CHAPTER 4

MAGNETIC TRANSITION IN CeP AND STRUCTURAL PHASE TRANSITIONS IN CeX (X = P, Se, Te) UNDER HIGH PRESSURE

4.1 INTRODUCTION

4.1.1 Solid state phenomenae in cerium compounds

The f-block element Cerium (Ce) and its compounds have been of interest to researchers of condensed matter as they contain rich physics and chemistry. Some of the fascinating aspects of these materials are as follows:

i) In cerium hydrides and chalcogenides, the 4f electron is localised.

ii) In CeP, the 4f electron possesses some itinerancy.

iii) The inter-metallic compounds of Ce exhibit nearly band-like character.

iv) There are controversial interpretations regarding the double-peak structure in valence band photoemission spectra (PES).

v) The mechanism of the structural phase transitions observed in rock-salt type cerium monopnictides and monochalcogenides needs to be understood in greater detail.

vi) Cerium compounds exhibit various solid state phenomenae such as Rudderman - Kittel - Kasuya - Yoshida (RKKY) interaction, Kondo interaction, crystal field effects, intermediate valences, heavy fermion character and complex magnetic phase diagrams.
In cerium compounds, hybridisation plays a significant role as 5d level is slightly lower in energy than 6s and 4f according to Aufbau principle. The group theoretical justification for this proximity was given by Novaro (1973). This gives rise to d-f mixing which is of 'on-site' type. In some pnictides, the 4f bands are located close to the Fermi level $E_F$ yielding some hybridisation with the valence p-electrons of pnictogen. This is said to be 'p-f' mixing which is of 'inter-site' type. On the other hand, the smooth spherical distribution of s-states makes them not suitable for hybridisation with 4f states. Direct f-f interaction is not expected as Ce-Ce separation is sufficiently large in these compounds to prevent such interaction. In a recent review, Benedict (1995) enumerated the pressure induced structural transitions in monopnictides and monochalcogenides of cerium.

### 4.1.2 Earlier studies on CeP

At ambient pressure, CeP crystallises in NaCl-type (B1) structure. It is antiferromagnetic (AFM). It shows a series of transitions under pressure as listed below:

i) Kasuya (1994) reported that CeP shows FM ordering around 0.86 GPa at 30K and that the compound is a low carrier system.

ii) Okayama et al (1993) performed electrical resistivity measurements on single crystalline CeP and reported a transition from dense Kondo FM state to normal metallic (NM) state around 5 GPa.

iii) According to Jayaraman et al (1976), CeP undergoes an electronic transition in which it changes from silvery gray color to a purple color around 9 GPa, which is related to the delocalisation of 4f-electron.
iv) Leger (1993) carried out high pressure x-ray diffraction (HPXRD) experiment on CeP and reported a structural transition from B1 to B2 phase around 19 GPa.

There are different reports on the conductivity of CeP by various authors. From the electrical resistivity measurements, Okayama et al (1993) showed that CeP is a metal. On the other hand, from optical absorption studies, Hulliger (1979) reported that thin films of CeP showed semiconducting property with an energy gap of 1.1 eV. In addition, Hulliger and Hull (1970) speculated a pressure-induced delocalisation of the 4f electron in the cerium monopnictides. The value of magnetic moment of CeP at zero field was found to be around 0.79 $\mu_B$ using magnetization studies by Kuroda et al (1993).

The first experimental evidence of a double-peaked structure due to f-emission in the valence band emission spectrum for the cerium pnictides was reported by Franciosis et al (1981) and Gudat et al (1982). The data for cerium pnictides indicated a peak about 0.5 eV below $E_p$ and another peak about 3 eV below $E_p$. The feature near 0.5 eV has a full width at half maximum (FWHM) of 0.6 eV and the one at 3 eV has a FWHM of 1 eV. Franciosis et al (1981) interpreted their spectra for the Ce-pnictides in terms of a screening model.

Freeman et al (1987) calculated the band density of states (DOS) for CeP using self-consistent linearized augmented plane wave (LAPW) method within the warped muffin-tin (WMT) approximation. Their results indicated the following features. There is a two-peaked structure from about -5 eV upto just below $E_p$ which results from the pnictide p-bands. There is also a broad Ce d-band DOS starting just about where the pnictide p-bands leave off and extending well above the scale of the plots. Just above $E_p$ are the two peaks resulting from the f-orbitals. However, the calculations by Freeman et al (1987) included the pnictide s-states in the core. Freeman

Norman et al (1984) re-interpreted the double-peaked 4f structure in CeP using a model in which the peak near the Fermi level is caused by a 4f photohole screened by 4f electrons and the deeper 4f peak by 4f holes poorly screened by Ce 5d or ligand electrons. For these systems, it was concluded that the more itinerant the 4f peak at greater binding energy. The most itinerant 4f states occur in CeN and the least in CeBi.

