work much better in the semiconductor phase, since upon replacement of the independent centers by a periodic lattice, only a smearing out of the level takes pace in a narrow band that is unimportant for the problem of the phase transition. However, the description of the semiconducting phase of VMC with the help of the Anderson Hamiltonian usually requires the introduction of self-consistent fields and meets with the inconsistencies considered in Sec. 2. In particular, in order to avoid the problem of the lifting of spin degeneracy in the filling of the localized level, it is appropriate to return to the spinless model.[7,8]

We first recall that, considering the Coulomb sf interaction in the self-consistent field approximation, we can obtain both continuous and jumpwise transitions from the state with $\langle n_f \rangle = 1$ to $\langle n_f \rangle = 0$, depending on the relation of the parameters. For the chalcogenides of Sm and Tm, this will be simultaneously a semiconductor-metal transition; but if we take hybridization into account, then the transition takes place between states with non-integer valence.[7,8,21,22] However, the choice of method of introduction of the mean field very strongly affects the behavior of the system. In addition, there exists an exact solution of the Falicov problem at $g_k = 0$ which gives only a continuous transition.[23]

We can investigate the behavior of the system in the case of a final hybridization from the side of the dielectric phase, not introducing the self-consistent field, but making the approximations in the effective Hamiltonian (24) which are made in the initial Hamiltonian in the framework of the standard VMC theory, i.e., discarding the fourth and sixth terms in it.[4] As a result, we have the Hamiltonian

$$H = E_i \sum_\sigma \tilde{N}_\sigma + (2E_i + U) \tilde{N}_2 + \sum_{\kappa\sigma} E_\kappa \tilde{c}_{\kappa\sigma}^+ \tilde{c}_{\kappa\sigma} + U_{ic} \sum_{\kappa\kappa'} \sum_{\sigma\sigma'} \tilde{N}_\sigma \tilde{c}_{\kappa\sigma}^+ \tilde{c}_{\kappa'\sigma'}. \quad (30)$$

Here E_κ and $\tilde{c}_{\kappa\sigma}$ correspond to the actual states of the continuum which can be obtained by the method of diagonalization of H_c (18). This Hamiltonian is identical in form with the Falicov Hamiltonian, but the sf-hybridization is taken into account exactly in its derivation. In it we have made the approximation of the contact character of the sf-Coulomb interaction that is usual in UMC theory, and have set $U_i = $ const, although in reality this integral depends on the level E_i: with decrease in the depth of the level, the fraction of the f-states in $\tilde{\varphi}_d(r)$ falls off but the fraction in $\tilde{\varphi}$ (r) increases, which can be seen already from (19). This simplification is not basic, since one can show that the ground term in $U_{ic}(\kappa\kappa')$ is actually factored out and the problem of the Green's function of the κ electrons admits an exact solution of the same type as the Hewson-Riseborough solution.[23]

Thus, using the Hewson-Riseborough method for the Hamiltonian (30), we obtain an expression for the average number of electrons in the localized state as a function of the chemical potential at $T = 0$:

$$\tilde{N}_i = \left[N_i - N \int^\mu S_0(\omega) d\omega \right] \Big/ \left[1 + N \int^\mu S_1(\omega) d\omega \right]. \quad (31)$$

Here S_0 is the density of states of the free continuum, and S_1 is the additional density of states arising from Coulomb scattering. The quantities S_0 and S_1 generally depend on the location of the level E_i in the forbidden band, but for qualitative consideration of the problem this is again unimportant. It is important that, as in the Hewson-Riseborough case, Eq. (31) allows only a continuous transition to the metallic state, which represents simply a "squeezing out" of the f level from the gap, unaccompanied by any discontinuities or exciton effects.

Thus, our consideration confirms the conclusion that in the Anderson model there is no "stripping" of the level E_i, and its appearance in the theory is connected exclusively with the splittings in the Coulomb term of the Hamiltonian (30).[7,8,21,22] However, it should be noted that a more accurate account of the "exciton" averages also gives only a smooth transition to the metallic phase (D. I. Khomskiĭ, private communication). All these arguments can be added to the arguments against the use of the mean field approximation in VMC summed up in Sec. 2.

In spite of the apparent similarity of the Hamiltonian (30) with the Hamiltonian of Falicov, our "exact" solution differs from the similar solution of Hewson-Riseborough because it is not the bare level but the actual localized level that is squeezed out into the band (in Eq. (31), we have $\langle N_i \rangle$ and not $\langle n_f \rangle$). Thanks to this, non-monotonicity in the occupation numbers still takes place, although it differs from the usual dependence in cases of continuous (Fig. a) and jumpwise (Fig. b) transitions in the mean field approximations. The number of electrons at the level E_i apparently changes jumpwise from 1 to 0 as $E \to E_c$ (the dashed line in Fig. c). But the average number of f-electrons here at the site $\langle n_f \rangle$ falls off monotonically with breakup of the level and generally approaches zero in correspondence with (14) and (19) as $E \to E_c$. (The solid curve in Fig. c; on the drawings, the occupation numbers of are plotted as a function of the location of the bare level E_f). However, strictly speaking, our description is suitable only for the case in which the level E_i is occupied and there are no free carriers in the band; therefore the immediate vicinity of the transition and, in addition, the metallic region cannot be described. Furthermore, the transition of carriers into the band is accompanied by the appearance of charged f-ions and, consequently, a departure from the bottom of the conduction band of the shallow impurity levels to which the carriers are attracted. In any case, it is clear that first, at suffi-
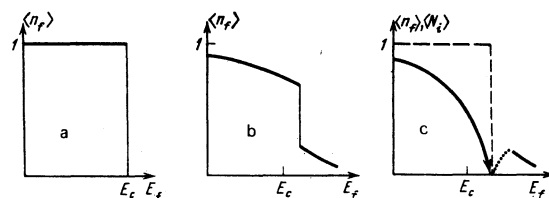

