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## Configuration Mixing in the Groundstate of Ce

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### ABSTRACT

4f electrons at the beginning of the rare earth series are weakly bound yet highly localized. Their virtual excitations create core change fluctuations which strongly enhance excitonic effects. The dynamic interaction lead to a new groundstate which may be viewed as a boundstate of a 4f electron and an f-exciton. The 4f-hole Greens' function is also strongly modified and shows two poles instead of one pole in the one-electron picture. The photoemission experiments and the x-ray edge absorption experiments in cerium and its metallic compounds are explained in this model. The new groundstate also provides a basis for the understanding of the  $\gamma$ - $\alpha$  phase transition of Cerium.

The electronic structure of elements immediately preceding the rare-earth series is characterized by a sudden and dramatic change in the wavefunction of f-like electrons. For atoms with nuclear charge less than Lanthanum the 4f-wavefunctions (unoccupied in the atomic groundstate) are hydrogenic and have their maxima well outside the 5d and 6s valence electrons. Self-consistent field one-electron calculations like Hartree-Fock or Local Density Functional (LDF) theory yield 4f radii of  $\sim 10$  a.u. or more. As the nuclear charge is increased past Lanthanum the nuclear attraction can overcome the centrifugal barrier sufficiently to allow for a strongly localized boundstate. Unlike the outer s,p,d wavefunctions, the 4f wavefunction has no orthogonality requirements and therefore collapses extremely close to the nucleus and lies well inside of even the core-like 5s and 5p wavefunctions (see Fig. 1). This atomic wavefunction-collapse was first studied by M. Goeppert Mayer<sup>1</sup> in 1941 who found that the Thomas-Fermi potential has the form of a two-well potential separated by a barrier. The coexistence of two different atomic states for Lanthanum with the same nominal electronic configuration ( $6s^2 4f$ ) was conjectured by Band and Fomichev<sup>2</sup> in 1980 on the basis of self-consistent Dirac-Fock calculations. Several related experimental results on borderline elements like La, Ce and Pr have been reported and have been attributed to anomalously large configuration interactions.<sup>3</sup> While all these studies reveal an intrinsic instability of the electronic structure of the *atom* as a function of nuclear charge, it is *a priori not* clear whether similar instabilities can occur in solids, where extended atomic-like states ( $r \geq 5$  a.u.) are strongly modified by neighboring atoms.

In recent years several anomalous experimental results have, however, been reported in experiments on Ce-metal and its compounds, raising questions about the nature of the groundstate and the excitation spectra of this borderline element.<sup>4-12</sup> These experimental results are also relevant for the understanding of the isostructural  $\gamma$ - $\alpha$  phase-transition of fcc Ce.<sup>13</sup> It has been conjectured early that this phase transition is associated with the valence instability of the Ce 4f electron and that it may be explainable by the promotional model<sup>14</sup> in analogy to other valence instability transitions such as the S-M transition in SmS.<sup>15</sup>

In the promotional model the two configurations  $f^n(s,d)^m$  and  $f^{n-1}(s,d)^{m+1}$  are thought to be nearly isoenergetic so that a small change in external parameters (temperature or pressure) can change the groundstate. The formal equivalence of the latter configuration with a metallicly screened 4f-hole implies then that photoemission from the 4f-level should occur at the Fermi level.

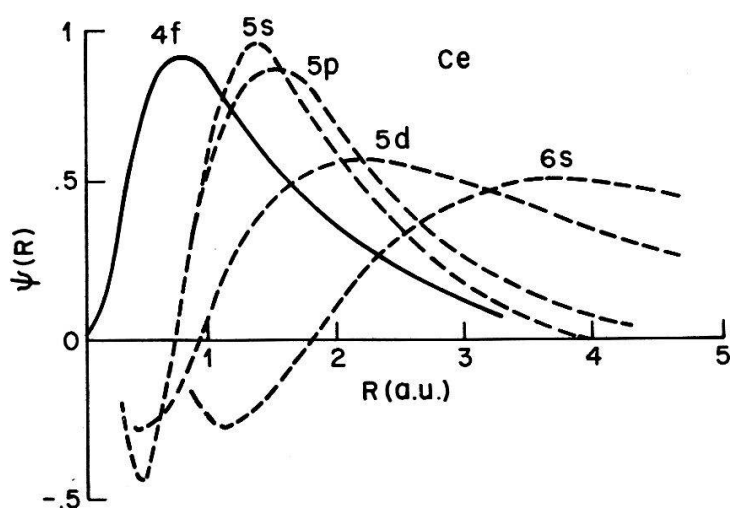


Fig. 1 Radial wavefunctions of neutral atomic Ce as calculated within the local density functional scheme.