A similar two-peak structure is seen in the bremsstrahlung isochromat spectroscopy (BIS) (Allen et al 1983) in cerium compounds.

Kasuya et al (1992) applied the concepts of Wigner crystal and magnetic polaron model in order to explain some anomalous properties of CeP.

Thus, the survey indicates that there has been no quantum mechanical ab-initio calculations of magnetic moment of CeP and a theoretical study of the pressure - induced phase transitions exhibited by CeP. The present study aims to fill up this void.
4.1.3 Earlier studies on CeSe

The compound cerium selenide CeSe also crystallises in B1 phase at ambient pressure. Under ambient conditions, it is dense Kondo compound and is antiferromagnetic (AFM) with saturation magnetic moment of $0.57\mu_B$ as determined by neutron scattering experiments (Donni et al 1993). Thus, CeSe has a value of magnetic moment less than that of CeP (Kuroda et al 1993) for which it is $0.79\mu_B$. This is due to the stronger f-d hybridisation in CeSe which increases its Kondo temperature $T_k$ relative to the RKKY - magnetic temperature $T_{RKKY}$.

CeSe undergoes a structural transition to B2 type phase around 18 GPa (Leger 1993). This is investigated in the present study using TBLMTO-ASA method. There are a number of reports in literature on the PES of metallic CeSe (Lässer et al 1980, Gudat et al 1982, Oyamada et al 1993 and Lynch and Weaver 1987). These studies established that there is only a single 4f-related peak around a binding energy of 2.3 eV with FWHM of 0.7 eV. These results indicate that the double peaks present in CeP are absent in CeSe.

On the theoretical side, Kioussis et al (1991) reported the band structure at ambient pressure using LMTO method with WMT approximation by treating 4f states in the core, thus excluding the hybridisation of f electrons with those of p and d states. Dönni et al (1992) studied the anisotropic exchange and spin dynamics in CeSe.

4.1.4 Earlier studies on CeTe

Ott et al (1979) found, by neutron diffraction, that CeTe is AFM with an ordered moment of $0.3 \pm 0.1 \mu_B$. This indicates that CeTe is less magnetic than CeP or CeSe. Kioussis et al (1991) performed computational studies on CeTe and concluded that the increase in the band f-hybridization
places CeTe at the borderline between magnetic and non-magnetic behaviour. This is due to higher Kondo temperature relative to RKKY temperature. Band theory (Lim et al 1991 and Lim and Cooper 1991) showed little success in calculating the magnetic moment and in explaining the giant magneto optic effect owing to its heavy fermion character (Ott et al 1979).

Gudat et al (1981) used synchrotron radiation to carry out PES studies on metallic CeTe and reported that there is a single 4f-related peak around an apparent binding energy of 2.5 eV with FWHM of 0.7 eV. As in CeSe, in this compound CeTe also, there was no clear evidence for a second 4f related feature.

4.1.5 **Outline of the present study on CeX (X=P, Se, Te)**

The present chapter aims at

i) the calculation of band structure and magnetic moment of CeP in ferromagnetic state.

ii) the total energy calculations and equation of state (EOS) studies for the pressure induced transitions:

a) from FM to NM state in CeP
b) from B1 to B2 phase in CeP
c) from B1 to B2 phase in CeSe
d) from B1 to B2 phase in CeTe.

In order to compute the band structures, TBLMTO-ASA method was used.

Amongst the cerium monopnictides, only CeP has been studied in the present thesis as the higher monopnictides CeAs, CeSb and CeBi exhibit
complex magnetic phase diagrams. For example, CeSb shows as many as 14 types of magnetic orderings in the low-temperature regime (Chattopadhyay et al 1994). Of the cerium monochalcogenides, CeS does not exhibit pressure induced structural transition (De and Chatterjee 1989) and hence it has not been investigated in the present study.

4.2 PRESENT STUDY ON CeP

4.2.1 Method of calculations for CeP

Self-consistent spin polarized electronic structure calculations were performed for FM state of B1 phase. The methodology for spin polarized calculations is as adopted for Fe_3Pt by Rajagopalan et al (1995). The electron configurations of 6s^2 5d^1 4f^4 (Ce) and 3s^2 3p^3 (P) were used. The R/W values were chosen to be 1.27 (Ce), 1.0 (P) and 0.780 (ES). The other details of the calculations are as described for ThX (X = P, As, Sb). Accordingly, 512 k^*-points were sampled in the entire Brillouin zone and von Barth and Hedin exchange correlation scheme was employed. All relativistic corrections except that due to spin-orbit coupling were employed.

