

## Self-Interaction Corrected, Local Spin Density Description of the $\gamma \rightarrow \alpha$ Transition in Ce

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We show that, in contrast to local spin density, the self-interaction corrected local spin density provides a correct description of the  $\gamma$  phase of Ce metal. It correctly accounts for the volume and magnetic moment collapse at the  $\gamma \rightarrow \alpha$  transition, in good agreement with experiment.

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The isostructural (fcc $\rightarrow$ fcc)  $\gamma \rightarrow \alpha$  transition in Ce metal is associated with  $\sim(15-17)\%$  volume collapse, as well as a magnetic moment collapse [1]. This first order transition has a phase boundary terminating at a critical point which makes Ce a special case among elemental metals. At low temperatures and normal pressures  $\alpha$ -Ce is the stable phase. This transition has received a lot of attention throughout the years and several models have been proposed to explain it. The most well known are the promotional model [2], the Mott transition model [3], and the Kondo volume-collapse (KVC) model [4]. The promotional model involves a promotion of the Ce  $4f$  electron to the  $5d$  conduction-band state. However, positron annihilation experiments probing the electron density have not found any substantial difference in the number of  $4f$  electrons across the transition [5]. This was confirmed by Glötzel [6] whose first local spin density (LSD) calculation showed no substantial change in the  $4f$  occupation number. Similar conclusions could be drawn from the subsequent calculations performed within the local density approximation [7]. However, none of those calculations could reproduce the characteristics of this first order isostructural transition, and no stable  $\gamma$  phase was found. What those calculations showed, in agreement with experimental evidence, is the formation of a magnetic moment for the volumes in the neighborhood of  $\gamma$ -Ce, indirectly implying the localized nature of the  $f$  electrons in this phase. In the Mott transition model the  $4f$  electrons are treated as localized and nonbonding in the  $\gamma$  phase, whereas in the  $\alpha$  phase they are considered to be itinerant and bonding. This implies that the energy needed to destroy the  $f$  local moment in the  $\gamma$  phase is surmounted at the phase transition by the energy gained on an  $f$  band formation in the  $\alpha$  phase. This model is consistent with positron annihilation experiments suggesting delocalization of the  $4f$  electrons in  $\alpha$ -Ce into a band state [5]. The KVC model uses the localized orbitals to describe both  $\alpha$ -Ce and  $\gamma$ -Ce. The use of the Anderson impurity Hamiltonian is an important aspect of the model [8], leading to quantitative understanding of both the high-energy spectroscopic and low-energy thermodynamic properties of Ce. The essence of the KVC model is the coupling between the  $4f$  states and the conduction-

band states that drives the system through the transition. In this model the change in Kondo energy of  $\sim 60$  meV provides the small energy quantity needed to describe the  $p$ - $V$  phase diagram. According to Allen and Liu [9], *it is the Kondo spin fluctuation energy and entropy in Ce that are responsible for the  $\alpha$ - $\gamma$  transition*. Eriksson *et al.* [10], by implementing the orbital-polarization formalism, involving orbital and spin quenching, have reproduced certain features of the  $\gamma \rightarrow \alpha$  transition. In this formalism the itinerant states are used to describe both phases, and one deals with fourteen partially occupied  $4f$  orbitals that sum up to 1.

In this Letter we apply an *ab initio* approach to the  $\gamma \rightarrow \alpha$  transition in Ce, provided by the LSD and self-interaction corrected (SIC) LSD formalisms. We concentrate on the first principles self-consistent total energy calculations as a function of the lattice parameter.

