was estimated from the change of the work function of the electrons leaving the surface. The minima on curves 2 and 3 appeared after the buildup of the first and second atomic layers of copper, and their depth, as seen from the figure, depended on the annealing temperature.

According to data obtained by the SED method,[6] the copper atoms evaporated at room temperature on the (110) face of the tungsten single crystal form in the first layer a regular lattice that duplicates the substrate structure. The next two layers also duplicate this structure, but the agreement between the substrate and the film decreases gradually. The minima on curves 2 and 3, which represent in final analysis the dependence of the specularity coefficient p on the copper concentration, is observed when the translational symmetry is restored on the surface. At large copper concentrations, the agreement vanishes gradually and the oscillations of p attenuate.

The character of the reflection of the conduction electrons from the surface of the metallic crystals thus depends on the type of the diffraction processes that are realized on the conductor boundary. If the translational symmetry on the crystal surface is preserved, the electron reflection can be close to specular.

[1]A. F. Andreev, Usp. Fiz. Nauk 105, 113 (1971) [Sov. Phys. Usp. 14, 609 (1972)].
[2]R. F. Greene, transl. in: Poverkhnostnye svoĭstva tverdykh tel (Surface Properties of Solids), Mir, 1972, p. 127.
[3]P. P. Lutsishin, O. A. Panchenko, and A. A. Kharlamov, Zh. Eksp. Teor. Fiz. 64, 2148 (1973) [Sov. Phys. JETP 37, 1083 (1973)].
[4]O. A. Panchenko, P. P. Lutsishin, and Yu. G. Ptushinskiĭ, Zh. Eksp. Teor. Fiz. 66, 2191 (1974) [Sov. Phys. JETP 39, 1079 (1974)].
[5]O. A. Panchenko, A. A. Kharlamov, and Yu. G. Ptushinskiĭ, Zh. Eksp. Teor. Fiz. 67, 780 (1974) [Sov. Phys. JETP 40, 386 (1975)].
[6]E. Bauer, H. Poppa, G. Todd, and F. Bonczek, J. Appl. Phys. 45, 5164 (1974).
[7]V. G. Peschanskiĭ and M. Ya. Azbel', Zh. Eksp. Teor. Fiz. 55, 1980 (1968) [Sov. Phys. JETP 28, 1045 (1969)].
[8]V. V. Shishkov, G. I. Aleksandrova, M. V. Pikunov, and N. I. Strigina, Fizika i khimiya obrabotki materialov 4, 43 (1975).
[9]R. M. Stern, Appl. Phys. Lett. 5, 218 (1964).
[10]O. A. Panchenko and P. P. Lutsishin, Zh. Eksp. Teor. Fiz. 57, 1555 (1969) [Sov. Phys. JETP 30, 841 (1970)].
[11]J. W. Rayleigh, Proc. London Math. Soc. 17, 4 (1885).
[12]L. D. Landau and E. M. Lifshitz, Teoriya uprugosti (Theory of Elasticity), Nauka, 1965, Sec. 24. [Pergamon, 1971].

Translated by J. G. Adashko

Valence-change transitions in rare-earth compounds

A. N. Kocharyan and D. I. Khomskiĭ

P. N. Lebedev Physics Institute, USSR Academy of Sciences

(Submitted March 5, 1976)
Zh. Eksp. Teor. Fiz. **71**, 767–777 (August 1976)

The effect of exciton phenomena on the properties of localized impurity states and on the characteristics of electronic phase transitions with change of valence in rare-earth metals and compounds is considered. It it shown that Coulomb interaction between localized f-electrons and conduction electrons may broaden the narrow f-levels; this broadening depends (in contrast to the width of the virtual levels in the Anderson model) on the position of the E_0 level with respect to the Fermi energy; the width is maximal at $E_0 = \epsilon_F$. It is shown that if this effect is taken into account the f-level near ϵ_F may become stabilized and states with an intermediate valence may arise. In this case two consecutive phase transitions of the γ-α-α' type can occur in Ce under pressure. The influence of compressibility of the lattice is taken into account. The shapes of the phase diagrams of substances like Ce or SmS are discussed qualitatively.

PACS numbers: 71.55.Dp, 71.80.+j

1. INTRODUCTION

Rare-earth (RE) ions, both in metals and in compounds, are characterized usually by a definite occupation of the internal $4f$ shell with an integer number of f electrons; their state can be described by corresponding atomic quantum numbers (spin, orbital angular momentum, etc.). Direct overlap of the wave functions of the f electrons on different centers is usually small and depends little on their properties.

There are, however, a number of systems in which states of different valence are close in energy (for example, Sm^{2+} and Sm^{3+} in SmS). In these cases, transitions are possible between such states when the external conditions (pressure, temperature, composition) are changed, or, in other words, an f electron can go over into the conduction band (process of the type $Sm^{2+} \rightarrow Sm^{3+} + s$ electron). This phenomenon is assumed to be the cause of the experimentally observed, in a number of substances, electronic phase transitions, such as $\gamma-\alpha-\alpha'$ transitions in Ce[1] or dielectric–metal transitions in SmS, SmSe, SmTe,[2] TmTe,[3], EuO.[4] These phase transitions are usually not connected with a change in the lattice symmetry. They can be either first-order transitions (SmS, EuO), or continuous transitions (SmSe, SmTe); the corresponding phase-equilibrium line can terminate at the critical point ($\gamma - \alpha$ transition in Ce).

