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Materials response to high pressures

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Abstract. There are many fascinating areas of research related to the response of materials at high static and dynamic pressures. The experimental range of compression achievable in the condensed state under pressure is much larger than the range of expansion achievable before melting by variation of temperature. The advances in the experimental techniques have been matched by the developments in the first principles theories and in computational resources. Studies of equation of state and of phase transitions in materials have helped to increase our basic understanding of the condensed state of matter, with possible applications in many fields, including nuclear technology. The current status of high pressure research is briefly reviewed, taking examples mainly from the work of our group at Trombay.

Keywords. Materials response; high pressures.

1. Introduction

The most basic effect of high pressure in materials is compression, which in turn brings about a reduction in the inter-molecular distances. Today, using a diamond anvil cell in the laboratory one can squeeze a material to almost one third of its initial volume. We can contrast this with a few percent variation that is all that is possible using temperature as the thermodynamic parameter. The reduction in the intermolecular distances affects and can, in fact, be used to tune inter-molecular forces operative in the materials. With large and reproducible compression achievable in the laboratories, one can change the intermolecular forces by almost two orders of magnitude higher than that of what is possible by the variation in temperature. Therefore, it follows naturally that high pressure investigations provide a very stringent test for the theoretical understanding of condensed matter. Further, under static pressures, the variation brought about in the inter-molecular interactions is cleaner as it does not have any statistical effects associated with higher temperatures. However, in the case of shock loading of materials, the compression is accompanied by a temperature rise. In general, the material response depends on the nature of pressure loading. This is understandable, as the nature of macroscopic as well as microscopic strain may be different under static and shock pressures (Duvall and Graham 1977; Jayaraman 1983; Chidambaram 1984). For example, for planar shocks, the macroscopic strain is uniaxial while under hydrostatic pressures it may be isotropic volume compression. General response of materials under high pressures is either the occurrence of phase transformations or just compression with consequent changes in the physical properties.

Figure 1 shows the essential difference in the response of materials under static pressures and under shock loading. From the same initial state and for the same volume compression one gets very different pressures in the isothermal static case (P_C) and along a Hugoniot in the dynamic case (P_H). In the latter case, under increasing compression more and more energy goes into heat, contributing to thermal pressure. As the Hugoniot traces a different path than an isotherm, the pressures of phase transformations may be quite different, even if the same transformation is seen in both cases. Furthermore, there are kinetics considerations. In general, one may observe different phenomena under static and shock compression. For example, shock compression may lead to shock induced cooling on molecular dissociation as observed in molecular nitrogen (Nellis *et al* 1984) and hydrogen (Holmes *et al* 1995). However, when there are no phase transformations one can determine the equation of state under both static and shock pressures. This information is very useful in many contexts. For example, this is required for understanding several issues relating to geophysics, astrophysics, plasma and nuclear physics. This is also a vital input into the hydrodynamic calculations for nuclear safety, fission/fusion energy systems, hypervelocity impacts and weapon development. Formally, the equation of state of any material may be represented by a relationship as follows

$$f(P,\ V,\ T) = 0, \tag{1}$$

where P, V, T are the pressure, specific volume and temperature, respectively. However, in general the state of compression is such that P should be viewed as the

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stress and V as the strain. The relationship between the stress and strain depends on the shear strength of the material. Below the elastic limit, deviatoric stresses increase with uniaxial strain such as in planar shocks, and beyond yield point these may either decrease or freeze at a value just before the yield point. In any case if the deviatoric stresses are small compared to the mean stress, then one can treat stress as pressure. However, if the yield strength of the material increases with pressure then treating stress as pressure may lead to erroneous values of other physical parameters derived from the experimental data, such as bulk modulus and its derivative, etc (Chidambaram 1996).

As mentioned above the second important aspect of material response at high pressures is the occurrence of phase transformations. Pressure-induced phase transitions invariably lead to phases of higher density. Also, because at higher pressures diffusion is reduced, due to increasing repulsive interatomic potentials, the occurrence of diffusion-controlled phase transformations are severely reduced. It has also been observed that in some cases the phase transitions which are nucleation and growth kind in one setting, say under hydrostatic pressures, may become very fast under shocks. This implies that the existence of shear strain provides some alternative routes for these transformations. An example of this kind is the graphite to diamond phase transformation (Erskine and Nellis 1992). Because most phase transformations observed under high pressures are not diffusive and therefore displacive, these can be characterized by the symmetry change across the phase transformation (Christy 1993; Gupta and Chidambaram 1994; Sikka and Sharma 1995).