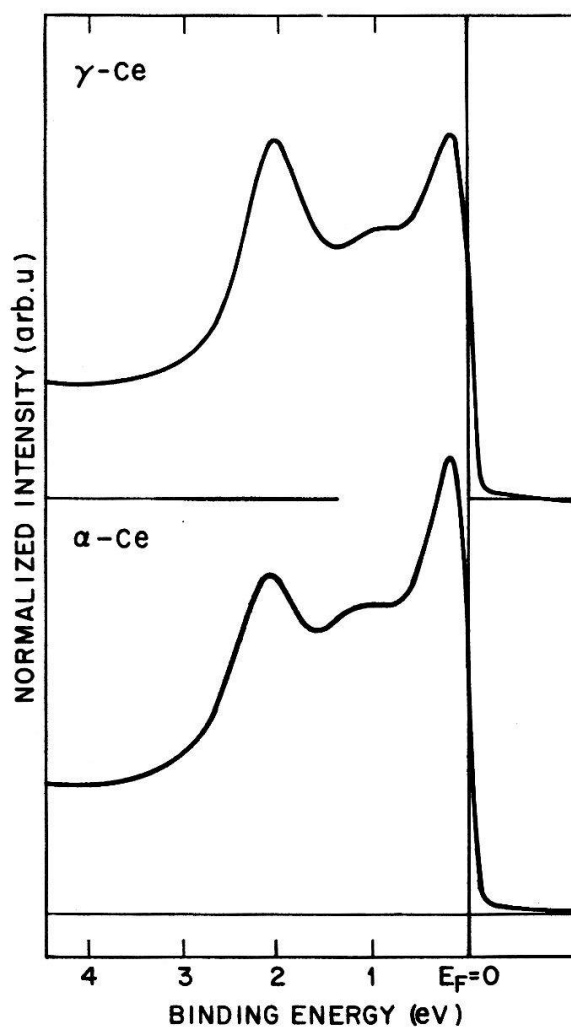


Fig. 2 Energy distribution curves of photoelectrons from  $\text{Ce}_{0.9}\text{Th}_{0.1}$  at photonenergy  $h\nu = 50$  eV.

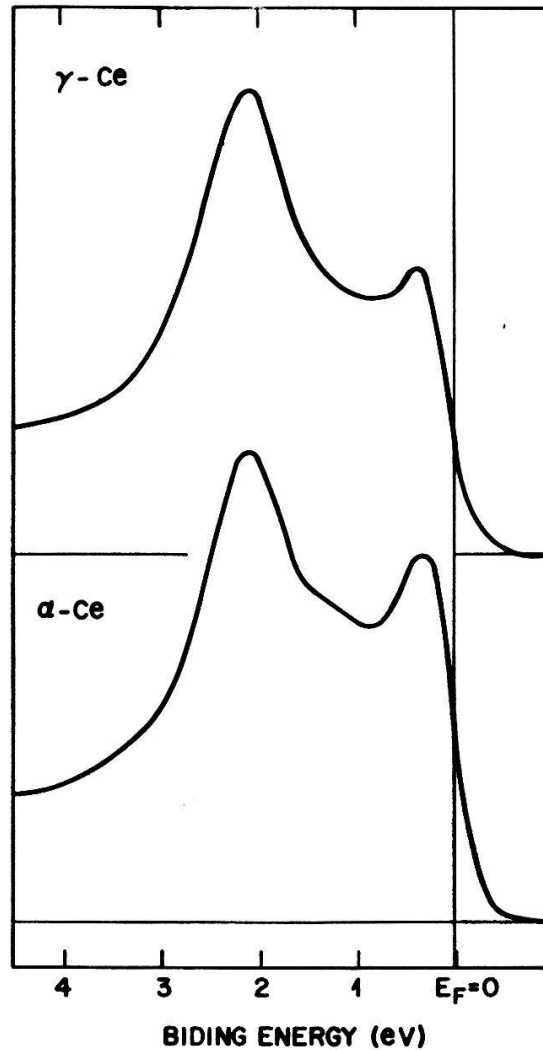


Fig. 3 Same as Fig. 2 but with  $h\nu = 122$  eV.

