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Phase transitions in cerium by pseudopotential methods

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Abstract

To study the phase diagram of cerium with ab initio molecular dynamics methods, we built and validated a pseudopotential for this element by Plane-Waves calculations. We present calculations of the equation of state and the high pressure phases. Our results are in fair agreement with all previous electron calculations and with experiment when the generalized gradient approximation (GGA) is used.

Keywords: Density functional theory; Pseudopotentials; f electrons; Plane wave calculations

1. Introduction

Cerium is one of the most fascinating elements of the periodic table showing a very rich phase diagram (Fig. 1). It has been studied extensively both experimentally and theoretically. It is the first lanthanide metal that has an appreciable occupation of the 4f states. Under various conditions of temperature and pressure, cerium is an antiferromagnet, a supraconductor, and the only pure element to exhibit pressure-induced isostructural transition, the well-known fcc α-γ phase transition at 0.7 GPa and 298 K with a volume collapse of ~16%. This phase transition might be related to an itinerant-localized transition of f electrons but is outside the scope of this work. Apart from this isostructural phase transition, the phase diagram is still controversial. The theoretical and experimental results on the crystal structure to which α-Ce transforms at 5 GPa are still confusing. According to the literature, the crystal structure in this 5–12 GPa region could be α′ (α-U; orthorhombic *Cmcm*; four atoms/cell) or α″(II) (monoclinic *C2/m*; four atoms/cell).

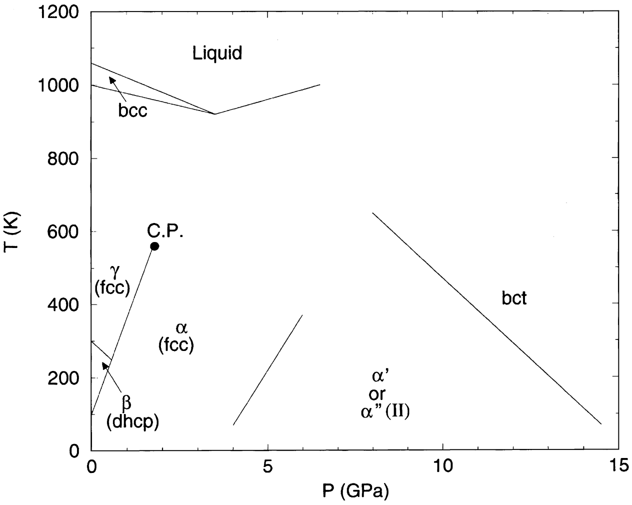

Fig. 1. Pressure versus temperature phase diagram for cerium.

Up to now, cerium has only been studied theoretically in all electron schemes and never in a pseudopotential scheme. Apart from limitations inherent to DFT-LDA (poor treatment of the electronic correlation), building a pseudopotential for heavy elements is still a challenge for various reasons (relativistic effects, localization of f electrons). But on a theoretical side, the Plane-Waves+Pseudopotential formalism is attractive because it offers a broader scope of study than all-electron calculations, such as ab initio molecular dynamics which allow to determine the crystal structure without any previous guess and should be accurate in the crystalline phases where f electrons are delocalized. Finding and understanding the structural properties of Ce metal are very important issues to obtain information on the nature of the 4f electrons.

In Section 2, the generation of our pseudopotential is explained. Section 3 deals with the calculations of the equation of state for cerium. In Section 4, we present the static study we performed for some high pressure phases. In Section 5, we present the conclusions of our calculations and the next steps to come in our work.

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2. Pseudopotential generation

We have generated two norm-conserving Trouillier–Martins [1] pseudopotentials in the Density Functional Theory formalism (Fig. 2):

- one in Local Density Approximation (LDA) using the Perdew–Zunger [2] exchange-correlation function (PZ);
- the other using Gradient Corrections to LDA (GGA: Perdew–Burke–Ernzerhof [3] exchange-correlation function (PBE 96)) and with non linear core correction (nlcc) [4].

The nonlinear core correction is added to take into account the spatial overlap between the core and the valence wavefunctions (especially in the case of the 4f wavefunction). For the GGA pseudopotential, we took a thinner grid to calculate our pseudopotential. The core electrons are treated in a scalar-relativistic formalism. We treated as valence states the 5s, 5p, 5d, 6s and 4f electrons and the cut-off radii are $r_{c5s}=1.29a_0$, $r_{c5p}=1.49a_0$, $r_{c5d}=1.99$, $r_{c4f}=1.99a_0$. For the 5s, 5p and 5d orbitals, the cut-off radius is taken just before the outermost maximum of the corresponding wavefunctions whereas for the 4f wavefunctions which is very localized we chose a radius larger than the outermost maximum of the wavefunction to obtain a softer pseudopotential in order to reduce the size of the plane waves basis set. A smaller value of r_{c4f} gave a more transferable and accurate pseudopotential but less rapidly convergent regarding the energy cut-off for the plane wave basis set. The value we have chosen can be seen as a compromise between transferability and convergence. We checked the transferability by calculating the logarithmic derivatives and by comparing with all-electron calculations for excited atomic states. The angular momentum component $l=0$ is taken as the local part. Both pseudopotentials need a 120 Ry cut-off for the plane wave expansion of wave functions. For all the structures that we have studied, we have optimized the Brillouin zone sampling, the Gaussian spreading for Brillouin zone integration and the crystallographic parameters.

