

# Electronic structure and thermoelectric power of cerium compounds at high pressure

N.V. Chandra Shekar<sup>a,\*</sup>, M. Rajagopalan<sup>b,1</sup>, J.F. Meng<sup>c</sup>,  
D.A. Polvani<sup>c</sup>, J.V. Badding<sup>c</sup>

<sup>a</sup> Material Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu 603102, India

<sup>b</sup> Max-Planck Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

<sup>c</sup> Department of Chemistry, Pennsylvania State University, University Park, PA 16802, USA

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## Abstract

The normal and high pressure thermoelectric power (TEP) of three cerium compounds are compared and the origin of the differences in their behaviour is discussed. CePd<sub>3</sub> shows a monotonic increase in thermopower as a function of pressure up to maximum pressure studied ~5 GPa. In sharp contrast, CeSn<sub>3</sub> shows an increase only up to 2–3 GPa and then starts decreasing. The ambient and high pressure behaviour is discussed by computing electronic structures of three Ce compounds, viz. CePd<sub>3</sub>, CeSn<sub>3</sub> and CeIn<sub>3</sub> using TB-LMTO method. The f-band width is larger in CeIn<sub>3</sub> as compared to the other two compounds, explaining the cause for its lower ambient TEP. The density of states of the f-band is maximum, narrower and the closest to the Fermi level in CePd<sub>3</sub> explaining its highest TEP. The band structure does not show much variation at higher compressions for CePd<sub>3</sub> and CeIn<sub>3</sub>. However, in the case of CeSn<sub>3</sub>, the band structure at higher compressions indicates an electronic topological transition, a possible cause for the pronounced peak TEP, observed in experiment.

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## 1. Introduction

The search for improved thermoelectric materials has renewed interest in thermoelectric power (TEP) measurements [1,2]. A variety of materials like skutterudites, intermediate valence compounds [3,4], semiconducting Bi–Sb alloys [5,6] and clathrates [7,8] have been studied and reported to have improved thermoelectric properties. In many of these compounds, pressure tuning of the electronic structure has demonstrated unprecedented thermoelectric figures of merit [3,9]. But reports on thermoelectric power under pressure are

scarce in literature. In the search for materials having higher thermoelectric power by means of pressure tuning, it is important to obtain better insight into the underlying mechanisms that cause changes in the thermoelectric power upon compression. Intermediate valence (IV) has been an interesting property of many rare earth (RE) intermetallic compounds [10,11]. It is believed that certain IV compounds go through the sequence: magnetically ordered trivalence, non-magnetic trivalence (Kondo effect), intermediate valence and tetravalence, as 4f level is gradually raised from well below  $E_F$  to well above  $E_F$  [10]. The intermediate valence state produces anomalies in many of the physical properties including thermoelectric power but is not understood fully yet [2,11]. Many cerium compounds show an increase in TEP at low pressures, which has been traditionally attributed to the valence transition of the cerium ion from trivalent to the tetravalent state

\* Corresponding author. Tel.: +91-4114-280347; fax: +91-4114-280081.  
E-mail address: chandru@igcar.ernet.in (N.V. Chandra Shekar).

<sup>1</sup> Permanent address: Physics Department, Anna University, Chennai, Tamil Nadu 600025, India.

Table 1  
Experimental parameters of three CeX<sub>3</sub> compounds

Compound	CePd <sub>3</sub>	CeIn <sub>3</sub>	CeSn <sub>3</sub>
Experimental (Å)	4.128	4.689	4.742
Structure	AuCu <sub>3</sub> type Pm3m, 221	AuCu <sub>3</sub> type Pm3m, 221	AuCu <sub>3</sub> type Pm3m, 221
Valence (experiment)	3.4 [10]	3.0 [10]	3.1 [10]
Bulk modulus (GPa) experiment	102 [13]	67 [14]	54 [10]
Kondo temperature (K) experiment	240 [14]	175 [15]	200 [16]
Thermopower (μV/K) experiment at STP	75	8 [12]	23
Transition pressure (GPa) experiment	–	–	2.5

[12]. The transition pressure is supposed to scale according to  $E_F - E_f$ , where  $E_F$  is the Fermi energy and  $E_f$  is the energy of the f-band centre. It is also known that in these compounds, the physical properties influenced by the Kondo temperature and compounds with similar temperatures might behave in the same fashion.

