

## RESEARCH ARTICLE

# Effect of pressure on the valency of cerium in cerium monochalcogenides and cerium monopnictides

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**Abstract:** Application of pressure on a material changes its properties due to the modification of the electronic states of the constituent atoms. Various effects of pressure on the properties of solid material have been identified, and valency change of an element in a compound is one of the effects of pressure. This study was aimed at finding the valency change as a function of pressure of some compounds. The valency changes of cerium in cerium monochalcogenides CeX (X = O and S) and cerium monopnictides CeX (X = P and As) as functions of pressure have been calculated utilising the reported data. For calculating the valency change of Ce, the reported experimental pressure-volume relationships of CeO, CeS, CeP and CeAs have been reproduced using the Birch equation of state. The corresponding pressure-volume relationships of these compounds for stable trivalent cerium have also been calculated using the same Birch equation. The change in valency is calculated by a technique, which considers the difference between the calculated and experimental lattice parameters at each pressure value of the concerned compound. Clear effect of pressure on the cerium valency has been obtained for each compound from the present calculation.

**Keywords:** Birch equation of state, cerium monochalcogenides, cerium monopnictides, valency change.

## INTRODUCTION

The application of hydrostatic pressure on a solid material has a direct effect on the extra-nuclear electronic states of the constituent atoms in the material. Various effects of pressure such as structural phase transition (Léger, 1993), unusual crystal lattice behaviour (Iwasa *et al.*, 1999; Hannan *et al.*, 2000), unusual electrical resistivity

(Okayama *et al.*, 1992) and the appearance of complicated magnetic phase (Hannan *et al.*, 2002; Osakabe *et al.*, 2002) have been reported.

In this study, we have focused on cerium monochalcogenides CeX (X = O, S, Se and Te) and cerium monopnictides CeX (X = P, As, Sb and Bi). Léger *et al.* (1987) have investigated the pressure-volume relationship and the crystallographic phase changes of these compounds by X-ray diffraction in diamond anvil cells at room temperature (Vedel *et al.*, 1986; Léger *et al.*, 1987; Léger, 1993). These compounds exhibit an unusual pressure-volume relationship in the wide pressure range from 0 to about 25 GPa. The pressure-volume relationships of CeX (X = O, S, Se and Te) have been reported by Léger (1993). The pressure-volume relationships of some selected compounds from both cerium monochalcogenides and monopnictides have been investigated using the Birch equation of state (Birch, 1947; Mito *et al.*, 2007) to calculate the valency change as a function of pressure (details are presented later in the text). In cerium monochalcogenides CeX (X = O, S, Se and Te), the volume of CeO decreases very rapidly with pressure up to 3 GPa, above which the rate of change exhibits a normal trend (Léger, 1993). The crystal structure of this compound up to 25 GPa remains the same (NaCl-type). The volume of CeS decreases smoothly up to a pressure of 27 GPa exhibiting the NaCl-type structure. CeSe also shows the NaCl-type phase up to 25 GPa but above 20 GPa a phase of CsCl-type structure appears with a volume change of 9 %. At 8 GPa, CeTe changes the structural phase from NaCl-type to CsCl-type (Léger, 1993).

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There are also reported works on the relative volume of cerium monpnictides CeX (X = P, As, Sb and Bi) as a function of pressure (Léger, 1993). CeP shows isostructural discontinuous transition at around 10 GPa, and above 20 GPa it exhibits a structural transition from NaCl-type to a CsCl-type structure (Vedel *et al.*, 1987; Léger, 1993). CeAs shows a sharp structural transition from NaCl-type to CsCl-type at about 18 GPa. CeSb exhibits a sharp structural transition from NaCl-type to body central tetragonal structure at 11 GPa. At 13 GPa, CeBi exhibits structural transition from NaCl-type to CsCl-type structure.

Crystal-lattice behaviour of CeSb has been extensively studied earlier (Hannan *et al.*, 2000) under various high pressures using a diamond-anvil cell (DAC). They observed an unusual shrinking of the crystal lattice below a certain critical temperature  $T_L$  in the paramagnetic region, which nearly corresponds to the resistivity anomaly temperature  $T_R$  as reported earlier (Okayama *et al.*, 1992).

Iwasa *et al.* (1999) measured the temperature dependence of the lattice constants of CeP and CeAs by X-ray diffraction. The lattice constants of CeP and CeAs show clear minima at 120 K and 90 K, respectively. These temperatures are close to the crystal field splitting energies of 160 K and 150 K of CeP and CeAs, respectively. Unusual temperature dependencies of the lattice constants in CeP and CeAs have been explained, assuming that the interatomic bond length between cerium ions of  $\Gamma_8$  state and pnictogens is shorter than that of  $\Gamma_7$  cerium ions (Iwasa *et al.*, 1999).