Table 1
Theoretical and experimental values of the equilibrium volume V and bulk modulus B for α-Ce from our pseudopotential calculations (PS), FP-LMTO calculations [5] and experimental data [6,7]

	V (Å^3)	B (GPa)
PS-LDA	23.30	58.7
FP-LMTO-LDA	22.74	60.5
PS-GGA-nlcc	26.30	43.0
FP-LMTO-GGA	26.05	48.7
Experiments	28–29	25–35

3. Equation of state

To check the validity of our pseudopotentials, we refer both to experiment and all previous electron calculations.

The first test was to calculate the equation of state for the experimental fcc phase.

Our results for the equilibrium volume and bulk modulus are shown in Table 1 together with results from all-electron FP-LMTO calculations [5] and experiment [6,7]. Our pseudopotential calculation agree with the all-electron calculations done in the same approximation for exchange-correlation.

In Fig. 3, we show the equations of state for Ce for both pseudopotentials and compare them with experimental data

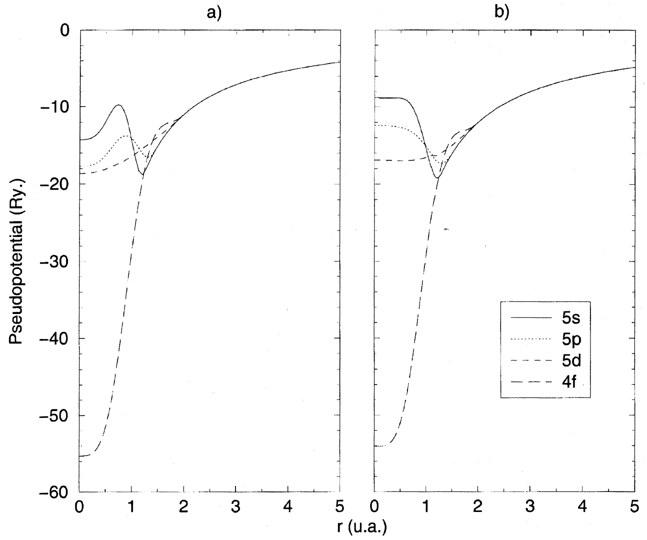

Fig. 2. Pseudopotential for every angular momentum in (a) LDA and in (b) GGA.

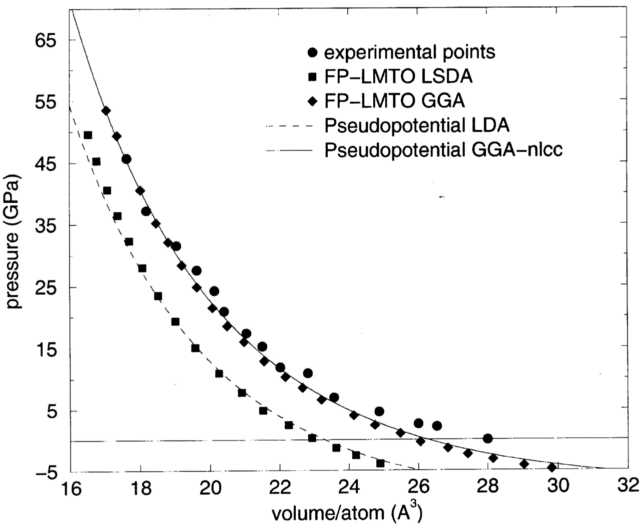

Fig. 3. Cerium 0 K equation of state (FP-LMTO calculations from Ref. [5] and experimental points from Refs [6,7]).

and all-electron calculations. The improvement when GGA replaces LDA is clear and the agreement of GGA calculation with experiment is fair.