In this paper, the behaviour of the thermoelectric power of CeX<sub>3</sub> (X = Pd, Sn and In), isostructural (cubic, AuCu<sub>3</sub>) and intermediate valence compounds as a function of pressure are compared. Table 1 lists the properties of CeX<sub>3</sub> compounds. It is worth noting the large difference in the thermoelectric power of the three compounds. The Kondo temperature of these compounds is in the vicinity of 200 K indicating possible similar properties and also reducing the possibility of any anomaly at room temperature because of Kondo correlation [17]. But the unusually high thermoelectric power of CePd<sub>3</sub> has received considerable attention and studies of its various alloys have been made [18,19]. It is also suggestive of the existence of Kondo resonance peak at  $E_F$  [2]. It is reported that in CePd<sub>3</sub> TEP does not change much with pressure [18].

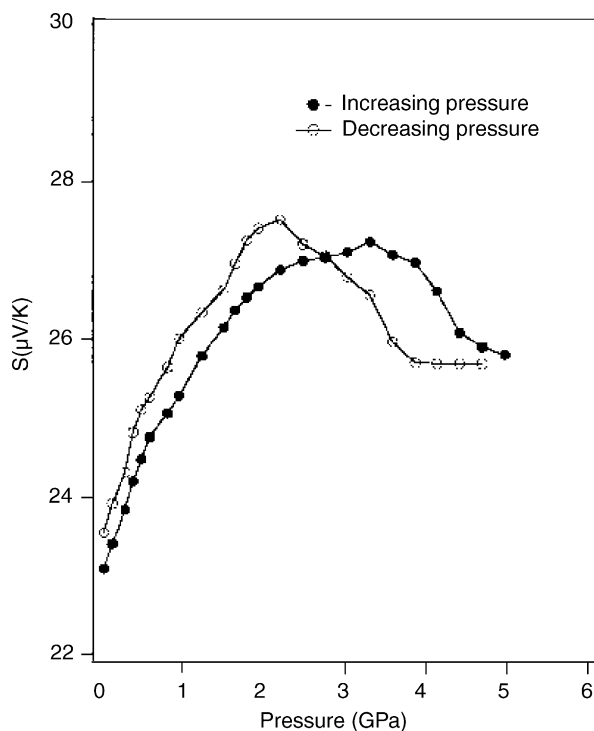


Fig. 1. Thermoelectric power of CeSn<sub>3</sub> as a function of pressure.

In sharp contrast, CeSn<sub>3</sub> has low TEP at ambient, but shows a peak at low pressure, which is attributed to the f-level pinned to  $E_F$  [12]. It is expected that compounds having similar Kondo temperatures will have similar properties. Electronic structure calculations [20,21] and recent photoemission spectroscopy experiments [17] do not address this difference in the TEP behaviour. Our objective was to repeat the measurements to confirm the high pressure-TEP behaviour of CePd<sub>3</sub> and CeSn<sub>3</sub>. Also in order to understand the trends in the ambient as well as high pressure behaviour of thermoelectric power, band structure calculations have been performed on three compounds, viz. CePd<sub>3</sub>, CeSn<sub>3</sub> and CeIn<sub>3</sub>.

## 2. Experiment and computation

The technique for measuring TEP under pressure on small samples of materials has been reported in detail [22]. Briefly, the pressure dependence is measured using the Mao–Bell diamond anvil cells at pressures between room pressure and 10 GPa. A culet size of about 1 mm and a gasket hole for