Non-spin polarized calculations were performed for NM(B1) state and B2 phase for the same number of k^*-points as used above. In the B2 phase, the R/W values of 1.1 (Ce) and 0.8745 (P) were used.

4.2.2 Ferromagnetic (FM) band structure of CeP

The spin-down and spin-up electron dispersion curves (bands) are plotted in Figures 4.1 and 4.2 along the high symmetry directions in the Brillouin zone. The overall profiles are similar. The low lying band is predominantly due to the 3s orbital of P. Above it lie the 3p bands of P. The 4f states of Ce lie close to E_p. The band structure indicates the metallicity of CeP as one of the 4f bands crosses E_p. Due to the localized nature of 4f electrons in FM state, the hybridization of f orbitals of Ce with the p states...
Fig. 4.1 ‘Spin-down’ electronic structure in FM state of CeP at ambient pressure
Fig. 4.2 ‘Spin-up’ electronic structure in FM state of CeP at ambient pressure
of P is absent at ambient pressure. The conduction band above $E_F$ is mainly due to 5d(Ce) states which hybridise with 4f (Ce) states.

### 4.2.3 DOS in FM state of CeP at ambient pressure

In Figures 4.3 to 4.9 the histograms of (i) total DOS, (ii) spin-down DOS, (iii) spin-up DOS, (iv) Ce-contribution to 'spin-down' DOS, (v) Ce-contribution to 'spin-up' DOS, (vi) P-contribution to 'spin-down' DOS and (vii) P-contribution to 'spin-up' DOS in FM state of B1 CeP are plotted at ambient pressure.

The total DOS in Figure 4.3 shows the double peaks due to 4f electrons which are resolved just above $E_F$ and is in good agreement with experiment (Franciosis et al. 1981, Weaver 1983). On the other hand, the total DOS with non-spin polarized calculations plotted in Figure 4.10 does not show the f peaks in resolved condition. This indicates that it is appropriate for the FM state of CeP to have been calculated by spin-polarized method for its electronic structure. It is also clear, from Figure 4.3, that the 4f level overlaps with the valence band which is in good agreement experiment (Croft et al. 1981).

In addition to the double-peak structure, the DOS plotted in Figure 4.3, exhibits the 3p (P) band feature between -0.37 and -0.17 Ry and a broad feature due to 5d (Ce) which starts around -0.1 Ry and extends well above the scale of the plot. All these characteristics agree well with PES experimental results (Franciosis et al. 1981 and Weaver, 1983) and previous calculations by Freeman et al. (1987).

The value of DOS at $E_F$ was found to be 92 states/Ry/Cell. The value of $N(E_F)$ indicates that CeP is not of heavy-fermion type. It can be pointed out that the spin-polarized PES was not reported by experiments in literature so far on this compound. Such an experimental work on CeP
Fig. 4.3 Total DOS in FM state of CeP at ambient pressure
Fig. 4.4 'Spin-down' DOS in FM state of CeP at ambient pressure
Fig. 4.5 'Spin-up' DOS in FM state of Ce at ambient pressure
Fig. 4.6 Contribution from cerium to ‘spin-down’ DOS in FM state of CeP at ambient pressure
Fig. 4.7 Contribution from cerium to 'spin-up' DOS in FM state of CeP at ambient pressure
Fig. 4.8 Contribution from phosphorous to ‘spin-down’ DOS in FM state of CeP at ambient pressure.
Fig. 4.9 Contribution from phosphorous to 'spin-up' DOS in FM state of CeP at ambient pressure
Fig. 4.10 Total DOS with non-spin polarized calculations on CeP
report would be highly useful to compare the placements of peaks in DOS histogram.

4.2.4 Magnetic moment calculation for transition in CeP from FM to normal metallic (NM) state

The magnetic moment of FM phase of CeP was calculated by spin-polarized technique using TBLMTO-ASA method at different cell volumes. At ambient pressure the value is found to be $0.678\mu_B$ which agrees well with experimental value \cite{Kuroda1993}. The calculated value of magnetic moment can be understood as follows.

The number of electrons in spin-down and spin-up states of various $l$-states (l-NOS) is given in Table 4.1. It shows, at ambient pressure corresponding to $V/V_0 = 1.0$, that there are 0.742 electrons in d-like spin-up state, 0.678 in d - like spin-down state, 0.851 in f-like spin-up state and 0.257 in f - like spin-down state. Thus, the contribution to magnetic moment is $0.064 \mu_B$/Ce-atom from d-states and $0.594 \mu_B$/Ce atom from f-states, yielding a net moment of $0.678 \mu_B$. This is in excellent agreement with experimental value given by Kuroda \textit{et al} (1993).