4. High pressure phases

For a further comparison with all electron data, we have also made a static study of some previously proposed high pressure phases (Fig. 4):

- α'
- α''(II)
- bct

We find that α (fcc) is the most stable phase at ambient pressure and α''(II) is more stable than α'. In LDA or in GGA, α' is always much higher in energy. The GGA calculations improve the equilibrium volume of the α phase but the relative stabilities do not change significantly. The fcc–bct structural transition is obtained at a volume of 20.6 Å^3 which corresponds to a transition pressure of 8.4 GPa in LDA and at a volume of 21.6 Å^3 and a pressure of 12.9 GPa. This is in agreement with the experimental transition pressures reported to occur between 10 and 13 GPa and the calculations of Ravindran et al. [8] who found a LDA transition pressure of 11.5 GPa and a GGA transition pressure of 14.5 GPa. We also note that the energy difference between bct and α''(II) is very small (less than 1 mRy).

5. Conclusion

We have shown that it is possible to construct a pseudopotential for an element with f electrons such as cerium.

We are exploring the phase diagram of these elements with ab initio molecular dynamics and hope to acquire a better knowledge of the role played by f electrons.

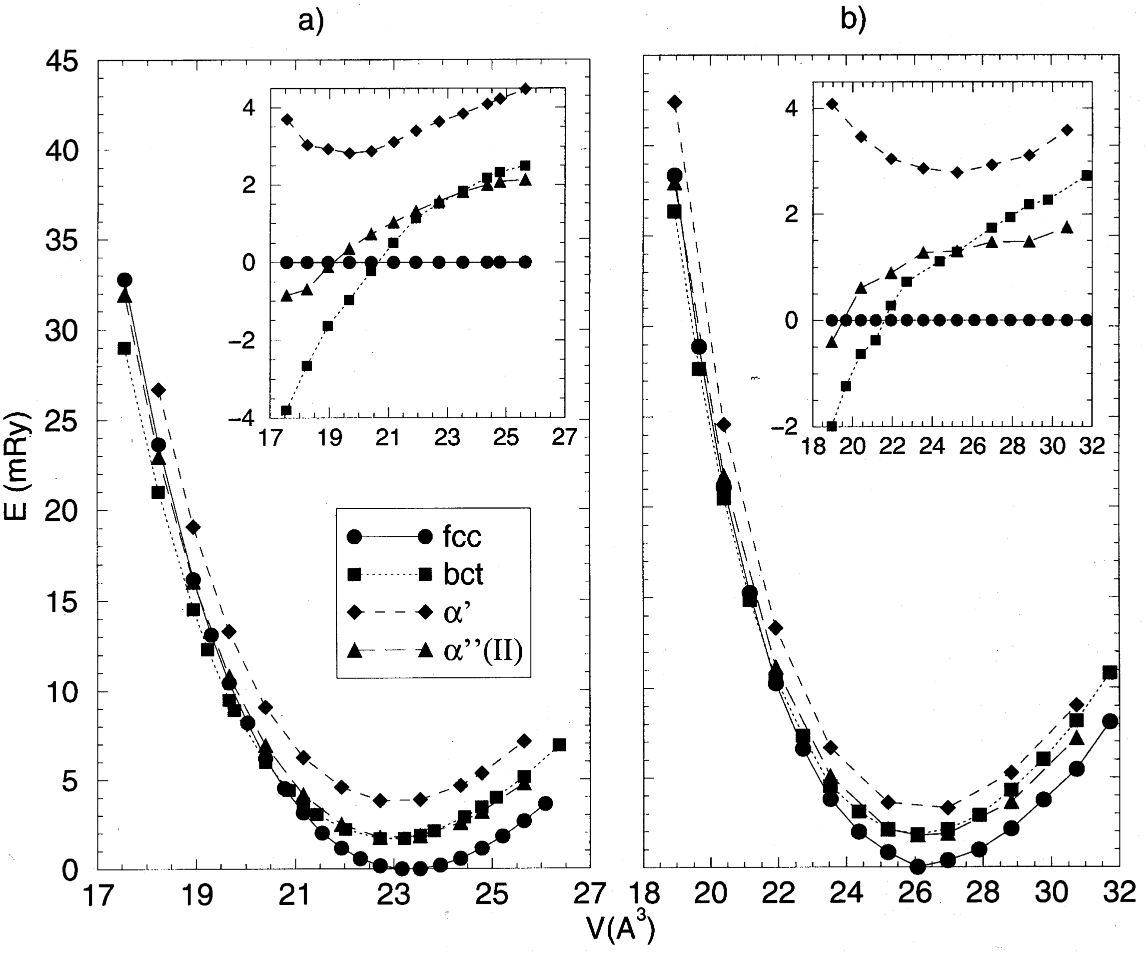

Fig. 4. The energy–volume curves in the α (fcc), α' (α-U), α''(II) (*C2/m*) and bct phases in (a) LDA and (b) GGA-nlcc. In inset are the energy–volume curves for the high-pressure phases of Ce relative to the α(fcc) phase.

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