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Ground and metastable states in γ-Ce from correlated band theory

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Abstract

The effects of electron correlation on the electronic structure and spin and orbital magnetic properties of the f.c.c. Ce were investigated using the relativistic (with spin–orbit coupling included) full-potential linearized augmented plane wave implementation of correlated band theory ('LDA+U'). Multiple energy minima of the LDA+U energy functional are obtained for γ-Ce. The lowest energy solution leads to a fully spin polarized 4f state and the lattice constant of γ-Ce. The higher energy local minima (additional self-consistent solutions) are shown to be strongly indicative of low-energy excitations.

Keywords: Electronic structure; Correlated band theory; Excitations; Ce

1. Introduction

The isostructural α–γ phase transition in Ce, and the character of the phases separately, have been the subject of continuous theoretical efforts for decades. Experimentally, the low temperature f.c.c. α phase of Ce transforms to the f.c.c. γ phase at high temperatures with a large increase in the volume. When pressure is applied, the crystal collapses back into the α phase in a first-order phase transition. The room temperature γ–α phase transition occurs at ≈7-kbar pressure with a decrease in the volume of ≈ 15%.

Several theoretical models have been suggested and they are described in some detail in Ref. [1]. The differences between the models arise from the different treatments for the Ce 4f electrons. The promotional model [2] assumed depopulation of the 4f level upon compression, but does not agree with the results of various experiments which indicate little change in the 4f occupation. Band structure calculations also indicate that promotion is too high in energy to drive the transition, and the 4f occupation remains near unity [3]. The Mott transition model [4] assumes the transformation of localized to band-like 4f state with the decrease in volume and is similar to the Mott–Hubbard metal-insulator transition. First principles calculations using the self interaction correction (SIC) to the LDA [5] produce total energy minima for localized (γ) and band (α) states with formally the same SIC total energy variational functional, and are in accordance with the Mott transition model. However, the use of atomic sphere approximation (ASA), which sphericalizes the potential and density within large atomic spheres, limits the ability of these calculations to produce a quan-

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titative total energy description of the system with highly non-spherically symmetric 4f electron charge/spin densities.

The other viable theoretical model is the Kondo volume collapse (KVC) model [6]. The essence of the KVC is an assumption of localized f states in both α and γ phases of Ce. The α phase consists of a mixed valence 4f state while the γ phase has almost integer 4f occupancy. The phase transition is due to the entropy contribution of the localized 4f state. The relation between KVC and Mott transition model was analyzed recently in Ref. [1] and quantitative arguments in favor of KVC model were provided.

The local (spin) density approximation (LDA) has had tremendous success in the quantitative description of a wide variety of solids [7], but the rare earths are extreme cases where the LDA description is inadequate. The 'correlated band theory' (LDA+U) approach has had much success in the treatment of correlated magnetic insulators where LDA results are incorrect. In this paper we explore not the γ–α transition per se, but the γ phase itself, by an application of the LDA+U approach that includes the following new features: (i) a full potential method is used, which enables the novel features we uncover; and (ii) the LDA+U method is applied to a metal where the interaction of the local orbitals with the conduction states is a central part of the physics. For the first time to our knowledge, multiple LDA+U energy minima (ground plus metastable states) are obtained within a specified broken symmetry, and we discuss how the various states are related to 4f excitations in the γ phase.

The LDA+U method (see Ref. [8] and references therein) is based on an energy which is a functional of the spin densities $\{\rho^s, s = \pm 1\}$, and the occupation matrices $\{n^s_{m,m'}\}$ of the 4f orbitals labelled by their azimuthal projections $m \equiv m_\ell$. There is every reason to expect that, within the allowed values of ρ^s and n^s, there can be local energy minima as well as the absolute minimum, which represents the ground state energy of the system. (Such local minima are rarely found within LDA except in magnetic systems.) The formal meaning of these local minima, as well as the formal underpinnings of the LDA+U approach itself, remains to be settled, but — like the Kohn–Sham eigenvalues (the band structure) which have little formal meaning but immense practical importance — these minima will be shown to bear a close relationship to local excitations of the 4f shell.

2. Computational results

Our results are based upon the full-potential linearized augmented plane wave method (LAPW) [9] as the basis for total energy calculations with the rotationally invariant LDA+U functional [10], and spin–orbit coupling (SOC) is included self-consistently [11]. Literature values [12] are used for the on-site repulsion $U = 6.1$ eV and exchange $J = 0.7$ eV (Slater integrals, $F_0 = 6.10$ eV, $F_2 = 8.34$ eV, $F_4 = 5.57$ eV, $F_6 = 4.12$ eV). Ferromagnetic spin alignment is assumed since local moments are present in paramagnetic high temperature γ phase of Ce [13].