As pressure is applied, the l-NOS of spin-up 'f' state and spin down 'f' state become nearly equal. In addition, the l-NOS in both spin-up and spin-down d-states increases slightly to get nearly equal population. As a result, the net magnetic moment becomes zero around $V/V_0 = 0.80$ corresponding to a pressure of 3.59 GPa.

Thus, CeP undergoes a transition from FM to NM state around 3.59 GPa, a value which is in good agreement with the experimental value reported by Okayma \textit{et al} (1993).
Table 4.1

Number of electrons (spin-down $\downarrow$ and spin-up $\uparrow$) (1-NOS/ formula unit) in various l-states at different reduced volumes in B1 phase of CeP

<table>
<thead>
<tr>
<th>$V/V_o$</th>
<th>Te</th>
<th>1-NOS</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$l_s$</td>
<td>$l_p$</td>
<td>$l_d$</td>
</tr>
<tr>
<td>1.00</td>
<td>0.155</td>
<td>0.245</td>
<td>0.678</td>
</tr>
<tr>
<td>0.95</td>
<td>0.153</td>
<td>0.254</td>
<td>0.711</td>
</tr>
<tr>
<td>0.90</td>
<td>0.152</td>
<td>0.265</td>
<td>0.744</td>
</tr>
<tr>
<td>0.85</td>
<td>0.150</td>
<td>0.278</td>
<td>0.787</td>
</tr>
<tr>
<td>0.80</td>
<td>0.149</td>
<td>0.295</td>
<td>0.817</td>
</tr>
</tbody>
</table>
In Table 4.2, the value of \( p \) is given as a function of pressure. In addition, the close agreement of the present 1-NOS results at ambient pressure with those by LAPW calculations (Freeman et al. 1987) can be seen in Table 4.3.

However, while comparing with the results of Freeman et al. (1987) in Table 4.3, it is to be recalled that s states of Ce were used in the core in their calculations. There is an excellent agreement in the 1-NOS of crucial l-states viz d (Ce) and f (Ce) between the present calculations and those by Freeman et al. (1987) as indicated in Table 4.3.

### 4.2.5 EOS studies for FM to NM transition under pressure in CeP

The self consistently calculated values of total energy in FM and NM states of B1 phase were fitted to Birch EOS in order to obtain pressure-volume relationship from which the enthalpy was calculated as a function of pressure. The present electronic structure calculations confirmed the FM phase at ambient pressure by showing minimum total energy for this phase when compared to NM phase. The pressure at which the enthalpies in the two states (FM and NM) are equal is the transition pressure \( P_m \) whose value is found to be 3.59 GPa which is in close agreement with the value reported by experiment (Kuroda et al. 1993). Table 4.4 gives \( P_m \), the bulk modulus \( (B_0)_\text{FM} \) at ambient pressure, volume collapse during the transition, equilibrium lattice constant \( a_0 \) and bulk modulus in NM phase \( B_{\text{NM}} \) and shows good agreement of these values those reported by experiments (Okayama et al. 1993 and Leger 1993). The present calculations showed an error of 3.15\% in the calculations of lattice parameter at ambient pressure.

In Figure 4.11, the magnetic moment is plotted as a function of cell volume. In Figures 4.12 and 4.13, the total energy as a function of cell volume and enthalpy as a function of pressure are plotted.
Table 4.2
Magnetic moment and density of states at Fermi level at different cell volumes in B1 phase of CeP

<table>
<thead>
<tr>
<th>V/V₀</th>
<th>μ(μₜ)</th>
<th>N(Eₚ) (States/Ry/Cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.678</td>
<td>92.107</td>
</tr>
<tr>
<td>0.95</td>
<td>0.556</td>
<td>65.801</td>
</tr>
<tr>
<td>0.90</td>
<td>0.385</td>
<td>57.949</td>
</tr>
<tr>
<td>0.85</td>
<td>0.073</td>
<td>60.002</td>
</tr>
<tr>
<td>0.80</td>
<td>0.007</td>
<td>46.268</td>
</tr>
</tbody>
</table>
Table 4.3
1-NOS for CeP at ambient pressure compared with the LAPW-supercell calculations

<table>
<thead>
<tr>
<th>1-NOS</th>
<th>Present study</th>
<th>LAPW study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce - s</td>
<td>0.311</td>
<td>0.13</td>
</tr>
<tr>
<td>Ce - p</td>
<td>0.491</td>
<td>0.17</td>
</tr>
<tr>
<td>Ce - d</td>
<td>1.420</td>
<td>1.04</td>
</tr>
<tr>
<td>Ce - f</td>
<td>1.108</td>
<td>1.02</td>
</tr>
<tr>
<td>P - s</td>
<td>0.046</td>
<td>0.02</td>
</tr>
<tr>
<td>P - p</td>
<td>3.147</td>
<td>2.54</td>
</tr>
<tr>
<td>P - d</td>
<td>0.074</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 4.4

