

Computational condensed matter physics

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Abstract. In the high pressure laboratory at BARC, we are pursuing a program to study the behaviour of materials under static and dynamic pressures. Theoretical component has been an integral part for guiding and interpreting new experiments. The initial phase of such efforts was devoted to the development of equation of state models at arbitrary temperatures and matter densities. With the advent of diamond anvil cell device and the simultaneous provision for laser heating of the compressed samples for static high pressure studies, and with the improvements of the diagnostic techniques in dynamic shock methods, the focus of our studies switched over to the predictions and interpretations of phase transitions. Often these efforts have led to intense experimental studies and sometimes helped in resolving the controversies in data. We adopted the first principles electronic structure calculations for high pressure studies. Our work on the electronic topological transition in zinc led to many experimental and theoretical investigations. The results of electronic structure changes in similar metal cadmium shall be compared with existing understanding in Zn under pressure. Our studies on Nb and other compounds like intermetallics and borocarbides have revealed interesting electronic structure changes under pressure. However, the electronic structure based investigations of structural stabilities at high pressures involve tedious trial and error effort, which is avoided in the *ab initio* molecular dynamics simulations. The current status of our efforts in the use of this technique is illustrated with the example of quasicrystal based clusters.

Keywords. Pressure; electronic topological transition; equation of state.

1. Introduction

Pressure as a thermodynamic variable in condensed matter studies has become very important in recent past. In fact the research at high pressures has truly developed into an interdisciplinary area which has important implications for and in the areas of physics, chemistry, materials science, biology, engineering and technology. The main effect of pressure is to reduce the volume of a substance. Thus in some sense, it mimics the phenomena taking place during the cohesion of solids. Therefore significant changes are expected, and indeed found, in the electronic states, chemical bonding, and atomic packing of condensed matter (Jeanloz 1987; Mao and Hemley 1994).

In the high pressure physics laboratory at BARC we have been pursuing a program to investigate materials for their physical properties at high pressures with special emphasis on equation of state (EOS) and phase stability using both static and dynamic techniques (Godwal 1995; Chidambaram 1996; Sikka *et al* 1997). A brief mention of our past work on EOS will be made with the current trends in theoretical methods to study EOS and phase transitions. The introduction of linear methods in electron energy band theory and availability of supercomputers, or parallel processors as an alternative, have given boost to the computational physics. The current efforts are on the generalized gradient approximation (GGA) based

ab initio electronic structure calculations and molecular dynamics (MD) simulations. Our work on electronic structure will be illustrated in the present article, especially where our theoretical investigations have played important roles in the interpretation of experimental data, like resolving the discrepancies, understanding of the mechanism for the observed phase transitions [Th] and predictions and finding the cause of anomalies in physical properties [Zn, Cd, Nb, AuIn₂, YNi₂B₂C], etc. Finally, our simulations by *ab initio* molecular dynamics will be presented. These first principles MD simulations compared to band structure computations have a promise to avoid the tedious search of various structures for structural stability by trial and error in phase transition studies under pressure or temperature. We have employed both the orbital based (Car-Parrinello method) and density based *ab initio* MD simulations (Pearson *et al* 1993; Shah *et al* 1994; Smargiassi and Madden 1994) in our calculations. The current status of our efforts in the use of this technique is illustrated with the example of Al–Zn–Mg quasicrystal based systems like clusters and crystal approximants to investigate the crucial role played by glue atoms in propagating the icosahedral symmetry.

2. Equation of state (EOS)

One of the most important outputs of high pressure theory and experiments is the pressure–volume–temperature

relationship of materials termed the EOS, the utility of which for meaningful interpretation of physical and chemical phenomena at arbitrary temperatures and matter densities is well known (Chidambaram 1996; Sikka *et al* 1997). At extremely high temperatures or high pressures (for pressures in few hundreds of Megabars range), the various variants of statistical Thomas–Fermi–Dirac theories are adequate to generate the EOS (McCarthy 1965). For the pressures up to 1000 GPa we adopted the usual division of the internal energy and pressure into temperature independent and dependent contributions