The High Pressure Physics Laboratory at Trombay has been engaged in the study of materials under high pressures for almost three decades. Over the years several state-of-the-art experimental facilities have been built and used (Chidambaram and Sharma 1991; Sikka 1992, 1994). These include several kinds of diamond anvil cells, energy dispersive X-ray diffraction set up (Sikka *et al* 1989), image plate based angle dispersive X-ray diffraction (Meenakshi *et al* 1995) and now CCD based angle dispersive X-ray diffraction set up (Sinha *et al* 1998). In addition we have Raman scattering (Chitra *et al* 1995; Roy and Bansal 1998) as well as facilities for IR measurements (Chitra *et al* 1998) under static high pressures. Our first high pressure X-ray diffraction set up was based on WC anvils and Be gaskets (Vohra *et al* 1984). We also have facilities to measure transport properties up to 100 kbar under static pressures (Vijayakumar *et al* 1984a, 1986a). On the dynamic pressure side we have set up a gas gun facility (Gupta *et al* 1994) with which we can load materials to shock stresses of 400 kbar or so. These experimental developments have been well matched with the growth on the theoretical front. Now we have the capabilities to predict the P–V behaviour of materials very accurately using various first principles electronic structure (Gupta *et al* 1993) or molecular dynamics calculations (Somayazulu *et al* 1993). Of these the electronic structure calculations essentially permit one to compute total energy as a function of given structural parameters. Most of the schemes are based on density functional approach (Hohenberg and Kohn 1965) in the local density approximation with appropriate exchange and correlation corrections. These days the most common methods are either linear muffin tin orbital scheme (LMTO) (Anderson 1975; Skriver 1984) or the *ab initio* pseudo-potentials (Hamman *et al* 1979; Bachelet 1982). Most calculations using LMTO method are carried out in the ASA approximation. However, in the case of materials which do not have close packing, full potential LMTO is more accurate (Methfessel 1988). *Ab initio* pseudo-potential scheme has also been quite successful in predicting equation of state and phase stability quite accurately (Moriarity 1982; Godwal *et al* 1983). Of the molecular dynamics methods, first principles molecular dynamics calculations provide a direct information of structural changes as a function of external pressures (Car and Parinello 1989). However, presently one is limited by the computational resources as these permit calculations for a ensemble of a few hundred atoms. Because such a small system may not be successful in representing truly the bulk structural features, classical molecular dynamics using pair potentials continues to be used to probe several aspects of the material response (Robertson *et al* 1997).

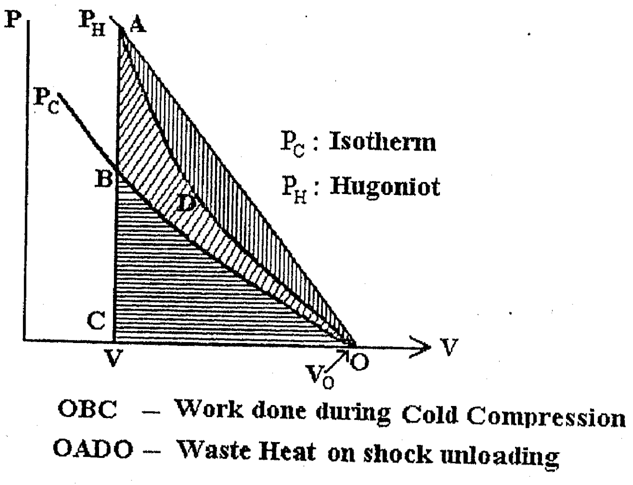

Figure 1. A schematic P–V diagram for the compression of material under isothermal (P_C) and shock loading (P_H).