Recently, we have explored the consequences of the self-interaction correction on the  $4f$  states in the distorted hcp Pr metal, where we have treated these states on equal footing with the conduction-band states [11]. We have found, in agreement with spectroscopies, that the  $4f$  band splitting in Pr into the occupied and unoccupied band complexes can be accounted for in the first principles band structure theory if the self-interaction of  $f$  electrons is removed. The unoccupied  $f$  bands strongly hybridize with the conduction bands creating extremely flat  $d$  bands at the Fermi level  $E_F$ , substantially increasing the density of states at  $E_F$ , and hence the agreement with the observed cyclotron masses, and providing the Fermi surface consisting of four sheets of predominantly  $d$  character, in agreement with de Haas-van Alphen experiment [12]. These results indicate that the SIC-LSD is capable of providing a correct description of the  $4f$  states in rare earth metals. The SIC-LSD formalism can discriminate between the localized and delocalized solutions, and always the ones providing an absolute minimum of the energy functional are chosen [13].

We have described the SIC-LSD formalism and its implementation in previous publications [11,14]. Here we just summarize the main points.

In the SIC-LSD formalism a general one-electron state  $\varphi_\alpha(\mathbf{r})$  satisfies the following wave equation:

$$[H^{\text{LSD}} - \delta V_{\alpha}(\mathbf{r})]\varphi_{\alpha}(\mathbf{r}) = \sum_{\alpha'} \varepsilon_{\alpha\alpha'} \varphi_{\alpha'}(\mathbf{r}), \quad (1)$$

where  $H^{\text{LSD}}$  is the usual LSD Hamiltonian and

$$\delta V_{\alpha}(\mathbf{r}) = 2 \int \frac{|\varphi_{\alpha}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}^{\text{LSD}}(|\varphi_{\alpha}(\mathbf{r})|^2, 0) \quad (2)$$

is the self-interaction correction to the usual LSD potential, and this correction vanishes for extended states. The second term in Eq. (2) is the local spin density approximation to the exchange and correlation potential, and the Lagrange multipliers  $\varepsilon_{\alpha\alpha'}$  ensure the orthogonality of  $\varphi_{\alpha}$ 's. There are several points to be made with respect to solving Eq. (1). First of all, one can convert it into a standard eigenvalue problem by employing the unified Hamiltonian concept [15]. The advantage is that from one matrix diagonalization one obtains *all* solutions and they are automatically orthogonal. Furthermore, one can make use of crystalline symmetry and solve this eigenvalue problem by means of one of the  $\mathbf{k}$ -space band structure methods. Here we employ the linear-muffin-tin-orbitals (LMTO) method, with the atomic sphere approximation (ASA) [16]. Applying SIC leads to the SIC-LMTO-ASA generalization of this method. The SIC potential becomes  $\mathbf{k}$  and band dependent, and it is important to construct a SIC potential compatible with a given crystalline symmetry. To accomplish that we apply symmetry operations and we sum up the  $\mathbf{k}$ - and band-dependent potential over all operations that turn a particular  $\mathbf{k}$  point in the irreducible wedge of the Brillouin zone (BZ) into an equivalent one, and divide by the number of these operations. This symmetrization procedure prevents the SIC potential to remove degeneracies of the relevant bands, as compared to the usual LSD band structure calculation. For the same reason one is restricted in the choice of the states to be self-interaction corrected. In the case of the fcc structure the sevenfold degenerate  $f$  multiplet is split into  $\Gamma'_2$  (singlet),  $\Gamma_{25}$  (triply degenerate), and  $\Gamma_{15}$  (triply degenerate) states, corresponding to  $A_{2u}$ ,  $T_{2u}$ , and  $T_{1u}$  representations, respectively. Since Ce has only one  $4f$  electron, then the choice of the state to be self-interaction corrected is unique, and this is precisely for the symmetry reasons. Moreover, in the angular momentum expansion of the potential only the spherically symmetric terms are retained.