$$E = E_c(V) + E_{\text{ion}}(V, T) + E_{\text{ex}}(V, T),$$

$$P = P_c(V) + P_{\text{ion}}(V, T) + P_{\text{ex}}(V, T).$$

Here the symbols c, ion and ex stand for cold (0 K), lattice thermal vibrations and electronic excitations, respectively. The zero degree isotherm is evaluated using density functional based electron band structure methods with the atomic numbers and crystal structure as input (Godwal *et al* 1983; Sikka *et al* 1997). The lattice vibration contribution in quasi-harmonic approximation is computed by Born–von Karman lattice dynamic theory and the electronic excitation term derived from low temperature expansions of Fermi–Dirac distribution function (Godwal *et al* 1983). The total energy and pressure evaluated using these equations are used in Rankine–Hugoniot relations to calculate the shock Hugoniot which represent the locii of all the points which can be reached by shocking a material from fixed initial conditions (Zel’dowich and Raizer 1967; Chidambaram 1996). Early on, we successfully calculated the shock Hugoniot equation of state of Al and were able to discriminate the two sets of shock data (Godwal *et al* 1979). These calculations were extended to many elements of interest for which the extensive shock data exist (Godwal *et al* 1983).

For the pressures in 1000 to 10000 GPa range, pressure and thermal ionization effects strongly controlled by atomic shell structure effects start dominating many physical properties. The orthogonality condition which keeps the core and conduction electrons apart also gets violated due to core ionization. The basic problem in this region is to obtain core ionization and core-conduction electron coupling and the resulting modified potential. For this difficult region which is known as ‘intermediate region’ in the literature the experimental data were sparse earlier and, in the absence of any existing theory, interpolation schemes were used between the experimental (pressures less than 1000 GPa) and high density Thomas–Fermi–Dirac region (McCarthy 1965). We approached this region from the solutions of the details of the ionization equilibrium by including the high density effects like pressure ionization, partition function cut off and lowering of the ionization potentials in Saha

ionization theory (Rouse 1971; Godwal 1983, 1995a, b). With new electronic charge and potential parameters the condensed matter theories were then employed for the calculation of shock Hugoniot EOS (Godwal *et al* 1981). In the absence of pressure and thermal ionization effects, this theory coincided with the model in the experimental region while in the high density region its predictions coincided with those of Thomas–Fermi–Dirac theories (McCarthy 1965). Many of the predictions made by this theory were later verified by the experiments (Volkov *et al* 1980; Godwal *et al* 1983, 1990).

3. Phase transitions

Pressure induced phase transitions have been the most important area of research with compression of about half easily achieved in most of the materials using the DAC. Hence the high pressure phase transitions have been extensively studied both theoretically and experimentally (Jayaraman 1983; Chidambaram 1996; Sikka *et al* 1997). The *ab initio* total energy calculations and first principles MD simulations have been going through rapid expansions during the last decade. The aim of these calculations have been to predict accurately structures and related ground state properties of solids without using any information from experiments. Hence they are ideally suited for the predictions of phase transitions, especially under the thermodynamic conditions not yet accessible to the laboratory experiments. We present below briefly some of our experimental and theoretical work on elemental solids (Th, Zn, Cd, Nb), and compounds (AuIn₂, and YNi₂B₂C) which emphasize the usefulness of the electronic structure calculations on identifying the underlying physical mechanism for the observed experimental phenomena, especially in the case of the electronic topological transitions (ETT) (Lifshitz 1960).

3.1 Elemental solids

3.1a *Thorium*: Thorium crystallizes in the face centred cubic (fcc) structure at ambient conditions. Vohra and Akella (1991) found that it undergoes fcc to body centred tetragonal (bct) structural phase transition around 100 GPa pressure. With the help of energy band structure calculations by the linear muffin–tin–orbital (LMTO) method (Andersen 1975; Skriver 1984; Christensen 1985), Rao *et al* (1992) studied the 5*f* band characteristic through the fcc-to-bct transition and found that the bottom of the band falls below the Fermi level (E_F) at the volume fraction of 0.6 (around 80 GPa pressure). It was thus established that the *f*-band occupation is central to this structural transition. It was also shown, by carrying out additional total energy calculations by restricting the LMTO expansion of the electron wave function up to angular momentum $l=2$ that Th is not spd-metal as

thought earlier, but it has contribution to bonding from the $5f$ band even at ambient pressure through hybridization. The exclusion of $l = 3$ term led to stabilization of the body-centred cubic (bcc) phase at ambient pressure, which continued to remain stable to the volume fraction of $V/V_0 = 0.4$. These findings were later re-confirmed by Johansson and coworkers (1995) using full potential (FP-LMTO) calculations. Our theoretical isotherms with and without inclusion of $5f$ electrons are compared in figure 1 with the experimental data of Vohra and Holzapfel (1993). The observed fcc structure and the EOS are consistent with the view that Th should be considered as spdf-metal belonging to heavier actinide group (Pa–Pu), and not as spd-transition metal belonging to the same group as Ti, Zr and Hf (Rao *et al* 1992; Sikka *et al* 1997).

