Electron-polaron effects in compounds with an unstable *f*-shell

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The appearance of a mixed valence and of heavy fermions is linked with features of the intratomic structure of elements with an unstable *f* shell. The double electron-polaron effect which arises here in the conduction band and in the *f*-electron cores can cause an anomalous increase in the state density at the Fermi level.

1. A mixed-valence state is known to occur in intermetallic compounds of lanthanides only in systems which contain ions of Ce (the nearest integer state of the *f* shell is $f^1_{5/2}$), Sm ($f^5_{5/2}$), Eu ($f^6_{5/2} f^1_{7/2}$) and Yb ($f^6_{5/2} f^7_{7/2}$), while in intermetallic compounds of the actinides an unstable valence is exhibited by compounds of U and Np. The heavy-fermion state, which is related to the mixed-valence state, is also observed in intermetallic compounds of Ce and U. These elements are distinguished from the other elements of the 4*f* and 5*f* series in that they have low-lying excited states of the same symmetry in which an *f* electron goes from a state of "orbital collapse," where it is localized in a very narrow potential well, at an orbit with a radius $\sim 1a_b$, to an "inflated" state, with a radius of (3–10) a_B, in a centrifugal well. In certain cases, free atoms and ions acquire states which are distributed between two wells of an effective potential $V_{\text{eff}}(r)$ (Refs. 1 and 2). In the 4*f* series, configurations which are labile with respect to decollapse are configurations with a single electron above a filled shell or subshell or with a single hole in them—i.e., precisely the elements listed above. In the 5*f* series, the transition to stable collapsed states is more gradual, taking up the first half of the series. This circumstance suggests that we attempt to relate the very concept of mixed valence (and also the anomalously large increase in the state density at the Fermi surface, ρ_f) in mixed-valence states and heavy-fermion systems with specifically the lability of the *f* shell in those cases in which the *f* electron is in a "shallow level in a deep well."[3]

2. It is believed that the *f* shells of rare-earth ions do not overlap in intermetallic compounds with a mixed valence and heavy fermions and that ρ_f is dominated by *fd* hybridization. Under certain conditions, many-electron processes involving a change in the structure of the continuum and which accompany *f-d* transitions lead to a significant narrowing of an *f* resonance. We believe (see also Ref. 7) that in addition to this electron-polaron effect, which is common to all systems in which narrow bands hybridize with broad bands, electron-polaron effects in the most unstable *f* shells, which are responsible for the appearance of a mixed valence and which make a positive contribution to the effective carrier mass, also occur in mixed-valence states and heavy-fermion systems.

In the customary approaches, mixed-valence states are associated with the transi-

tion of an electron from a f state with a "rigid" wave function $|f\rangle$: $f^p \to f^{p-1} + d$. In the borderline situation of electron collapse, however, there may be changes in the f-electron wave functions themselves, $|f\rangle \to |\tilde{f}\rangle$, upon a change in electron configuration. An alternative process (see also Ref. 8) also becomes possible: the capture of an extra electron by an atom

$$f^p + d \to \tilde{f}^{p+1}, \tag{1}$$

where $p = 1, 3$ for Ce and U, respectively. An instability of the f shell is manifested here by its pronounced relaxation upon the capture of an electron from the continuum as in (1). In a free U atom, where d represents states of the $6d$ shell, this relaxation is well known.[9] As a result, in the final state of reaction (1) the f-electron wave function may be greatly inflated (Fig. 1a) or may escape completely from the collapse state into an external Coulomb well (Fig. 1b), if the radius of the Wigner-Seitz cell is sufficiently large. In the latter case we are dealing with two types of f states ($f, \tilde{f}$) in a crystal; the existence of such states in an atom was mentioned in Ref. 9.

A two-well structure of the potential $V_f(r)$ (Fig. 1b) introduces mixed-valence properties even at a level of the free atom (or ion), as can be shown in a simple model with a Hamiltonian

$$H = \sum_{\mu} (\epsilon_f f_\mu^+ f_\mu + \epsilon_{\tilde{f}} \tilde{f}_\mu^+ \tilde{f}_\mu) + \sum_{\mu\mu'} (U_{ff} n_{f\mu} n_{f\mu'} + U_{\tilde{f}\tilde{f}} n_{\tilde{f}\mu} n_{\tilde{f}\mu'}) \tag{2}$$

(μ are the internal atomic numbers of the f electrons). In general, the wave function of an f electron is (cf. Refs. 3 and 10)

$$|\varphi_\mu\rangle = \alpha_\mu(n_f)\,|f_\mu\rangle + [1 - \alpha_\mu^2(n_f)]^{1/2} |\tilde{f}_\mu\rangle, \tag{3}$$

where n_f is the total number of f electrons and $\nu_f = |\alpha|^2 n_f$ is the number of electrons localized in an inner well. If, with $n_f = p$, the f electrons are in a state of collapse, and

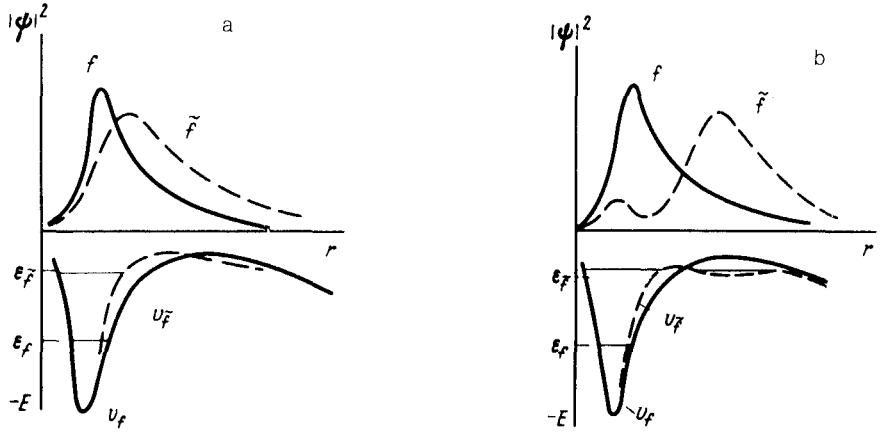

FIG. 1.

