

Pressure Induced Structural Phase Transition and Valence Change

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Abstract 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. In this work, we have studied the effect of pressure on the various properties of the material, such as structural behavior, crystal lattice behavior, magnetic behaviors of magnetic material and transport behavior like electrical resistivity. We have calculated the Ce valency change in some compounds of cerium monochalcogenides CeX ($X=O, S, Se$ and Te) and cerium monpnictides CeX ($X=P, As, Sb$ and Bi). In doing this task, we have reproduced the reported experimental pressure-volume relationships of the compounds 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. Clear effect of pressure on the cerium valency has been realized for each compound from the present calculation.

Keywords Cerium monochalcogenides, Cerium monpnictide, Birch equation of state, Valency change

1. Introduction

Hydrostatic pressure on a solid material has direct effect material changes its properties due to the modification of the electronic states of the constituent atoms of the material. Various effects, such as structural phase transition, unusual crystal lattice behavior, unusual resistivity, appearance of complicated magnetic phase etc. of pressure have been reported earlier [1-4, 9-10, 15-24]. Some of these effects are highlighted blow. Two members of cerium monochalcogenides CeX ($X=O, S, Se$ and Te), CeSe and CeTe change structure from NaCl-type to CsCl-type at about 20 GPa and 8 GPa, respectively with the increase of pressure [1]. There are also reported works on relative volume of cerium monpnictides CeX ($X=P, As, Sb$ and Bi) as a function of pressure [1]. CeP shows isostructural discontinuous transition at around 10 GPa, and above 20 GPa it exhibits a structural transition from NaCl-type to CsCl-type structure [1, 2]. 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.

The structural phase transition and unusual crystal lattice behavior are analyzed in the last few years [25-32]. There are

reported relative volume of uranium monochalcogenides UX ($X= S, Se$ and Te) as a function of pressure [1]. The volume of US decreases gradually up to 15 GPa. The data above this pressure scatter suggesting a transition, probably to an orthorhombic structure [3]. USe does not show any structural transition up to 20 GPa. UTe exhibits a NaCl to CsCl-type transition at 11 GPa with the increase of pressure. In uranium monpnictides, UAs and USb exhibit structural transitions from NaCl- to CsCl-type at 17 GPa and 9 GPa, respectively [1].

If we apply high pressure on a material, its properties change due to the modification of the electronic states of the constituent atoms of the material. The structure of the material may be changed due to the application of the high pressure. Unusual crystal lattice behavior with temperature is also observed as a consequence of the application of pressure. The magnetic behaviors of magnetic material may be changed due to pressure. Transport behaviors like electrical resistivity, specific heat may also change due the effect of pressure

2. Calculation of Valance Change Due to Pressure

2.1. Relative Volume of Monochalcogenides as a Function of Pressure

Leger *et al.* investigated the pressure-volume relationship and the crystallographic phase changes of cerium monochalcogenides and monpnictides by X-ray diffraction in diamond anvil cells at room temperature [1, 11, 12].

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Fig.1 shows the experimental change of relative volume of cerium monochalcogenides as a function of pressure [1]. The volume of CeO decreases very rapidly with pressure up to 3 GPa, above which the rate of change exhibits normal trend. The crystal structure of this compound up to 25 GPa remains the same (NaCl-type). The volume of CeS decreases smoothly up to the pressure of 27 GPa with 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 to CsCl-type.

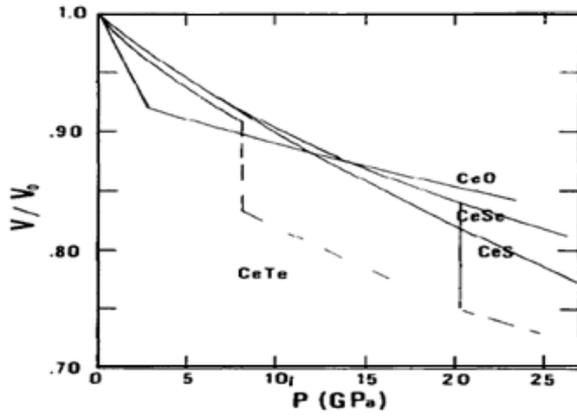


Figure 1. Experimental change of relative volume of cerium monochalcogenides with pressure (solid line: NaCl-type structure, dashed line: CsCl-type structure) [1]