3.1b Zinc and cadmium: Zinc and cadmium are unique among hcp metals, having unusually large c/a axial ratio at ambient condition ($c/a = 1.856$ and 1.886 , respectively). The large deviation from the ideal c/a value of 1.633 causes anisotropies in many of their physical properties, some of which are attributed to the changes in the Fermi surface (FS). Both these metals exhibit giant Kohn anomaly (GKA) at ambient pressure (Kohn 1959; Kagan *et al* 1983). The application of pressure alters the FS topology, transport and other physical properties, and have led to intense theoretical and experimental studies of these materials under compression (Meenakshi *et al* 1992; Potzel *et al* 1995; Takemura 1995; Morgan *et al* 1996).

The anomaly in the variation of the axial ratio and electrical resistance of Zn with pressure was first reported

around 7 GPa (Lynch and Drickamer 1965), but a later experiment could not find the anomaly up to 32 GPa (Schulte *et al* 1991). Due to this controversy, we calculated the change in the axial ratio for Zn under pressure from the first principles total energy calculations based on the LMTO method (Meenakshi *et al* 1992). These calculations showed that volume dependence of the axial ratio changes slope around the relative volume of 0.92, and the details of the electronic band structure revealed that the anomaly is related to the appearance of maximum in the density of states (DOS) at E_F . Takemura (1995) later observed that the volume dependence of the c/a ratio changes slope at $V/V_0 = 0.893$. Also Potzel *et al* (1995) have recently detected an anomaly in the Mössbauer spectrum of Zn at 6.6 GPa and 4.2 K. Their scalar-relativistic linear augmented plane wave calculations verified that the anomaly is related to the topological change of the FS around the L symmetry point of the Brillouin zone (BZ) and at this pressure it leads to the destruction of the GKA (Potzel *et al* 1995; Steiner *et al* 1996). Moreover, the anomaly observed in the recent neutron inelastic scattering experiments has also been interpreted in the similar way (Morgan *et al* 1996). However, the occurrence of the anomaly in Zn in the high pressure angle-dispersive X-ray diffraction (ADXRD) experiments (Takemura 1995) at the $\sqrt{3}$ value of (c/a) , for which significant degeneracies in the reciprocal lattice vectors occur for the hcp structure, cast doubts on ETT as the sole cause of the anomaly. In order to remove this ambiguity we undertook studies on similar metal Cd as it also exhibits GKA at normal pressure. The details are reported elsewhere (Godwal *et al* 1997c), and we briefly summarize the key results below.

We employed the same theoretical formalism as used for Zn (Meenakshi *et al* 1992) and predicted two anomalies in Cd (see figure 2). The first anomaly is around $V/V_0 = 0.95$ although it is not observed in the experimental data (Lynch and Drickamer 1965; Schulte *et al* 1991; Takemura 1997). However, around this pressure, our measurement of thermoelectric power (TEP) showed a broad maximum (Vijayakumar *et al* 1997), and based on our LMTO calculations, this corresponds to appearance of additional K-point needles in the FS (third zone electron sheet). The second anomaly occurs at $V/V_0 = 0.85$ and is also seen in the recent experimental data of Takemura (1997), and also in the earlier data of Lynch and Drickamer (1965), but not in the work of Schulte *et al* (1991). However, at this pressure, there is no ETT to destroy the GKA although theoretical calculations support the presence of ETT in Zn (Meenakshi *et al* 1992; Potzel *et al* 1995; Steiner *et al* 1996). This reveals that electronic structure of Cd under pressure is different from that of Zn, which is in contrast to the currently speculated view that the FS topologies of Zn and Cd under pressure are identical. Our calculations show a continuous and slow transfer of electrons from d -like to s -like states