Before discussing some specific examples, we shall briefly summarize some recent developments in the area of high pressures. For static high pressures, the development of the double hotplate (Shen *et al* 1996), where the material under pressure is heated with a YAG laser from both the sides, is a significant experimental development. Earlier procedure of heating was from one side (Ming and Bassett 1974), though it provided high temperatures, upto 6000 K (Boehler 1993; Saxena *et al* 1995; Yoo *et al* 1995), yet the results obtained were ambiguous as there were uncertainties in the sample characterization due to large temperature gradients. Now uniform temperatures up to 3000 K can be achieved within a high pressure sample of ~ 20 μm diameter and 10 μm thickness (Mao *et al* 1997). This can be accurately probed by a finer 3 × 6 μm X-ray microprobe from synchrotron sources. The second development is of determination of single crystal elasticity tensor of materials from the X-ray diffraction data obtained under non-hydrostatic compression of a polycrystalline material (Singh *et al* 1998). Further this is the only method that permits the determination of these elastic constants at high pressures in the megabar range. For shock experiments, earlier data obtained from laser shocks were considered less accurate due to non-planarity of shocks and pre-heating of the material ahead of shock front. With recent improvements in the beam smoothening and other experimental developments, reliable absolute equation of state can now be obtained to very high pressures using laser shocks (Da Silva 1997; Gupta and Sharma 1997). Also after several years, careful X-ray diffraction experiments are now being carried out for planar shocks using gas guns (Rigg and Gupta 1998). Obviously these experiments provide direct information about lattice strains unlike in the earlier work using laser shocks where one has to make several plausible approximations for the nature of the shock wave. Also shocked hydrogen has been shown to become metallic (Weir *et al* 1996), though under static pressures this metallization continues to elude scientists (Edwards and Ashcroft 1997). The highest pressures up to which the experimental investigations have been carried out have not changed much since the last review by Sikka *et al* (1997). For the sake of completeness, we mention these here. For static pressures, a pressure of ~ 5 Mbar has been claimed in a diamond anvil cell (Ruof and Luo 1990) and a simultaneous laser heating in a diamond anvil cell to 2 Mbar, 5000 K has been achieved (Boehler 1993; Yoo *et al* 1995). Therefore now one can create the conditions in a diamond anvil cell which compare well with the centre of the earth. Multi-anvil presses have been used for larger samples up to a pressure ~ 400 kbar (Utsumi *et al* 1998), while neutron scattering has now been carried out up to a pressure of 25 GPa using a Paris-Edinburgh cell (Klotz *et al* 1998). On the dynamic pressure side, gas guns and chemical explosives have been used for equation of state measurements up to ~ 10 Mbar (Ahrens 1993). Lasers have been used to load materials up to ~ 750 Mbar (Cauble *et al* 1993). And using impedance matching technique, materials have been investigated up to a pressure of 5000 Mbar using nuclear explosives (Vladimirov *et al* 1984).

2. Phase transitions

Over the years our group at Trombay has investigated a large number of materials—metals and alloys, inorganic materials and organic materials. A large number of phase transformations, both under static as well as shock loading have been investigated. For example, the phase transformations have been investigated in Be (Vijayakumar *et al* 1984b), Na (Sankaran *et al* 1992), Si (Olijnyk *et al* 1984; Sharma and Sikka 1985), Ge (Olijnyk *et al* 1984), Ti (Gyanchandani *et al* 1990a), Zr (Gyanchandani *et al* 1990b), Hf (Gyanchandani *et al* 1990c), Hg and CdHg alloys (Vijayakumar *et al* 1986a; Sharma *et al* 1987), $InAu_2$ (Godwal *et al* 1997), La–Th alloys (Vijayakumar *et al* 1986b), Yb (Gyanchandani *et al* 1987), Th (Rao *et al* 1992), Zn (Meenakshi *et al* 1992), Cd (Godwal *et al* 1998), $LiKSO_4$ (Sankaran *et al* 1988), $AlPO_4$ (Sankaran *et al* 1990; Somayazulu *et al* 1994a; Garg and Sharma 1999; Sharma *et al*, to be published), $FePO_4$ (Joshi *et al* 1997; Murli *et al* 1997), GeO_2 (Somayazulu *et al* 1994a; Suresh *et al* 1994), SiO_2 (Chaplot and Sikka 1993; Somayazulu *et al* 1994b), KTP (Somayazulu *et al* 1994c), $Ni(OH)_2$ (Chitra *et al* 1998), resorcinol (Sharma *et al* 1985; Deb *et al* 1993), para-dichlorobenzene (Sankaran *et al* 1986), admantine (Sikka *et al*, to be published) etc. Many of these phase transformations have been investigated experimentally as well as theoretically. Here we shall briefly present a few of these.

