Pressure-induced phase transition and electronic structure of curium pnictides: *Ab initio* calculations

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ABSTRACT

We report an *ab initio* calculation of pressure-induced structural phase transition and electronic properties of the NaCl-type Cm-based pnictides namely CmX (X = N, P, As, Sb and Bi). The total energy as a function of volume is obtained by means of self-consistent tight-binding linear muffin tin orbital (TB-LMTO) method by performing spin and non-spin polarized calculation. Magnetically the CmX compounds are stable in ferromagnetic (FM) state and their crystal structure is NaCl-type at ambient condition. From the present study, we predict a structural phase transition from ferromagnetic (FM) NaCl-type (B_1 phase) structure to ferromagnetic CsCl-type (B_2 phase) structure for curium pnictides in the pressure range of 51.0–10.0 GPa (CmN to CmBi). The pressure-induced transition is found to be first order. The band structure and density of states (DOS) are plotted in FM-B_1 phase and FM-B_2 phase. Apart from this the ground-state properties like magnetic moment, lattice parameter and bulk modulus are calculated and compared with the available theoretical and experimental results.

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1. Introduction

The actinide (An) monopnictides and monochalcogenides provide a series of chemically similar compounds in which crystal properties depend on the An–An separation and exhibit new phenomena due to iterant *f*-electron. Therefore, such properties, which are dependent on, or influenced by the degree of 5*f* orbital overlap or their interactions are expected to be quite sensitive as the outer shell electrons are much less spatially extended than the valence *s*, *p*, *d* orbitals. In addition to chemical bonding, solid-state properties such as magnetic ordering due to the coupling between actinide species are also known to be dependent on the degree of 5*f* overlap [1]. Most of the actinide monopnictides crystallize in NaCl-type (B_1) structure. The structural phase transition at high pressure in actinides pnictides (AnX, X = N, P, As, Sb) have been investigated in recent years with great interest. The majority of the actinides and lanthanides compounds exhibit non-integral valency at high pressure and display numerous allotropic structure and properties which can be, in general, interpreted in terms of valance fluctuations arising from instability of *f*-electrons [2–8]. A phenomena of interest in these compounds is the hybridization of the *f* electron which is an important parameter and leads to complex properties such as Kondo-like, magnetic anisotropy or intermediate valance

behavior and is responsible for their unusual properties [2,9,10]. Several monopnictides of Th, U, Np and Pu, which have the B_1-type crystal structure, have been investigated previously both experimentally [11–18] and theoretically [5,19–21]. The high-pressure phase transition pressures, hysteresis behavior during pressure release and nature of the compressibility, elastic and phonon properties of these compounds have also been reported.

Experimental studies on curium pnictides to measure lattice parameters have been carried out by Damien et al. [22] by using X-ray powder diffraction technique. The high-pressure behavior of curium monobismuthide (CmBi) has been reported up to 48 GPa by Gensini et al. [23], which reveals that CmBi crystallizes in the NaCl-type crystal structure at room temperature and undergoes a first-order phase transition from its NaCl-type (B_1) to CsCl-type (B_2) structure at 12.0 GPa with a volume collapse of 16%. They have also reported the bulk modulus (B_0) to be 54.0 GPa at ambient condition. Milman et al. [24], who carried out theoretical study on curium pnictides, have reported that these solids are ferromagnetic and weakly metallic. They have also reported theoretical study on CmBi based on density functional theory by using CASTEP code and found the structural phase transition pressure from B_1 to B_2 to be 14.2 GPa with relative volume collapse of 8.0%. Ground state electronic structure and properties of curium nitride (CmN) have been reported by Petit et al. [25] by using LMTO method within self-interaction corrected local spin-density approximation (SIC-LDA) and predicted B_0 to be 154.0 GPa. Structural phase transition and high-pressure behavior of CmBi have also been reported by Jha

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and Sanyal [26] by using three body interaction potential. They reported that CmBi undergoes a structural phase transition from B_1 to B_2 phase at pressure of 12.0 GPa. Recently, Rached et al. [27] have used FP-LMTO method to calculate structural and elastic properties of CmBi.

In the present paper, we have performed both spin- and non-spin polarized electronic band structure calculations using first principles tight-binding linear muffin tin orbital (TB-LMTO) method at ambient as well as at high pressure to understand the stability of magnetic and non-magnetic (NM) phases, structural and electronic properties of curium pnictides. We show that these solids crystallize in NaCl-type structure and stable in ferromagnetic phase. At high pressure they remain ferromagnetic but undergo first-order structural phase transition from B_1 to B_2 phase in the pressure range of 10.0–51.0 GPa. We further report the electronic band structure (BS) and density of states (DOS) in respective minority and majority spin channels.