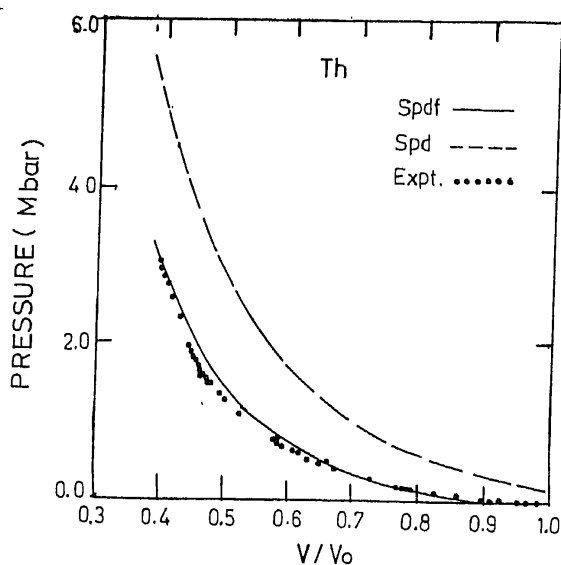


Figure 1. 0 K isotherm of thorium. The curve referred as spd is for the case when f -orbital is suppressed in the calculation. Experimental data (Vohra and Holzapfel 1993) are shown for comparison.

under compression, and the turn-over in the $4d$ partial pressure contribution to bonding from negative (filled band) to positive around this anomaly due to increase in the $d-d$ overlap. Moreover, when we analyzed using universal EOS, the experimental data on Zn (Takemura 1995) and Cd (Takemura 1997), it showed deviations from linearity in Zn at the observed anomaly, and in Cd around the first anomaly. These findings are consistent with the view that the universal EOS should show deviation from linearity whenever an electronic transition occurs (Sikka 1988). Note that our prediction of two anomalies in Cd is consistent with the later FPLMTO-GGA calculations of Novikov *et al* (1997) who find anomalies in the c/a ratio at $V/V_0 = 0.95$ and 0.85 .

Uncertainties still exist in Zn regarding ETT as the cause of anomaly in c/a variation with pressure. Based on the recent LDA electronic structure calculations, Fast *et al* (1997) claim that the electronic states around the K-point of the BZ are responsible for the observed anomaly. Also, Novikov *et al* (1997) based on the FPLMTO-GGA calculations find the anomalies in the pressure dependence of c/a near experimental values for both Zn and Cd, and also obtain similar anomalies in electric field gradient. However, their studies do not support the destruction of GKA due to ETT. On the experimental side, the recent high pressure room temperature neutron inelastic experiments of Klotz *et al* (1998) up to 9.4 GPa, do not support the ETT and destruction of GKA. However, the need of the hour is to carry out the high pressure experiments at very low temperatures to reduce the smearing of the Fermi distribution function which dampens the anomalies due to ETT. It will be ideal to

carry out the high pressure Fermi surface measurements at low temperatures to identify directly the possibility of ETT under pressure in Zn.

3.1c Niobium: The group VB transition metals such as vanadium, niobium and tantalum are particularly interesting because of their superconducting properties, and for the anomalies in the phonon dispersion curves. Fermi surface topologies of the VB group transition metals were studied by Mattheiss (1970) using non self-consistent augmented plane-wave method. The effect of pressure on the electronic structure of niobium was first studied by Anderson *et al* (1981) by the self-consistent augmented plane-wave method. They found that Fermi surfaces of Nb at 6 GPa, and at 26 GPa are similar. Recent superconducting transition temperature (T_c) measurements under compression up to megabar pressures (Struzhkin *et al* 1997) using highly sensitive magnetic susceptibility technique show two anomalies in Nb, one near 5 GPa and the other in the 60–70 GPa range. However, the high pressure static and dynamic experiments of Akahama *et al* (1991) show that the ambient pressure body centred cubic (bcc) structure of Nb is stable up to 170 GPa. Hence any change in T_c may mainly be due to changes in the electronic structure. Motivated by these observations, we have carried out the electronic structure calculations of Nb in the bcc phase as a function of pressure.

We employed the first principles full potential linear muffin tin orbital (FPLMTO) method as per Methfessel's (1988) version. Hedin-Lundquist (1971, 1972) local density approximation (LDA) was employed.