It is quite interesting that near the transition the RE ions are characterized by partial occupation of the f level, i.e., they have a non-integer (intermediate) valence. Thus, in the metallic phase of SmS the valence of Sm is equal to 2.7; in Ce, the γ phase is a phase with intermediate valence, which varies with pressure from ~ 3.7 near the $\gamma - \alpha$ transition to ~ 3.85 at ~ 50 kbar, where a second phase transition is observed into a phase α' with valence 4 (empty f level).[1)]

The theoretical description of these phenomena usually starts out from the model of two bands: strongly localized f electrons and conduction electrons (we shall call them for brevity s electrons, although in these substances they have more readily a d or sd character). The simplest and most attractive is Falicov's model,[8] which connects the transitions with the influence of the Boulomb interaction between the f and s electrons (in this approach we can take into account also lattice effects[9,10]).

The analysis of[8] makes it possible to describe a number of qualitative characteristics of electron phase transitions, such as their jumplike or smooth character and the phase-equilibrium line shape for the $\gamma - \alpha$ transition, including the critical point. The initial form of this model, however, is subject to one significant shortcoming: in first-order transitions the number of f electrons changes jumpwise by unity, i.e., it does not describe states with intermediate valence. Nor is it possible to obtain in the usual approach the second phase transition in Ce, of the $\alpha - \alpha'$ type.

States with intermediate valence were obtained within the framework of the Falicov model in[11,12] with account taken of the hybridization of the f and s levels. This factor leads to a non-integer occupation of the f level; the transition itself becomes somewhat smeared out in this case.

It turns out, however, that besides the usual hybridization, analogous consequences can result also from the Coulomb $f-s$ interaction itself. An examination of this effect is in fact the purpose of the present paper. It will be shown that the Coulomb interaction can lead under certain conditions (when the f level E_0 lies near the Fermi level ε_F), besides to a jumplike transition, to an additional broadening of the f level and by the same token can imitate the influence of hybridization. Allowance for this circumstance also leads to the appearance of a state with intermediate valence, which is analogous in many respects to the "excitonic dielectric."[13] A second phase transition from such a phase into a phase with integer valence (of the type of the $\alpha - \alpha'$ transition in Ce) then becomes possible. Within the framework of the developed approach, it is possible to describe in a unified manner the various possible types of phase transitions, obtain states with intermediate valence, and explain qualitatively the main features of the observed phase diagrams.

The principal results of the present paper were reported at the All-Union Conference on Low-Temperature Physics; a brief exposition was given in[14]. Similar ideas wherein hybridization increases as a result of excitonic effects were also advanced recently by Zaslavskiĭ *et al.*,[15] and were used to consider magnetic properties of transition metals.

2. FORMULATION OF MODEL

For the sake of argument we shall discuss a system of the Ce type, where the occupied f level crosses the conduction band. All the results can be easily transferred to the case of systems such as SmS, where the f level goes over under pressure from the forbidden band to the conduction band and where the electronic transition is simultaneously a dielectric–metal transition. The Hamiltonian of the model in question is

$$H = \sum_{k,\sigma} \varepsilon_k a_{k\sigma}^+ a_{k\sigma} + E_0 \sum_{n,\sigma} b_{n\sigma}^+ b_{n\sigma} + \frac{1}{N} \sum_{k,n,\sigma} (V_{kn} a_{k\sigma}^+ b_{n\sigma} + \text{H.c.}) + \frac{1}{N} \sum_{k,k',n,\sigma,\sigma'} g(k,k',n) a_{k\sigma}^+ a_{k'\sigma} b_{n\sigma'}^+ b_{n\sigma'} + U \sum_n b_{n\uparrow}^+ b_{n\uparrow} b_{n\downarrow}^+ b_{n\downarrow}. \quad (1)$$

The first term is the energy of the conduction electrons, the second is the energy of the localized f electrons, the third is the $f-s$ hybridization, the fourth describes the repulsion of the f and s electrons, and the last describes the intra-atomic repulsion of two f electrons.

In order not to complicate the exposition, we introduce in the main part of the article some additional simplifications. As is known, at large U the repulsion of the f electrons causes them to become localized.[16] We, like Falicov *et al.*,[8] shall use this circumstance directly, assuming that the f level can be occupied not more than once, and therefore omit the last term; at the same time we shall omit the spin indices. The results of the general analysis are given in Sec. 4 and in the Appendix.

We assume the hybridization matrix elements to be independent of the number of the site, $V_{kn} = V$. This approximation corresponds in fact to the fact that the metal is regarded as an aggregate of "impurities" situated at each site of the lattice. This description of REM is widely used[17]; it permits a close analogy with the Anderson model.[18] We assume correspondingly also $g(k,k',n) = g$.

