States with intermediate valence in rare-earth compounds

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A variational method is used to consider the influence of the electron-phonon interaction on electronic phase transitions in rare-earth compounds. It is shown that allowance for polaron effects smooth out the transition and leads to stabilization of states with intermediate valence.

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Electronic phase transitions (EPT) with change of valence, due to the transition of f electrons into the conduction band, were observed in a number of rare-earth compounds (Ce, SmS, TmSe).[1] It is customary to use in the description of the corresponding phenomena two models, the electron-electron interaction model[2,3] and a model that attributes the transition to interaction of the electrons with the lattice.[4,5] Both approaches lead in the simplest self-consistent field approximation (SCFA) usually to first-order transitions between states with integer valence. The smearing of the transition and the appearance of states with fractional number n of f electrons per center (the so called states with intermediate valence) appear in this case only as a result of hybridization of the f and s electrons[6,7] [1)] or as a result of the sufficiently large width of the s band.

It was shown in [8] that if one goes beyond the framework of the SCFA in the electron-electron interaction model, then the appearance of states with intermediate valence is made possible by local (exciton) correlations. We shall show below that, analogously, allowance for the local (polaron) effects in the electron-phonon interaction also leads to stabilization of states with intermediate valence in the case of EPT.

Polaron effects for an individual impurity were investigated in [9], where only the case of limiting localization was considered (the deformation of the lattice followed instantaneously the electronic state of the center, i.e., it assumed two values corresponding to $n=0$ or 1), and also in [10], where another limiting case was considered, wherein on account of the fast f-s transitions due to hybridization, the deformation turns out to correspond to the average number of the f electrons, just as in the SCFA. We shall construct a general scheme that interprets the situation between these extreme cases, and consider the dependence of the corresponding regime on the position of the f level and on the number of f electrons, as well as the reaction of these effects on the development of the EPT.

The analysis will be based on a very simple model, wherein the s band is approximated by a narrow s level,[2] while the phonons and the electron-phonon interaction are assumed to be local[2)]. The Hamiltonian of the model is

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$$H = \sum_i \{\epsilon a_i^+ a_i + E_0 f_i^+ f_i + V(a_i^+ f_i + \text{h.c.}) + \omega b_i^+ b_i - g f_i^+ f_i (b_i^+ + b_i)\}. \quad (1)$$

Here a^+, f^+, b^+ are the production operators of the s and f electrons and the phonons, respectively; the last term describes the deformation of the lattice (the change of the ion radius) as a function of the number of f electrons on the center.

We use a variational method and seek the wave function on the center in the form

$$|\psi_i> = u_i a_i^+ |0> ||\beta_a>> + v_i f_i^+ |0> ||\beta_f>>, \quad u_i^2 + v_i^2 = 1. \quad (2)$$

Here $\|\beta\gg$ is the coherent state of the phonons with eigenvalue β satisfying the conditions

$$b||\beta>> = \beta||\beta>>, \quad <<\beta||\beta'>> \exp\left\{-\frac{|\beta|^2}{2} - \frac{|\beta'|^2}{2} + \beta^* \beta'\right\}. \quad (3)$$

The meaning of the wave function (2) is that different electronic states of the center correspond to different lattice deformations; the reaction of the lattice, however, is not instantaneous and is incapable of following completely the fast f-s transitions due to hybridization, so that the values of β_a, β_f, and n must be determined in a self-consistent manner.

The energy (1) averaged over the wave functions (2) is a function of three variational parameters: β_a, β_f, and $v^2 = n_f \equiv n$ ($u^2 = 1-n = n_s$) (we assume hereafter that all the centers are equivalent and omit the site label i). Taking (3) into account, this functional takes the form

$$F = (1-n)(\epsilon + \omega\beta_a^2) + n(E_0 + \omega\beta_f^2 - 2g\beta_f) - 2Ve^{-\frac{(\beta_a - \beta_f)^2}{2}} \sqrt{n(1-n)}. \quad (4)$$

The SCFA corresponds to the choice $\beta_a = \beta_f = \beta$; it is easy to verify that minimization of (4) with respect to β yields in this case $\beta_{\text{SCFA}} = gn/\omega$, and the energy $f(n)$ takes the form

$$F_{\text{SCFA}} = \epsilon + n(E_0 - \epsilon) - \frac{g^2}{\omega} n^2 - 2V\sqrt{n(1-n)}, \quad (5)$$

from which follows a first-order transition with increasing E_0 at sufficiently weak hybridization V ($2V < g^2/\omega$).