The calculated electronic band structure at normal pressure is similar to those available in the literature (Mattheiss 1970; Anderson *et al* 1981). Accordingly, the energy bands of Nb are similar to those of other group VB transition metals, V and Ta, the main differences being the width and position of the d bands, and the $s-d$ band separation. We have calculated the total energies by changing atomic volume from 133.5 a.u.^3 to 85 a.u.^3 . The equation of state (EOS) of Nb obtained by using these total energies (not shown here and the details will be published elsewhere, (Palanivel *et al* 1999)) agrees well with the experimental data of Akahama *et al* (1991) as well as with shock data (Kinslow 1970). The details of electron energy bands have also been studied at different compressed volumes up to the volume corresponding to about 60 GPa pressure.

To explain the observed anomaly in T_c of Nb at 5 GPa, Struzhkin *et al* (1997) very recently have suggested that it is due to change in the Fermi surface topology due to shift of a band near Fermi energy (E_F). According to them, the two third zone Fermi surface sheets may touch to form a neck along $\Gamma N(\Sigma)$ direction at ambient pressure, which means that the minimum of the third band along Σ is at higher energy than E_F . They then attribute the T_c anomaly to the disappearance of this neck as the d -band lowers

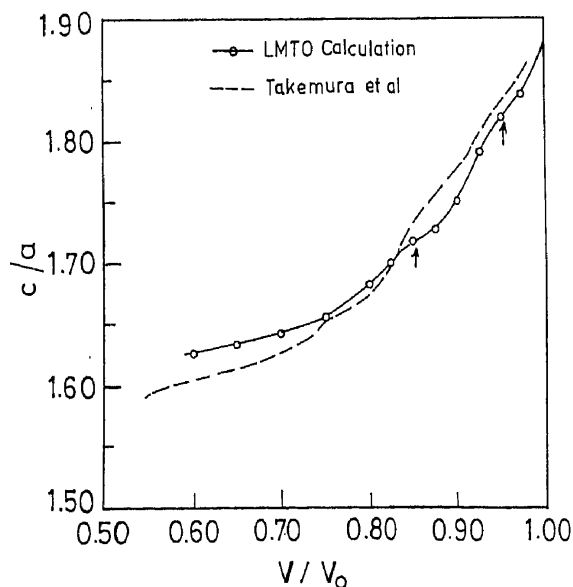


Figure 2. Comparison of the calculated (c/a) variation with relative volume compression (V/V_0) and the experimental data (Takemura 1997) for cadmium.

with respect to E_F under compression, and touches it at 5 GPa. The present FPLMTO calculations show that the minimum of the relevant band (see figure 3a) is below, E_F , and thus the necks do not exist in Nb at normal pressure. We also found that the shift of this band with respect to E_F along Σ is relatively small in the pressure range of 0 to 5 GPa. Note that there is no other experimental evidence of these necks in Nb.

Thus we conclude that in contrast to the suggestion of Struzhkin *et al* (1997), the experimentally observed anomaly in T_c at 5 GPa is not due to ETT. This anomaly may be due to uniaxial stresses in the sample, which is also the alternative suggestion given by Struzhkin *et al* (1997). Note that the d energy level Γ_{25}' crosses E_F at a volume compression V/V_0 of about 0.8 (see figure 3b), which corresponds to about 60 GPa pressure. This ETT is in good agreement with the second anomaly in T_c observed experimentally (Struzhkin *et al* 1997) in the 60–70 GPa pressure range, and supports the interpretation of Struzhkin *et al* (1997).

3.2 Intermetallics

3.2a $AuIn_2$: We are carrying out a program to investigate intermetallics for their high pressure behaviour by using both theory and experiments. In particular, our interest in $AuIn_2$ is due to the observed anomaly of a change in the slope of the melting curve near 3 GPa pressure (Storm *et al* 1996), which generally indicates a phase transition. As many of the halides and oxides pertaining to the geophysical interest occur in the same structure, phase transformation studies of $AuIn_2$ under compression are useful to give indications of high pressure phases of these oxides and halides. Motivated by these factors, we carried out the ADXRD (with imaging plate), electrical resistivity, and TEP measurements on