It is easy to verify that the principal results remain in force also when account is taken of the periodicity in the location of the centers. Moreover, it can be shown[19,20] that when account is taken of the strong interelectron correlation and the ensuing localization of the f electrons, the features of the "impurity" model are duplicated to a great extent here, too.

Thus to separate the main features we consider first a spinless model with Hamiltonian

$$H = \sum_k \varepsilon_k a_k^+ a_k + E_0 \sum_n b_n^+ b_n + \frac{V}{N} \sum_{k,n} (a_k^+ b_n + \text{H.c.}) + \frac{g}{N} \sum_{k,k',n} a_k^+ a_{k'} b_n^+ b_n. \quad (2)$$

3. VIRTUAL STATE WITH VARIABLE WIDTH FOR ONE IMPURITY

We consider first the case of one impurity with a localized electron. In accordance with (2), its description differs from the Anderson model in that the $f-s$ interac-

tion is taken into account. The hybridization term in (2) causes the ground state of the wave functions of the f and s electrons to become mixed, so that besides the mean values $\langle a_k^+ a_k\rangle = n_{ks}$ and $\langle b^+ b\rangle = n_f$, the "anomalous mean values" $\langle a_k^+ b\rangle$ become different from zero (they can be called "excitonic"). Consequently it is necessary to take them into account also in the $f-s$ interaction term. We shall therefore subdivide the equations of motion in a manner that separates these mean values, a procedure equivalent to the substitution

$$ga_k^+ a_{k'} b^+ b \to ga_k^+ \langle a_{k'} b^+\rangle b + \text{H.c.} \tag{3}$$

Obviously, the obtained terms have the same structure as the hybridization terms in (2). Here, however, in contrast to the hybridization constant V, the corresponding parameters must be determined in a self-consistent manner. In essence, the separation of the anomalous mean values (3) is fully analogous to the similar procedure in an excitonic dielectric.

Using the separation (3), the equation of motion for the Green's function take the form

$$\begin{aligned} E\langle\langle b|b^+\rangle\rangle &= \frac{1}{2\pi} + E_0\langle\langle b|b^+\rangle\rangle + \tilde V^* \sum_k \langle\langle a_k|b^+\rangle\rangle, \\ E\langle\langle a_k|b^+\rangle\rangle &= \varepsilon_k\langle\langle a_k|b^+\rangle\rangle + \tilde V\langle\langle b|b^+\rangle\rangle. \end{aligned} \tag{4}$$

Here

$$\tilde V = V + \Delta, \qquad \Delta = g\sum_{k'}\langle a_{k'} b^+\rangle. \tag{5}$$

From (4) we obtain in the usual manner

$$G_{ff} = \langle\langle b|b^+\rangle\rangle = \frac{1}{2\pi}\left(E - E_0 - \sum\frac{|\tilde V|^2}{E-\varepsilon_k}\right)^{-1}, \tag{6}$$

$$G_{fs}^k = \langle\langle a_k|b^+\rangle\rangle = \frac{\tilde V}{E-\varepsilon_k}\langle\langle b|b^+\rangle\rangle. \tag{7}$$

Writing down

$$\sum_k \frac{|\tilde V|^2}{E-\varepsilon_k} = \mathrm{P}\sum_k \frac{\tilde V^2}{E-\varepsilon_k} - i\pi|\tilde V|^2\sum_k \delta(E-\varepsilon_k)$$

and omitting, as usual, the real part (the level shift due to it merely renormalizes E_0), we obtain from (6) the state density of the f electrons

$$\rho_f(E) = \frac{1}{\pi}\frac{\Gamma}{(E-E_0)^2+\Gamma^2}, \tag{8}$$

where

$$\Gamma = \pi|\tilde V|^2\sum_k \delta(E-\varepsilon_k) = \pi\rho(V+\Delta)^2, \tag{9}$$

and from (7) we obtain the equation for the self consistency for the anomalous mean value of Δ (5):

$$\Delta = g\sum_k\langle a_k b^+\rangle = -g(V+\Delta)\int\left\{\left\langle\left\langle\sum_k a_k|b^+\right\rangle\right\rangle_{E+i\varepsilon} - \left\langle\left\langle\sum_k a_k|b^+\right\rangle\right\rangle_{E-i\varepsilon}\right\}dE = -(V+\Delta)\frac{g\rho}{2}\ln\frac{(E_0-\varepsilon_F)^2+\Gamma^2}{\xi_0^2}. \tag{10}$$

Here $\xi_0 \sim \varepsilon_F$ is the cutoff energy.

It is seen from (10) that even at $V=0$ there can exist a nontrivial solution corresponding to a nonzero "excitonic hybridization":

$$\Gamma_{exc} = \pi\rho\Delta^2 = [(\xi_0 e^{-1/g\rho})^2 - (E_0-\varepsilon_F)^2]^{1/2}. \tag{11}$$

In accordance with (11), $\Delta \neq 0$ if the f-level lies sufficiently close to ε_F, $|E_0-\varepsilon_F| < E_c = \xi_0 e^{-1/g\rho}$; the width of the level is maximal when the f level crosses the Fermi energy. At $V\neq 0$, as seen from (10), the level is always broadened, but again Γ is maximal at $E_0 = \varepsilon_F$.