The photoemission spectra of various Ce-based systems thought to be mixed valent is, however, more complicated. A strong feature associated with 4f-emission usually occurs for binding energies between 2-3 eV.<sup>5</sup> This binding energy value is compatible with an extrapolation of results of Nd- and Pr-based systems,<sup>16</sup> it has been deduced from comparing trends in heats of formation of various tri- and tetra valent metals<sup>17</sup> and it can be approximately calculated as difference between self-consistently screened states containing different numbers of 4f-electrons.<sup>18</sup> In addition to this feature at 2-3 eV below the Fermi level a number of Ce-compounds with nominally either one f-electron or mixed valence character reveal a *second* feature near  $E_F$ . The strength of this second feature varies for different compounds. Especially intriguing are the results on  $Ce_{0.9}Th_{0.1}$  which as a function of decreasing temperature transforms from the  $\gamma$ -phase to the  $\alpha$ -phase.<sup>7</sup> The alloying of Th into Ce enables this transition to be studied under normal pressure

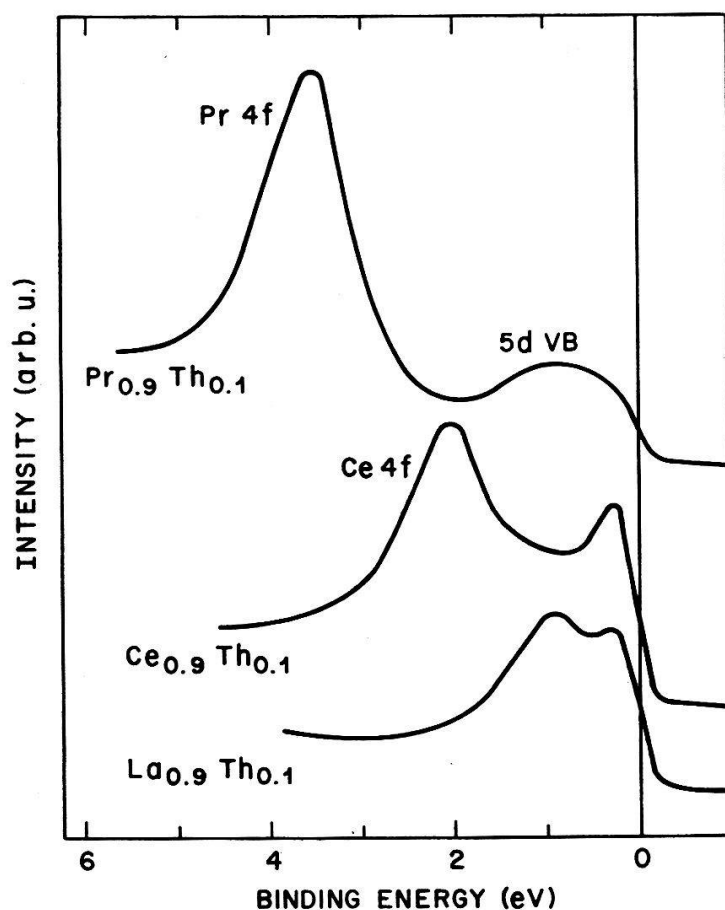


Fig. 4 Comparison of results for  $\text{Pr}_{0.9}\text{Th}_{0.1}$ ,  $\text{Ce}_{0.9}\text{Th}_{0.1}$  and  $\text{La}_{0.9}\text{Th}_{0.1}$  at  $h\nu = 70$  eV. (all from ref. 8).

conditions. The data are shown in Figs. 2-4 for photon-energies of 50 eV and 122 eV. These energies were chosen to enhance the intrinsically weak emission from 4f states over 5d, 6s valence emission by optimizing the energy dependent cross-section<sup>7</sup> and making use of resonance effects involving 4d core levels.<sup>19</sup>

The results show a pronounced two-peak structure which, remarkably remains essentially unaltered through the  $\gamma$ - $\alpha$  transition. This fact is in accord with various other experimental findings, i.e., Compton scattering,<sup>20</sup> positron annihilation<sup>21</sup> and neutron scattering<sup>22</sup> which all suggest that there is essentially *no* change in the number of tightly-bound 4f electrons at the  $\gamma$ - $\alpha$  transition. This is clearly inexplicable in the promotional model and alternative models for the transitions have been suggested involving the idea of a Mott-transition<sup>17</sup> in the f-electron system or associating the volume collapse with the Kondo state.<sup>23</sup>