2.1 *Transition metals*

For transition metals, the rare earths and the actinides, the occupancy of *d* and *f* bands plays a vital role in stabilizing a structure. Pettifor (1970), and subsequently others (Williams, unpublished; Miedema and Nilsson 1983), showed that for the 3d transition metals the structure is decided by the occupancy of *d* band as represented by the number of electrons in the 3d band (N_d). Under high pressures various bands move and broaden by different amounts resulting in a transfer of electrons from one band to another. And generally this transfer is from *s* and *p* bands to *d* and *f* bands, thereby changing the nature of bonding and consequently the relative stability of phases. In 3d transition series, particularly on Ti, Zr and Hf, our group has carried out extensive investigations. This work started with studies of the ω phase in Ti and Zr in the seventies (Sikka *et al* 1982). Ti transforms from hcp (α) to the simple hexagonal (ω) phase in the pressure range 2·9–7·5 GPa while, for Zr, transformation to the ω phase occurs between 2·1 and 6·0 GPa (Sikka *et al* 1982). In both the materials the ω phase is metastable and is retained on release of pressure. Detailed band structure calculations showed that the stability of the ω phase is related to $s \rightarrow d$ transfer (Vohra *et al* 1979). Mechanism of $\alpha \rightarrow \omega$ transformation has also been studied in detail. From the orientation relations between the α and ω phases in pressure-treated Ti and Zr foils, Usikov and Zilbershtein (UZ) (1973) suggested that the α phase goes to the ω phase via an unstable β phase. And the existence of this intermediate β phase was demonstrated for Ti–V alloys by Vohra *et al* (1981) through selected area diffraction on the foils of pressure treated Ti-10% V alloys. For pure Zr this was shown to be true by Gupta *et al* (1985) using neutron diffraction. Earlier work, particularly relating ω phase has been presented in an extensive review by Sikka *et al* (1982). Subsequent orientational relationship (OR) studies on shocked Zr, carried out by Kutsar *et al* (1990), agreed with those of Usikov and Zilbershtein. But in a later study, Song and Gray (SG) (1995) claimed to have observed new ORs between α and ω phases in shocked Zr. However, Jyoti *et al* (1997) showed that the ORs of SG is a subset of ORs of UZ. These studies therefore suggest that the mechanism of α to ω phase transformation is identical for both static and shock compression (Jyoti *et al* 1997).

In shock experiments, McQueen *et al* (1971) observed discontinuities in the shock velocity (U_s) versus particle velocity (U_p) data of Ti, Zr, and Hf at 17, 26 and 40 GPa, respectively. Generally these are indicative of phase transitions. To understand these features fully, Gyanchandani *et al* (1990b) carried out total energy calculations using LMTO–ASA method. For Zr they found that α phase transforms to ω phase at ~ 5 GPa, in reasonable agreement with the experiments. Calculations predicted the existence of a new $\omega \rightarrow \beta$ phase transformation at higher pressures. This was subsequently observed at ~ 30 GPa under static high pressures (Xia *et al* 1990a). view of this, the 26 GPa discontinuities in U_s–U_p ation in Zr is attributed to the $\omega \rightarrow \beta$ phase trans- mation. In contrast to Zr, Ti showed no $\omega \rightarrow \beta$ phase nsformation up to very high pressures (Gyanchandani *al* 1990b). This has also been confirmed by subsequent atic pressure experiments (Xia *et al* 1990b), thereby uggesting that the low pressure shock Hugoniot of Ti may not be accurately determined. Later experiments have proven this to be true (Gray *et al* 1993). In Hf the calculations predicted (Gyanchandani *et al* 1990c) an $\alpha \rightarrow \beta$, while the experimental results showed sequential $\alpha \rightarrow \omega \rightarrow \beta$ phase transformations. On incorporation of Madelung correction the calculations showed an $\alpha \rightarrow \omega$ phase transformation at 36 GPa and $\omega \rightarrow \beta$ phase change at 55 GPa. These are in agreement with the experimental results.