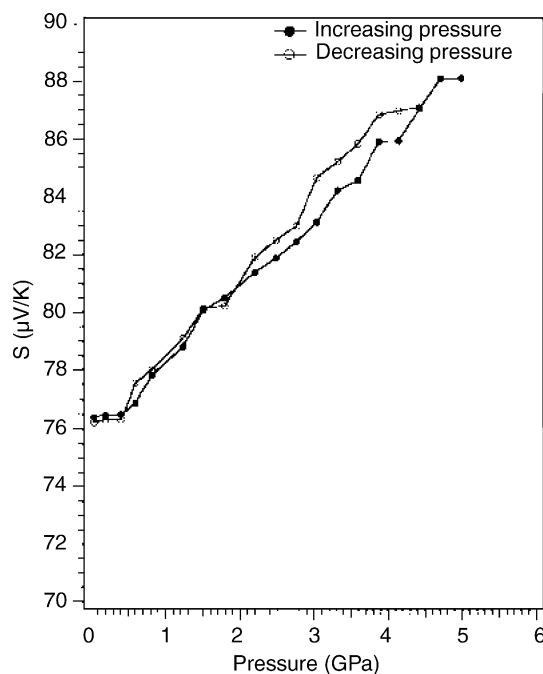


Fig. 2. Thermoelectric power of CePd<sub>3</sub> as a function of pressure.

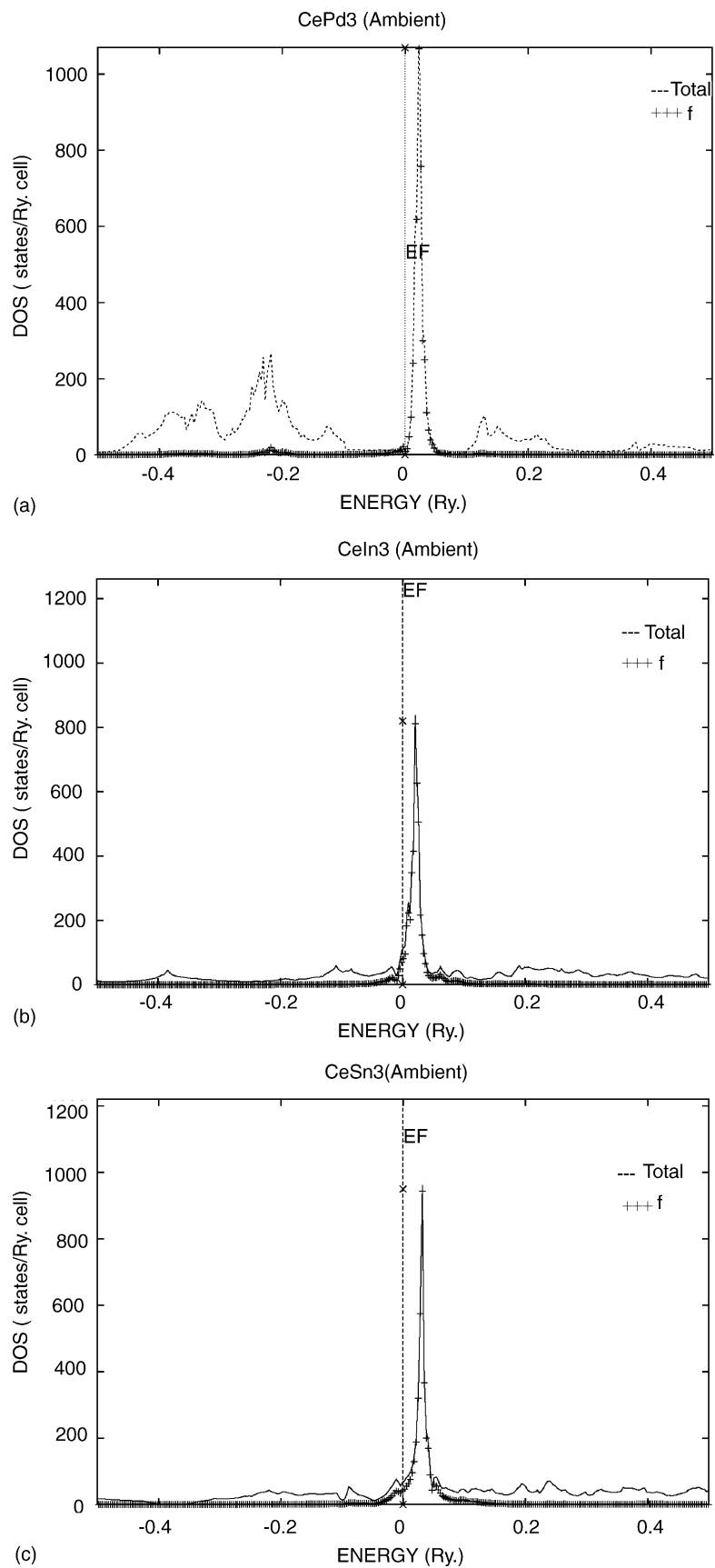


Fig. 3. (a–c) Total and partial f-density of states CePd<sub>3</sub>, CeIn<sub>3</sub> and CeSn<sub>3</sub>.