ϵ_f is an excited state for them, the addition of an extra f electron will have the consequence that the wave function will be partially "squeezed out" into the outer well, with a consequent decrease in the total energy of the atom. These events will lead to an effective decrease in ν_f; i.e., the number of *localized* electrons may decrease, rather than increase, during process (1). Minimizing the total energy with respect to ν_f with trial function (5), we find limitations on the value of this parameter:

$$p - {}^{1}/_{p} < \nu_f < p + 1, \tag{4}$$

which means $0 < \nu_f < 2$ for Ce and $2.66 < \nu_f < 4$ for U. This fractional value of ν_f corresponds to a mixed-valence state.

In the free atom, according to Ref. 1, a mixed-valence state arises as a "transitional" state in a narrow interval ΔZ between two integer values of the atomic number Z which correspond to a change in the nature of the f state from inflated (Coulomb) to collapse. In a crystal, a mixed valence may arise because of a change in the conditions at the boundary of the Wigner-Seitz sphere for an f ion and metallic screening. In this picture, we find a fairly natural explanation for both the static properties (e.g., the lattice constant) and the dynamic properties (e.g., the photoemission) of these systems. In particular, the total number of electrons with f symmetry may change insignificantly upon, say, a γ-α transition in Ce, while the relative number of electrons localized in a core, ν_f, will decrease.

3. Core polarization can contribute substantially to the narrowing of the resonance $\Gamma_f - \Gamma_f^*$ along with the traditional "Tomonaga narrowing."[4-6] Only electron-hole pairs with characteristic times $\tau < \tau_0$, where τ_0 is the tunneling time of an electron in the case of *fd* tunneling, participate in the change in the structure of continuum states which accompanies the motion of a slow particle through a crystal.[6,11] The lowest-energy processes are cut off because of the finite lifetime of the electron at a site: $\tau_f \sim \hbar(\Gamma_f^*)^{-1} \gg \tau_0$. In a similar way, a distinction is drawn between fast and slow core relaxation processes that accompany reaction (1). Processes which involve a polarization of inner shells and which are fast in comparison with τ_0 accompany the tunneling almost adiabatically, having little effect on the amplitude of the tunneling. The change in the structure of the f shell (f-$\tilde{f}$ processes) occurs through the excitation of low-lying d states with energies[10] $\lesssim 1$ eV and of Coulomb nf levels in the "external" well, with energies[1] $\sim R_y/n^2$, $n \gtrsim 5$, so that processes involving relaxation of the f shell during tunneling can be treated in the antiadiabatic approximation, as can processes involving a change in the structure of the continuum. The many-electron tunneling integral then takes the form

$$V_\mu^*(k) = \langle \psi_{band} \mid \tilde{\psi}_{band} \rangle \langle \psi_f \mid \tilde{\psi}_f \rangle^p \langle \psi_k \mid V \mid \psi_{f\mu}^{\sim} \rangle \equiv R_{band}(V^*) R_f^p V, \tag{5}$$

where, as before, the tilde means a structural change in the final state of reaction (1). The factor reflecting the nonorthogonality of continuum states depends on V^* by virtue of the cutoff which we mentioned above at the low-energy limit by the energy $\sim \Gamma_f^* = \pi\rho_0(V^*)^2$. From (5) we find

$$V^* = R_f^{p/(1-b)}(V/D)^{b/(1-b)}V, \qquad b = \sum_l (2l+1)(\delta_l/\pi)^2 - (2\delta_3/\pi), \tag{6}$$

where the δ_l are the phase shifts in the scattering of the conduction electrons by the potential of the f electrons, and $D \sim \rho_0^{-1}$ is the width of the d band.

In an atomic electron-polaron effect, as in the band effect, there are two trends: On the one hand, the presence of the external well in $V_f(r)$ leads to a decrease in the effective potential barrier, since an electron tunnels out of state $|\varphi\rangle$ in (3), not out of $|f\rangle$ [an effect which is analogous to a contribution to (6) which is linear in δ_3]. On the other hand, the "shaking" of the other f electrons causes a narrowing of the resonance. The extent of this narrowing increases with increasing fraction of f states in the function φ and with increasing number of f electrons, p (values $R_f \sim 0.1$ are given for the nonorthogonal integrals in f atoms in Ref. 1). The competition between these two factors can result in the wide variety of values of $\Gamma_f^* \sim \rho_0 (V^*)^2$ which are observed in mixed-valence compounds and, possibly, in heavy-fermion systems containing uranium (this model is not directly applicable to heavy-fermion systems based on cerium, where the valence of the f ions is essentially an integer).

On the whole, the new concept proposed here, which relates the appearance and features of states with a mixed valence and, possibly, heavy fermions to the lability and nonadiabatic nature of atomic shells, seems to be able to furnish a natural explanation of many aspects of the behavior of these systems.

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