We have thus found that as a result of allowance for the excitonic effects connected with the $f-s$ interaction, the effective width of the impurity level, in contrast to the usual Anderson model, turns out to be variable: the level is strongly smeared out when it lies close to ε_F. This result can be compared with the experimental data,[21] according to which levels that lie deep under the Fermi surface are quite sharp, and only the levels close to ε_F exhibit a noticeable width. The considered effect can manifest itself in a number of properties of the magnetic impurities: in the magnitude of the indirect exchange, in the influence of these levels on the superconductivity,[22,23] in magnetic–nonmagnetic impurity transitions.[21] A rough qualitative estimate shows that at $\xi_0 \sim \varepsilon_F \sim 5$ eV and at a dimensionless Coulomb constant $g\rho \sim \frac{1}{4}-\frac{1}{5}$ the level width reaches values on the order of $\Gamma \sim 0.04-0.1$ eV, which is close in order of magnitude to the experimental value for the Ce impurity in La; thus, the considered effect can explain the level broadening even without resorting to lattice hybridization.

4. ELECTRONIC PHASE TRANSITIONS IN RARE-EARTH METALS AND COMPOUNDS

We proceed now to consider concentrated systems with large numbers of f electrons. In this case, owing to the $f-s$ interaction, even the relative positions of the f level and the s band can change with changing number of f electrons. In simplest form, this effect can be seen by taking into account this interaction in the Hartree-Fock approximation,[8] $ga^+ab^+b \to gn_s b^+b + gn_f a^+a$. It is seen that in this case there is simply a renormalization of the f and s levels, $E_0 \to E_0 + gn_s$, $\varepsilon_k \to \varepsilon_k + gn_f$, which depends on the number of f electrons n_f and s electrons $n_s = n_0 - n_f$, where n_0 is the total number of the electrons per center. It is precisely this factor, as shown in[8] which can lead to jumplike transitions when the f level moves (i.e., when E_0 is altered, for example, by pressure). The value of n_f itself is determined in this approach by the self-consistency equation; when simultaneous account is taken of the excitonic effect we shall need, thus, solve a coupled system of equations for n_f and Δ.

In accordance with the foregoing, we now take into account (first with the model (2)) both factors, the excitonic hybridization described in Sec. 3, and the self-consistent renormalization of the levels; we effect accordingly in the $f-s$ interaction the following separation of the terms:

$$\frac{g}{N}\sum_{k,k',n} a_k^+ a_{k'} b_n^+ b_n \to g n_s \sum_n b_n^+ b_n + g n_f \sum_k a_k^+ a_k + \frac{1}{N}\sum_{k,n} (\Delta a_k^+ b_n + \text{H.c.}). \quad (12)$$

In the second member we have left out here the terms with $k = k'$; it is easy to show that allowance for these terms leads only to a renormalization of the hybridization matrix element.

Inasmuch as in the assumed model (2) the interaction and hybridization matrix elements do not depend on the number n of the site, all the centers turn out to be equivalent, and the summation over n reduces simply to the multiplication by the number of centers N. It is easy to verify that this leads in all equations simply to cancellation of the factor $1/N$ in the hybridization term. Since the subscript n can be left out in the manipulations, both the equations of motion for the Green's function and their solutions will take a form exactly analogous to (4)–(7), with replacement of E_0 by $E_0 + gn_s$ and of ε_k by $\varepsilon_k + gn_f$. Accordingly, the density of states of the f electrons is equal to

$$\rho_f(E) = \frac{1}{\pi}\frac{\Gamma}{(E - E_0 - gn_s)^2 + \Gamma^2}, \quad (13)$$

where $\Gamma = \pi\rho(V+\Delta)^2$, and the self-consistency equation for Δ again yields, just as (10) and (11), the following width at $V = 0$:

$$\Gamma = \pi\rho\Delta^2 = \{(\xi_0 e^{-1/g\rho})^2 - [E_0 + gn_s - \varepsilon_F(n_f)]^2\}^{1/2}. \quad (14)$$

Here, however, it is necessary also to take into account the fact that the very position of the Fermi level depends on n_f and changes when the f electrons go over to the conduction band. At constant density of states of the s electrons ρ we have $\varepsilon_F(n_f) = \varepsilon_F(1) + (1 - n_f)(1/\rho - g)$.

Starting from (13), we obtain an equation for n_f:

$$n_f = \int_{-\infty}^{\varepsilon_F(n_f)} \rho_f(E)\,dE = \frac{1}{\pi}\operatorname{arcctg}\frac{E_0 + gn_s - \varepsilon_F(n_f)}{\Gamma}. \quad (15)$$

In the absence of excitonic mean values (at $\tilde{V} = V$), Eq. (15) coincides with that obtained earlier in[12]. As shown there, depending on the ratio of the parameters, this equation leads to a change of E_0 or else to a first-order transition with $n_f \neq 1$ and $n_f \neq 0$ in the vicinity of the transition, or to merely a smooth variation of n_f.