Results for FM to NM transition in CeP under pressure

<table>
<thead>
<tr>
<th></th>
<th>Present study</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_m$ (GPa)</td>
<td>3.59</td>
<td>5</td>
</tr>
<tr>
<td>$(B_0)_{FM}$ (GPa)</td>
<td>59.49</td>
<td>65</td>
</tr>
<tr>
<td>$\Delta V/V_0$ (%)</td>
<td>6.6</td>
<td>10.5</td>
</tr>
<tr>
<td>$a_0$ (Å)</td>
<td>5.7194</td>
<td>5.9058</td>
</tr>
<tr>
<td>$B_{NM}$ (GPa)</td>
<td>104</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig. 4.11 Magnetic moment of CeP as a function of reduced volume
Calculated total energy as a function of cell volume in FM and NM states of CeP
Variation of enthalpy with pressure for FM to NM transition in CeP
fter the FM to NM transition, the compound is still in B1 phase. of NM state is marked by the pronounced hybridisation between d 3p (P) bands as seen in the electronic structure profile 4 of NM state just after the transition. There will be a slight f to transfer also during the transition. The total DOS, contributions m Ce and P in NM state are plotted in Figures 4.15 to 4.17.

pression-induced B1 to B2 transition in CeP by total energy calculations

he total energies per unit cell in B1 (NM) and B2 phases were rch EOS. The total energies, pressures and enthalpies are plotted 4.18 to 4.20. The results such as transition pressure $P_t$, volume uiring the transition are shown in Table 4.5 and are found to be in ement with those reported by experiment (Leger 1993).

eger (1993), who performed the HPXRD experiments and reported a B2 transition in CeP, pointed out that the Hill's criterion (Hill not be applied to the volume behaviour of cerium compounds under n order to test the criterion, the Ce-Ce distances were calculated ing TBLMTO method and are given in Table 4.6.

as seen in Table 4.6, Ce-Ce distance in NM phase remained above Thus, Hill theory is not suitable to be applied for the FM to NM induced by pressure in the case of CeP.

Generally, one cannot prove or disprove delocalisation from study only. A complementary study such as of optical, magnetic al properties is necessary to decide upon that issue. However, $et al$ (1992) pointed out that there is a case where a structural g gives strong indication to the occurrence of f-delocalisation. This se of the isostructural volume collapses under pressure. As
Electronic structure in NM state of B1 phase of CeP just after the magnetic transition
4.15 Total DOS of CeP in NM state of B1 phase just after the magnetic transition
Ce-projected DOS in NM state of B1 phase just after the magnetic transition
Fig. 4.17 P-projected DOS in NM state of B1 phase just after the magnetic transition
Fig. 4.18 Calculated total energies versus cell volume in B1(NM) and B2(NM) phases of CeP
Fig. 4.19 Equation of state for B1(NM) and B2(NM) phases of CeP. Experimental data points are from Leger (1993)
Fig. 4.20 Enthalpy as a function of pressure in B1(NM) and B2(NM) phases of CeP
Table 4.5
Results of pressure induced B1 to B2 transition in CeP

<table>
<thead>
<tr>
<th></th>
<th>Present study</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_r$ (GPa)</td>
<td>18.5</td>
<td>19</td>
</tr>
<tr>
<td>$\Delta V/V_0$ (%)</td>
<td>11.89</td>
<td>10.5</td>
</tr>
<tr>
<td>B in B2 phase (GPa)</td>
<td>96.15</td>
<td>-</td>
</tr>
<tr>
<td>Case</td>
<td>Ce-Ce distance (Å)</td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>--------------------</td>
<td></td>
</tr>
<tr>
<td>Hill limit for Ce</td>
<td>3.40</td>
<td></td>
</tr>
<tr>
<td>In FM state at ambient pressure</td>
<td>4.185</td>
<td></td>
</tr>
<tr>
<td>In NM state just after transition</td>
<td>3.884</td>
<td></td>
</tr>
<tr>
<td>In B2 phase just after transition</td>
<td>3.233</td>
<td></td>
</tr>
</tbody>
</table>
mentioned in section 4.1.2, Jayaraman et al (1976) reported that, in CeP, there is an isostructural volume collapse of 8% around 9GPa.

The total DOS in B2 phase just after the transition is plotted in Figure 4.21.