We shall in this paper present a theory of the electronic ground- and excited states of Ce with particular emphasis on the characteristic *two-peak* signature in the photoemission spectra. As we shall show, the dynamic interactions

induced by strong core charge polarizations lead to a complete breakdown of any characterization in terms of one-electron states. The new stable groundstate may be viewed as the boundstate of a 4f electron and an f-exciton.<sup>24</sup> This configurationally mixture state leads to two poles in the 4f-hole Greens function and thus presents a natural explanation of the photoemission experiments. The model contrasts a model by Liu and Ho<sup>25</sup> which invokes screened and unscreened 4f-holes and also another model recently proposed by Gunnarsson and Schonhammer<sup>26</sup> in which the large degeneracy of the f-level plays the central role. Both these models are excited state models, while we propose here a modification of the ground state. We will also comment on the  $\gamma$ - $\alpha$  phase transition, in which we believe the features of the new mixed groundstate play an essential role.

We begin by defining an effective one-electron Hamiltonian of a rare-earth describing all valence f-states ( $\mu$ ), i.e. localized 4f as well as delocalized 5f,6f ... etc, in addition to s,d valence electrons ( $k$ )

$$H_0 = \sum_{\mu} \epsilon_{\mu} c_{\mu}^{\dagger} c_{\mu} + \sum_k \epsilon_k c_k^{\dagger} c_k \quad (1)$$

Focusing on the f-electron subspace (1st term) we assume that for  $\mu = 4f$  the correct inclusion of all one-electron energies yields an appropriately broadened level about 2-3 eV below the Fermi level. Note that this situation would not be given by bandstructure-like calculations which, because of the "open shell" structure of Ce would place the f-level at and above the Fermi-level. An appropriately modified Hartree-Fock picture has been given by Bringer.<sup>27</sup> States with 5f,6f, ... etc. character form a continuum starting at the bottom of the s,d-band at about -4 eV. However the region of strong attractive f-like phase shifts which leads to a high f-like density of states begins of about 5-10 eV higher energies.<sup>29</sup>

We next consider excitations of the 4f electron. We are primarily interested in the attractive electron-hole interaction for a hole in  $\mu = 4f$  and the electron scattering from  $\mu'$  to  $\mu'' \neq 4f$

$$H_1 = \sum_{\mu'\mu''} V_{\mu\mu'\mu''} c_{\mu'}^{\dagger} c_{\mu} c_{\mu}^{\dagger} c_{\mu''} \quad (2)$$

We estimate the Coulomb interaction,  $V$  from local density functional (LDF) calculations on renormalized atoms to be only of the order of a few tenths of eV.

In addition, however, the creation of a 4f hole produces large core charge fluctuations. As seen in Fig. 1 the 4f wavefunction lies spatially well inside the 5s and 5p core electrons which therefore strongly relax upon 4f ionization. To describe these relaxations consider  $\hat{H}_2$  which represents the Coulomb scattering

between any  $\mu$ -state and the core states  $(m, m')$

$$\hat{H}_2 = \sum_{\mu\mu', mm'} W_{\mu\mu', mm'} c_m^\dagger c_m c_{\mu'}^\dagger c_{\mu} \quad (3)$$

For scattering from 4f to the higher f-states, the largest matrix elements  $W$  occur, as discussed above when  $m$  are the outermost (5s,5p) core states and  $m'$  the unoccupied valence states. These valence-band states usually have a rich orbital momentum character, but the matrix elements are largest for initial and final states with the same orbital momentum character i.e., involving only the symmetric breathing mode of the core. Accordingly only the admixing of the localized 4f states to higher f-like states is considered. Moreover, we will assume a manifold of states in which the total number of electrons with localized f-character is one or zero (i.e. the  $U \rightarrow \infty$  limit). This ensures that we can neglect the large Coulomb interactions between electrons in 4f-like intermediate states.

Provided we work at energies smaller than the characteristic resonance frequencies of the  $m$  to  $m'$  transitions ( $\geq 30$  eV) we can eliminate these  $(m)$  states obtaining an effective polarization Hamiltonian involving only the  $\mu$ -states<sup>30</sup>

$$H_2 = \sum U_{\mu\mu'\mu''\mu'''} c_{\mu'''}^\dagger c_{\mu''} c_{\mu'}^\dagger c_{\mu} \quad (4)$$

with attractive interactions

$$U = - \sum_{m, m'} \left| \frac{W_{\mu\mu' m m'} W_{m m' \mu'' \mu'''}}{E_m - E_{m'}} \right| \quad (5)$$