Because of an explicit orbital dependence of the SIC potential [see Eq. (1)] it is required that the SIC-LSD energy functional is stationary under unitary transformations among the occupied orbitals  $\varphi_{\alpha}(\mathbf{r})$ . This requirement adds the following set of equations,

$$\langle \varphi_{\alpha} | \delta V_{\alpha} - \delta V_{\alpha'} | \varphi_{\alpha'} \rangle = 0, \quad (3)$$

to the eigenvalue problem in terms of the unified Hamiltonian. This set of equations has to be satisfied for every pair  $\alpha, \alpha'$  in every iteration of the self-consistency (SCF) cycle of the eigenvalue problem. Therefore, in the SIC-LMTO-ASA band structure scheme one has to employ a

two-level SCF to reach convergence for both the total energy and wave functions. Equation (3) is often referred to as the localization criterion [17], since it takes care that the orbitals  $\varphi_{\alpha}$  possess the optimal degree of localization for the absolute minimum of the SIC-LSD energy functional. It also implies the Hermiticity of the Lagrange multipliers matrix, so that it can be diagonalized providing the SIC-LSD eigenvalues. The SIC-LSD eigenvalues obtained by diagonalizing the unified Hamiltonian matrix agree very well with those provided by diagonalizing the Lagrange multipliers matrix. This gives one confidence that employing the unified Hamiltonian concept, and overcoming the evaluation of the Lagrange multipliers matrix, is a sensible choice.

We have performed semirelativistic spin-polarized calculations with and without self-interaction correction, using SIC-LMTO-ASA and LMTO-ASA, respectively, for a number of lattice parameters. The calculations have been performed in two energy panels, each one using its own set of standard (unscreened) LMTO *spdf*-basis functions. The lower panel has included the semicore  $5p$  bands and the upper panel the valence  $6s$ ,  $5d$ , and  $4f$  bands. The respective basis sets have differed in the choice of the energy expansion parameters  $\varepsilon_{\nu l}$ . In all calculations we have used 525  $\mathbf{k}$  points in the irreducible part of the BZ, and we have generated all equivalent  $\mathbf{k}$  points in the BZ by applying symmetry operations. Such a large number of  $\mathbf{k}$  points has been essential to self-consistently converge results for the lattice parameters in the vicinity of the  $\gamma \rightarrow \alpha$  transition in Ce, especially with respect to the value of the magnetic moment.

In Fig. 1(a) we present both the LSD and SIC-LSD total energy curves as a function of the volume. The SIC-LSD curve's minimum occurs virtually at the volume of  $\gamma$ -Ce, and it crosses the LSD curve at the volume for which the LSD magnetic moment goes to zero [see Fig. 1(b)]. Note that the SIC-LSD moment also persists after the crossing of the curves. The theoretical volume of the  $\gamma$  phase is  $\sim 0.2\%$  smaller than the experimental volume, indicating that the SIC-LSD correctly describes a stable  $\gamma$  phase of Ce. The latter statement is strengthened by good agreement of the calculated and experimental  $p$ - $V$  curves for the  $\gamma$  phase, although the calculated pressure curve lies still higher than the measured curve, with a bulk modulus of 340 kbar at the theoretical lattice constant. The minimum of the LSD curve lies 5 mRy higher than that of the SIC-LSD curve, and it underestimates by about (9–10)% the volume corresponding to the  $\alpha$  phase of Ce metal. One can see that LSD fails to provide a correct description of the  $\alpha$  phase, also giving much too low a theoretical volume. Moreover, the agreement with experiment of the calculated pressure curve for  $\alpha$ -Ce is not as good as in the case of  $\gamma$ -Ce. The bulk modulus of the  $\alpha$  phase, evaluated at the theoretical lattice constant, is 443 kbar. A common tangent construction gives a *positive* transition pressure of  $\sim 17$  kbar, as opposed to  $-8$  kbar, the value obtained by extrapolating from the