CeSb shows a complicated magnetic pressure-temperature phase diagram (Chattopadhyay *et al.*, 1994; Osakabe *et al.*, 2002). The magnetic pressure-temperature phase diagram of CeP is more complicated than that of CeSb (Hannan *et al.*, 2002). The resistivity of CeP exhibits a surprisingly pressure sensitive behaviour (Okayama *et al.*, 1992). At ambient pressure, the sharp pointed peak at about 10 K is due to the antiferromagnetic phase transition. The resistivity passes through a minimum at about 23 K, a broad maximum at around 80 K and then it decreases with increasing temperature. This is a typical magnetic dense Kondo behaviour. At ambient pressure, there is a sharp pointed peak for CeAs corresponding to the Néel temperature 7.7 K (Okayama *et al.*, 1992). A broad maximum is also observed at around 60 K with a Kondo type behaviour in the higher temperature region. Enormous enhancement of the electrical resistivity of CeSb is seen near 30 K at pressures above 3 GPa. The peak

value of resistivity increases with increasing pressure, and at 7 GPa it reaches a value nearly 23 times as large as that at the ambient pressure (Okayama *et al.*, 1992). CeBi exhibits a sharp pointed peak near 30 K associated with the magnetic phase. At pressures higher than 3 GPa, however, the sharp pointed peak changes into a hump and shows a tendency to disappear gradually with increasing pressure (Okayama *et al.*, 1992). All of the features mentioned above have been driven by the application of various hydrostatic pressures on the compounds.

In this study the valency change of Ce in some compounds of cerium monochalcogenides CeX (X = O, S, Se and Te) and cerium monpnictides CeX (X = P, As, Sb and Bi) with the change of pressure has been calculated. In doing this, the reported (Léger, 1993) experimental pressure-volume relationships of the compounds have been reproduced by using the Birch equation of state. The corresponding pressure-volume relationships of these compounds for stable trivalent cerium have also been calculated using the same Birch equation. The clear effect of pressure on the cerium valency has been realised for each compound from the present calculation.

## CALCULATION OF VALENCY CHANGE DUE TO PRESSURE

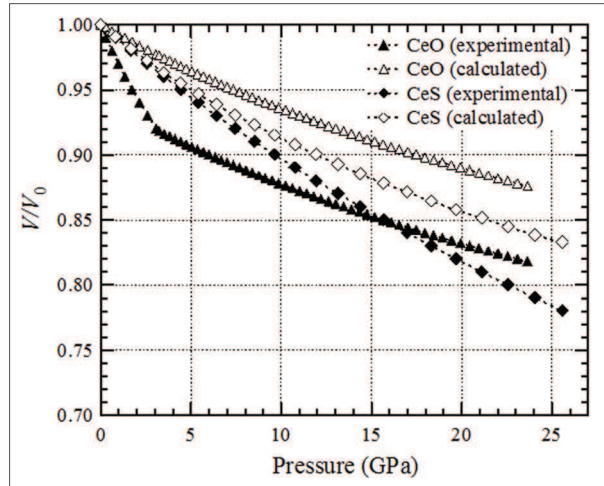
### Reproduction of experimental relative volume

The experimental pressure-volume relationship, as reported by Léger (1993), can be fitted using the Birch equation of state (Birch, 1947; Mito *et al.*, 2007) as written below:

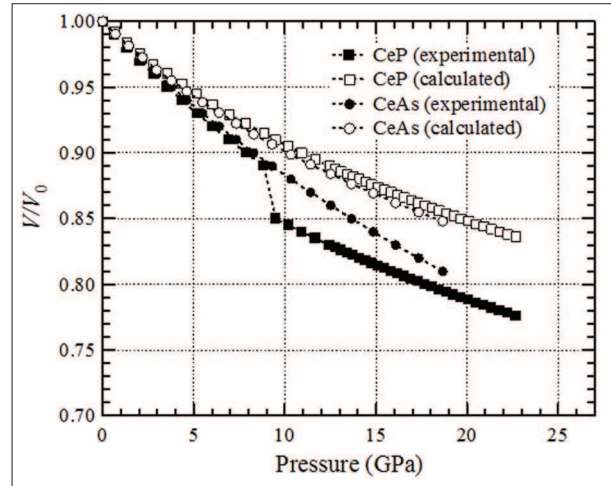
$$P(y) = \frac{3}{2} B_0 (y^{-7/3} - y^{-5/3}) \left[ 1 - \frac{3}{4} (B^* - 4) (1 - y^{-2/3}) \right], \quad \dots(1)$$

where  $P$  is the pressure,  $y = V/V_0$  is the relative volume,  $B_0$  is the Bulk modulus and  $B^*$  is the pressure derivative of the Bulk modulus. The values of  $B_0$  and  $B^*$  come as fitting parameters. So if the fitting parameters are known, the experimental trend (data) of the relative volume as a function of pressure can be reproduced.