We consider now the behavior of the system with account taken of the excitonic hybridization (at $V = 0$). Substituting (14) in (15), we can reduce (15) to the form

$$\xi_0 e^{-1/g\rho}\cos \pi n_f = \tilde{E}_0 - \tilde{\varepsilon}_F - 2\tilde{g}(n_f - 1). \quad (16)$$

We have introduced here the notation $\tilde{E}_0 = E_0 + g(n_0 - 1)$, $\tilde{\varepsilon}_F = \varepsilon_F(1)$ (the position of the f level and the Fermi energy when the f level is occupied, $n_f = 1$) and the renormalized coupling constant $\tilde{g} = g - 1/2\rho$. From a graphic solution of Eq. (16) we see that when the f level moves upward (actually $\tilde{E}_0(p) = E_0 + cp$, see Sec. 5) the number of f electrons changes from 1 to 0. In this case, depending on the value of the constant $\tilde{g}$, different cases are possible: 1) the transition is smooth if the interaction is weak; 2) at a stronger interaction, two successive transitions with an intermediate-valence phase between them are possible, Fig. 1a; 3) finally, at a still stronger interaction, one strong transitions of first order is possible without a significant intermediate valence.

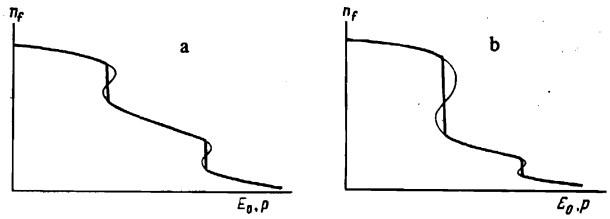

FIG. 1. a) Dependence of the number of f electrons n_f on the position of the level E_0 (or on the pressure p) at intermediate values of the interaction constant g in (16); b) the same in accordance with Eq. (17) or when account is taken of the variation of the density of states of the s electrons with pressure.

A similar equation results also from an analysis based on the complete Hamiltonian (1). When the correlation of the f electrons is taken into account by Hubbard's method, it takes the form (see the Appendix)

$$\xi_0 \exp\left\{-\frac{2}{g(2-n_f)\rho}\right\}\cos\frac{\pi n_f}{2-n_f} = \tilde{E}_0 - \tilde{\varepsilon}_F - 2\tilde{g}(n_f - 1). \quad (17)$$

Equation (17) leads in general outline to the same result as (16), but an asymmetry, as shown in Fig. 1b, appears in the solution (see also Sec. 5).

We see thus that simultaneous allowance for the level shift and for the broadening, which result from the Coulomb interaction of the f and s electrons, yields a variety of types of phase transitions. In particular, excitonic hybridization can stabilize the phase with intermediate valence, with the f level secured near the Fermi level.

The physical cause of this behavior can be easily understood. Direct interaction of the f and s electrons, of the density–density type, causes integer values $n_f = 0$ and $n_f = 1$ to be favored (roughly speaking, the interaction energy is $E_{\text{int}} = gn_f(1 - n_f)$); it is this which causes the tendency to a jumplike transition. However, when the f level is far from ε_F, its width in accordance with (11) is small. On the other hand, if the f level lies near ε_F, then it acquires an appreciable width. As a result, the density of the f states smears out and the kinetic energy of the occupied f states becomes lower. This effect acts in opposition to the influence of the interaction energy and can stabilize the f level near ε_F, leading to a phase with intermediate valence.

5. ALLOWANCE FOR THE COMPRESSIBILITY OF THE LATTICE

In the foregoing we chose as the parameter the position of the f level E_0. Actually, E_0 depends on the specific volume v, while phase transitions are observed in reality with changing pressure p. We change over below, in analogy with[9,10], to the variable p and take at the same time account of the lattice compressibility. We assume here that the only quantity dependent on the

volume v is $E_0(v) = E_0(v_0) - a(v - v_0,\ a > 0$. Actually the relative locations of the f level and of the conduction band (which in SmS has seemingly the character of the t_{2g} subband of the $5d$ band, and in Ce has a mixed sd character) depends on the atomic volume primarily because of the change of the splitting of the d-subbands by the crystal field, and also because of the broadening of the conduction band; the change of ρ will be neglected for simplicity. The electronic part of the total energy at an f-electron number n_f (or an f-hole number $\nu = 1 - n_f$) takes in the simplest approximation the form

$$\mathscr{E} = [\varepsilon_F - E_0]\nu - (g - 1/\rho)\nu^2. \tag{18}$$

Adding to (18) the elastic energy and changing over to the variable p, we write down the enthalpy of the system

$$H = \mathscr{E} + pv = [\varepsilon_F - E_0]\nu - (g - 1/\rho)\nu^2 + {}^1/_2\varkappa(v - v_0)^2 + pv. \tag{19}$$