The organization of the paper is as follows: Section 2 describes the method of calculation of electronic band structure and phase transition pressure. In Section 3 potentially interesting results with some predictions are discussed. The corresponding Sections 3.1 and 3.2 deal with the structural and electronic, magnetic properties of CmX at ambient and at high pressure, respectively. Finally in Section 4, we have recapitulated the results.

2. Method of calculations

The total energy, band structure and density of states for curium pnictides are calculated in non-magnetic (NM) and ferromag-netic (FM) states, similar to our earlier work [28–30] using TB-LMTO method [31,32] within the local-density approximation (LDA) [33]. van Barth and Hedin [34] parameterization scheme has been used for exchange correlation potential. Curium pnictides (CmX) crystallize in the NaCl-type structure (space group, $Fm\bar{3}m$, No. 225) and magnetically stable in the FM state. In the FM ground state, curium and non-metal atoms are located at positions: Cm: $(0,0,0)$ and X: $(0.5,0.5,0.5)$. The structure of the high-pressure phase is CsCl-type (space group, $Pm\bar{3}m$, No. 221) with positions at Cm: $(0,0,0)$ and X: $(0.5,0.5,0.5)$. As mentioned earlier [28–30] TB-LMTO method works well for the close-packed structures and since curium pnictides belongs to NaCl-type structure, which is not a close-packed structure, therefore, two equivalent empty spheres were introduced at positions $(0.25,0.25,0.25)$ and $(0.75,0.75,0.75)$ in such a way that they do not break the crystal symmetry [35]. However, the CsCl-type structure (high-pressure phase) being a close-packed one, no empty sphere was need for calculations. Total energy (per formula unit) was calculated for curium pnictides in these two structures. The Wigner–Seitz sphere was chosen in such a way that the sphere boundary potential is minimum and the charge flow between the atoms is in accordance with the electro-negativity criteria. The $\mathbf{E}$ and $\mathbf{k}$ convergence were also checked. The tetrahedron method of Brillouin zone integration has been used to calculate the total density of states. The total energy has been computed by reducing the volume from $1.05V_0$ to $0.55V_0$, where V_0 is the equilibrium cell volume. The calculated total energy was fitted to the Birch equation of state [30] to obtain the pressure volume relation. The pressure is obtained by taking volume derivative of the total energy. The bulk modulus $B_0 = -V_0\,\mathrm{d}P/\mathrm{d}V$ is also calculated from P–V relation.

Table 1
Calculated equilibrium lattice parameter a_0 (au), Bulk modulus (B_0) in GPa, phase transition pressure (P_t) in GPa and magnetic moment (μ_B) of curium pnictides in B_1 and B_2 phases.

Solids	Lattice parameter (a_0) in au	Bulk modulus (B_0) in GPa	Phase transition (P_t) in GPa	Relative volume (V/V_0) in %	Magnetic moment (μ_B)
CmN					
B_1 phase present	9.3702	154.4	50.9	5.0	6.91
Experimental	9.4997[a]	154.0[b]	–	–	7.02[c]
Other	9.5356[d]	–	–	–	7.24[d]
B_2 phase present	5.5981	198.8			6.99
CmP					
B_1 phase present	10.3167	94.6	36.4	7.0	6.90
Experimental	10.8528[a]	–	–	–	–
Other	10.9057[d]	–	–	–	7.20[d]
B_2 phase present	5.8326	111.3	–	–	6.81
CmAs					
B_1 phase present	10.8063	82.4	29.7	6.8	6.85
Experimental	11.1249[a]	–	–	–	6.58[c]
Other	11.1608[d]	–	–	–	6.80[d]
B_2 phase present	6.1404	97.3			6.78
CmSb					
B_1 phase present	11.4643	75.2	21.2	7.8	6.80
Experimental	11.7020	–	–	–	–
Other	11.8128[d]				6.68[d]
B_2 phase present	6.5379	78.6	–	–	6.3
CmBi					
B_1 phase present	11.9218	53.3	11.4	10.0	6.78
Experimental	11.9583[e]	54[e]	12.0[e]	16.0	–
Other	11.9583[d]	49[d]	14.2[d]	8.0[d]	6.76[d]
			12.0[f]	13.0[f]	
	11.4462[g]	69.2[g]	5.32[g]	2.46	
B_2 phase present	6.8307	67.4	–	–	6.89
Other		70[d]	–	–	
	6.8862[g]	72.6[g]			

[a] Ref. [22].
[b] Ref. [25].
[c] Ref. [1].
[d] Ref. [24].
[e] Ref. [23].
[f] Ref. [26].
[g] Ref. [27].

