

Comment on:

**Electronic Structure of Cerium in the Self-Interaction Corrected Local Spin Density Approximation** by *A. Svane*, to appear in Phys. Rev. Lett., February 21, 1994, and

**The Self-Interaction Corrected Local Spin Density description of the  $\gamma \rightarrow \alpha$  transition in Ce** by *Z. Szotek, W.M. Temmerman, and H. Winter*, to appear in Phys. Rev. Lett., February 21, 1994

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The  $\gamma \rightarrow \alpha$  phase transition in Ce metal has been studied extensively both experimentally and theoretically. This transition is unique in being isostructural (fcc $\rightarrow$ fcc) and it is associated with  $\sim 15$ – $17$  % volume collapse, as well as, a magnetic moment collapse [1]. It 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, this model is difficult to reconcile with the cohesive properties of Ce [3] as well as with photoemission data [5]. Moreover, positron annihilation experiments probing the electron density have not found any substantial difference in the number of  $4f$  electrons across the transition [6]. This was confirmed by Glötzel [7] 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 [8]. 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 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 [6]. No quantitative description of cerium within the Mott transition picture at finite temperature has been presented.

In the Kondo volume collapse model [9] the transition is assumed to be governed by spin screening of the localized  $f$ -electrons by the ( $spd$ ) conduction electrons. In this model the  $\gamma$ -phase consists of essentially unscreened localized moments, while the  $\alpha$ -phase consists of screened moments. The screening of a localized  $f$ -electron is accomplished by the non- $f$  valence electrons on the neighbouring atoms forming a spin singlet with the  $f$ -electron and is then controlled by the  $f$ -( $spd$ ) hopping matrix elements. This screening is well understood for an isolated localized moment [10] but till now the effect of a periodic array of local moments has not been described. In the calculation of the Kondo volume collapse model [9] it is assumed that the results for the single moment case (in particular the strong dependence of the screening energy on volume) can be carried over to the lattice case. With this assumption it has been shown that the detailed characteristics of the  $\gamma \rightarrow \alpha$  phase transition, including the occurrence of a critical point, may be explained [9]. In accordance with the Kondo volume collapse model, the photoemission experiments on cerium are well accounted for with the Anderson impurity model [11]. Both the Mott transition model and the Kondo volume collapse model agree that the  $\gamma$ -phase of cerium consists of localized  $f$ -electrons, while the dispute is over the nature of the  $\alpha$ -phase.

Eriksson et al. [12], 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 one.

The papers by Svane and Szotek et al. apply an *ab initio* approach to the  $\gamma \rightarrow \alpha$  transition in Ce, provided by the LSD and self-interaction corrected (SIC)-LSD formalisms. They concentrate on the first principles self-consistent total energy calculations as a function of the lattice parameter.

The self-interaction corrected local-spin-density approximation [13] is an *ab initio* electronic structure scheme, which describes static Coulomb correlation effects much better than the LSD approximation. This has been demonstrated in studies of the Hubbard model [14], in applications to 3d monoxides [15] and  $\text{La}_2\text{CuO}_4$  [16] and hydrogen solid [17]. In the papers

commented upon here Svane and Szotek et al. demonstrate that this scheme is also capable of describing  $\gamma$ -Ce properly and in fact provides a unified *ab initio* framework for studying both the  $\alpha$ -phase and the  $\gamma$ -phase of cerium.

In the SIC-LSD one subtracts from the LSD total energy functional  $E^{LSD}$  the self-Coulomb,  $U[n_i]$ , and self-exchange-correlation energy,  $E_{xc}^{LSD}[n_i]$ , for each occupied orbital, where  $n$  is the total spin-density of the electrons, while  $n_i$  is the spin-density of the  $i$ 'th occupied electron orbital. The rationale is that  $E^{LSD}$  erroneously includes the self-interaction of each electron, which is then corrected for in the SIC-LSD energy functional  $E^{SIC}$ . The self-interaction vanishes for extended states, for which reason the SIC-LSD energy functional is identical to the LSD energy functional in the entire region of configuration space corresponding to Bloch-like one-particle wavefunctions. The possibility exists, however, that different local minima of  $E^{SIC}$  containing localized wavefunctions can be found with a lower total energy than the LSD-like local minimum.

The two papers differ in the implementation of the SIC-LSD formalism. Svane has implemented the SIC-LSD approximation within the linear-muffin-tin-orbital (LMTO) method in the tight-binding representation [18] and with the atomic-spheres approximation (ASA). The SIC-LSD energy functional is minimized by using a simple steepest descent iterative scheme for the localized states and subsequently solving the secular equation for the itinerant states in the subspace orthogonal to the localized states. Szotek et al. have taken an advantage of the unified Hamiltonian concept [19] and converted the minimization of the SIC-LSD energy functional into a standard eigenvalue problem which by making use of crystalline symmetry they have solved applying the standard unscreened linear-muffin-tin-orbitals method, with the atomic sphere approximation [20]. With respect to technical details of the calculation both papers differ in the choice of the energy panels and the symmetry of the  $f$  band states to be self-interaction corrected. Despite that, and what is most reassuring, both papers reach very much the same conclusions concerning the important physical issues of Ce.

These papers demonstrate, for the first time, that it is possible from first principles calculations to obtain two energy minima corresponding to the  $\alpha$ -phase and the  $\gamma$ -phase, respectively. Since, both curves represent local minima of the same energy functional a phase transition is predicted to take place. It is significant that the energy difference between the two minima, corresponding to either localized or delocalized  $f$ -electrons, is in mRy range allowing for a low-pressure transition between the phases, in agreement with experimental evidence. Disregarding some sensitivity of the relative positions of the LSD and SIC-LSD total energy minima and the actual value of the transition pressure to the choice of the energy panels and basis functions 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 stiffness of both the  $\alpha$ -phase and the  $\gamma$ -phase around  $P = 0$  as well as the  $P = 0$  volume of the  $\alpha$ -phase are not well reproduced within the present formalism which may be taken as an indication that still some effects, as e. g. Kondo screening, have not been properly described. These calculations correctly account for the disappearance of

the magnetic moment at the transition and give the theoretical volume collapse of  $\sim 23-24$  %. The reason for the 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 [21], suggesting the sensitivity of this hopping integral to the volume. In the  $\gamma$ -Ce 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  $E_f$ . These papers show that the strong hybridization effects of the  $f$  electrons are the driving force behind the  $\gamma \rightarrow \alpha$  transition in Ce, in agreement with both the KVC and the Mott transition models. Suffices 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,  $\sim 10$  %, 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 system as  $\alpha$ -Ce. The inclusion of Kondo screening of the localized moments within the SIC-LSD description is a difficult task. The SIC-LSD formalism relies, as the LSD, on a single Slater determinant description. One may presume quantum fluctuations to be improperly described in cases where they are significant. Therefore, at this stage one could not draw final conclusions with respect to the nature and degree of localization of the  $4f$  electrons in the non-magnetic  $\alpha$ -phase. Nevertheless, the main result of these papers, i.e., a successful *ab initio* description of the  $\gamma$ -Ce, is an important contribution to a better understanding of the  $\gamma \rightarrow \alpha$  phase transition in Ce.

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