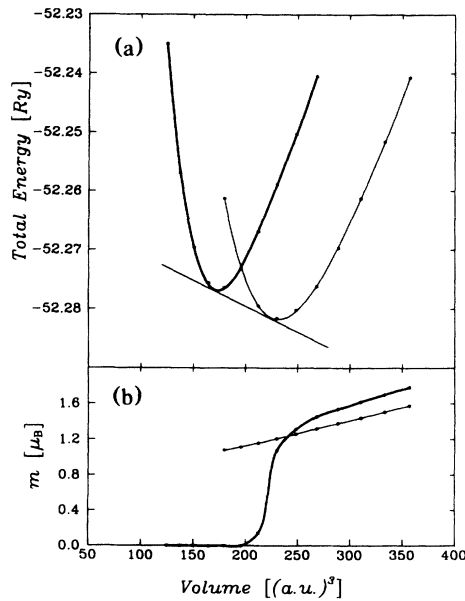


FIG. 1. The SIC-LSD (thin solid curve) and LSD (thick solid curve) total energy (a) and magnetic moment  $m$  (in Bohr magneton  $\mu_B$ ) (b), as a function of volume. The common tangent line is also shown in (a).

phase diagram to  $T = 0$  K [18]. The theoretical volume collapse is  $\sim 23\%$ , as compared to the experimental values of about  $(15\text{--}17)\%$  [1]. We believe that the reason for such overestimation of the volume collapse primarily lies in the failure of the LSD to better describe  $\alpha$ -Ce. The LSD fails to describe the  $\alpha$  phase as well, as the SIC-LSD describes the  $\gamma$  phase. This is probably not surprising due to the fact that the  $\alpha$  phase is still a strongly correlated system, and the LSD would substantially overestimate the value of the  $f$ - $f$  hopping integral. However, the LSD has been successful in describing high-pressure phases of Ce [19], suggesting the sensitivity of this hopping integral to the volume.

It should be mentioned that it is the number of basis functions used in the lower (semicore) panel that influences the relative positions of the LSD and SIC-LSD total energy curves minima. Including only the  $s$  and  $p$  LMTO's makes the LSD curve 3.0 mRy lower in energy than the SIC-LSD curve, thus leading to a *negative* transition pressure of  $-11$  kbar. Adding  $d$  functions shifts the SIC-LSD minimum below the LSD minimum with the relative difference of 1.5 mRy between the corresponding minima and the transition pressure of 3 kbar. Including also the  $f$  functions makes the SIC-LSD minimum 5 mRy lower than that of the LSD curve with the transition pressure of  $\sim 17$  kbar. Moreover, the inclusion of the  $f$  functions is crucial for obtaining the theoretical lattice constant of the  $\gamma$  phase nearly equal to the experimental value (as compared to the  $spd$  calculation, adding the  $f$ -basis function changes the equilibrium volume of  $\gamma$ -Ce by 2.8%, and of  $\alpha$ -Ce by 0.8%). The sensitivity of the relative positions of the LSD and SIC-LSD total energy

minima to the choice of basis functions is disturbing and might be solved in the future by use of the downfolding technique [20]. Nevertheless, this sensitivity does not seem to affect our qualitative conclusions concerning the physics of the  $\gamma \rightarrow \alpha$  phase transition.

Disregarding uncertainties in the actual value of the transition pressure, and the relative positions of the LSD and SIC-LSD total energy curves minima, these *ab initio* calculations correctly reproduce the crucial characteristics of this first order  $\gamma \rightarrow \alpha$  transition, and especially the SIC-LSD describes the  $\gamma$  phase extremely well. The overestimation of the volume collapse seems to be mostly due to the LSD. This is the first time that the  $\gamma \rightarrow \alpha$  transition could be described in terms of the *ab initio* calculations within the density functional theory. Moreover, it is significant that in this description the energy difference between the two phases is in mRy range.

Analyzing further the total energy curves in Fig. 1, one should note that these are the localized solutions that give lower total energies for the volumes in the vicinity of the  $\gamma$  phase. At the crossing point of the two energy curves both the localized and delocalized solutions give the same total energy, and from that point on the nonmagnetic, delocalized solutions give lower energies. The crossing point of the two total energy curves is extremely dependent on the choice of the exchange-correlation potential, and it is crucial to use the Ceperley-Alder exchange-correlation potential [13] to correctly account for the disappearance of the magnetic moment at the transition.