In contrast to the direct Coulomb elements  $V$  in eqn. 1 the effective interactions  $U$  are strong. Direct atomic calculations give  $W$ 's of about 10 eV which in turn give  $U$ 's of order -2 eV. The combination of  $(V+U)$  can thus produce strong excitonic effects associated with the excitation of a 4f electron. The effects discussed so far mainly result from two features which are particular to border-line rare-earth atoms: a) the 4f electrons have a small ionization energy, i.e. a few eV characteristic for valence electrons, but b) they are strongly localized on a scale characteristic for core electrons and do therefore strongly couple to high energy polarization modes (i.e. core charge fluctuations). The origin of the interactions  $V$  and  $U$  is diagrammatically illustrated in Fig. 5.

With these ingredients we now consider a reduced Hamiltonian  $H_{\text{eff}}$  in the space of two kinds of states, first the groundstate of the one-electron problem (with the 4f level occupied) denoted by  $|0\rangle$  and with energy value taken as 0. Secondly, we consider the continuum of states  $c_{\mu}^\dagger c_{4f} |0\rangle$  formed from a localized 4f hole and the electron in the state  $\mu$  with energy  $\epsilon_{\mu}$ . As discussed above this





expectation values  $\langle c_\mu^+ c_{4f} \rangle_\xi$  are finite and coupling to the Hartree-Fock like pole  $|0\rangle$  occurs. The lower pole (A) corresponds to an eigenstate which is a symmetric linear combination of the original 4f state and of exciton states

$$\psi_A \sim \left( a + b \sum_{\mu} g_{\mu} c_{\mu}^+ c_{4f} \right) |0\rangle . \quad (9)$$

The wavefunction corresponding to the new pole (B) is accordingly

$$\psi_B \sim \left( b - a \sum_{\mu} g_{\mu} c_{\mu}^+ c_{4f} \right) |0\rangle \quad (10)$$

In (9) and (10)  $g_{\mu}$  is the exciton envelope wavefunction which together with the

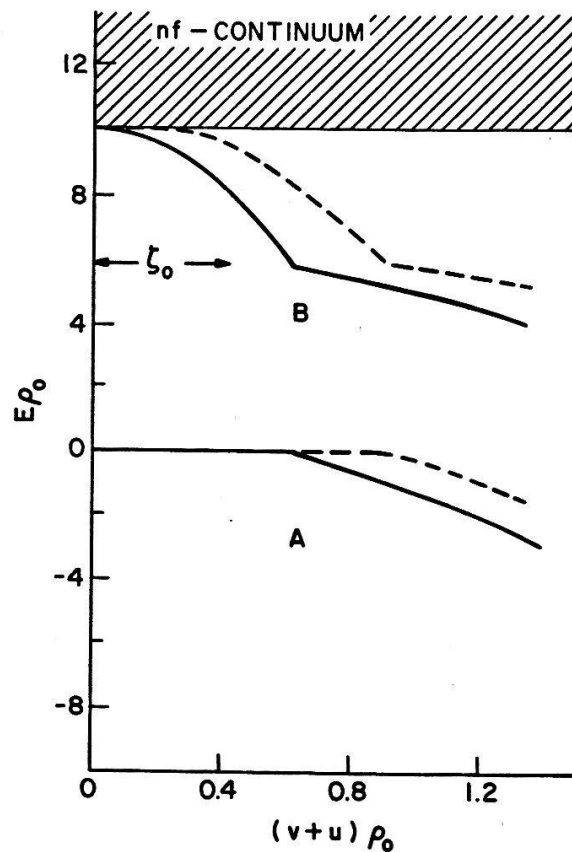


Fig. 6 Variation of the A and B poles in the one hole Greens' function for increasing coupling strength. Two model densities of states are considered for the continuum, constant  $\delta = \delta_0$  (full line) and free-electron  $\delta = \frac{3}{2} \delta_0 \sqrt{E}$  (broken line).

weights  $a$  and  $b$  is obtained from the eigenvectors of  $H_{\text{eff}}$ .

While the instability of the normal state  $|0\rangle$  can only be seen through a many-body treatment as above, the existence of a localized exciton state and the quantitative plausibility of the ideas above may be illustrated through a self-consistent variational one-electron calculation. We have accordingly carried out self-consistent variational LDF calculations of the renormalized Ce-atom embedded into the crystal. First results were presented in ref. 32. We have since extended these calculations to the use of a 3-parameter variational trial function for the  $f$ -like states. Similar to ref. 32 we find *two* stable solutions, one corresponding to the state  $|0\rangle$  and the other corresponding to  $\sum_{\mu} g_{\mu} c_{\mu}^{+} c_{4f} |0\rangle$ . The two wavefunctions are depicted in Fig. 7 (lower panel) together with the variational energy of the system as a function of wavefunction extent (upper panel).