Recent first principles electron structure calculations by Rao *et al* (1999) on the relative stability of various phases of iron at high pressures and high temperatures is another example of the predictive power of such calculations. They showed that the proposed orthorhombic structure (Andrault *et al* 1997) in the pressure range 40–100 GPa at temperatures 1500–2400 K is unstable with respect to the hcp and fcc phases. Recent experiments confirm the non-observation of orthorhombic phase (Shen *et al* 1998).

2.2 *Pressure induced amorphization*

Over the last one decade several materials were shown to become amorphous under high pressures. In our laboratory we discovered this phenomenon while trying to identify pressure induced crystalline phase transitions in $LiKSO_4$ with the help of X-ray diffraction (Sankaran *et al* 1988). Instead we found that beyond ~ 12 GPa, crystalline diffraction pattern loses all sharp Bragg peaks. Another interesting feature is that the diffraction pattern re-emerges on release of pressure. After this observation, several more compounds were investigated in our laboratory and were shown to become amorphous under compression. These include $AlPO_4$ (Sankaran *et al* 1990; Somayazulu *et al* 1994a; Garg and Sharma 1999; Sharma *et al*, to be published), GeO_2 (Somayazulu *et al* 1994a; Suresh *et al* 1994), $FePO_4$ (Joshi *et al* 1997; Murli *et al* 1997). The last two compounds were also shown to become amorphous under shock compression (Suresh *et al* 1994; Joshi *et al* 1997). Understanding of this interesting phase transformation was aided by several molecular dynamical calculations (Chaplot and Sikka 1993; Somayazulu *et al* 1993, 1994b, c) as well as through a simple physical model of competition of close packing and the structural frustration arising from unfavourable kinetics (Sikka and Sharma 1992). Our extensive molecular dynamics calculations demonstrated that the high pressure amorphous phase has higher cation–anion coordination (Somayazulu *et al* 1993). For SiO_2 it was also shown that the P–V curve of the high density amorphous phase matches well with the experimental results. Therefore, the high pressure phase is the amorphous phase and not stishovite (Somayazulu *et al* 1994d). Using these MD calculations, it was shown as to how MD results can be utilized to relate to experimental X-ray diffraction results to determine the high pressure structures in quartz (Somayazulu *et al* 1994b). Physically the emergence of an amorphous phase was shown to be related to the steric hindrances (Sikka and Sharma 1992; Sikka *et al* 1994). We know that in general, high pressure favour close packing. However if the shape of the molecules is such that the access to the expected crystalline phase is hindered, then the material may amorphize (Sikka and Sharma 1992). It was shown that the pressure of amorphization matches well with the pressure at which nearest non-bonded atoms reach a limiting value. For example for O–O there are two limits (Sikka *et al* 1994), one the normal limit = 2·8 Å at which the distortion of the constituent unit becomes significant. The second is the extreme limit beyond which it is energetically very costly to reduce the O–O distances and this is 2·6 Å. Figure 2 shows the O–O distance as calculated in one of our recent MD calculation on $AlPO_4$ (Garg and Sharma 1999). The error bars represent the statistical variation of O–O distances over the MD ensemble. We note that at ~ 30 GPa, some O–O distances reach the extreme limit and thus $AlPO_4$ amorphizes. Prior to that at ~ 15 GPa, some O–O distances reach the normal limit and a recent Raman measurement indicates the existence of phase transformation at this pressure (Gillet *et al* 1995). The extensive body of work on the pressure induced amorphization of materials has been reviewed by Sharma and Sikka (1996) recently.