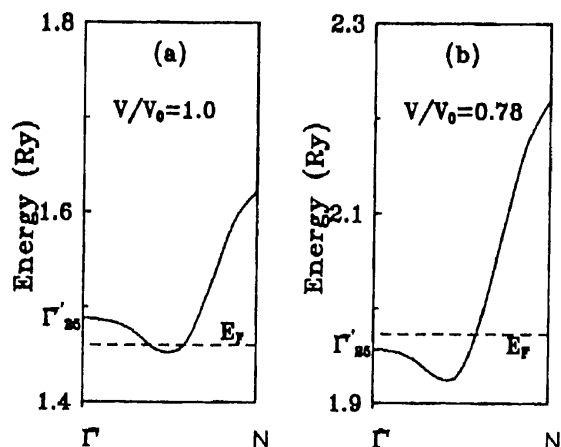


Figure 3. Electron energy band along $\Gamma N(\Sigma)$ in Nb at (a) ambient pressure, and (b) at volume compression V/V_0 of 0.78. The broken lines denote the respective Fermi levels (E_F).

$AuIn_2$ (Godwal *et al* 1997a). The electrical resistivity is structureless, though decreases rapidly and the sign of the slope changes near 3 GPa, whereas the TEP increases rapidly near 2 GPa pressure. But, the ADXRD measurements rule out the structural changes up to 8 GPa. Thus the isostructural electronic structure changes appear to be responsible for the observed anomalies. For further insight, we carried out the LMTO calculations in the CaF_2 structure under compression. The details of the calculations were presented elsewhere (Godwal *et al* 1997a). A significant result obtained is the crossing of an extremum (maximum) of an electron energy band through Fermi level (E_F) as pressure varies (see figure 4a). Also, our universal EOS (Rose *et al* 1984) estimates show deviations from linearity in the 2–4 GPa pressure range (figure 4b) indicating electronic transition (Sikka 1988). Thus our electronic structure calculations reveal that the anomalies in the melting curve and the transport properties are due to ETT.

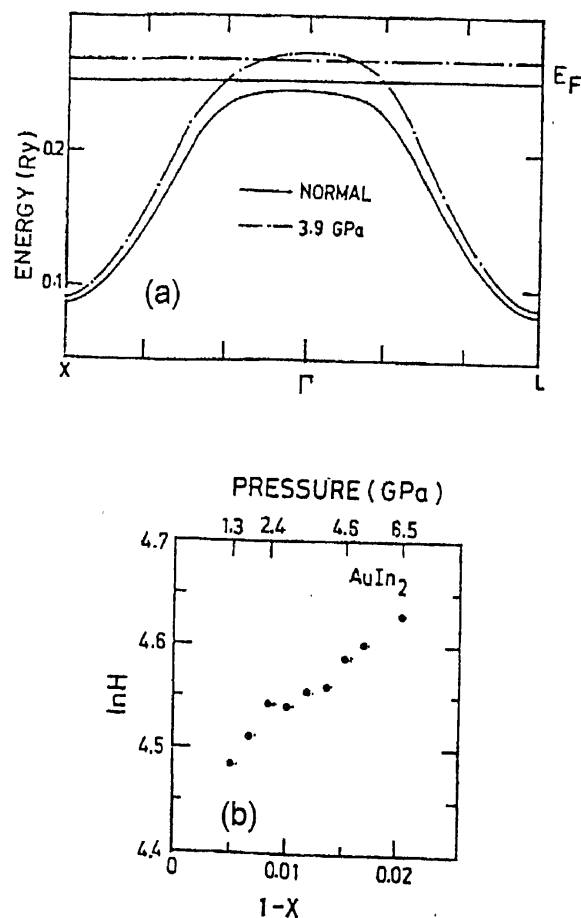


Figure 4. (a) Shift of the energy band maximum at $\Gamma_{2'}'$ across the Fermi level (E_F) from the occupied to the unoccupied region under pressure; (b) the universal equation of state for $AuIn_2$ by electronic structure calculations. Departure from linearity in the curve occurs in the pressure range of 2 to 4 GPa. The pressure values at a few compressions are shown.