The key to finding the various solutions (local minima) is to start from atomic densities and different 'guesses' for the 4f occupation matrices n^s and then obtain self-consistently both spin/charge densities and occupation matrices. As an intuitive guess for 4f occupations we use the fully spin-polarized state ($\mathrm{Tr}\, n^\uparrow = 1$, $\mathrm{Tr}\, n^\downarrow = 0$) and choose various orbital characters for $n^\uparrow_{m,m'}$.

2.1. Ground state

The calculated equilibrium lattice constant (Table 1) is very close to the experimental value of γ-Ce at zero pressure and room temperature. It is consistent

Table 1
The equilibrium lattice constant (a, a.u.) and bulk moduli (B, kbar) as a result of LDA+U calculations

	LAPW	LMTO-ASA [5]	LMTO-ASA [18]		Exp. [5]
	LDA+U	SIC	f-Core LDA	f-Core GGA	
a	9.83	9.58	9.69	10.02	9.76
B	296	310	312	288	210, 244

with recent findings that the use of Hubbard U leads to the equilibrium lattice constant equal to that of the Pu localized δ phase [14]. The calculated bulk modulus is ~25% larger than the experimental value, similar to other calculations that have treated the localized character of the 4f state in γ-Ce.

For the γ phase (lattice constant, $a = 9.7556$ a.u.) we found the lowest energy solution to be fully spin polarized with the f occupation of 1.044. The orbital dependence of the spin-majority occupation matrix is shown in Table 2. The LDA+U value of spin magnetic moment in γ-Ce, 1.1 μ_B, is significantly enhanced in comparison with the LDA value (0.5 μ_B). The LDA+U absolute value of orbital magnetic moment in γ-Ce is almost five times larger than produced by LDA (0.4 μ_B). The spin and orbital magnetic moments are anti-aligned in accordance with the third Hund's rule.

The electronic density of states for the γ-Ce ground state is shown in Fig. 1 in comparison with the result of relativistic (with SOC) LDA calculations. The f-majority peak at the bottom of the valence band (≈ 2.5 eV below the Fermi level) indicates the position of the localized 4f state, in quantitative agreement with the resonant photoemission measurements [15]. The difference between LDA+U and LDA is due to the localization of the 4f state, which removes both majority and minority 4f states from the vicinity of the Fermi level. Since the 4f state is not well separated from the valence band (Fig. 1) we conclude that in spite of its localized character the 4f state in γ-Ce cannot be treated as core-like.

The LDA+U does not reproduce the α-Ce equilibrium lattice constant (9.163 a.u.). Instead, the total energy is increasing with the decrease in volume in agreement with SIC calculations when f-state localization is assumed. The LDA results of LMTO-ASA calculations [5,18] underestimate the value of equilibrium lattice constant by $\approx 5\%$ and the use of full potential calculations makes agreement with the experiment even worse ($\approx 7\%$). The situation is improved by the use of GGA instead of LDA [18]. However, the ability of LDA (GGA) to reproduce the equilibrium lattice constant close to α-Ce does not mean that LDA provides its complete quantitative description. It rather indicates the strong mixing between the conduction band and f-states in

Table 2
The elements of the occupation matrix $n_{m,m'}$ (spin-majority) (initial assignment n^0 and self-consistent n^{scf}); spin ($2\langle S_z\rangle$), orbital ($\langle L_z\rangle$) moments and the total energy increase with respect to the ground state (ΔE, meV) for different LDA+U self-consistent solutions in the order of increasing total energy[a]

$n^0_{m,m'}$			$n^{scf}_{m,m'}$			$2\langle S_z\rangle$	$\langle L_z\rangle$	ΔE
Solution 1								
m, m'	−2	2	m, m'	−2	2	1.18	−1.87	0
−2	1	0	−2	0.960	0.143			
2	0	0	2	0.143	0.030			
Solution 2								
m, m'	−3	1	m, m'	−3	1	1.18	−0.75	19
−3	1	0	−3	0.438	−0.484			
1	0	0	1	−0.484	0.552			
Solution 3								
m, m'	−1	3	m, m'	−1	3	1.18	0.001	52
−1	1	0	−1	0.737	−0.423			
3	0	0	3	−0.423	0.253			
Solution 4								
m, m'	0		m, m'	0		1.14	−0.004	232
0	1		0	0.979				

[a] Only those elements of occupation matrix which are bigger than 0.01 are shown. The spin-minority occupation matrix is almost zero since there is a complete spin-polarization of the 4f-shell.