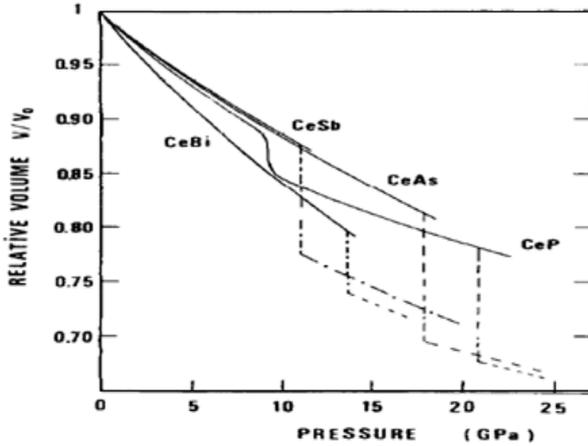


Figure 2. Experimental change of relative volume of cerium monopnictides with pressure (solid line: NaCl-type structure, dashed line: CsCl-type structure, dashed line with dot: body centered tetragonal structure) [1]

Figure 2 shows the experimental change of relative volume of cerium monopnictides as a function of pressure [1]. CeP shows isostructural discontinuous transition at around 10 GPa, and above 20 GPa it exhibits a structural transition from NaCl-type to CsCl-type structure [1, 2]. The unit-cell volume of CeAs decreases continuously with pressure upto 18 GPa and then a sharp structural transition from NaCl-type to CsCl-type occurs. CeSb shows almost

the same pressure dependence of unit-cell volume as the CeAs upto 11 GPa, then it shows a sharp structural transition from NaCl-type to body central tetragonal structure. The slope of the pressure-dependent unit-cell volume curve of CeBi is higher than that of CeAs. At 13 GPa, CeBi exhibits structural transition from NaCl-type to CsCl-type structure.

2.2. Reproduction of Experimental Relative Volume

The experimental pressure-volume relationship, as shown in Figs. 1 and 2, can be fitted using the Birch equation [13, 14] as written below:

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

where $y=V/V_0$ 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 we know the fitting parameters, we can reproduce the experimental trend (data) of the relative volume as a function of pressure.

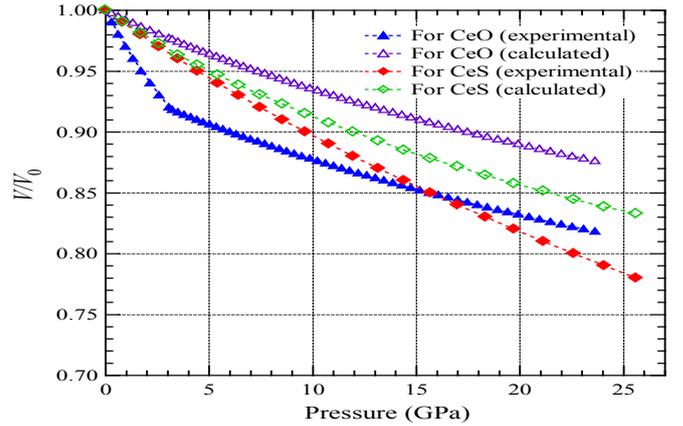


Figure 3. Reproduced experimental pressure-volume curves of CeO and CeS (solid triangles and solid diamonds) and the corresponding calculated curves (open triangles and open diamonds) for stable trivalent cerium in the compounds

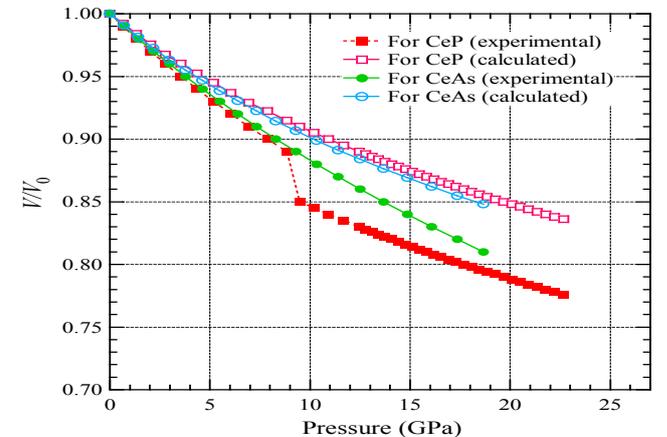


Figure 4. Reproduced experimental pressure-volume curves of CeP and CeAs (solid squares and solid circles) and the corresponding calculated curves (open squares and open circles) for stable trivalent cerium in the compounds

The reproduced experimental relative volumes for CeO and CeS are shown in Fig. 3 by solid triangles and solid diamonds, respectively. The values of the parameters B_0 and B^* used for CeO are 30 GPa and 5, respectively and for CeS are 82 GPa and 2.25, respectively [1].