3.2b YNi_2B_2C : The new family of borocarbide superconductors have been extensively investigated recently (Mazumdar *et al* 1993; Cava *et al* 1994; Nagarajan *et al* 1994; Meenakshi *et al* 1996). Some of their distinct properties are: short B–C separation (1.46 Å), near ideal tetrahedral coordination of Ni and B atoms, and short Ni–Ni separation (2.45 Å), i.e. shorter than in Ni-metal. Also, the variation of their superconducting transition temperature (T_c) with pressure is interesting as most of the lanthanide borocarbides show linear dependence, with the slope changing sign between Lu and Tm in the series. The high pressure electronic structure studies are desirable as they might identify the features in the electronic spectrum which lead to these systematic changes in T_c with pressure. Also, as these changes affect the transport properties like electrical resistance and thermoelectric power (TEP), we also carried out these measurements under pressure. Moreover, we measured the ADXRD at high pressures to look for any structural change, and to obtain the EOS. The theoretical calculations were carried out by the tight binding LMTO (TB-LMTO) (Andersen and Jepsen 1984) and the FPLMTO methods (Wills and Cooper 1987).

We found rapid decrease in resistivity with pressure up to about 2 GPa, and a smooth weak pressure dependence thereafter up to 8 GPa, suggesting absence of structural transition. But the TEP measurements showed a peak in the 2–4 GPa pressure range, which indicates significant changes in the electronic DOS at E_F . Absence of structural transition in this pressure region was further confirmed by our ADXRD measurements. We observed no structural phase change up to 16.4 GPa, and YNi_2B_2C was found to retain its ambient phase; the carbon filled variant of $ThCr_2Si_2$ type tetragonal structure (space group $I4/mmm$). The EOS obtained from the lattice parameter measurements with the ADXRD set up is shown in figure 5. The measured (P – V) data compare reasonably well with our TB-LMTO calculations. Both the experimental P – V data and the theoretical estimates yielded the bulk modulus of 200 GPa. Also shown in figure 5, are the EOS curve from the FPLMTO (Meenakshi *et al* 1998) calculations which agree better with the experimental data. Moreover, the FPLMTO calculations on other borocarbide $LuNi_2B_2C$ also give almost coinciding curve with that of YNi_2B_2C . Our calculations also showed that the boron component of DOS is reduced at E_F on compression, apart from the usual band broadening effect, as the peak in the vicinity of E_F moves away from it (see Meenakshi *et al* 1998, for details). This feature would predict a fall of T_c with pressure in YNi_2B_2C (Mattheiss *et al* 1994). However in the pressure range up to 2 GPa, the change in the boron component of DOS at E_F , as obtained by our calculations, is so small that almost no change in T_c is expected. This is consistent with the available experimental data (Schmidt and Braun 1994; Alleno *et al* 1995).

4. *Ab initio* molecular dynamics

The first principles electronic structure based total energy calculations can determine the most stable structure at high pressures from the chosen candidate structures, but might fail to locate one of the lowest free energy, as the search is only by trial and error. The MD simulations can locate the structure giving global minimum energy by employing standard techniques like simulated annealing (Kirkpatrick *et al* 1983). However, the bonding characteristics generally could change drastically under pressure, and hence the *ab initio* MD simulations would be preferred. But the coupled density functional MD calculations based on Kohn-Sham equations (Kohn and Sham 1965) demand unmanageable computer power for complex systems, as one has to carry out the calculations for unoccupied electron states though not used anywhere in the self-consistent process. This drawback reduces the efficiency of the computations by at least an order of magnitude. Alternatively, the direct minimization of total energy keeps track of occupied electron orbitals only. Starting with any arbitrary set of trial electron orbitals, one can iteratively upgrade them to get the minimum of total energy, and the set of orbitals at the minimum energy represents the Kohn-Sham solution. Further, to study the dynamics of ions, their positions can be included as additional variables and the structural relaxation can be treated as a global minimization problem. Car and Parrinello (1985) treated coefficients of electron wavefunctions and ionic positions as though they formed a dynamical system and the corresponding phase space is explored by MD simulations. The constant pressure (variable cell) simulations by this method can identify the high pressure phase transitions in solids (Focher *et al* 1994). We are adapting these methods for high pressure studies. The current status of our efforts in the use of this