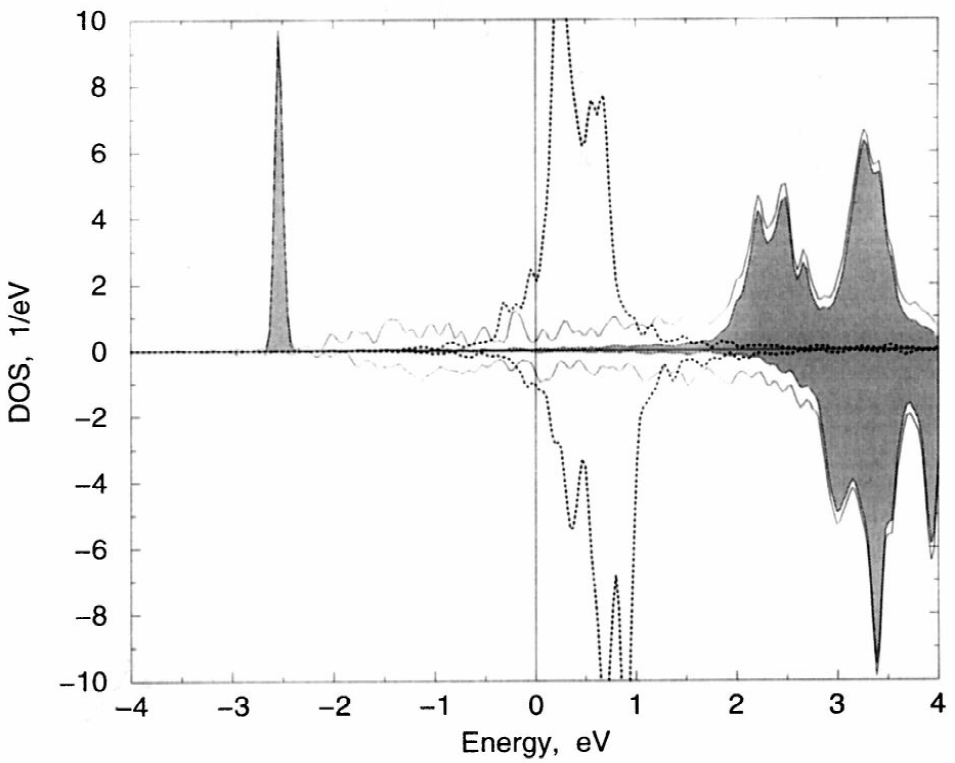

Fig. 1. Spin-resolved total and partial 4f densities of states for ordered γ-Ce. The majority are plotted upwards, the minority downwards. The 4f partial DOS from LDA is dotted. The full line gives the LDA + U DOS, with the 4f contribution filled in. The 4f DOS peaks near the Fermi level in both spins are well removed from the Fermi level by LDA + U.

α-Ce but neglects the electron correlations. As was already mentioned [1], there is considerable experimental evidence of correlated character of f-electrons in α phase which is strictly beyond LDA (GGA), SIC and LDA + U static 'mean-field' treatment.

2.2. Metastable states

As mentioned above, several self-consistent solutions corresponding to different (local) minima of the LDA + U energy functional are possible. Different minima must be searched for by exploring various regions of the underlying space. Our initial and final (self-consistent) majority spin occupation matrix elements are shown in Table 2.

The values of $n^{s}_{m,m'}$ at a LDA + U minimum can be considered as corresponding to mean-field-like projections (in the Fock space) of many-body wavefunctions on the single-particle angular basis set. The interpretation is much simpler for an f^1 ion than it would be for a multi-electron ion because the $\{m_l, m_s\}$ and $\{J, J_z\}$ representations are unitarily related. In the simple crystal-electric-field (CEF) model for the paramagnetic Ce^{3+} ion [17] the ground state is formed by one of the Γ_7 and $\Gamma_8^{1,2}$ doublets from $J = 5/2$ multiplet [16]. In order to compare the CEF model [17] with the LDA + U results, we apply to the LDA + U solutions the unitary transformation from $\{m_l, m_s\}$ representation to $\{J, J_z\}$ representation with $J = 5/2,7/2$. The states from Table 2 are then classified as follows.

2.2.1. Solution (1) — ground state

It has 96% $m_l = -2$, with 3% $m_l = 2$ mixed in. The transformation to $\{J, J_z\}$ representation yields 69% of $|5/2, -3/2\rangle$ and 1% of $|5/2, 5/2\rangle$ states from $J = 5/2$ multiplet, plus 27% of $|7/2, -3/2\rangle$ and 3% of $|7/2, 5/2\rangle$ states from $J = 7/2$. We conclude that solution 1 consists of 70% states from the $J = 5/2$ multiplet which are the linear combina-

tion of the CEF levels Γ_7 and Γ_8^1, and 30% states from the $J = 7/2$ multiplet.

