CHAPTER 6

CONCLUSIONS

Self-consistent total energy calculations employing TBLMTO-ASA method together with Birch equation of state studies were used to study the pressure-induced phase transitions in ThX (X = P, As, Sb), CeX (X = P, Se, Te) and NpX (X = As, Te).

The total energies are computed for the two phases (B1 and B2) as a function of cell volume by TBLMTO method and fitted to Birch equation of state. From the computed enthalpies the transition pressures are computed for ThP, ThAs and ThSb. The transition pressures (26.6, 26.2 and 12.5 GPa) are in good agreement with the experimental results. In addition, the bulk modulus in the two phases, lattice parameter and volume collapse are also obtained and compared with the available results.

Spin and non-spin polarized calculations are performed on CeP to obtain the total energies in the B1 phase. The total energies are fitted to Birch equation of state. From this study, it is found that CeP undergoes a transition from FM to NM state around 3.59 GPa, which is in agreement with the experimental observation. It is observed that there is a gradual transfer of f-like electrons from spin-down to spin-up states under pressure. At a volume compression of around 0.8V₀ corresponding to a pressure of 3.59 GPa, populations in the spin-down and spin-up f-states become nearly equal which signifies a transition from FM to NM state. The DOS histogram exhibited a double peak structure due to 4f electrons of Ce which are in agreement with PES results and other theoretical reports. In addition, the
ground state properties like bulk modulus, lattice parameter are also obtained and compared with available results.

Similar calculations on NpAs and NpTe indicated the transition pressures to be 19.8 and 10 GPa respectively.

The following conclusions can be drawn from these results.

i) The LDA formalism was found to yield the ground state properties like lattice parameter, transition pressure and bulk modulus for ThX (X = P, As, Sb) and CeSe and CeTe. The LSDA framework explained the pressure induced phase transitions in CeP, NpAs and NpTe well.

ii) The magnetic moment for CeP calculated by LSDA is in close agreement with experimental report. This may be due to the fact that the 4f level in CeP contains one electron only. On the other hand, the magnetic moments of NpAs and NpTe are slightly over estimated due to the higher population in 5f level of Np. An overall examination of the results indicates that the spin-orbit effects which were not taken into account in the calculation have no or little role to play in a study concerned with structural properties.

iii) The origins of the mechanisms that drive the compounds to B2 phase from B1 phase can be commented upon. In the case of ThX (X=P,As,Sb), CeSe, CeTe, NpAs and NpTe, the pressure-coordination rule is found to be applicable. That is, the compound remains in B1 state with coordination number 6 over the pressure range in which the ratio of cation to anion radius remains between 0.42 and 0.71. The compound goes to B2 phase with a coordination number 8 at the transition pressure of the compound. Hill's theory proposed for magnetic phase transitions in the compounds of
cerium, uranium, neptunium and plutonium was based on an analysis in the values of Ce-Cc, or An-An distances. However, this criterion being more than two and half decades old, can be probed for its validity in the light of new experimental data on the phase stability of the compounds. Present electronic structure studies showed that the Hill's criterion is good for 5f electron compounds such as NpAs and NpTe but not for their 4f counterparts such as CeP. This is due to that CeP transforms into NM state from FM state despite that Ce-Ce distance remains above the Hill limit in NM phase.

iv) Only in the case of CeP there is evidence for the delocalisation which is the driving mechanism for the B1 to B2 transition. Thus, pressure induces itinerancy in CeP.

v) The variations in interatomic distances during the transitions are found to be playing a significant role in these compounds. Such analysis was carried out for 4 compounds viz ThAs, ThSb, NpAs and NpTe for which experimental results on interatomic distances are available. As a result of the transition, the distance between neighbouring metal atoms decreased and that between metal and non-metal atoms increased. This weakens the d-f / p-f interaction and leads to the geometrical effects resulting in the B1 to B2 transition.

vi) The bulk moduli $B_0$ of the compounds studied showed some systematics. While $B_0$ varies as a function of cell volume $V_0$ at ambient pressure for thorium monopnictides, it scales with the reciprocal of $V_0$ in the case of cerium compounds studied.

vii) The band structure given by the electron dispersion curves and histograms of DOS are similar in these compounds in their broad
features. However, the bands sink down in energy in the case of monochalcogenides as a chalcogen has one electron in its p state than pnictogen.

viii) The finer details of DOS in CeX compounds are of special interest as they exhibit double peaks due to 4f in case of CeP but not in the case of CeSe and CeTe. These results are in excellent agreement with the PES experiments reported by various authors.

ix) The present calculations took the hybridisation effects into account by treating 4f and 5f states in valence configuration while the previous calculations in the literature gave little importance to hybridisation in these compounds.

x) A few qualitative indications can be inferred from the present results on the question of applicability of various models to the compounds. A weak coupling (between f and d bands) model seems to be applicable for FM phase of CeP. The p-f mixing model explains the band profiles of the chalcogenides CeSe, CeTe. The d-f hybridisation may be governing the electronic structure in NpAs. Promotional picture, where an f electron is promoted to the conduction band increasing the metallic valence by one, is not found to be the case for the compounds studied. However, it is also pointed out that the calculation of a few band parameters such as mixing matrices is necessary to make concluding remarks on such models.

A few comments on future scope for research on these compounds can be made. Spin-polarized PES experiments on CeP, NpAs and NpTe would be highly useful for precise comparison of results on DOS by calculations. Fermi surface studies under pressure may settle the question of delocalisation in these compounds.