The reproduced experimental relative volumes for CeO and CeS are shown in Figure 1 by solid triangles and solid diamonds, respectively. The values of the parameters  $B_0$  and  $B^*$  used for CeO are 30 GPa and 5, and for CeS are 82 GPa and 2.25, respectively (Léger, 1993). The calculation for the reproduction of the experimental data has been done by IGOR Pro software (Version 4.0).



**Figure 1:** Reproduced experimental pressure-volume curves of CeO and CeS (solid triangles and solid diamonds) and the corresponding calculated curves (open triangles and open diamonds) for stable trivalent cerium in the compounds.



**Figure 2:** Reproduced experimental pressure-volume curves of CeP and CeAs (solid squares and solid circles) and the corresponding calculated curves (open squares and open circles) for stable trivalent cerium in the compounds.

The reproduced experimental relative volumes for CeP and CeAs using equation (1) are shown in Figure 2 by solid squares and solid circles, respectively. The values of the parameters  $B_0$  and  $B^*$  used for CeP are 64 GPa and 3, and for CeAs are 69 GPa and 2.6, respectively (Léger, 1993).

#### Theoretical relative volume for stable trivalent cerium

Two compounds, CeO and CeS, from the category of cerium monochalcogenides have been selected. For trivalent stable cerium in CeO the parameters  $B_0$  and  $B^*$  are 125 GPa and 5.4, and in CeS they are 85 GPa and 5.4, respectively (Léger, 1993). Using these parameters in equation (1), the relative volumes of CeO and CeS as a function of pressure have been calculated. The calculated relative volumes are presented in Figure 1 by open triangles and open diamonds.

For trivalent stable cerium in CeP the parameters  $B_0$  and  $B^*$  are 78 GPa and 5.4, and in CeAs they are 72.44 GPa and 5.4, respectively (Léger, 1993). The relative volumes of CeP and CeAs as a function of pressure have been calculated using equation (1). The calculated relative volumes are presented in Figure 2 by open squares and open circles.

#### Calculation of valency change

It is assumed that the valency of cerium in cerium monochalcogenide and cerium monopnictide compounds varies linearly with the lattice parameter,  $a$  (Léger, 1993). The increase of the valency,  $x$  above 3+ can be calculated by the following relation.

$$x = \frac{\{a_{\text{calc}}^{3+}(P) - a_{\text{exp}}^{3+x}(P)\}}{\{a_{\text{calc}}^{3+}(P_0) - a_{\text{calc}}^{4+}(P_0)\}}, \quad \dots(2)$$

where  $a_{\text{calc}}^{3+}(P)$  is the calculated lattice constant at pressure  $P$  with cerium valency 3+,  $a_{\text{exp}}^{3+x}(P)$  is the experimentally observed lattice constant at pressure  $P$  with cerium valency 3+x,  $a_{\text{calc}}^{3+}(P_0)$  is the calculated lattice constant at ambient pressure with cerium valency 3+ and  $a_{\text{calc}}^{4+}(P_0)$  is the calculated lattice constant at ambient pressure with cerium valency 4+.

In the calculation, the cerium coordination must be taken into account and the following cerium radii with a coordination of six, for *fcc* structure, are used:  $r_{\text{Ce}}^{3+}(P_0) = 1.034 \text{ \AA}$ ,  $r_{\text{Ce}}^{4+}(P_0) = 0.85 \text{ \AA}$  (Léger, 1993).

So, for NaCl-type cubic lattice we can write

$$a_{\text{calc}}^{3+}(P_0) - a_{\text{calc}}^{4+}(P_0) = 2 \{r_{\text{Ce}}^{3+}(P_0) - r_{\text{Ce}}^{4+}(P_0)\}$$

$$= 2(1.034 - 0.85) \text{ \AA} = 0.368 \text{ \AA}$$

So, equation (2) becomes

$$x = \frac{\{a_{\text{calc}}^{3+}(P) - a_{\text{exp}}^{3+x}(P)\}}{0.368} \quad \dots(3)$$

$$\text{or } x = \frac{a_{\text{calc}}^{3+}(P_0) \left\{ \frac{a_{\text{calc}}^{3+}(P)}{a_{\text{calc}}^{3+}(P_0)} - \frac{a_{\text{exp}}^{3+x}(P)}{a_{\text{calc}}^{3+}(P_0)} \right\}}{0.368}, \quad \dots(4)$$

where  $a_{\text{calc}}^{3+}(P_0)$  is the lattice parameter of the concerned *fcc* lattice at ambient pressure.