The stability of a particular structure is decided by the minima of the Gibbs energy (enthalpy at absolute T). The phase transition pressure P_t can be obtained by matching enthalpies of both structures such that the difference of enthalpy become $\Delta H = H_{B_2} - H_{B_1} = 0$, at transition pressure (P_t).

3. Results and discussion

3.1. Structural properties

Both the structural and magnetic stabilities are determined by calculating the total energies in NaCl-type structure by performing spin-polarized (ferromagnetic) and non-spin polarized (non-magnetic) configurations. A plot (not shown) between total magnetic (FM) and non-magnetic (NM) energies as a function of volume reveals that the Cm-pnictides are stable in FM state only, and do not undergo to NM state at high pressure.

The equilibrium cell volumes for curium pnictides in FM state at ambient pressure are estimated to be 176.35, 273.40, 313.95, 379.46 and 426.77 au^3 and corresponding lattice parameters calculated are 9.3702, 10.3167, 10.8063, 11.4643 and 11.9218 au for CmN, CmP, CmAs, CmSb and CmBi, respectively, and compared with the experimental [23] and theoretical [24] values in Table 1. Similar calculations were also performed for CsCl-type structure. In Fig. 1(a)–(e), we have plotted variation of total energy with V/V_0 for both B_1 and B_2 phases. One can notice from Fig. 1 that at ambient condition curium pnictides are stable in FM-NaCl-tpye structure but under compression these compounds undergo structural phase transition to FM-CsCl-type structure. The equation of states in terms of pressure variation of relative volume change is given in Fig. 2 for curium pnictides. In case of CmN, we have predicted a phase transition pressure of 50.9 GPa with relative volume collapse of 5.0%. There are no experimental and theoretical studies reported up till now, and hence our results could not be compared. Similar phase transitions in CmP, CmAs, CmSb and CmBi from the present calculations are also predicted, at pressures 36.4, 29.7, 21.2 and 11.4 GPa with relative volume collapse of 7.0%, 6.8%, 7.8% and 12.0%, respectively. We, however, could compare our results in the case of CmBi with other theoretical work [24,26,27], who have reported similar (B_1 to B_2) transition pressure of 12.0, 14.2 and 5.32 GPa with corresponding relative volume collapse of 13.0, 8.0 and 2.46%, respectively, and experimental data reported by Gensini et al. [23] who have also observed B_1 to B_2 phase transition at a pressure of 12.0 GPa with relative volume collapse of 16.0%. Detailed theoretical and available experimental data are summarized in Table 1. It is revealed from Table 1 that in the case of CmBi, for which most of the experimental data are available, our calculated results from TB-LMTO method on phase transition pressure (P_t) deviates only (−) 5%. However, the theoretically predicted value of P_t from density functional theory reported by Milman et al. [24] deviates (+) 18% from the experimental results. Also, it can be emphasized the predicted results for other four pnictide compounds will prove to be reasonably accurate when such measurements will be done in future.