Minimizing (19) with respect to v, we obtain from the condition $\partial H/\partial v = 0$

$$v - v_0 = -(a\nu + p)/\varkappa, \tag{20}$$

$$H_{min}(\nu) = \left[\varepsilon_F - E_0(v_0) - \frac{a}{\varkappa}p\right]\nu - \left(g - \frac{1}{\rho} + \frac{a^2}{2\varkappa}\right)\nu^2 - \frac{p^2}{2\varkappa}. \tag{21}$$

Thus, as the result of allowance for the compressibility of the lattice we find, first, that the f level moves linearly upward with pressure and, second, that a factor $a^2/2\varkappa$ is added to the Coulomb interaction. Combining these results with the statements made in Sec. 4, we see that the main conclusions remain in force, and the conditions for the first-order transition become easier (the effective interaction increases, $g \to g + a^2/2\varkappa$). At a sufficient value of the term $a^2/2\varkappa$, the jumplike transition is possible even without allowance for the Coulomb interaction at $g = 0$. This explanation of the transitions in RE compounds, based on the pure lattice mechanism, was proposed in[24,25].

A similar analysis can be carried out also with the allowance for the dependence on the volume of the width of the band W and the density of states ρ. It is qualitatively easy to understand that, since, W increases upon compression and ρ decreases, the conditions for the jumplike transition

$$g + \frac{a^2}{2\varkappa} - \frac{1}{\rho} > 0$$

become worse and the jump of the valence in the second phase transition discussed in Sec. 4 will be smaller (see Fig. 1b) and may vanish completely, so that this transition becomes smooth. This factor can be connected with a jump of n_f that is smaller in the $\alpha - \alpha'$ transition of Ce than in the $\gamma - \alpha$ transition, and also with the smooth behavior of the valence in the metallic phase of SmS.

6. DISCUSSION OF RESULTS

The main result of this study, which is contained in Secs. 3 and 4, reduces to the fact that when the f–s interaction is taken into account the width of the virtual levels in the metal becomes variable, going through a maximum when the f level crosses the Fermi level. This can influence both the properties of the magnetic impurities and in particular the transitions with changes of valence in REM and their compounds, leading in particular to the possibility of two successive phase transitions and to states with intermediate valence. A phase with intermediate valence is described in this approach to a considerable degree in analogy with the excitonic dielectric,[13] being characterized by a nonzero "anomalous mean value" of Δ. Such an interpretation explains also certain characteristic features of phase diagrams of the considered systems.

One can expect first of all that with increasing temperature the "order parameter" Δ will decrease and at a certain temperature it may vanish. The material will then go over to the "normal" state with a number of electrons close to an integer (smeared out, of course, by the temperature). This behavior corresponds to that experimentally observed in Ce, where an intermediate phase α goes over with increasing T into an integer-valence phase γ or α' ($dT_c/dp > 0$ for the transition $\gamma - \alpha$ and $dT_c/dp < 0$ for $\alpha - \alpha'$).

The positive slope of the $\gamma - \alpha$ equilibrium line is usually attributed to the larger spin entropy of the γ phase; from this point of view, however, one could expect $dT_c/dp > 0$ also for the $\alpha - \alpha'$ transition, inasmuch as in the α' phase there vanishes that small fraction of the f electrons which had still remained in the α phase. One can assume that owing to the smaller specific volume of the α' phase the lattice entropy in it should also be smaller (provided that the phonon frequencies do not soften significantly because of the possible change in the lattice symmetry). This contradiction can likewise be resolved, in particular, by using the procedure described in the present paper.

A similar situation takes place also in SmS,[26] where the high-temperature phase corresponds to a dielectric with nonmagnetic ions Sm^{2+}, and the low-temperature phase corresponds to a metal with Sm^{3+} ions having $J = \frac{5}{2}$ and accordingly a larger a spin entropy. This result is attributed[27] to the contribution of the higher-excited states of the ions; there is, however, also a possible explanation based on the fact that the metallic phase with intermediate valence is characterized by an additional "excitonic" ordering, which is violated with increasing T.

It is of course difficult to justify rigorously the generalized self-consistent-field approximation used in the present paper, particularly for heavy f-holes. One can hope, however, that it accounts correctly for the main qualitative features of the considered phenomenon, and it can be assumed, in particular, that it is suitable at not too small values of n_f (cf.[10]). In the least, it seems promising that even in the simplest form the model under consideration yields qualitative results that are close in form to those observed in experiment.

In conclusion, we are deeply grateful to L. V. Keldysh and E. G. Maksimov and also to V. L. Ginzberg and the participants of the seminar under his direction for useful discussions.