4.3 PRESENT STUDY ON CeSe

4.3.1 Non-spin polarized calculations for CeSe

Donni et al (1993) reported that the compound CeSe has a magnetic moment of 0.57 \( \mu_B \) only which is less than the value of 0.79\( \mu_B \) expected from the crystal field ground state doublet as in the case of CeP. A pressure induced magnetic transition is unknown in the case of CeSe. Hence, non-spin polarized calculations were performed on CeSe. The valence configurations of \( 6s^25d^14f^1 \) (Ce) and \( 4s^24p^4 \) (Se) were used. The R/W values of 1.314 (Ce), 1.01 (Se) and 0.705 (ES) were used in B1 phase and 1.08 (Ce) and 0.904 (Se) in B2 phase. The calculations were performed in a manner similar to that adopted for ThX described in Chapter 3.

4.3.2 Electronic structure of CeSe in B1 phase at ambient pressure

The electron dispersion curves of CeSe in B1 phase along the high symmetry directions are shown in Figure 4.22. The three bands around -0.4 Ry originate from the Se-4p states and are fully occupied. A chalcogen atom has 4 electrons in its p-orbital while a pnictogen has only 3 electrons in its p-orbital. This causes the p-derived bands of CeSe to sink far below \( E_F \) when compared to that of cerium pnictide. The bands dominating the hybridisation induced properties in the cerium chalcogenides are largely derived from 5d (Ce) states.
Fig. 4.21 Total DOS in B2 phase of CeP just after the structural transition
Fig. 4.22 Electronic structure of CeSe in B1 phase at ambient pressure
4.3.3  DOS in CeSe in B1 phase at ambient pressure

The total DOS of CeSe in B1 phase at ambient pressure is plotted in Figure 4.23. It depicts the following features

i) 4p (Se) states lie between -0.5Ry and -0.35Ry.

ii) There is a small pocket due to Ce-5d derived states in occupied region just below E_F and a broad feature of 5d (Ce) states in unoccupied region spread over the scale of the plot.

iii) The doublet is not resolved. It is in accordance with the view expressed by Lynch and Weaver (1987) that there is no evidence for second 4f peak in the case of cerium monochalcogenides. This is due to localised character of 4f electron.

All these features agree with the PES results of Gudat et al (1981). The non-zero value of N(E_F) in CeSe in B1 phase at ambient pressure indicates the metallicty of the compound. There has been a report of electronic structure calculations on CeSe at ambient pressure by Kioussis et al (1991) using LMTO method in WMT approximation. However, Kioussis et al (1991) treated the 4f level of Ce in core states and did not allow them to hybridise with band states. On the other hand, the present calculations with TBLMTO-ASA method were performed by including f electron of Ce in valence configuration thus allowing hybridisation between f and d states of Ce.

4.3.4  EOS studies for pressure-induced B1 to B2 transition in CeSe

The total energies, obtained for B1 and B2 phases at different cell volumes, were fitted to Birch EOS. The results are given in Table 4.7 and
Fig. 4.23 Total DOS of CeSe in B1 phase at ambient pressure
Table 4.7
Results of B1 to B2 transition in CeSe under pressure

<table>
<thead>
<tr>
<th></th>
<th>Present study</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_t$ (GPa)</td>
<td>16.46</td>
<td>18.0</td>
</tr>
<tr>
<td>$\Delta V/V_0$ (%)</td>
<td>9.7</td>
<td>9.0</td>
</tr>
<tr>
<td>$B_0$ (GPa) in B1 phase</td>
<td>67.06</td>
<td>76 ± 4</td>
</tr>
<tr>
<td>$a_0$ (Å)</td>
<td>5.8439</td>
<td>5.9757</td>
</tr>
<tr>
<td>$B$ (GPa) in B2 phase</td>
<td>87.94</td>
<td>-</td>
</tr>
<tr>
<td>Ce-Ce distance (Å) in B1 phase at ambient pressure</td>
<td>4.234</td>
<td>4.24</td>
</tr>
</tbody>
</table>
a good agreement is found with experiment (Leger 1993). The total energies, pressure-volume relation and enthalpies as a function of pressure are plotted in Figures 4.24 to 4.26. Scholosser and Ferrante (1991) reported that the application of 'Universal Equation of State' (UEOS) (Vinet et al 1989) applied to CeSe gives $B_0 = 90.67$ GPa. This indicates that Birch EOS used in the present studies gives better value of $B_0$.

The DOS histogram of CeSe in the high pressure B2 phase are plotted in Figure 4.27.

4.4 PRESENT STUDY ON CeTe

4.4.1 Method of calculation for CeTe

CeTe has a small magnetic moment of 0.3 $\mu_B$ (Ott et al 1979) and the electronic structure calculations by Kioussis et al (1991) placed the compound on the border line between the magnetic and non-magnetic behaviour. Hence, non-spin polarized calculations were performed at 512 K$^3$-points in the entire Brillouin zone in both B1 and B2 phases. The R/W values used are 1.284 (Ce), 1.057 (Te) and 0.704 (ES) in B1 phase and 1.0 (Ce) and 1.0 (Te) in B2 phase.