2.3 *Mechanism of phase transformations*

As mentioned earlier, most of the phase transformation observed under pressure are not diffusive and therefore of the reconstructive kind. Instead these are by and large displacive, involving correlated atomic movement of atoms. Therefore, it is possible to classify these transformations in terms of symmetry changes. These symmetry systematics also help one to identify the path of atomic movements necessary for the phase change. Further for many of these transformations one could either use Landau theory of second order or that of transcendental order parameter or modifications thereof to understand these symmetry changes. Also these symmetry changes provide the orientation relations between the various variants of the daughter phase and thus provide a further support for understanding the mechanisms of phase transformations. An example of this kind has already been given above in the context of the α to ω phase change in the transition metals. Here we shall briefly mention two more closely related examples, viz. of pure Hg and CdHg alloys (Vijayakumar *et al* 1986; Sharma *et al* 1987) and Na (Sankaran *et al* 1992). At ambient conditions Cd exists in hcp phase while Hg and CdHg alloys can be stabilized in body centred tetragonal phase. At high pressures these are expected to transform to hcp phase and have been shown to do so. This is a fast transition and one can correlate two structures through a simple geometric construction shown in figure 3. Further these two structures can be shown to be related through softening of a phonon mode $TA_1(110)\ \langle 1\bar{1}0 \rangle$. Figure 3 can also be used to understand a bcc to hcp phase transformation, which takes place in Na at low temperatures (Sankaran *et al* 1992). Our frozen phonon calculations for Hg and CdHg alloys suggested that the mode does not soften at the pressures corresponding to the phase transformations. This can be rationalized in terms of coupling of relevant strains and this coupling lowers the pressure of phase transformation and the transformation becomes of the first order and continues to be displacive (Sharma *et al* 1987). These ideas can also be utilized in explaining phase transformation in CdS. Cadmium sulfide which exists in wurtzite structure is known to transform under static

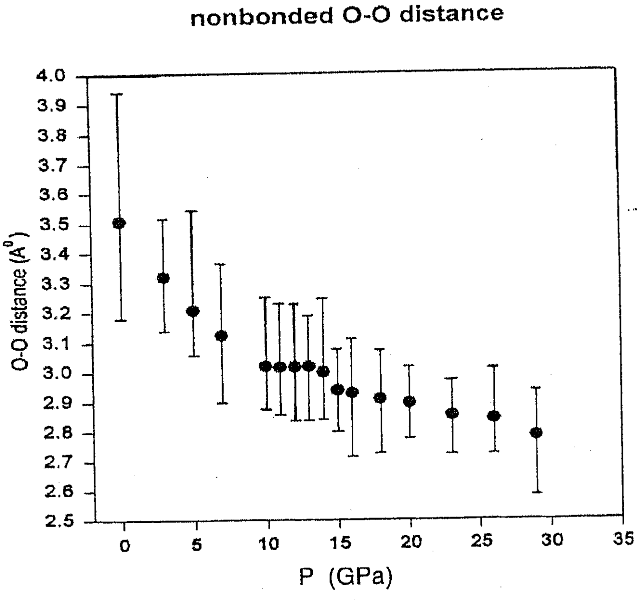

Figure 2. Computed non-bonded O. . .O separation in $AlPO_4$ under hydrostatic compression (Garg and Sharma 1999).

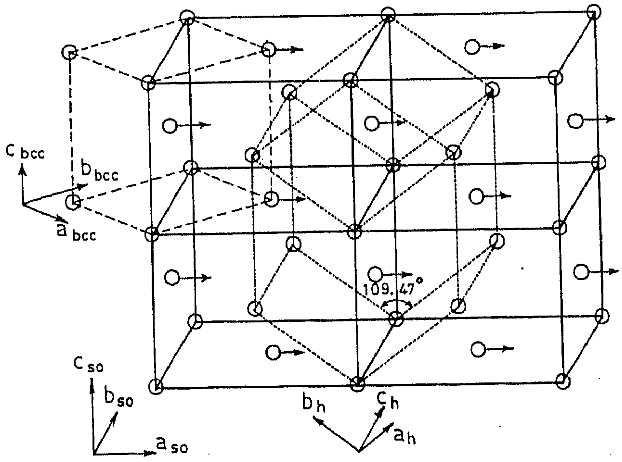

Figure 3. A geometric representation of the path of phase transformation from a body centred cubic (bcc) or bct to a hexagonal close packed structure as in Na (Sankaran *et al* 1992), and Hg (Vijayakumar *et al* 1986; Sharma *et al* 1987), respectively. A reversal of similar atomic movements can be used to explain a hcp to fcc phase transformation in CdS (Sharma and Gupta 1998). The intermediate phase is a distorted orthorhombic cell.

pressures to rock-salt (fcc) structure. Same transformation also takes place under shock loading along the crystallographic c- and a-axis (Sharma and Gupta 1998). It is shown that here too the mechanism is very similar to what is displayed in figure 3, except that now the atomic movements are from a hexagonal structure to fcc, through an intermediate orthorhombic structure.