Apart from this, the equilibrium lattice parameters and bulk modulus in both B_1 and B_2 phases are also tabulated in Table 1 and compared with the available experimental and theoretical results which reveal that our calculated values of lattice constant for all the five Cm-pnictide crystals agree reasonably well with the measured one. The calculated bulk modulus of CmN and CmBi agree excellently with the measured values, reported so for [23,25]. In addition, the magnetic moment at equilibrium in FM-NaCl phase is also calculated from the present study and shown in Table 1. It can be seen that the contributions to the magnetic moment comes entirely from Cm atom rather than non-metal pnicto-
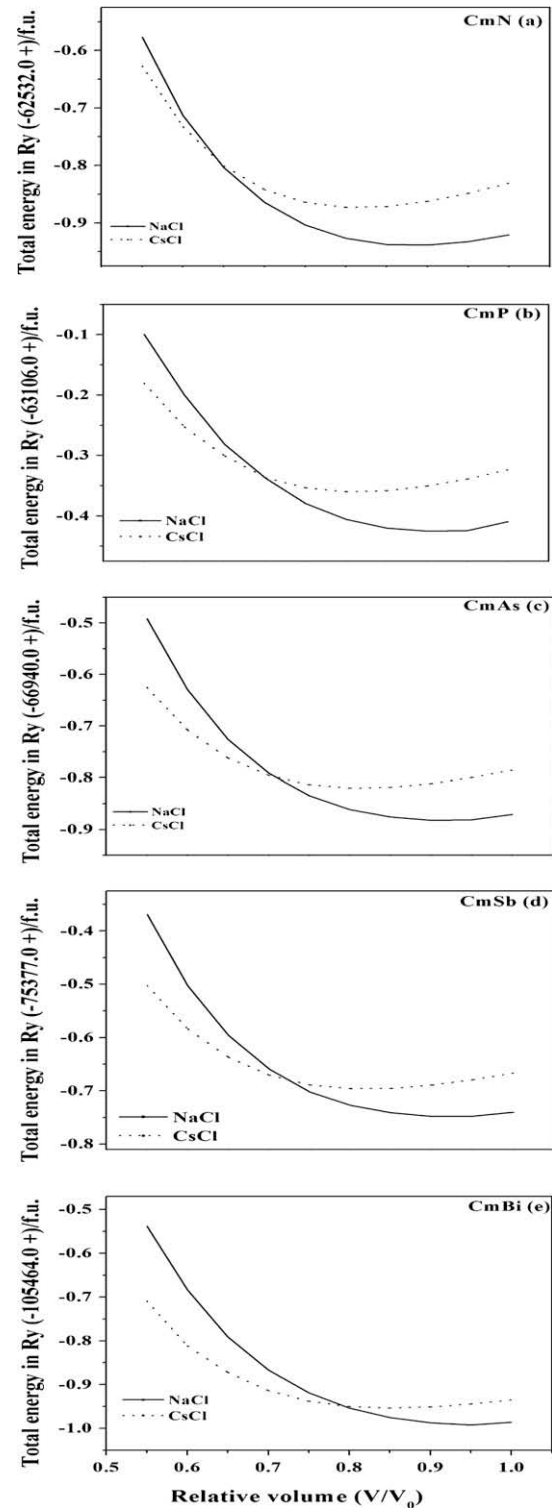

Fig. 1. (a)–(e) Variation of total energy with relative volume for FM-B_1 phase and FM-B_2 phase for curium pnictides.

gen atom. The calculated values of magnetic moments of curium pnictides are compared with the available experimental [23] and other theoretical results [24], which show a good agreement.

3.2. Electronic properties

We have carried out spin-polarized electronic band structure calculations for the curium pnictides namely; CmX (X = N, P, As,
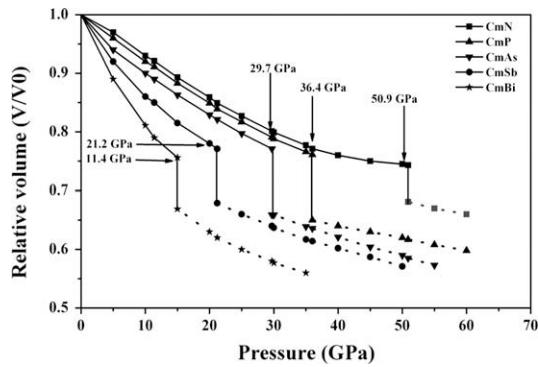
Fig. 2. Equation of states for curium pnictides. Solid line represents B_1 and dotted line represents B_2 phase.

Sb, Bi) in their B_1 and B_2 phases. As discussed earlier, the CmX compounds are ferromagnetic and weakly metallic in nature. We have therefore, calculated the band structure (BS) and density of states (DOS) in majority- and minority-spin channels at ambient as well as at high pressure. For the sake of discussion on electronic properties of Cm-pnictides, we have presented BS and DOS diagram for CmN in Figs. 3–6. Figs. 3 and 4 illustrate a combined picture of BS and DOS of minority, majority spin channels, respectively, in NaCl-phase under ambient conditions. From these figures one can notice a weakly metallic nature of CmN. In Fig. 3, the lowest lying bands around -1.5 Ry are due to 'p'-like states of Cm, and the next lowest energy bands are due to 's'-like states of N, which lie around -1.0 Ry. The bands in the valence band just below the Fermi level (E_F), in the range of -0.5 to 0.0 Ry, arise due to N 'p'-like states. Also, in Fig. 3, for the minority-spin case, Cm 'f'-like states can also be seen above the Fermi level (cluster of solid lines), which hybridize with Cm 'd'-like states. A small crossover of Cm 'd'-like states at 'X' point can be seen. While for the majority spin case (Fig. 4) the localized Cm 'f'-like states (cluster of solid lines) can be seen below E_F, and joining with N 'p'-like states. The crossover of Cm 'd'-like states in 'G–X' direction can be also seen. In general,
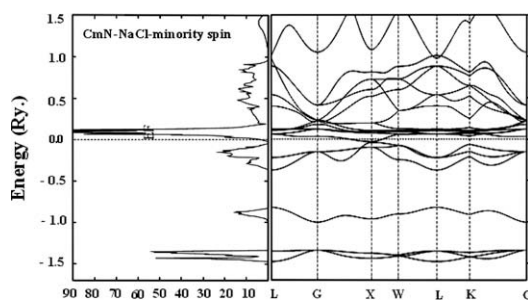