APPENDIX

The general system of equations for the Green's function in the model (1) takes the form

$$E\langle\langle b_\sigma|b_\sigma^+\rangle\rangle=\frac{1}{2\pi}+(E_0+gn_s)\langle\langle b_\sigma|b_\sigma^+\rangle\rangle+U\langle\langle b_{-\sigma}^+b_{-\sigma}b_\sigma|b_\sigma^+\rangle\rangle+\sum_k(V^*+\Delta_\sigma^*)\langle\langle a_{k\sigma}|b_\sigma^+\rangle\rangle, \tag{A1}$$

$$E\langle\langle a_{k\sigma}|b_\sigma^+\rangle\rangle=(\varepsilon_k+gn_f)\langle\langle a_{k\sigma}|b_\sigma^+\rangle\rangle+(V+\Delta_\sigma)\langle\langle b_\sigma|b_\sigma^+\rangle\rangle, \tag{A2}$$

$$E\langle\langle b_{-\sigma}^+b_{-\sigma}b_\sigma|b_\sigma^+\rangle\rangle=\frac{n_{f-\sigma}}{2\pi}+(E_0+gn_s)\langle\langle b_{-\sigma}^+b_{-\sigma}b_\sigma|b_\sigma^+\rangle\rangle+U\langle\langle b_{-\sigma}^+b_{-\sigma}b_\sigma|b_\sigma^+\rangle\rangle+\sum_k(V^*+\Delta_\sigma^*)\langle\langle b_{-\sigma}^+b_{-\sigma}a_{k\sigma}|b_\sigma^+\rangle\rangle$$

$$-\sum_k\{(V^*+\Delta_\sigma^*)\langle\langle a_{k-\sigma}b_{-\sigma}^+b_\sigma|b_\sigma^+\rangle\rangle-(V+\Delta_\sigma)\langle\langle b_{-\sigma}a_{k-\sigma}^+b_\sigma|b_\sigma^+\rangle\rangle\}. \tag{A3}$$

We have introduced here the notation $n_s=\sum_{k\sigma}\langle a_{k\sigma}^+a_{k\sigma}\rangle$, $n_{f\sigma}=b_\sigma^+b_\sigma$, $n_f=n_{f\sigma}+n_{f-\sigma}$, $\Delta_\sigma=g\sum_k\langle a_{k\sigma}b_\sigma^+\rangle$ and split off the $f-s$ interaction term, in analogy with (12). Just as in Sec. 4, by virtue of the equivalence of all the sites, we have left out the site label n. We have retained in (A1) the terms describing the strong correlation of the electrons at one center. In contrast to the simple Hubbard model,[16] besides the terms of the type $\langle\langle b_{-\sigma}^+b_{-\sigma}b_\sigma|b_\sigma^+\rangle\rangle$, we retain also the function $\langle\langle b_{-\sigma}^+b_{-\sigma}a_{k\sigma}|b_\sigma^+\rangle\rangle$, which characterizes the correlation of the s and f electrons and describes in essence multiple scattering of the f electron by one center.[19,20] The equation of motion for it is of the form

$$E\langle\langle b_{-\sigma}^+b_{-\sigma}a_{k\sigma}|b_\sigma^+\rangle\rangle=(\varepsilon_k+gn_f)\langle\langle b_{-\sigma}^+b_{-\sigma}a_{k\sigma}|b_\sigma^+\rangle\rangle+(V+\Delta_\sigma)\langle\langle b_{-\sigma}^+b_{-\sigma}b_\sigma|b_\sigma^+\rangle\rangle-\sum_{k'}\{(V^*+\Delta_\sigma^*)\langle\langle a_{k'-\sigma}b_{-\sigma}^+a_{k\sigma}|b_\sigma^+\rangle\rangle-(V+\Delta_\sigma)\langle\langle b_{-\sigma}a_{k'-\sigma}^+a_{k\sigma}|b_\sigma^+\rangle\rangle\}. \tag{A4}$$

Carrying out in the last two terms of (A3) and (A4) a splitting in the form

$$\langle\langle a_{k'-\sigma}b_{-\sigma}^+a_{k\sigma}|b_\sigma^+\rangle\rangle=\langle a_{k'-\sigma}b_{-\sigma}^+\rangle\langle\langle a_{k\sigma}|b_\sigma^+\rangle\rangle,$$

taking V and accordingly $\langle a_{k\sigma}b_\sigma^+\rangle$ to be real, and using the Hermiticity conditions, we easily verify that the corresponding terms cancel each other both in (A3) and (A4). Solving the resultant closed system of equations, we get

$$\langle\langle b_\sigma|b_\sigma^+\rangle\rangle=\frac{1}{2\pi A}\left[1+\frac{Un_{f-\sigma}}{A-U}\right], \tag{A5}$$

where

$$A=E-E_0-gn_s-\sum_k\frac{(V+\Delta_\sigma)^2}{E-\varepsilon_k-gn_f},$$

$$\langle\langle a_{k\sigma}|b_\sigma^+\rangle\rangle=\frac{V+\Delta_\sigma}{E-\varepsilon_k-gn_f}\langle\langle b_\sigma|b_\sigma^+\rangle\rangle. \tag{A6}$$

In the case of strong $f-f$ interaction, $U\to\infty$, the result simplified and we obtain for the Green's function the expression

$$\langle\langle b_\sigma|b_\sigma^+\rangle\rangle=\frac{1-n_{f-\sigma}}{2\pi A}, \tag{A7}$$

which differs from the results of the model (2) actually only in the presence of the usual factor $(1-n_{f-\sigma})$ of the Hubbard model. From (A7) and (A6) we easily obtain in the paramagnetic case, $n_{f\sigma}=n_{f-\sigma}=\frac{1}{2}n_f$, an expression for the parameter

$$\Gamma=\pi\rho\Delta^2=\{[\xi_0\exp(-2/g(2-n_f)\rho)]^2-[E_0+gn_s-\varepsilon_F(n_f)]^2\}^{1/2} \tag{A8}$$

and an equation for n_f:

$$n_f=\frac{2-n_f}{\pi}\operatorname{arcctg}\frac{E_0+gn_s-\varepsilon_F(n_f)}{\Gamma}, \tag{A9}$$

from which we obtain Eq. (17).