2.2.2. Solution (2)

Roughly equal amounts of $m_l = -3$ and $m_l = +1$ in this solution indicates coupled $j_z = -5/2$ and $j_z = 3/2$ states. It consists of 55% of states from $J = 5/2$ multiplet (combinations of the CEF levels Γ_7 and Γ_8^1) and 45% of states from $J = 7/2$.

2.2.3. Solution (3)

This involves admixture of $m_l = -1$ with 25% $m_l = +3$, which transforms to an admixture of 42% of $|5/2, -1/2\rangle$ ($|\Gamma_8^2\rangle$) state with 58% of $|7/2, 7/2\rangle$.

2.2.4. Solution (4)

Pure $m_l = 0$, corresponds to the combination of 42% of $|5/2, 1/2\rangle$ ($|\Gamma_8^2\rangle$) state with 58% of $|7/2, 1/2\rangle$, and lies 232 meV above the ground state.

There are several important reasons why our solutions do not correspond directly to CEF levels as normally considered: (i) the standard CEF picture assumes that the effective CEF magnetic Hamiltonian commutes with the total angular momentum operator *J*, while the LDA+U effective Hamiltonian (see Ref. [8] and references therein) does not. As a result, the $J = 5/2$ and $J = 7/2$ states are mixed in the LDA+U solutions; (ii) the CEF picture assumes ideal cubic symmetry, whereas a 4f state in γ-Ce is actually surrounded by 12 atoms whose own moments are oriented randomly, hence breaking cubic symmetry; (iii) the non-cubic nature of the 4f density perturbs the conduction electron density, which leads to a non-cubic local field; and (iv) in our calculations we have artificially ordered the spins of the magnetic ions and allowed orbital moments, which reduces the site symmetry to tetragonal.

The comparison between LDA+U calculated splitting scheme with the results of inelastic neutron scattering experiments [19] is shown in Fig. 2. It is seen that solutions 1–3 lie well within the range of low-energy excitations peak and reflect the mixed CEF and spin–orbit excitations. The energy position of solution 4 (232 meV) agrees well with the experimental inelastic peak at 260 meV. This peak is usually interpreted as the spin–orbit excitation ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ [19]. Our calculations suggest that this interpretation is oversimplified since the states from

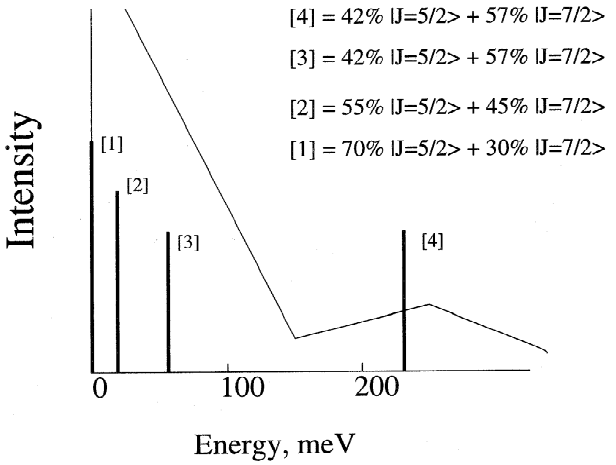

Fig. 2. Schematic sketch of the experimental inelastic neutron scattering intensity in comparison with the energy positions of LDA+U calculated ground and excited states [1].

both lower ${}^2F_{5/2}$ and first excited ${}^2F_{7/2}$ multiplets are mixed in the ground and excited states of γ-Ce. The spectrum from present LDA+U calculations is in better agreement with the experiment [19] than previously reported results of SIC calculations [20] (86–100 and 130 meV).

Recently, Solovyev et al. [21] proposed a correction to the LDA+U total energy functional [22] when SOC is included and non-collinear magnetic configurations are considered. This correction accounts for additional contributions to the exchange energy due to non-zero spin-off-diagonal elements of the occupation matrix $\{n_{m,m'}^{s,-s}\}$. We included the corrections and found that the spin-off-diagonal occupations have minute effects on the values of spin and orbital magnetic moments, and the total energies (less than 2 meV).

3. Conclusions

To summarize, we have obtained the ground and three metastable states from relativistic (with spin–orbit coupling) spin-polarized full-potential LDA+U calculations for f.c.c. Ce. The ground state has equilibrium lattice constant of γ-Ce. Our calculations reproduce the localized character of 4f states in γ-Ce, which however cannot be treated as a part of the atomic core. Analysis of various LDA+U solutions

allows us to make a comparison between correlated band theory results and CEF model. Interpreted as excitation energies, these total energy differences between LDA + U solutions are in reasonable agreement with the experimental data.

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