Summary and Future Scopes

The thesis has presented the *ab-initio* electronic band structure calculations to examine high pressure behaviour of binary systems LiH, MgO and LaN under pressure. Most of such binary systems have been reported experimentally/theoretically to undergo B1 to B2 structural transition under pressure [1-3]. In LiH and MgO, we also predict the B1 to B2 structural phase transition under pressure, however, unlike LiH and MgO, in LaN, the B1 phase is found to undergo a transition to lower symmetry B10 (which is a distortion of B2 phase) phase at ~ 25.8 GPa, which is in agreement with experimental observations of Schneider *et al* [4]. Further, we have predicted that the B10 phase will transform to B2 structure at pressures above 169 GPa, upon further compression. The occurrence of the low symmetry B10 structure before the stabilization high symmetry B2 phase has been explained by invoking the symmetry breaking mechanism. Apart from these theoretical studies, experimental shock compression study on elemental solid copper has also been presented in the thesis. The aim of this shock compression study was to determine the dynamic yield strength and spall strength of polycrystalline copper at strain rates of ~$10^4$/s. The main results of the studies conducted on these materials and presented in different chapters of the thesis are summarized below:

Total energy calculations on the binary system LiH, MgO and LaN have been carried out to investigate the possibility of B1 $\rightarrow$ B10 $\rightarrow$ B2 phase transition sequence under pressure. At ambient conditions, each of these systems exists in rocksalt type structure (B1 phase). For LiH and MgO, the theoretical analysis predicts the B1 to B2 (CsCl type structure) structural transition at a pressure of ~ 327 GPa and ~ 535 GPa, respectively, whereas for LaN, the B1 phase transforms to B10 (a tetragonal phase, which can be regarded as distortion of B2 phase) phase at ~ 25.8 GPa, in close agreement with
the experimental value of 22.8 GPa [4]. The B10 phase is found to be stable up to ~ 169 GPa and beyond this pressure the B2 phase becomes favorable over the B10 phase. The stability of the low symmetry tetragonal phase in LaN has been associated to symmetry breaking mechanism induced lowering of total energy.

Further, adding thermal corrections to the first principles 0K energies at various hydrostatic compressions, the 300K isotherm have also been determined. Apart from this, the pressure dependent elastic moduli for B1 phase have also been calculated for LiH, MgO and LaN. Various thermophysical properties such equilibrium volume, bulk modulus, its pressure derivative, Debye temperature, elastic constants and Gruneisen parameter at zero pressure have been derived from these calculations and compared with the available experimental data.

In LiH apart from static lattice calculations, the lattice dynamic calculations have also been performed up to ~ 150 GPa and phonon spectra have been determined as a function of pressure. The phonon frequencies for different modes at various Brillouin zone points have been obtained as a function of pressure and compared with the experimental data [5,6]. Additionally, unlike that predicted by Zhang et al. [7] on the basis of their lattice dynamic calculations, we do not find any attenuation in the TA(X) phonon mode at ~ 200 GPa. *In-situ* high pressure Raman measurements up to pressures more than 200 GPa will be required to resolve this discrepancy.

For MgO, apart from investigations under hydrostatic compressions, the calculations have been extended to determine the ideal [001] compressive and tensile strength under two uniaxial loading conditions, namely “uniaxial strain condition” and “uniaxial stress condition”. The compressive strength is determined to be ~ -283 GPa and -115 GPa, respectively, for the two conditions. The ideal tensile strength is determined be ~ 20 GPa and 11 GPa, respectively, for the two loading conditions. There are further
scopes to continue these kinds of studies in various other crystallographic directions such as [011], [111]. In addition to this the determination of ideal shear strength along different crystallographic directions of MgO single crystal is also an open question.

As far as prediction of crystal structure at high pressures in these binary solids is concerned only three structures B1, B2 and B10 have been taken for study, the possibility of any other high pressure structures may require testing of still more phases, specially for LiH and MgO, as there are no high pressure experiments on these materials up to the predicted B1 to B2 transition pressures. It is quite challenging to guess and perform total energy calculations for all the plausible structures to predict the high pressure phases of materials theoretically. For a new material (with only knowing the constituent atoms) without prior knowledge of its crystal structure, one has to carry out the total energy calculations as a function of pressure for all the possible candidate structures which may be the structures of analogous system or new structures guessed from chemical intuition. The plot of total energy versus pressure will show the structures which are lower in energy compared to other phases corresponding to particular compression and thereby the possibility of the stability of energetically higher structures can be cancelled out. In this way the ground state phase corresponding to the global minima as well as high pressure phases associated with the local minima and the corresponding structural transformation sequence with compression can be determined. But problem arises when some unexpected structure or hitherto unknown structure get stabilized at high pressure; as is the case for the high pressure B10 phase in LaN system. So, here, reliable structure prediction capabilities of computer simulation are necessary which will work without any prior knowledge, assumption or intuition of the system [8]. Simulated annealing [9-11], minima hopping [12] and metadynamics [13-15], evolutionary algorithm USPEX (Universal Structure Predictor: Evolutionary Xtallography) [16-18] etc. are some of the methods which have been applied in recent past to explore the stable crystal structure relaxing the randomly produced structures. These methods are implemented in the sophisticated simulation computer codes such as USPEX[19], CALYPSO[20], XtalOpt[21], to predict crystal structure.
Further, all these theoretical calculations are based on the DFT. Despite the improvements in various approximations in DFT, it has its own limitations. There are difficulties in using DFT to properly describe intermolecular interactions; charge transfer excitations; transition states, global potential energy surfaces and some other strongly correlated systems; and in calculations of the band gap of some semiconductors. The exchange-correlation potentials which are used in DFT calculations are not exact and these are some approximations to the true picture. This produces some inherent error in these calculations. The transition metals, the lanthanides, and the actinides has vacant inner orbital (the $d$- orbital and $f$- orbital are partially filled) and these atoms and their compounds are difficult to simulate theoretically and sometime give results which are away from the experimental observations.

In the experimental front, the yield strength and fracture strength of polycrystalline copper has been measured under both the quasistatic loading condition and high strain rate loading condition with strain rates $\sim 10^4/s$. The yield strength and fracture strength (maximum stress that the material can withstand before fracture) measured in quasistatic experiments is 0.13 GPa and 0.22 GPa, respectively. However, these quantities measured at strain rates of $\sim 10^7/s$ generated in plate impact experiments are 0.14 GPa and 1.32 GPa, respectively. These results suggest that the yield strength of copper shows marginal increase with increasing strain rates up to $10^4/s$, whereas the fracture strength increases by $\sim 6$ times as compared to that measured at quasi static condition. Further, the nanoindentation analysis of the as received and shock treated samples suggested that the effect of shock treatment is to increase the hardness of this material by $\sim 20\%$.

Finally, the plate impact experiments carried out in copper to generate compressions as well as tensions at high strain rates using the Gas Gun facility are quite difficult as the rise time of pressure is of order of few tens of nanoseconds and duration pressure pulse in the material is extremely small (a few microseconds). All the
measurements are to be completed successfully within this short time. In addition to this, the experiments are destructive in nature with most of the parts of the experimental assembly including various type of sensors need to prepared a fresh for each shot. This thesis reports the measurements of yield strength and fracture strength of polycrystalline copper under high strain rate conditions generated in shock wave experiments carried out using the gas gun facility. It will be interesting to perform similar investigations in single crystal copper subjected to shock loading along different crystallographic directions e.g. [100], [110] and [111], as above mentioned mechanical properties are expected to be dependent on the shock loading along a specific crystallographic axis.
Reference