The reproduced experimental relative volumes for CeP and CeAs using Eq. (1) are shown in Fig.4 by solid squares and solid circles, respectively. The values of the parameters B_0 and B^* used for CeP are 64 GPa and 3, respectively and for CeAs are 69 GPa and 2.6, respectively [1].

2.3. Theoretical Relative Volume for Stable Trivalent Cerium

We have selected two compounds, CeO and CeS, from the category of cerium monochalcogenides. For trivalent stable cerium in CeO the parameters B_0 and B^* are 125 GPa and 5.4, respectively, and in CeS they are 85 GPa and 5.4, respectively [1]. Using these parameters, we have calculated (using Eq. (1)) the relative volumes of CeO and CeS as a function of pressure. The calculated relative volumes have been presented in Fig. 3 by open triangles and open diamonds.

For trivalent stable cerium in CeP the parameters B_0 and B^* are 78 GPa and 5.4, respectively, and in CeAs they are 72.44 GPa and 5.4, respectively [1]. The relative volumes of CeP and CeAs as a function of pressure have been calculated using Eq. (1). The calculated relative volumes have been presented in Fig. 4 by open squares and open circles.

2.4. Calculation of Valence Change

There is a linear variation of the cerium valency in the cerium monochalcogenide and cerium mononictide compounds with the lattice parameter, a [1]. The increase of the valency, x , can be calculated from the following relation [1].

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

where $a_{\text{calc}}^{3+}(P)$ is the calculated lattice constant at pressure P with cerium valance 3+, $a_{\text{exp}}^{3+x}(P)$ is the experimentally observed lattice constant at pressure P with cerium valance 3+x, $a_{\text{calc}}^{3+}(P_0)$ is the calculated lattice constant at ambient pressure with cerium valance 3+ and $a_{\text{calc}}^{4+}(P_0)$ is the calculated lattice constant at ambient pressure with cerium valance 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: $r_{\text{Ce}}^{3+}(P_0) = 1.034 \text{ \AA}$, $r_{\text{Ce}}^{4+}(P_0) = 0.85 \text{ \AA}$ [1].

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, Eq. (2) becomes

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

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

$$x = \frac{\left[\frac{a_{\text{calc}}^{3+}(P)}{a_{\text{calc}}^{3+}(P_0)} - \frac{a_{\text{exp}}^{3+x}(P)}{a_{\text{calc}}^{3+}(P_0)} \right]}{0.368},$$

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

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

$$x = \frac{\left[\left\{ \frac{V_{\text{calc}}(P)}{V(P_0)} \right\}^{1/3} - \left\{ \frac{V_{\text{exp}}(P)}{V(P_0)} \right\}^{1/3} \right]}{0.368}$$

where $V_{\text{calc}}(P) = \{a_{\text{calc}}^{3+}(P)\}^3$ is the calculated volume of the unit cell at pressure P with cerium valance 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 valance 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:

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

3. Results & Discussion

In the present work we have studied the effect of pressure on the valency change of some compounds. Fig.5 shows the calculated valency of Ce, as calculated using Eq. (6), in CeO, CeS, CeP and CeAs as a function of pressure. For CeO, the valency of Ce rapidly increases with the increase of 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 increase of 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 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+.

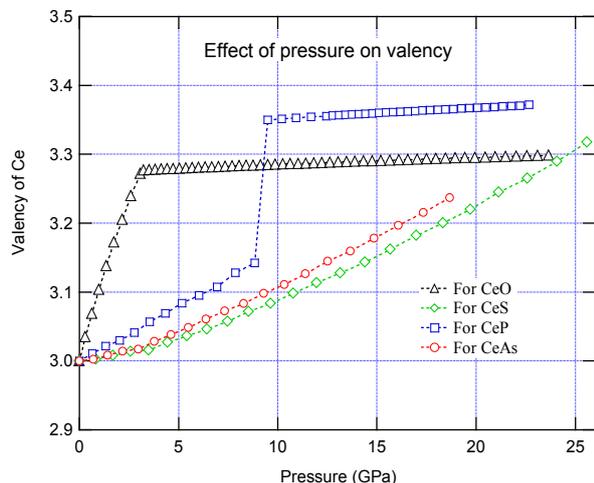


Figure 5. Valency of Ce in CeO, CeS, CeP and CeAs

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. That is, the environment around the Ce in a compound is solely responsible to drive how the valency of Ce in the compound will change.

4. Conclusions

The pressure-dependent volume behaviors of cerium monochalcogenides and monpnictides have been studied in details. A method for the calculation of valency change of cerium in these compounds adopting the Birch equation of state has been introduced. Our calculation shows clear effect of pressure on the valency change. We interpreted that the environment around the Ce in a compound is solely responsible to drive how the valency of Ce in the compound will change.

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