In Figs. 2(a) and 2(b) we present, respectively, the LSD and SIC-LSD total densities of states for the theoretical lattice parameters of the  $\alpha$  and  $\gamma$  phases. In  $\alpha$ -Ce, as described by the LSD, the unoccupied  $4f$  band states strongly hybridize with the  $5d$  and other valence bands, contributing substantially to the total density of states at the Fermi energy  $E_F$ . In  $\gamma$ -Ce, on the other hand, the  $4f$  states are split into the occupied states, occurring at about  $-7.5$  eV below  $E_F$ , and the unoccupied states at about 1 eV above  $E_F$ . As a result of this splitting the hybridization of the unoccupied  $4f$  states with the valence bands is extremely small. Moreover, these densities of states imply a huge change in the one-electron contribution to the total energy between the  $\alpha$  and  $\gamma$  phases. Indeed, the one-electron sum in the  $\gamma$  phase is by 1164 mRy lower than in the  $\alpha$  phase. However, the respective total energies differ by 5 mRy only. This is because in the  $\gamma$  phase the gain of 1443 mRy in Coulomb energy is balanced by the loss of 720 mRy in kinetic energy and 718 mRy in exchange-correlation energy. From these numbers one can see that there is a competition between the large on-site  $f$ - $f$  Coulomb interaction, on the one hand, and the  $f$  hybridization, on the other hand. In the  $\gamma$  phase the on-site  $f$ - $f$  Coulomb interaction wins, leading to a localization of the  $f$  electrons which manifests itself through an appearance of the low lying  $f$  peak in the density of states.

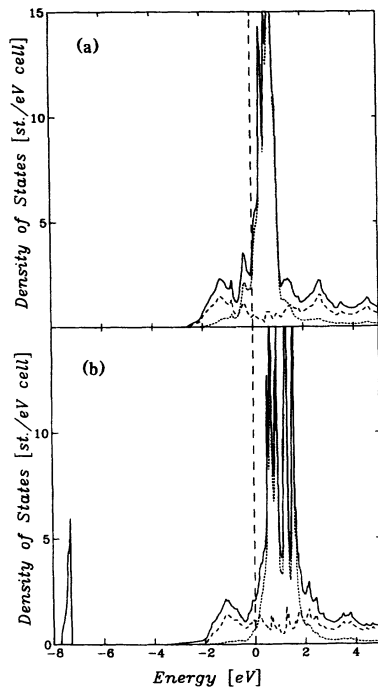


FIG. 2. The LSD (a) and SIC-LSD (b) total density of states. The dashed curves are the  $d$  contributions to the total density of states, while the dotted curves correspond to the  $f$  contribution.

Summarizing, our results show that the strong hybridization effects of the  $f$  electrons are the driving force behind the  $\gamma \rightarrow \alpha$  transition in Ce. This leads to an energy lowering of the nonmagnetic state below the magnetic state at small volumes. Within this *ab initio* approach the SIC-LSD also provides the mechanism for switching off the  $4f$  contribution to cohesion at the phase transition. The SIC-LSD treats on equal footing both the *band-f* hybridization and the  $f$ - $f$  hopping, and that is true for all the  $f$  states. These *ab initio* calculations do not discriminate between either the KVC or the Mott transition model. They correctly account for the hybridization change at the transition, in agreement with both models. Suffices it to say that the SIC-LSD provides a correct description of the  $\gamma$  phase and leads to a small energy difference between the two phases. The large underestimation of the equilibrium volume of  $\alpha$ -Ce could be interpreted as an indication of missing correlations due to the Kondo screening. Equally well, however, one could argue that LSD would normally overestimate the  $f$ - $f$  hopping integral and bonding of such strongly correlated systems as  $\alpha$ -Ce. Therefore, at this stage one cannot draw final conclusions with respect to the nature and degree of localization of the  $4f$  electrons in the nonmagnetic  $\alpha$  phase.

Similar calculations, using a very different implementation of the SIC-LSD formalism, have independently been performed by Svane who reached very much the same conclusions as the ones presented here [21].

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