the same size were used. Typical sample dimensions were  $700 \mu\text{m} \times 50 \mu\text{m} \times 50 \mu\text{m}$ . Monoclinic  $\text{ZrO}_2$  was used as the pressure-transmitting medium. A focused Nd-YLF infrared laser beam is used to induce a temperature gradient. An error analysis indicates that the resolution in the TEP measurement,  $\Delta S/S$ , is approximately 0.008. Pressure is measured by the ruby fluorescence method [23].

We have carried out electronic structure calculations on  $\text{CePd}_3$ ,  $\text{CeSn}_3$  and  $\text{CeIn}_3$ , in order to compare the electronic structure for three compounds and to look for any systematics. Within the framework of density functional theory, the electronic structure calculations are performed using the TB-LMTO approach [24,25]. The exchange-correlation potential within the local density approximation is calculated using the parameterization scheme of von Barth and Hedin [26]. We have used the scalar relativistic approach that includes the mass velocity and Darwin corrections, but omits the spin-orbit couplings. All K space integrations are performed with the tetrahedron method [27] and the self consistency in the charge density is obtained with 624 irreducible K points. The basis set consists of 6s, 5d and 4f orbitals for Ce and 5s, 5p and 4d orbitals for Sn and In, and 5s and 4d orbitals for Pd. The 6p orbitals of Ce are treated by the down folding technique. The combined corrections terms are also

included which account for the non-spherical shape of the atomic spheres and the truncation of the higher partial waves inside the spheres were included so as to minimize the errors in the LMTO method. The Wigner–Seitz sphere radii are chosen in such a way that the sphere boundary potential is minimum and the charge flow is in accordance with the electro negativity criteria.

### 3. Results and discussion

Thermoelectric power  $\text{CePd}_3$  and  $\text{CeSn}_3$  have been studied up to 5 GPa. At ambient,  $\text{CePd}_3$  has a high thermoelectric power of about  $75 \mu\text{V/K}$  (there are reports up to  $125 \mu\text{V/K}$ ),  $\text{CeSn}_3$  shows about  $23 \mu\text{V/K}$  and  $\text{CeIn}_3 \sim 8 \mu\text{V/K}$  [12]. Under pressure, all three compounds show increase in thermopower. However, in  $\text{CeSn}_3$  TEP starts decreasing by  $\sim 2.5$  GPa (Fig. 1). The coefficient of thermoelectric power is  $\sim 0.03/\text{GPa}$  for  $\text{CePd}_3$ ; whereas, for  $\text{CeSn}_3$  it is  $\sim 0.07/\text{GPa}$  up to 2.5 GPa. Our experiments show that the increase observed in  $\text{CePd}_3$  continues even up to 10 GPa [28] which is in contrast to the belief that TEP stays constant with pressure [18]. Also, the increase observed in  $\text{CePd}_3$  is of the same order of magnitude as in  $\text{CeSn}_3$  Fig. 2. In  $\text{CeSn}_3$ , TEP reached a maximum of about  $27 \mu\text{V/K}$  and started decreasing, confirming one of the earlier results [12]. The experiments were