Minimization of the total expression (3) yields three equations for the quantities β_a, β_f, and n. Analytic and numerical investigations of these equations, the details of which we omit, lead to the following conclusions:

1. If the f level is far from the Fermi level (far from ϵ in this model) we have $\beta_a \approx \beta_f$ at $E_0 \ll \epsilon$ we have $n \approx 1$ and $\beta_a \approx \beta_f \approx g/\omega$; at $E_0 \gg \epsilon$ we have $n \approx 0$ and $\beta_a \approx \beta_f \to 0$). The SCFA regime ($\beta_a = \beta_f$), however, is not reached rigorously even at large V.

2. As E_0 approaches ϵ, the difference $\beta_f - \beta_a$ increases, and the effective hybrid-

ization $\tilde{V}=V\exp\left\{-\frac{(\beta_a-\beta_f)^2}{2}\right\}$ is accordingly decreased progressively (this corresponds to the polaron narrowing of the virtual f level in the more realistic models). The decrease is maximal at $E_0=\epsilon$.

Despite the appearance of hybridization, which might seem to increase the tendency to a jumplike transition (cf. (5)), the EPT becomes smoother in comparison with the SCA predictions. Thus, at $g<2\omega$ the transition is smooth for all values of Z down to the very smallest.

4. In the general case, ambiguous solutions of rather complicated type are possible, but those usually realized are states with maximum and minimum values of n, between which first-order transitions take place.

5. When account is taken of the finite width of the s band, stabilization of states with $E_0\approx\epsilon_F$ and with intermediate values of $n(\approx\frac{1}{2})$ is possible. Transitions to this state can be jumplike.

Let us explain qualitatively why allowance for the local effects in the electron-phonon interaction smears out the transition and stabilizes states with intermediate valence. In the absence of interaction and hybridization, the EPT turns out to be smooth as the f level moves: $n=1$ at $E_0<\epsilon_F$, then E_0 coincides with ϵ_F until all the f electrons go over to the conduction band, after which $n=0$ (the hybridization can only smear out this transition even more). In the SCFA, at sufficiently strong interaction, this process becomes jumplike: the more electrons go over to the s band, the smaller the average lattice parameter (the smaller $\langle b\rangle=\beta_{\text{SCFA}}=\frac{g}{\omega}n$), as a result of which the effective energy of the f level increases additionally as further excitation of the f level increases additionally as further excitation of the f electrons into the conduction band becomes easier. On the other hand, when polaron effects are considered, in the extreme situation when the lattice realigns itself instantaneously ($\beta_f=g/\omega,\beta_a=0$), the energy levels of the centers with $n=1$ and $n=0$, while displaced, remain fixed and do not depend on the states of the neighboring centers; by the same token, the situation becomes analogous to the case of interacting electrons, wherein the transition is smooth. In the general case, since some intermediate situation is realized ($\beta_a\neq0$, but $\beta_a\neq\beta_f$), and since furthermore β_a and β_f are themselves dependent on n, different regimes are possible, but the tendency to stabilization of the states with intermediate valence on account of local effects is preserved.

We note in conclusion that polaron suppression of f-s transitions and stabilization of local states with different ion radii can in principle favor their spatial ordering in substances with intermediate valence (an analogous crystallization of f electrons on account of long-range Coulomb interaction in these systems was proposed by L. V. Keldysh). It would be of great interest to attempt to observe the corresponding spatial correlation in experiment, say with the aid of neutron scattering.

[1]For simplicity we refer to the s band, although actually the conduction band is more readily d-like.
[2]In addition to the model-based arguments, there are also a number of experimental indications[11,12] that s d states in rare-earth compounds are local to a considerable degree.

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