Variable *f*-level width and valence-change transitions in cerium compounds

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A new model explains the abrupt transitions to an intermediate-valence phase in rare-earth compounds on the basis of an increase in the s–f hybridization and an increase in the width of the f level with increasing pressure. In particular, the model explains some recent results on the properties of cerium compounds [J. W. Allen *et al*., Phys. Rev. Lett. **46**, 1100 (1980); M. Croft *et al*., Phys. Rev. Lett. **46**, 1104 (1981)].

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Some important new results reported simultaneously in two recent experimental papers[1,2] may change substantially our understanding of electronic phase transitions involving a valence change, which occur in rare-earth compounds of cerium. Specifically, photoemission measurements have shown that (first) the f level in cerium compounds apparently lies well below the Fermi level and (second) this level shifts relatively slightly as the valence-instability point is approached. Croft *et al.*[2] have suggested that it may be not so much the shift of the f level (as has been believed) as its broadening, which is important in the valence-change transitions observed in many rare-earth compounds when doped or subjected to pressure. There are also direct experiments[3] which show that the width of the f level increases by a factor of more than three in $Ce_{1-x}Th_x$ at the transition to the intermediate-valence phase (which is similar to the γ-α transition in cerium).

The theoretical models, which have been discussed for such transitions (see, for example, the review article by Khomskiĭ[4]), lead to the conclusion that the s-f hybridization V, which broadens the f level, spreads out and smooths the transition. The hybridization, however, has been assumed to remain constant during compression. In this letter we will work from a simple model to study the effect of a change of the f-level width on the valence transition, and we will show that under certain conditions this change in width in fact promotes an abrupt transition.

The situation may be described qualitatively as follows. We assume that in the initial state, with $P=0$ and with a specific volume $v=v_0$, the f level lies a distance $E_f(v_0)=E_0$ below the Fermi level and has a width $\Gamma_0=\pi\rho V_0^2$. We assume that compression causes this level to move upward and to become broader. The broadening is accompanied by a decrease in the number of filled f states, n_f (Fig. 1), and this decrease causes a decrease in the average lattice constant, because the ions have a smaller radius without the f electron. This further compression causes an even greater increase in the width of the f level, which leads to a further decrease in n_f; this "feedback" may cause the transition to become abrupt.

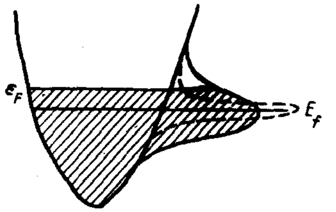

FIG. 1. Compression-induced change in the filling of the f level. Dashed curve–Initial virtual f level; solid curve–f level broadened during compression; ϵ_F–Fermi level; hatching–filled states.

To put the analysis in more specific terms, we will adopt a very simple local model. It has been shown in a series of studies[5,6] that this model gives a generally satisfactory description of the basic characteristics of mixed-valence compounds. In this model the conduction band is replaced by the s level, and the hybridization is assumed to be local:

$$H = \sum_i \{ E_s a_i^+ a_i + E_f f_i^+ f_i + V(a_i^+ f_i + \text{H.c.}) \} , \qquad (1)$$

Here a_i and f_i are the operators representing the s and f electrons at lattice site i, and we will set $E_s = 0$ below. (Analysis of this model and of the more realistic model with a broad s band shows that the basic qualitative results are the same.[6]) We consider the dependence of the parameters E_f and V on the volume $\bar{v} = v - v_0$; in the simplest case,

$$E_f = E_o - \gamma \bar{v}, \quad V = V_o - \alpha \bar{v} \quad (E_o < 0, \ V_o > 0,, \ \gamma, \alpha > 0). \qquad (2)$$

The lattice-deformation energy $Bv^{-2}/2$ should also be added here.

With Hamiltonian (1), the problem can be solved by elementary methods; the energy of this system, which is equal to the sum of electronic and lattice parts, is

$$\mathcal{E}(v) = \frac{E_f}{2} - \frac{1}{2}\sqrt{E_f^2 + 4V^2} + \frac{B\bar{v}^2}{2} . \qquad (3)$$

From (3) we find the equation of state, $P = -\partial\mathcal{E}/\partial v$, and also the condition for instability of the system (a first-order transition):

$$\frac{dP}{dv} = -B + \frac{2(V_o\gamma - E_o\alpha)^2}{[E_f^2 + 4V^2]^{3/2}} > 0 . \qquad (4)$$

Condition (4) is satisfied most easily in the case $\bar{v}_c = (E_0\alpha + 4V_0\gamma)/(\gamma^2 + 4\alpha^2)$; in this case, (4) becomes

$$(\gamma^2 + 4\alpha^2)^{3/2} > 4B|V_o\gamma - E_o\alpha| , \qquad (5)$$

which is a necessary and sufficient condition for an abrupt transition. It is easy to see that a slight increase in hybridization with increasing pressure (a small value of α) hinders the satisfaction of condition (5), but at larger values of α this condition is satisfied more easily, and an increase in hybridization contributes to an abrupt change. The requirement that the transition occur at a positive pressure ($\bar{v}_c < 0$) imposes a restriction

$$a < a_{max} = \frac{|E_0|\gamma}{4V_0} . \tag{6}$$

A check shows that conditions (5) and (6) are not contradictory. It can be seen from (6), in particular, that for a real discontinuity there must be a shift of the f level ($\gamma \neq 0$). Formally, condition (5) could be satisfied with $\gamma = 0$, but in this case the transition would occur in the nonphysical region $P < 0$, at the point at which the hybridization $V(\nu)$ crosses zero and changes sign—an absolutely unrealistic situation (a similar false transition has been observed by Entel *et al.*[7]).[2)]

In summary, analysis of a simple model confirms the qualitative arguments above and shows that an increase in the s-f hybridization or in the width of the f level upon compression promotes an abrupt transition with a change in valence, under certain conditions. Such a transition would occur from a state with a rather deep f level, i.e., from a phase with $n_f \approx 1$ (a pressure-induced increase in hybridization hinders a rise of the f level, and the cutoff occurs at larger values of $|E_0|$). The final state is one with an intermediate valence $n_f \approx 1/2$ (the f level rises toward the Fermi level and becomes significantly broader). These conclusions are in good qualitative agreement with the basic aspects of valence-change transitions, in particular, with the results of Refs. 1 and 2.

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[2)]It can be shown that the transition remains abrupt even if $V(\nu)$ is a constant-sign function. In this case the condition for a jump is that the rate of increase of the hybridization upon the compression be sufficiently high. Nonlinearity of the function $V(\nu)$ also contributes to a jump ($d^2V/d\nu^2 > 0$).

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