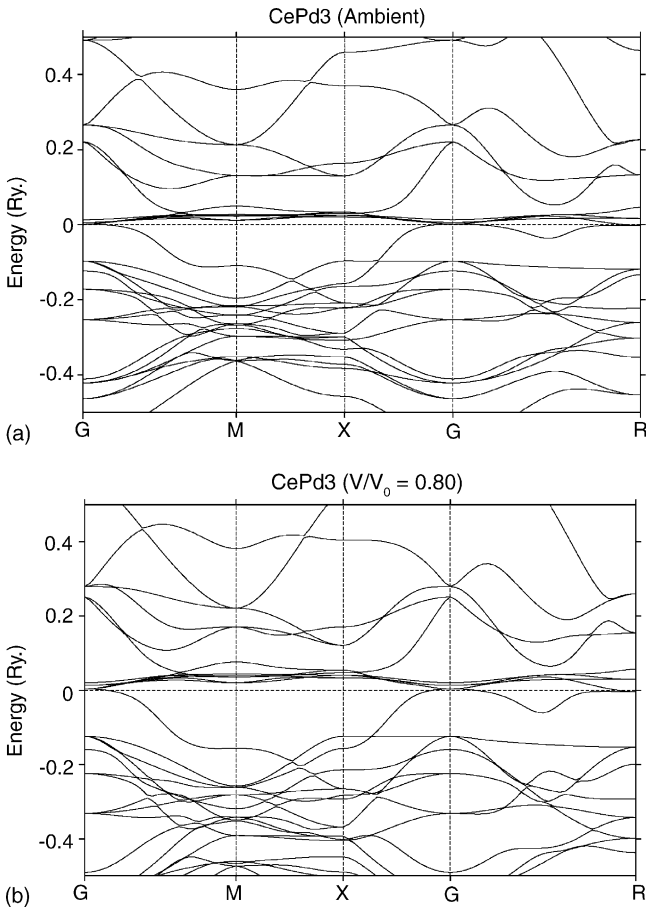


Fig. 4. (a and b) The band structures at  $1.00V_0$  (top) and  $0.80V_0$  (bottom) of  $\text{CePd}_3$ .

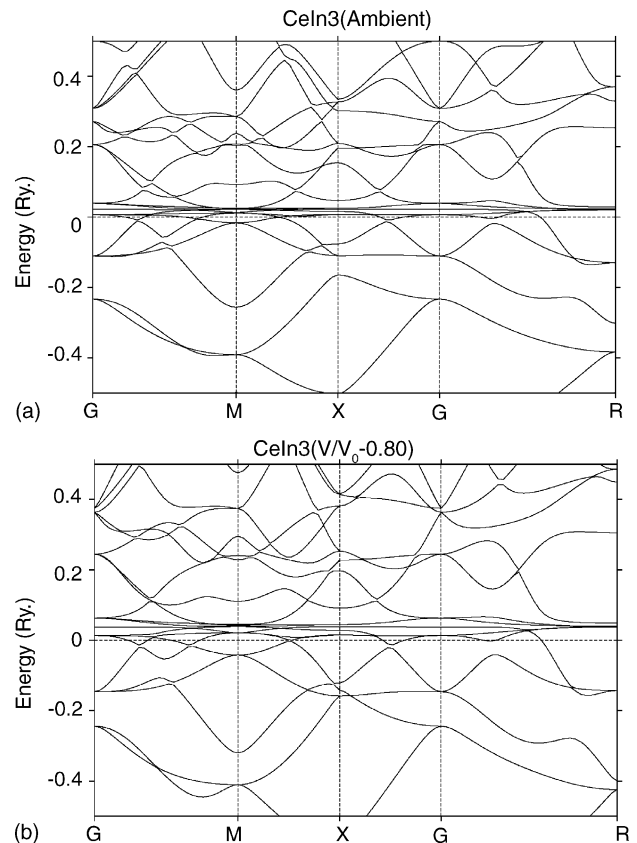


Fig. 5. (a and b) The band structures at  $1.00V_0$  (top) and  $0.80V_0$  (bottom) of  $\text{CeIn}_3$ .

carried out several times and the observations were reproducible. Looking at the results on cerium compounds, it is clear that TEP increases with pressure in general and in some compounds TEP peaks at pressure  $P_t$  and starts decreasing. This was believed to be caused by valence transition of the cerium ion in the respective compound and  $P_t$  the valence transition pressure [12].

The general increasing trend of the TEP under pressure for all the three compounds observed experimentally occurs as the f-band broadens and simultaneously moves away from the Fermi level into the conduction band. Experimentally it is observed that in the case of CePd<sub>3</sub> and CeIn<sub>3</sub> [12], the increase in high pressure-TEP continues up to higher pressures; whereas, in CeSn<sub>3</sub> it stops at a pressure of  $\sim 2.5$  GPa and thereafter starts decreasing. The f-electrons possess very high kinetic energy and effective mass and as they become more and more itinerant their contribution increases TEP. But at the same time, the band is also moving away from the Fermi level and their significance in controlling transport properties might decrease. It will be interesting to see the fate of TEP at higher pressures; although, the TEP measurements are known to be difficult to perform above 10 GPa. It is predicted that at high enough pressures the increasing TEP in CePd<sub>3</sub> and CeIn<sub>3</sub> might stop as f-band moves sufficiently

