The role of pressure in elastic properties of cerium

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Abstract. Cerium 4f electrons are peculiar in being spatially localized with a radial extent much smaller than that of 5s and 5p semicore states, yet having an energy in the region of valence 6s and 5f electrons. Two phases, α and γ, of cerium are under debate in terms of different properties like elastic properties or phase transition properties. The mechanical and elastic properties of cerium have generated substantial interest over the years both experimentally and theoretically. Theoretical studies, concerned with the lattice dynamics, which may be of use, as it is expected from the electron-phonon interaction, and plays a significant role during the γ → α transition, are very limited.

The aim of the present work is to study the behavior of lattice dynamics and elastic constants under increasing pressure using first-principles methods within linear response approach for the face-centered cubic (fcc) γ-cerium and shed some light on the interrelationship among the elasticity and phonons and understand the role of phonons in the phase transition. Our calculations reproduce zero pressure lattice dynamical and elastic properties of cerium with a very good precision.

1. Introduction
The story about the one of the most interesting elemental crystals, cerium, and its isostructural phase transition from its γ to its α phase around 0.8 GPa, after several decades, finally closes in. Up to date, two mechanism are commonly used to describe the electronic nature of this phase transition: the Mott transition model and the Kondo-Volume-Collapse (see reference [1] and references therein for a more detailed description).

The question about the role of the lattice dynamics in this phase transition has been posed already in late 70’s by Stassis et al. [2]. Based on their inelastic neutron scattering experiments, they have found that the phonon spectrum of γ-Ce is softer than it should be, when compared to the spectrum of thorium using the Lindemann homology rule [3]. These softening features were more pronounced in the phonon modes which are more sensitive to the influence of pressure in the elastic limit. More specifically, these are the modes which, in the elastic limit, involve the elastic constants $c_{11}$ and $c_{12}$, which in turn, determine the bulk modulus. And, not surprisingly, the bulk modulus in γ-Ce exhibits a dramatic decrease with increasing pressure [4,1]. On the ground of these results and the pressure dependence of the thermal displacements, measured by Jeong et al. [5], one can conclude that lattice dynamics and electron-phonon coupling play an important role in the explanation of the $\gamma \rightarrow \alpha$ phase transition and elastic instability in the elemental crystal of Ce [6].

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A few theoretical studies have already been employed in order to illuminate the role of lattice dynamics. Huang and Chen [7] have calculated the phonon dispersion curves in the γ-Ce, but only at zero pressure. Still, they managed to reproduce, using the Haman scheme norm conserving pseudopotential method, the soft branches in the phonon dispersion curves. A very recent combined study by Krisch et al. [8] measured, using inelastic X-ray scattering, and calculated, using the \textit{ab initio} projector augmented wave approach, the phonon dispersions at various pressures in both \textit{γ} and \textit{α} phases of Ce. This way, they were, by comparison, able to note the significant changes in phonon dispersions through the phase transition, confirming the important role which lattice dynamics and electron-phonon interaction play in this case. This facts were the motivation for our work: to study in more detail the lattice dynamics and elastic properties across the \textit{γ} → \textit{α} phase transition in Ce. A detailed analyses of the electron-phonon interaction is currently in progress.

In a cubic lattice the bulk modulus depends on the shear modulus and the elastic constant \(c_{11}\). Since it is known that the shear modulus is relatively insensitive to the applied hydrostatic pressure [4], the softening of the bulk modulus should be a consequence of the softening of \(c_{11}\), which is connected with the longitudinal phonon modes. We have, thus, tried to calculate the elastic constants, in order to confirm that there indeed exists the softening of the \(c_{11}\) constant. Longitudinal and shear moduli have been precisely measured by ultrasonic experiments by Decremps et al. [1], showing an anisotropic behavior of \(γ\)-Ce with respect to the propagation of elastic waves. This property was already predicted by Stassis et al. on the basis of Born-von Karman force constant model [2]. Furthermore, ultrasonic measurements show the softening of the longitudinal modulus with increasing pressure, while the shear modulus is almost constant in the whole stability interval of the \textit{γ} phase of Ce crystal. All these elastic properties should be reproduced by our \textit{ab initio} calculations.

2. Methods
In our study, we used standard \textit{ab initio} methods based on DFT [9] and DFPT [10] as implemented in the ABINIT [11] code. We used pseudopotentials to substitute the all-electron potentials, plane waves to expand the wave functions and Monchhorst-Pack meshes [12] of k-points to represent the integrations over the reciprocal space. Of the available pseudopotential schemes, we used Troullier-Martins LDA [13] ones (4 valence electrons) for the elastic properties of Ce and Hartwigsen-Goedecker-Hutter LDA [14] ones (12 valence electrons) for the lattice dynamics. Each studied property was converged with respect to the number of the plane waves and k-points in the Brillouin zone: elastic constants under 1 GPa and phonon frequencies under 1 cm\(^{-1}\). Above convergences were reached using the plane wave energy cut-offs of 60 and 80 Ha for the elastic constants and phonon frequencies, respectively, and using the \(8×8×8\) and \(6×6×6\) k-point meshes for the elastic constants and phonon frequencies, respectively. Marzari’s “cold smearing” scheme was used for the occupation of electronic level with the smearing energy of 0.005 Ha. Elastic constants and phonon dispersions were calculated using the standard response function methods, as described in Refs. [15] and [10], respectively. Our equilibrium lattice constant of \(γ\)-Ce is 9.99 Bohr, which is in good agreement with experimental [2] and previous theoretical [7] results of 9.75 Bohr and 9.94 Bohr, respectively.