The coupling in Ce is large enough to also well localize the excitonic part of the wavefunction. We thus believe that for Ce and intermetallic Ce compounds the Fermi-level and the coupling matrix elements are such that the new, configurationally mixed groundstate is realized. Since the exciton is also well localized the broadening of the A and B poles will be small and the Fermi-level will be pinned to the upper B-resonance. The count of strongly localized  $4f$  electrons is slightly less than unity distributed over the *two* resonances. The "condensation" of an  $f$ -exciton of more delocalized character (see Fig. 7) is provided by electron-transfer from the  $s,d$  reservoir. The exact amount depends in detail on the Coulomb coupling strength, on the position of the Fermi-level and on the broadening.

The spectral distribution for  $f$ -like electrons as seen by a photoemission experiment is given by the one-hole Greens' functions

$$G_f(\omega) = \left[ \frac{Z_A}{\omega - E_A + i\delta} + \frac{Z_B}{\omega - E_B + i\delta} \right] \theta(\omega - E_F) \quad (11)$$

exhibiting a *two-peak* structure. The model thus provides a natural explanation for the valence photoemission data on Ce and Ce based compounds. Similarly the existence of two poles in the valence spectrum will modify core level spectra as can be discussed in terms of shake-up or down processes.<sup>33</sup>

Inverse photoemission experiments (BIS) probe the unoccupied states as one electron is added to the (unoccupied) system. In a simple model this electron can either be added into a localized  $4f$ -orbital and the associated Coulomb