4.4.2 Electronic structure of CeTe in B1 phase at ambient pressure

The electron dispersion curves (bands) of CeTe in B1 phase at ambient pressure are given in Figure 4.28 along high symmetry directions in the BZ. The overall profile of the band structure is similar to CeSe in B1 phase. However, the 5s (Se) states lie below -1 Ry and are not plotted in this diagram. The valence band region is mostly by the 5p (Te) derived bands which lie between -0.2 Ry and -0.4 Ry. In the conduction band regime, there is hybridisation between 4f (Ce) and 5d (Ce).
Fig. 4.24 Calculated total energies at different cell volumes in B1 and B2 phases of CeSe
Fig. 4.25 Equation of state of CeSe. Experimental data points are from Leger (1993)
Fig. 4.26 Enthalpy as a function of pressure for the B1 to B2 transition in CeSe
Fig. 4.27 Total DOS of CeSe in B2 phase just after the transition
Fig. 4.28 Electronic structure of CeTe in B1 phase at ambient pressure.
4.4.3 DOS of CeTe in B1 phase at ambient pressure

The total DOS histogram of CeTe in B1 phase at ambient pressure is shown in Figure 4.29. The overall profile of the DOS of CeTe is similar to CeSe.

The DOS histogram depicts the following features:

i) 5p-like bands in valence band region lie below E_F between -0.4 and -0.3 Ry,

ii) one prominent 4f peak with a satellite peak just above E_F as in CeSe in B1 phase.

iii) a broad feature due to 5d (Ce) spanning over the region from -0.18 Ry and extending over the scale of the plot.

These features agree well with the report of Gudat et al (1981) and Lynch and Weaver (1987). In case of CeTe, Kioussis et al (1991) performed calculations using LMTO within WMT approximation at ambient pressure with 4f (Ce) in core states, thus not allowing for hybridisation effects. But, the present TBLMTO-ASA calculations treated f electrons to be in the valence configuration only.

4.4.4 EOS studies on CeTe for the study of B1 to B2 transition under pressure

The total energies in B1 and B2 phases were fitted to Birch EOS in order to calculate transition pressure P_t, volume reduction during the transition ΔV/V_0, bulk modulus B_0 in B1 phase lattice constant a_0 at ambient pressure and the bulk modulus B in B2 phase at the transition pressure which are indicated in Table 4.8. The results are in general agreement with Leger (1993).
Fig. 4.29 Total DOS of CeTe in B1 phase at ambient pressure
Table 4.8
Results of B1 to B2 transition in CeTe under pressure

<table>
<thead>
<tr>
<th></th>
<th>Present study</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_t$ (GPa)</td>
<td>15</td>
<td>8</td>
</tr>
<tr>
<td>$\Delta V/V_0$ (%)</td>
<td>7.6</td>
<td>8.5</td>
</tr>
<tr>
<td>$B_0$ (GPa)</td>
<td>72.13</td>
<td>76 ± 4</td>
</tr>
<tr>
<td>$B$ (GPa)</td>
<td>71.40</td>
<td>-</td>
</tr>
<tr>
<td>$a_0$ (Å)</td>
<td>6.1709</td>
<td>6.3449</td>
</tr>
</tbody>
</table>
The error in the calculation of $a_0$ was found to be 2.7%. The total energy as a function of cell volume, pressure-volume relationship and enthalpy at various pressures are plotted in Figure 4.30 to 4.32. As the anion-size increases from Se to Te, one would expect the transition pressure of CeTe to decrease when compared with CeSe and the same trend is expected in the values of $B_0$ and $\Delta V/V_0$ between the two compounds. This trend has been established by the present TBLMTO-ASA calculations. The DOS of CeSe in B2 phase at transition pressure is plotted in Figure 4.33. The Fermi energy, DOS at Fermi energy and 1-NOS in B1 and B2 phases at different pressures in CeTe are given in Table 4.9. These results indicate that there is no appreciable transfer of electrons during the phase transition.

4.5 BULK MODULI OF CeX (X=P, Se, Te)

The bulk moduli of the cerium monochalcogenides and cerium monopnictides vary linearly with $(1/V_0)$ (where $V_0$ is the volume of the unit cell) as plotted in Figure 4.34.

The cerium compounds have generally a lower bulk modulus $B_0$ than the corresponding lanthanum ones. For example, a comparison between the thorium monopnictides ThX (X=P, As, Sb) studied in Chapter 3 and the CeX (X=P, Se, Te) is made in Table 4.10.