3. Results
3.1 Lattice dynamics
Since the elastic instability in the \textit{γ} phase of Ce is connected with the soft phonon branches, phonon dispersion curves should show lowered frequencies for the longitudinal modes and transversal modes at L and W points of the Brillouin zone. Figure 1, which represents the calculated full phonon dispersions of \(γ\)-Ce at zero pressure, shows clearly that it is so, although the calculated phonon branch at L point is not as soft as in experiments. As these phonon modes are connected with the \(c_{11}\) and \(c_{12}\) elastic constants in the elastic limit, we should expect to find the softening behavior of these elastic constants with increasing pressure (see subsection 3.2). No significant changes in the phonon dispersions of \textit{γ} phase can be seen at the pressure of 0.8 GPa. More specifically, there are no soft modes
which go to zero frequency at the phase transition, which, in turn, also indicates that it is the first order phase transition.

![Figure 1. Phonon dispersion curves of $\gamma$-Ce at 0 Gpa. Circles represent the experimental data obtained by Stassis et al. (reference [2]).](image)

3.2 Elastic properties

The influence of the hydrostatic pressure on the calculated elastic constants is shown in figure 2(a). It can be clearly seen that with used pseudopotential method, one cannot reproduce the softening of the $c_{11}$ constant as expected from experiments [2,5]. The zero pressure values of the elastic constants, on the other hand, are in an excellent agreement with the experimental values, which was not obtained in any previous theoretical study, up to our knowledge (see table 1).

![Figure 2. Pressure dependence of (a) elastic constants: $c_{11}$ (○), $c_{12}$ (◊) and $c_{44}$ (Δ). There is no expected softening of the $c_{11}$. (b) bulk modulus; (c) longitudinal modulus; (d) shear modulus. In figures (b), (c) and (d) calculated values are presented by □ and experimental [1] by ○.](image)

Consequently, the calculated bulk modulus shows no softening with increasing pressure (Fig. 2(b)). Since longitudinal modulus depends on the bulk modulus, it should also show the softening trend with increasing pressure [1]. Our pseudopotential approach fails here, too (figure 2(c)). Oppositely, shear
modulus is structured in such a way that the softening behavior of the \( c_{11} \) constant and the bulk modulus is not apparent. It is almost insensitive to the pressure. Here our calculations correctly describe its dependence on pressure (figure 2(d)), because only the difference between the trends is important and not the trends themselves. Our calculations correctly predict the anisotropy in the propagation of the elastic waves, although not in the same measure as experiments.

| Table 1. Elastic constants \( c_{ij} \), bulk B, longitudinal \( \rho V_{2L}^2 \) and shear \( \rho V_{2S}^2 \) modulus at zero pressure. |
|---------------------------------|---------------------------------|---------------------------------|-----------------|-----------------|-----------------|
| \( c_{11} \) (GPa)           | \( c_{12} \) (GPa)             | \( c_{44} \) (GPa)             | B (GPa)         | \( \rho V_{2L}^2 \) (GPa) | \( \rho V_{2S}^2 \) (GPa) |
| Present                        | 32.5                           | 17.2                           | 14.3            | 22.3            | 37.8            | 11.7           |
| Exp. [2]                       | 24.1                           | 10.2                           | 19.4            | 14.8            |                 |                |
| Exp. [1]                       |                                |                                | 20.6            | 35.6            | 11.2            |                |
| Exp. [16]                      |                                |                                | 21.0            |                 |                 |                |
| Theor. [7]                     | 37.9                           | 26.4                           | 20.9            | 30.2            | 5.8             |                |

It is altogether still not clear why the calculated \( c_{11} \), B and \( \rho V_{2L}^2 \) agree so well at zero pressure, while at the same time do not follow the correct behavior with increasing pressure. It is the authors’ presumption that the possible reason lies in the pseudopotential used. It has been checked, that the pressure does not increase the energy of the outer core electrons, which would make them more valence-like electrons, and which, thus, would had to be included into the valence bands.

4. Conclusions

Pseudopotential \textit{ab initio} calculations of high pressure properties of \( \gamma \)-Ce should have had a part of elucidating the roles of lattice dynamics and elasticity in the phase transition occurring at about 0.8 GPa. Although our calculations correctly reproduced the softer phonon branches in the phonon dispersions and elastic constants (and consequently the bulk modulus) at zero pressure, they failed to reproduce the behavior of the elastic properties, as found in the experiments, at higher pressures. The underlying reason of this is still unknown to the authors. One of the possible reasons is the use of inadequate pseudopotential during the study of the elastic constants.

Nevertheless, the found characteristics of the lattice dynamical and elastic properties indicate that the electron-phonon interaction plays a significant role in the studied phase transition. The calculations of the pressure dependence of this interaction are currently under way.

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