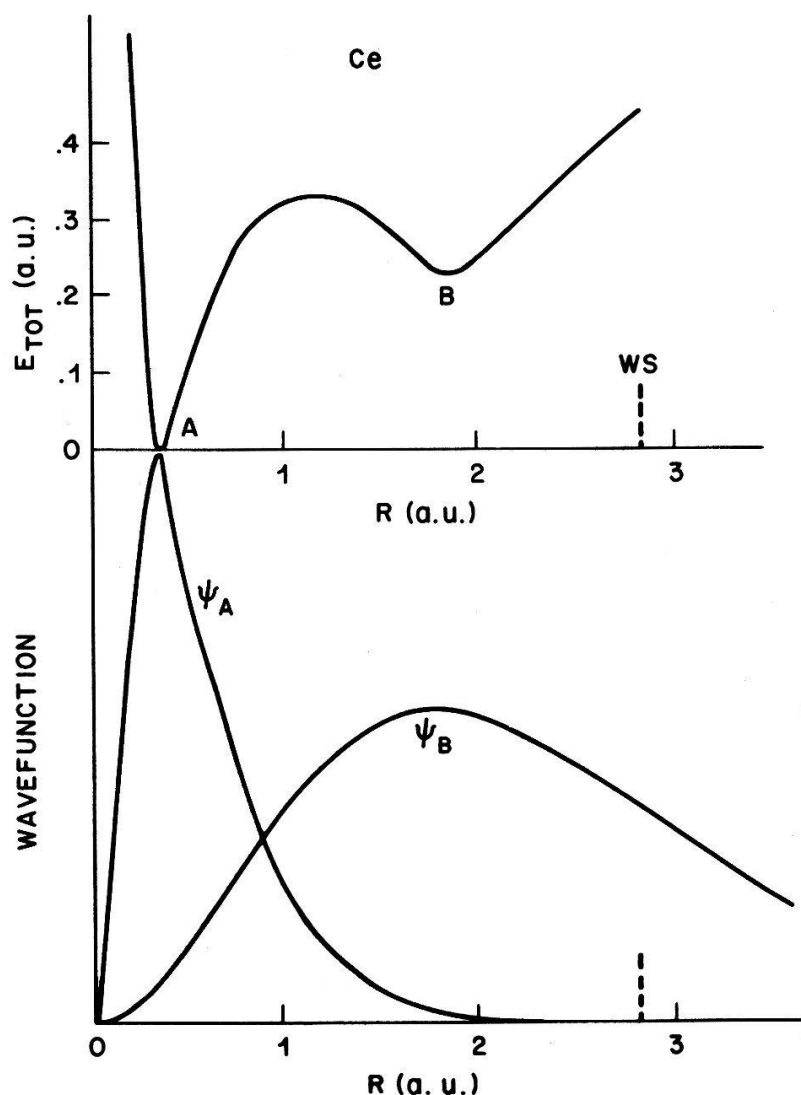


Fig. 7 Calculated total energy (top) of  $4f^1sd^3$  atomic Ce as a function of a 3-parameter 4f wavefunction using the self-consistent local density functional scheme.  $R$  is the radial position of the maximum of the total wavefunction. The lower panel shows the two stationary solutions at  $R \approx 0.4$  a.u. and  $R \approx 1.9$  a.u. Details of a similar calculation are discussed in ref. 32.

repulsion  $U$  is large<sup>16-18,29</sup> ( $\sim 6$  eV) or it can be added into the more delocalized excitonic state for which the Coulomb repulsion is about 4-5 times smaller.<sup>29</sup> We thus expect multiple peaks in BIS spectra on Ce compounds as well. Recent experimental data support this simple picture.<sup>34</sup>

As one goes in the one-electron picture from Ce to Pr and to heavier rare-earths the binding energy of the 4f electron increases and the Fermi-level drops further below the onset of the  $nf$ -continuum. The conditions for the

condensation described here are therefore less likely to be met. Closest to Ce is neutral Pr with one 4f electron and La with a core-hole. These model the final states in x-ray absorption experiments for core -p to valence -d (followed by a fast relaxation into 4f) transitions in  $Ce^{4+}$  and  $La^{3+}$  compounds. The experiments<sup>7</sup> show two edges, separated by about 8 eV, which are connected to the A and B resonances discussed above.

We now examine the  $\gamma$ - $\alpha$  phase transition in somewhat more detail. Although we have no quantitative theory of the transition, the following general picture is compatible with the electronic structure model we developed above. From the measured  $dP/dT$  and the volume change one can deduce  $\Delta S = 1.5 k_B$ ,  $P\Delta V \approx 22$  meV,  $T\Delta S \approx 38$  meV and  $\Delta U \approx 16$  meV at  $T = 300K$  and  $P = 7$  m bar.<sup>13</sup> The lower internal energy of the compressed  $\alpha$ -phase is consistent with thermal expansion arguments. Specific heat measurements<sup>35</sup> on the  $\alpha$ -phase show a linear behavior with  $\gamma \approx 13$  mj/mole  $^{\circ}K^2$ . Our conclusion from photoemission data is that in both phases the Fermi-level is pinned to the B-resonance. With a volume change of 15% the Fermi-level will however move slightly upwards according to bandstructure calculations.<sup>28</sup> This may result in a small shift within the B-resonance in addition to a broadening of that resonance. Since the B-resonance is near the Fermi level it dominates both the entropy and the susceptibility. The entropy, therefore is proportional to  $T/W$  for  $T \ll W$  and constant for  $T \gtrsim 0(W)$ , where  $W$  is the width of the resonance. If the width of the resonance increases in going from the high volume ( $\gamma$ ) to the low volume ( $\alpha$ ) phase, there is a temperature region in which the contribution  $-TS$  to the free-energy is changing linearly in the  $\gamma$  phase and quadratically in the  $\alpha$  phase. The possibility for an iso-structural  $\gamma$ - $\alpha$  transition thereby appears. Quantitatively a factor of two increase in the width of the resonance (for transition at the lowest pressure) is quantitatively in accord with the phase transition data as well as the change in susceptibility at the phase transition.

The understanding of the phase transition requires only that there be a resonance near the Fermi level which broadens at the transition. Another model with this feature has been proposed by Allen and Martin<sup>23</sup> who, however, attribute the resonance near the Fermi-energy to a "Kondo-resonance."