far from the Fermi level. Our computations support the belief that the transition pressure, the pressure where TEP may stop its upward trend, increases in the sequence CeSn<sub>3</sub>  $\rightarrow$  CeIn<sub>3</sub>  $\rightarrow$  CePd<sub>3</sub> as  $E_F - E_f$  increases [12]. It is speculated that the transition pressures may be higher in the case of In and Pd compounds. It seems as though the f-electrons are itinerant in all three systems and the f-band is the farthest from the Fermi level for CeSn<sub>3</sub>.

The gross features of our calculated electronic properties are compared well with earlier calculations [20,21,29–31]. But it is known that the position and width of f-level is sometimes misleading and depends on the computation method and code. The value  $E_F - E_f$  is much larger in CeIn<sub>3</sub> and CeSn<sub>3</sub> as compared to CePd<sub>3</sub>. This clearly explains the higher value of TEP in CePd<sub>3</sub>. The f-band width is the highest in the case of CeIn<sub>3</sub>, which means that relatively the effective mass of the electrons are smaller, explaining its lowest ambient TEP. However, in the case of Pd and Sn compounds the bandwidths are similar. These trends correctly predict the observations in our experiments. Fig. 3(a–c) shows the total as well as the partial f-density of states (dos) of all three compounds and gives the idea as to how far f-band is from the Fermi level. It is evident that the contribution of f-band is maximum in the vicinity of the Fermi level.