In the mechanism of phase transformations, do the proposed intermediate structures have any physical significance or these just provide a convenient geometric relationship? Sharma and Sikka (1985) had proposed an intermediate orthorhombic structure in a soft mode mechanism of pressure induced phase transformation between β-tin and primitive hexagonal phase. This has now been experimentally observed in tin and its alloys (Ivanov *et al* 1991). Similarly an orthorhombic structure was hypothesized for mechanistic path between bct to hcp transformation in Hg and CdHg alloys. The existence of this phase has also been confirmed since then (Schulte and Holzapfel 1998). For CdS too it seems that the proposed path is a physical reality and not just a geometric convenience (Knudson and Gupta 1998). Therefore, we conclude that whenever a specific structure is hypothesized based on sound physical requirements, then that structure is likely to be observed by careful experimentation.

3. Shock temperature

We mentioned in the introduction that unlike under the static compression, the shock loading is accompanied by a temperature increase. Basically this temperature increase reflects the adiabatic nature of the compression. For shock loaded gases the temperature increase is likely to be quite high, as a significant part of the compression energy will be converted into kinetic energy of the molecules. For liquids and solids one can expect a relatively less temperature increase, as in these phases a significant part of compression energy is converted into the potential energy. How much of the total compressive energy gets converted into heat? It is a difficult question for which no microscopic understanding is yet available. We shall briefly mention some of the relevant concepts here. If we describe the shock front as a sharp stress discontinuity, then due to the conservation of mass, momentum and energy the material ahead and behind the shock front are related by Rankine–Hugoniot equations, viz.

$$U_s \rho_0 = \rho_1 (U_s - U_p), \tag{2}$$

$$P_1 - P_0 = \rho_0 U_s U_p, \tag{3}$$

$$E_1 - E_0 = \tfrac{1}{2} (P_1 + P_0)(V_0 - V), \tag{4}$$

re U_s is the shock front velocity, U_p the particle velocity in the compressed region, P, ρ, E and V are longitudinal stress, density, internal energy and volume, respectively and quantities with subscript 0 and 1 represent the unshocked and shocked regions. The locus of all final states which can be accessed from a given initial state is the Rankine–Hugoniot curve. If we take $P_0 = 0$, then in figure 1 the triangle OAC represents the increase in the internal energy on shock compression. If the compression to volume V was carried out isothermally, then the increase in the internal energy would have been the curved triangle OBC. Then the difference between the area of triangle OAC and OBC represents the internal energy which has been converted into the heat. Of course we have made an assumption that the nature of the final strain states at A and B are same. However, in general there would be differences in the microstructure and defects, such as vacancies and dislocations etc as their number may be much higher in a shocked sample. Therefore a small part of the internal energy difference may be stored in these defects.

For a planar shock, physically it seems reasonable to assume that immediately after the shock front the state of strain will be uniaxial. If the stress deviators are large enough to cause the plastic deformation, this microscopic uniaxial strain will transform to almost hydrostatic strain (Chidambaram 1984). For most of metallic samples the Hugoniot elastic limit (HEL) is small and hence this represents the most likely situation in metallic systems. Thus for materials which have been loaded to stresses well beyond HEL, the state B in figure 1 corresponds to that of almost isotropic uniform