$$\text{or } x = \frac{a_{\text{calc}}^{3+}(P_0) \left[ \left\{ \frac{V_{\text{calc}}(P)}{V(P_0)} \right\}^{1/3} - \left\{ \frac{V_{\text{exp}}(P)}{V(P_0)} \right\}^{1/3} \right]}{0.368}, \quad \dots(5)$$

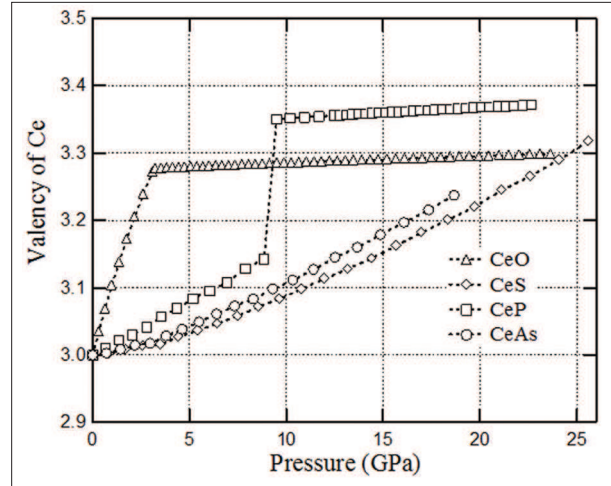
where  $V_{\text{calc}}(P) = \{a_{\text{calc}}^{3+}(P)\}^3$  is the calculated volume of the unit cell at pressure  $P$  with cerium valency  $3+$ ,  $V_{\text{exp}}(P) = \{a_{\text{exp}}^{3+x}(P)\}^3$  is the experimentally observed volume of the unit cell at pressure  $P$  with cerium valency  $3+x$  and  $V(P_0) = \{a_{\text{calc}}^{3+}(P_0)\}^3$  is the calculated volume of the unit cell at ambient pressure with cerium valance  $3+$ .

The valency of Ce at pressure  $P$  is calculated from the following relation:

$$\text{Valency} = 3 + \frac{a_{\text{calc}}^{3+}(P_0) \left[ \left\{ \frac{V_{\text{calc}}(P)}{V(P_0)} \right\}^{1/3} - \left\{ \frac{V_{\text{exp}}(P)}{V(P_0)} \right\}^{1/3} \right]}{0.368} \quad \dots(6)$$

## RESULTS AND DISCUSSION

The effect of pressure on the valency change of some compounds is presented in this article. In Figures 1 and 2, there is a big difference between the experimental and calculated pressure-volume curves. This difference is due



**Figure 3:** Valency of Ce in CeO, CeS, CeP and CeAs.

to the enhancement of valency above  $3+$  with pressure, as can be seen from equation (6). Figure 3 shows the valency of Ce calculated using equation (6), in CeO, CeS, CeP and CeAs as a function of pressure. For CeO, the valency of Ce rapidly increases with the pressure, and at about 3 GPa the valency is  $3.27+$ . Above 3 GPa the valency is almost pressure independent up to 23.5 GPa. The valency of Ce in CeS increases non-linearly with the pressure, and at about 25.5 GPa the valency is  $3.31+$ . For CeP, the valency of Ce increases almost linearly with the increase of pressure, and at 9 GPa the valency becomes  $3.14+$ . Above this pressure, the valency suddenly increases to  $3.35+$  at about 9.5 GPa due to isostructural valence-phase transition, and then the valency is almost pressure independent up to 22.5 GPa. In the case of CeAs, a continuous non-linear increase of valency with the increase of pressure is found, and at 18.5 GPa the Ce valency is  $3.23+$ . It is seen that in any group of compounds, the valency change does not depend on the group, but it is dependent on the particular sample of the group.

## CONCLUSION

In this study a method adopting the Birch equation of state has been introduced for the calculation of valency change of cerium in CeO, CeS, CeP and CeAs. Our calculation shows a clear effect of pressure on the valency change, and the maximum valency change of  $0.37+$  is found for the change of pressure of 22.6 GPa for CeP. The valency change of cerium with pressure in any compound under a certain group is found to be independent of the group. That means, the environment around the Ce in a compound is solely responsible for the change of the valency of Ce in the compound.

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