FIG. 1.

ciently large values of E_f in the allowed band the dependence $\langle n_f \rangle$ (E_f) should be approximately the same as in drawing b, and second, all the non-monotonicities around the point E_c are essentially connected with the single-site model and have no direct relation to the phase transitions in the rare-earth metal chalcogenides.

Evidently, within the framework of the single-node model, the VMC problem cannot be solved. One must consider a periodic system, for which there is a simple canonical transformation both in the semiconducting and in the metallic phase. The approach to the semiconducting phase, proposed in the present paper, is generalized without difficulty, and if the intra-atomic Coulomb interaction of the hybridized electrons in the narrow band originating from the level E_f it becomes the Hubbard approach but its width increases upon approach of E_f to E_c. It is clear that this picture has little in common with the single-site case. Thus, as a qualitative conclusion, one can note that the exact solution of the problem of the semiconducting phase of VMC in the single-center approximation demonstrates the weakness of this model no less clearly than the approximate consideration with the help of splittings of the self-consistent field demonstrates its worth.

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APPENDIX

The canonical transformation (16) gives

$$c_d = \tilde{c}_d \cos\gamma + \sum_k u_k \tilde{c}_k \gamma^{-1} \sin\gamma,$$

$$c_k = \tilde{c}_k + \gamma^{-2}(\cos\gamma - 1) u_k \sum_{k'} u_{k'} \tilde{c}_{k'} - \gamma^{-1}\sin\gamma\, u_k \tilde{d}, \qquad (A.1)$$

$$\gamma^2 = \sum_k u_k^2$$

(for simplicity, we assume the coefficients u_k to be real, generalization to the case of complex u_k is trivial; the index σ is omitted, since the operator e^S does not mix states with different spin projections). Substituting (A.1) in H_1 (15), we find

$$\frac{E_d - 2T\,\mathrm{tg}\,\gamma + Z\,\mathrm{tg}^2\,\gamma}{1 + \mathrm{tg}^2\,\gamma} = E_i, \qquad (A.2)$$

$$u_k \gamma^{-1}\{(E_d - Z)\sin\gamma\cos\gamma - (E_k - Z)\sin\gamma + T(\cos^2\gamma - \sin^2\gamma)$$
$$- T\cos\gamma\} + g_k\cos\gamma = 0, \qquad (A.3)$$

$$T = \gamma^{-1}\sum_k u_k g_k, \qquad Z = \gamma^{-2}\sum_k u_k^2 E_k.$$

The left side of Eq. (A.3) is the coefficient for $c_k^* c_d$ in H_1. Multiplying (A.3) by u_k and summing over k, we get

$$T(1 - \mathrm{tg}^2\,\gamma) + (E_d - Z)\,\mathrm{tg}\,\gamma = 0. \qquad (A.4)$$

With account of (A.4), the expression (A.3) transforms to

$$\gamma g_k + T u_k - u_k(E_k - Z)\,\mathrm{tg}\,\gamma = 0. \qquad (A.5)$$

Simultaneous solution of (A.2), (A.4), and (A.5) gives

$$u_k = \frac{\gamma g_k}{(E_k - E_i)\,\mathrm{tg}\,\gamma}, \qquad \mathrm{tg}^2\,\gamma = M',$$

and also (17) and (18).

It must be emphasized that in the derivation, essential use was made of the condition of the existence of a localized level in the forbidden band [Eq. (A.2)]; therefore the canonical transformation in the given form is applicable only to the case of Anderson impurities in the semiconductor.

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[1] Since the matrix element g_k projects the state of the continuum on the space corresponding to the symmetry of the bare wave function of the electron of the unfilled shell[6], the distortion affects only the components with $l = 1, 2$ for impurities of transition metals in tetragonal semiconductors and with $l = 3$ systems of the type SmS (cf. Ref. 14).

[2] However, even in this case, at low density of the free carriers, when one can make use of the gas approximation to take into account a strong, short-range potential, the effective single-site interaction turns out to be small.[15]

[3] In solving numerically the problem for the model of semielliptic density of the states in the nondegenerate model and in the Hewson approximation, we have not found solutions with a localized moment.

[4] The conditions under which these terms are insignificant were discussed in Sec. 3. We add to this disscussion the remark that discarding the hybridization with polar states in the presence of free carriers can turn out to be a not entirely harmless operation, since Hamiltonians of this type are nonanalytic in the hybridization constant (see, for example, Refs. 24 and 25). However, this remark should be addressed to all authors engaged in the CVV problem.

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