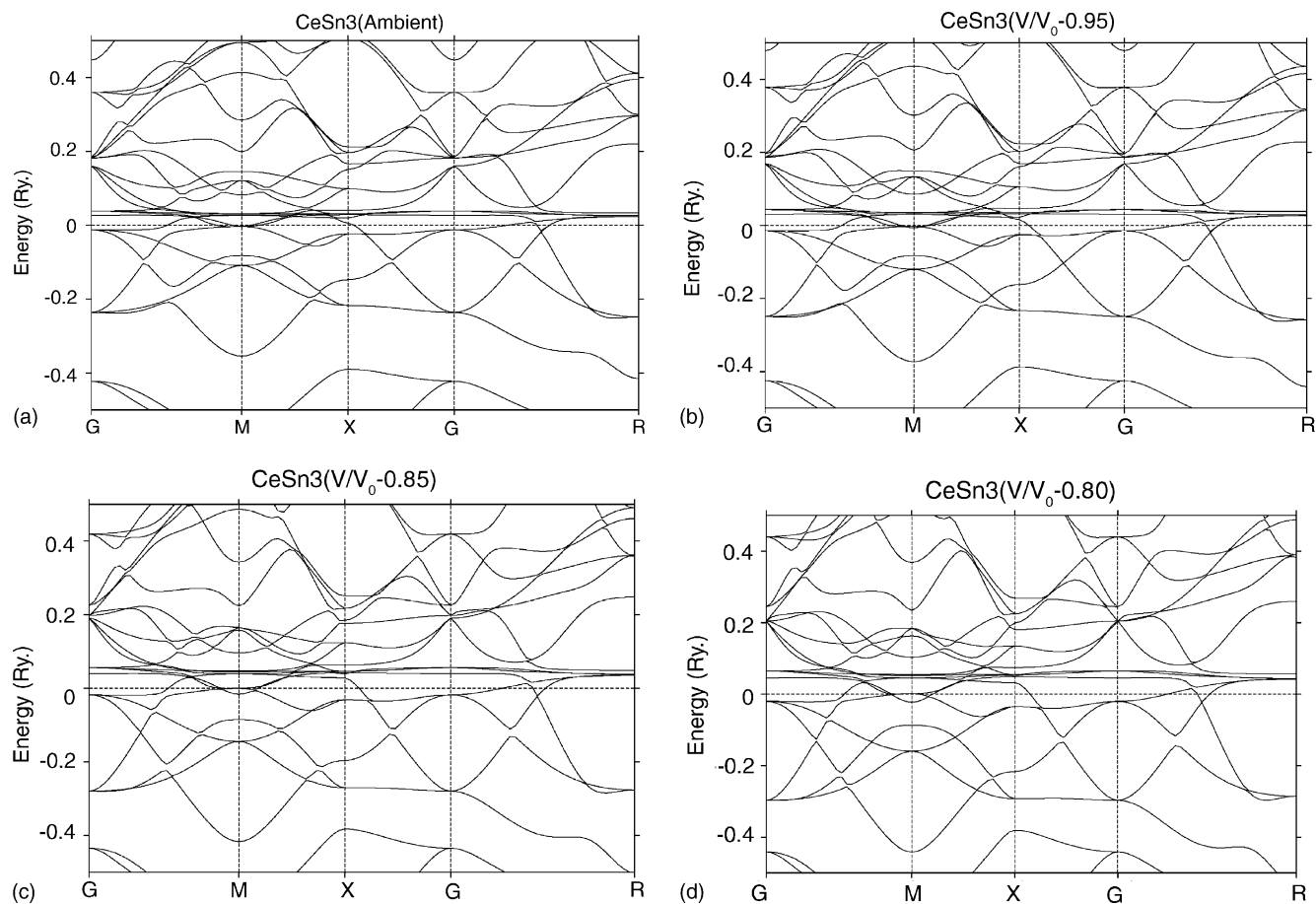


Fig. 6. (a–d) The band structures at  $1.00V_0$ ,  $0.95V_0$ ,  $0.85V_0$  and  $0.80V_0$  of CeSn<sub>3</sub>.

In an attempt to understand the high pressure TEP behaviour observed in CePd<sub>3</sub>, CeIn<sub>3</sub> and CeSn<sub>3</sub>, calculations were carried out for compressions at 0.95V<sub>0</sub>, 0.90V<sub>0</sub>, 0.85V<sub>0</sub> and 0.80V<sub>0</sub>, where V<sub>0</sub> is the equilibrium unit cell volume. In CePd<sub>3</sub>, one does not observe much change in the band structure under compression as can be seen by band dispersion curves plotted for ambient equilibrium cell volume and 0.80V<sub>0</sub>, shown in Fig. 4(a and b). From the figure, it can be seen that along the 'G' direction f–d type of band moving, rather slowly, up. Fig. 5(a and b) shows the band structure for CeIn<sub>3</sub> and this compound also does not show any drastic change with pressure. The general featureless behaviour of the two compounds, possibly indicate the stability under the action of pressure. The compounds do not show any structural transitions under pressure up to the maximum pressure studied.

However, calculations reveal interesting features in CeSn<sub>3</sub>. Fig. 6(a–d) shows the band structure at ambient and reduced volumes for CeSn<sub>3</sub>. It is seen that along the 'M' direction a f–d type of band is almost tangential to the Fermi level, coming down at 0.95V<sub>0</sub>. This indicates electronic transition, also called electronic topological transition (ETT). Such transitions are reported in several intermetallics [32]. It is also reported that ETT can induce a pronounced peak in the thermoelectric power (TEP), since TEP depends upon the derivative of the density of states at Fermi level [33]. This differs from the belief that the cause for large increase in TEP in CeSn<sub>3</sub> at low pressure is due to the valence change of the cerium ion.

In summary, high-pressure thermoelectric power measurements were carried out for CePd<sub>3</sub> and CeSn<sub>3</sub> and TB-LMTO calculations on CePd<sub>3</sub>, CeIn<sub>3</sub> and CeSn<sub>3</sub> were done. CePd<sub>3</sub> shows an increase in TEP up to the maximum pressure studied ~5GPa. CeSn<sub>3</sub> shows an increase only up to ~2–3 GPa and then starts decreasing. The large difference in the ambient TEP between the compounds is understood by comparing the calculated f-band width and its proximity to the Fermi level. High-pressure electronic structure of CePd<sub>3</sub> and CeIn<sub>3</sub> do not show any gross variation under compression. However, we observe electronic topological transition in CeSn<sub>3</sub> in the pressure regime where a pronounced increase in TEP is observed in the experiment around ~2.5 GPa. It is clear that ETT plays an important role in enhancing the TEP; and hence, this correlation needs to be understood further.

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