[1)]The data on the $\alpha-\alpha'$ transition are not completely clear: it has been assumed at first[5] that this transition, just as $\gamma-\alpha$, is isomorphic, fcc–fcc. A statement was made later[6] that the phase has a different lattice symmetry. There are, however, considerations[7] according to which the lower symmetry of the α' phase in[6] might have been due to non-uniformity of the pressure.

[1]E. King, J. A. Lee, I. R. Harris, and T. F. Smith, Phys. Rev. **B1**, 1380 (1970).
[2]A. Jayaraman, V. Narayanamurti, E. Bucher, and R. G. Maines, Phys. Rev. Lett. **25**, 368 (1970).
[3]A. Chatterjee, A. K. Singh, and A. Jayaraman, Phys. Rev. **B6**, 2285 (1972).
[4]A. Jayaraman, Phys. Rev. Lett. **29**, 1674 (1972).
[5]E. Franceschi and G. L. Olcese, Phys. Rev. Lett. **22**, 1299 (1969)
[6]F. H. Ellinger and W. H. Zachariasen, Phys. Rev. Lett. **32**, 773 (1974).
[7]H. Balster and J. Wittig, J. Low Temp. Phys. **21**, 377 (1975).
[8]L. M. Falicov and J. C. Kimball, Phys. Rev. Lett. **22**, 997 (1969); R. Ramirez and L. M. Falicov, Phys. Rev. **B3**, 2425 (1971).
[9]B. Alascio and A. Lopez, Solid State Commun. **14**, 321 (1974).
[10]K. Miyamoto and T. Nagamiya, J. Phys. Soc. Jap. **38**, 726 (1975).
[11]B. Alascio, A. Lopez, and C. F. E. Olmedo, J. Phys. **F 3**, 1324 (1973).
[12]A. N. Kocharyan and D. I. Khomskiĭ, Kratk. Soobsh. Fiz. **8**, 3 (1974).
[13]L. V. Keldysh and Yu. V. Kopaev, Fiz. Tverd. Tela (Leningrad) **6**, 2791 (1964) [Sov. Phys. Solid State **6**, 2219 (1965)].
[14]A. N. Kocharyan and D. I. Khomskiĭ, 18 Vsesoyuznoe soveshchanie po fizike nizkikh temperatur (18th All-Union Conf. on Low Temperature Physics), NT-18, Tez. Dokl., Kiev, 1974, p. 135; Solid State Commun. **18**, 985 (1976).
[15]G. M. Zaslavskiĭ, E. V. Kuz'min, and I. S. Sandalov, Zh. Eksp. Teor. Fiz. **67**, 1422 (1974) [Sov. Phys. JETP **40**, 707 (1975)]; E. V. Kuz'min and I. S. Sandalov, Zh. Eksp. Teor. Fiz. **68**, 1388 (1975) [Sov. Phys. JETP **41**, 691 (1975)].
[16]J. Hubbard, Proc. R. Soc. A **276**, 238 (1963).
[17]B. Coqblin and A. Blandin, Adv. Phys. **17**, 281 (1968).
[18]P. W. Anderson, Phys. Rev. **124**, 31 (1961).
[19]A. F. Barabanov, K. A. Kikoin, and L. A. Maksimov, Teor. Mat. Fiz. **25**, 87 (1975).
[20]A. N. Kocharyan and D. I. Khomskiĭ, Preprint FIAN, 1976.
[21]D. K. Wohlleben and B. K. Coles, in: Magnetism, ed. G. Rado and H. Suhl, **5**, 3 (1973).
[22]G. F. Ratto, B. Coqblin, and E. Galleani d'Agliano, Adv. Phys. **18**, 489 (1969).
[23]A. N. Kocharyan and D. I. Khomskiĭ, Fiz. Tverd. Tela (Leningrad) **14**, 2421 (1972) [Sov. Phys. Solid State **14**, 2093 (1973)].
[24]L. L. Hirst, J. Phys. Chem. Solids **35**, 1285 (1974).
[25]C. M. Varma and V. Heine, Phys. Rev. **B11**, 4763 (1975).
[26]K. Yu. Tonkov and I. L. Aptekar', Fiz. Tverd. Tela (Leningrad) **16**, 1507 (1974) [Sov. Phys. Solid State **16**, 972 (1975)].
[27]L. J. Tao and F. Holtzberg, Phys. Rev. **B11**, 3842 (1975).

Translated by J. G. Adashko