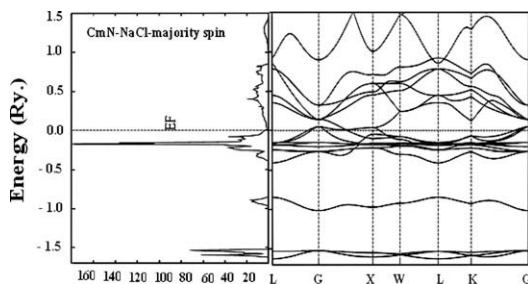**Fig. 3.** Band structure and density of sates in minority spin in B_1 phase for CmN.

Fig. 4. Band structure and density of states in majority spin in B_1 phase for CmN.
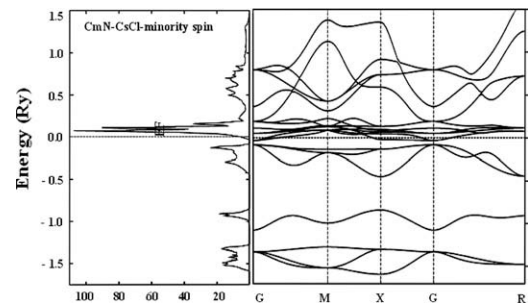

Fig. 5. Band structure and density of states in minority spin in B_2 phase for CmN.
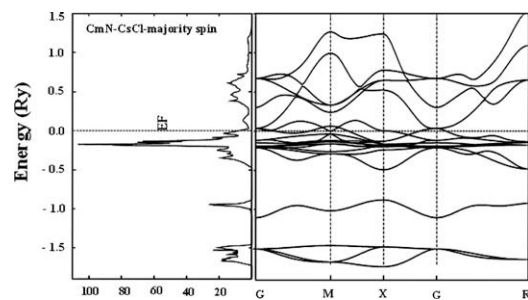

Fig. 6. Band structure and density of states in majority spin in B_2 phase for CmN.

Figs. 3 and 4 describe a weak metallic picture of CmN under ambient conditions.

As predicted in the preceding subsection, CmN undergoes a structural phase transition to the CsCl-type structure at the pressure of 50.9 GPa, we have, therefore, obtained band structure and density of states for the CsCl-type structure for minority and majority spins and presented in Figs. 5 and 6, respectively. It is found from Figs. 5 and 6 that all the states are very similar to those in the NaCl-type structure. As pressure is increased the lower energy bands are shifted to the higher energy side and more compressed bands are seen, which in the case of minority spins can be understood in terms of hybridization of Cm 'f'- and 'd'-like states. Nonetheless, in both the spins, CmN exhibits metallic nature, in the CsCl structure as well.

The band structure and density of states have also been obtained for rest of the Cm-pnictides. The band structure and density of states are very much similar to those of CmN, except much localized Cm f-like states. The Cm 'f'-like states at Fermi level, reveal more metallic of the rest of the Cm-pnictides as compared to CmN in minority spin.

4. Conclusions

In the present study, we have investigated the electronic and magnetic properties of curium pnictides. At ambient condition curium pnictides are found to be stable in the ferromagnetic state and crystallize in the NaCl-type structure at ambient condition. The CmX compounds undergo structural phase transition from FM-NaCl-type to FM-CsCl-type structure in the pressure range of 51.0–10.0 GPa (CmN to CmBi). High-pressure experimental studies are indeed needed to verify structural properties for curium pnictides. The high-pressure structural phase transition in CmBi is in good agreement with the experimental and theoretical results. The total energies are fitted to the Birch equation of state. The ground-state properties like lattice parameters, bulk modulus and magnetic moment are calculated and tabulated in Table 1. We have compared ground-state properties with available

experimental and theoretical results. The deviation between the calculated and experimental values may be due to the uses of LDA, which underestimate the ground-state properties. In addition, we have reported the band structures and density of states in both B_1 and B_2 phase for curium pnictides.

Acknowledgements

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