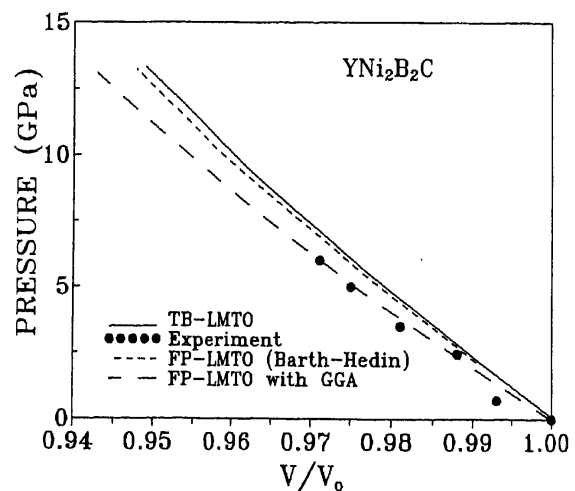


Figure 5. Equation of state for YNi_2B_2C . The curve for $LuNi_2B_2C$ by the FPLMTO calculations coincides with the dashed curve and hence is not shown separately.

technique will be illustrated below by a few examples at ambient pressure by constant volume MD simulations. We have employed both the orbital based (Car and Parrinello 1985) and the density based (Pearson *et al* 1993; Shah *et al* 1994; Smargiassi and Madden 1994) methods in our *ab initio* MD simulations, using the standard atomic pseudo-potentials of Bachelet-Hamann-Schluter (Bachelet *et al* 1982).

4.1 Orbital based *ab initio* MD

The first method (Car-Parrinello method) is based on the plane wave expansion of valence electron orbitals. We have implemented this orbital based *ab initio* MD scheme for constant volume simulations on BARC parallel processor ANUPAM. The program employs frequent transformations between reciprocal and direct spaces. Hence the direct and inverse fast Fourier transforms (FFTs) are parallelized (Jagadeesh *et al* 1996). By employing assembler coded FFTs, we get a speed-up of about 4 in the 8-node machine. We have applied parallelized C-P method to study the molten phase of sulphur. The calculated pair distribution function (Godwal *et al* 1997b) compares fairly well with the results of neutron diffraction experiments (Descotes and Bichara 1995). The constant pressure (variable cell) simulations are being implemented to compute thermodynamic properties and phase stability of materials.

4.2 Density based *ab initio* MD

The second method adopted in our calculations employs the plane wave expansion of the square root of total valence electron density (Pearson *et al* 1993; Shah *et al* 1994; Smargiassi and Madden 1994).

The density based MD simulations were carried out on clusters related to Al-Zn-Mg quasicrystal. Al was chosen at the centre of the cluster as our earlier study (Rao *et al* 1994) on the crystal approximants with Zn₄₈Mg₃₂ around different (Al, Zn, Mg and empty) central atoms in a bcc crystal structure had shown that Al atom at the central site would give the most stable system.

We carried out calculations on: (i) a cluster of 105 atoms; (ii) a cluster of 125 atoms; and (iii) a two-cluster system of 162 atoms which partially takes into account the effects of inter-cluster interactions.

Our 105 atom cluster calculations show that the atoms in the ideal icosahedral positions give stable structure though the energy differences are only marginal (about 1.7 mRy per atom). The calculated total energies for three different positions of atoms are given in table 1.

In the 125 atom calculations, only the glue atoms were moved in a molecular dynamic simulations. The cage of 101 atoms was not allowed to move from the ideal icosahedral position during these simulations. We find

Table 1. Total energies of a cluster of 105-atom at different positions of atoms by density based MD simulations.

Position of atoms	Total energy
Ideal icosahedral positions	- 230.280 Ry
Crystal approximant positions	- 230.102 Ry
Penrose tiling	- 229.127 Ry

that the distances of the glue atoms from the central atom have changed randomly from the initial values. We are studying in more detail, the effects of temperature on these results.

In the calculations with two clusters, only the static atom calculations were carried out for the total energies. The cages were always kept at the ideal icosahedral positions, and the glue atoms were considered at (i) ideal positions, (ii) crystal approximant positions (Guryan *et al* 1988; Henley and Elser 1986), (iii) a few intermediate positions, and (iv) a few extrapolated deviations from positions (i) to (ii). We found that neither the ideal nor the crystal approximant positions of glue atoms give the lowest energy though the differences are only of the order of a few mRy. These results support the recent model by Chidambaram (1999) for quasicrystals based on interacting clusters i.e. the clusters with ideal icosahedral symmetry force the 5-fold rotational symmetry on the overall structure, the glue atoms may not adhere to the long range rotational symmetry; and in the process they might as well get configurationally disordered in filling the inter-cluster regions.

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