Leger (1993) pointed out that, at the crystallographic B1 to B2 transition, the increase of the cerium radius will have a value of 0.12Å which is the same as the increase in Ce-X distance by 0.12Å only. Leger (1993) observed that in the case of CeP this increase was actually observed. But in other cases, such as CeTe, the Ce-X distance decreases by a value less than 0.12Å.
Fig. 4.30 Calculated total energies versus cell volume in B1 and B2 phases of CeTe
Fig. 4.31 Pressure-volume relationship for CeTe. Experimental data points are from Leger (1993)
Fig. 4.32 Enthalpy as a function of pressure in CeTe
Fig. 4.33 Total DOS of CeTe in B2 phase just after transition
Table 4.9

Fermi energy, density of states and partial number of states in B1 and B2 phases of CeTe at various pressures

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pressure</th>
<th>$E_F$ (Ry)</th>
<th>$N(E_F)$ (Ry/f.u.)</th>
<th>1-NOS (states/f.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ce</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>s</td>
</tr>
<tr>
<td>B1</td>
<td>Ambient</td>
<td>-0.076</td>
<td>1.08</td>
<td>0.36</td>
</tr>
<tr>
<td>B2</td>
<td>Just below $P_t$</td>
<td>0.019</td>
<td>1.11</td>
<td>0.36</td>
</tr>
<tr>
<td>B2</td>
<td>At $P_t$</td>
<td>-0.042</td>
<td>88.2</td>
<td>0.31</td>
</tr>
</tbody>
</table>
Table 4.10

Calculated values of bulk moduli of thorium and cerium binaries at ambient pressure

<table>
<thead>
<tr>
<th></th>
<th>AX</th>
<th>ThX</th>
<th>CeX</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>P</td>
<td>As</td>
<td>Sb</td>
</tr>
<tr>
<td>B₀(GPa)</td>
<td>137</td>
<td>118</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P</td>
<td>Se</td>
</tr>
<tr>
<td></td>
<td>59.49</td>
<td>67.06</td>
<td>72.13</td>
</tr>
</tbody>
</table>
Fig. 4.34 Ambient bulk modulus as a function of ambient cell volume in the cases of CeP, CeSe and CeTe.
4.6 SUMMARY OF RESULTS

The effect of pressure on rock salt type, cerium compounds CeP, CeSe and CeTe was investigated by means of first principles electronic structure calculations. In all the compounds, the Ce 4f electron is treated in valence configuration, thus allowing for hybridization effects in the band calculations. The pressure induced phase transitions were studied by means of total energy calculations using TBLMTO - ASA method and the salient features of the results are given below:

i) The transition from FM to NM state in CeP was found to occur around 3.59 GPa.

ii) CeP was found to undergo a structural transition from B1 phase to B2 phase around 18.5 GPa.

iii) The transition pressure for B1 to B2 transformation in CeSe was calculated to be 16.46 GPa.

iv) CeTe had shown the structural transition from B1 to B2 phase under a pressure of 15 GPa.

v) Spin-polarized ferromagnetic band structure for CeP at ambient pressure was given for the first time.

vi) Theoretical estimates of bulk moduli and lattice constants were provided for B2 phases of CeP, CeSe and CeTe for which experimental values are not available in literature.

vii) The band structures and total DOS and atom projected DOS histograms were calculated for all the 7 phases, namely, FM (B1), NM (B1), B2 of CeP; B1 and B2 of CeSe and B1 of B2 of CeTe.
viii) PES reports are available for all the three compounds in literature and were used to compare the present DOS results. However, experimental result of spin-polarized PES would be desirable for CeP. CeP showed clear double peaks for 4f features just above $E_F$ in its DOS. On the other hand, there is only a satellite peak associated with a prominent 4f peak just above $E_F$ in CeSe and CeTe. These results are in good agreement with experiments and previous calculations.

ix) The value of magnetic moment was calculated by ab-initio band theory to be 0.679$\mu_B$ for CeP. Hill's criterion was found to be invalid for the FM to NM transition in CeP.

x) The bulk moduli of the three compounds vary inversely as a function of unit cell volume.

xi) The results indicated that CeP has slightly itinerant f electron while CeSe and CeTe have highly localised f electrons.

xii) All the three compounds were found to be metallic.

Okayama et al (1993) stated that the origin of the electronic transition in CeP is uncertain and information on Fermi surface at the transition pressure would be desirable. Kasuya et al (1993) stressed the importance of the purity and stoichiometry of the low carrier compounds such as CeP for interpretation of results.

On the whole, the present calculations established that cerium compounds can be treated satisfactorily by one - electron theory for investigating the pressure - induced magnetic and structural phase transitions.