**REFERENCES**

- 1) M. Goeppert-Mayer, *Phys. Rev.* **60**, 184 (1941).
- 2) I. M. Band and V. I. Fomichev, *Phys. Lett.* **75A**, 178 I. M. Band, V. I. Fomichev and M. B. Trzhaskovskaya, *J. Phys. B (At. Mol. Phys.)* **14**, 1103 (1981).
- 3) See e.g. Z. B. Goldschmidt in "Handbook on the Physics and Chemistry of the Rare Earths," ed. K. A. Gschneidner and L. Eyring (North Holland, Amsterdam, 1978) vol. 1, p. 1 and G. Wendin and M. Ohno, *Physica Scripta* **14**, 148 (1976).
- 4) "Valence Fluctuations in Solids," ed. L. H. Falicov, W. Hanke, M. B. Maple (North Holland, Amsterdam, 1981).
- 5) "Valence Instabilities," ed. P. Wachter, H. Boppart (North Holland, Amsterdam, 1982).
- 6) T. M. Lawrence, P. S. Riseborough and R. D. Parks, *Rep. Prog. Phys.* **44**, (1981).
- 7) K. R. Bauchspiess, W. Boksch, E. Holland-Moritz, H. Launois, R. Pott and D. Wohlleben in ref. 4, p. 417.
- 8) R. D. Parks, N. Martensson and B. Reihl in ref. 5, p. 239 and references therein.
- 9) W. Gudat, M. Iwan, R. Pinchaux and F. Hulliger, ref. 5, p. 249.
- 10) J. W. Allen, S. J. Oh, I. Lindau, J. M. Lawrence, L. I. Johansson and S. B. Hagstrom, *Phys. Rev. Lett.* **46**, 1100 (1981).
- 11) M. Croft, T. H. Weaver, D. J. Peterman and A. Franciosi, *Phys. Rev. Lett.* **46**, 1104 (1981).
- 12) N. Martensson, B. Reihl and R. D. Parks, *Solid State Commun.* **41**, 573 (1982).

- 13) D. C. Kosenmaki and K. A. Gschneidner in "Handbook on the Physics and Chemistry of the Rare Earths," ed. K. A. Gschneidner and L. Eyring (North Holland, Amsterdam, 1978) Vol. 1, p. 337.
- 14) W. H. Zachariasen, *Phys. Rev.* **76**, 301 (1949), L. Pauling, *J. Chem. Phys.* **18**, 145 (1950), B. Coqblin and A. Blandin, *Adv. Phys.* **17**, 281 (1968), R. Ramirez and L. M. Falicov, *Phys. Rev.* **B3**, 2425 (1971), L. L. Hirst, *J. Phys. Chem. Solids*, **35**, 1285 (1974).
- 15) C. M. Varma and V. Heine, *Phys. Rev.* **B11**, 4763 (1975).
- 16) J. K. Lang, Y. Baer and P. A. Cox, *Phys. Rev. Lett.* **42**, 74 (1979).
- 17) B. Johansson, *Phil. Mag.* **30**, 469 (1974).
- 18) J. F. Herbst, R. E. Watson and J. W. Wilkins, *Phys. Rev.* **B13**, 1439 (1976), **B17**, 3089 (1978).
- 19) A. Zangwill and P. Soven, *Phys. Rev. Lett.* **45**, 204 (1980).
- 20) N. Kornstadt, R. Lässer and B. Längeler, *Phys. Rev.* **B21**, 1898 (1980).
- 21) D. R. Gustafson, J. O. McNutt and L. O. Roellig, *Phys. Rev.* **183**, 435 (1969).
- 22) R. M. Moon, W. C. Koehler, *J. Appl. Phys.* **50**, 2089 (1979).
- 23) J. W. Allen and R. M. Martin, *Phys. Rev. Lett.* **49**, 1106 (1982).
- 24) M. Schlüter and C. M. Varma, to be published.
- 25) S. H. Liu and K. M. Ho, *Phys. Rev.* **B26**, 7052 (1982).
- 26) O. Gunnarsson and K. Schönhammer, *Phys. Rev. Lett.* **50**, 604 (1983).
- 27) A. Bringer, ref. 4, p. 397.
- 28) D. Glötzel, *J. Phys.* **F8**, L163 (1978) W. E. Pickett, A. J. Freeman and D. D. Koelling, *Physica*, **102B**, 341 (1980).
- 29) These results are obtained from LDF renormalized atom calculations.
- 30) J. R. Schrieffer, "Theory of Superconductivity," W. A. Benjamin Inc., Reading, 1964.

- 31) D. Jerome, T. M. Rice and W. Kohn, *Phys. Rev.* *158*, 462 (1967).
- 32) M. Schlüter and C. M. Varma in ref. 5, p. 259.
- 33) G. Wendin and M. Ohno, *Physica Scripta* *14*, 148 (1976).
- 34) Y. Baer, H. R. Ott, J. C. Fuggle and L. E. DeLong, *Phys. Rev.* *B24*, 5384 (1981) E. Wuilloud, Y. Baer and M. B. Maple, to be published.
- 35) D. C. Koskimaki and K. A. Gschneidner, *Phys. Rev.* *B11*, 4463 (1975).