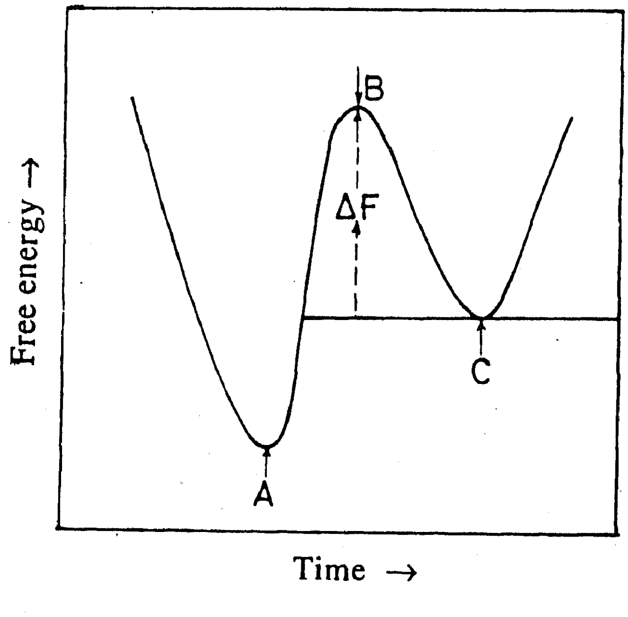

Figure 4. A schematic of shock compression model. Points A, B and C in free energy versus time represent an uncompressed, uniaxial compression and hydrostatic compression, respectively (Godwal *et al*, to be published).

strain. While at A, the strain is initially uniaxial and this quickly evolves to the hydrostatic strain. Figure 4 is a schematic of this. Godwal *et al* (to be published) have carried out first principles total energy calculations for Al using energy band structure calculations. Differences in the energy of instantaneous distorted state fct (from fcc ≡ state A) and hydrostatically compressed state (state B) was taken to be the heat. Table 1 summarizes the results of these calculations. The agreement seems reasonable, particularly at lower pressures.

4. Equation of state

As discussed above, we have experimentally determined the equation of state of various materials and some of these were mentioned in § 2 in the context of phase transformations. In this section we shall briefly discuss the theoretical status of the determination of the equation of state. At the fundamental level, the equation of state of a material is completely determined if we can find out the Gibb's free energy of a given system as a function of pressure. However, theoretically one calculates the total energy as comprising of E_c (the cold part at $T = 0$ K, primarily electronic energy), E_{lt} (representing the total energy due to the lattice thermal vibrations) and E_0 (V, T) (due to electronic excitations). Using various computational codes these contributions can be calculated. An extensive body of work done in Trombay has been reviewed in two publications (Godwal *et al* 1983; Sikka *et al* 1997). We shall mention here essentially two examples, one from sp metal aluminum and the other one thorium in which the *f* electrons play the most important role.

Experimentally the equation of state of Al is known up to ~ 2000 GPa. This range can be classified in three parts, viz. normal region ($P \lesssim 500$ GPa), high density region ($P > 10{,}000$ GPa) and the intermediate region. It is well known that in the normal region one could classify the electronic states as localized core and delocalized band states. In the high density region, Thomas–Fermi–Dirac theory is adequate for computations. However, the intermediate region is full of complexities as in this region pressure and thermal ionization of the localized states takes place. The first successful attempt to model this was by Godwal *et al* (1981), who used Saha ionization theory to incorporate the ionization effects characteristic of the intermediate region. Figure 5 shows the relative contributions of various phenomena to the total pressure (Sikka *et al* 1997). The computed equation of state of Al is compared with the experimental data in figure 6. The experimental point shown by the solid circle in the intermediate region was obtained by Volkov *et al* (1980) after the calculations had been completed. Its excellent agreement with the theoretical results confirms the validity of the approach taken by our Trombay group.

Thorium, which exists in the fcc phase at ambient conditions has been shown to transform to the bct phase at a pressure of 80 GPa and at $V/V_0 = 0{\cdot}6$. Total energy calculations using ASA–LMTO by Rao *et al* (1992) and using full potential LMTO by Johanson *et al* (1995) have provided the understanding of this phase change. These calculations showed that this phase transformation occurs when the bottom of the 5*f* band falls below the Fermi level and therefore starts getting occupied. The comparison of the computed and experimental equation of state is shown in figure 7. Excellent agreement provides enormous confidence in the reliability of the computational accuracy and predictability.

Table 1. Calculation of shock temperature (Godwal *et al*, to be published).

	Shock temperature (K)	
Pressure (GPa)	Non-equilibrium model	Equilibrium model (deduced temperatures from experiments)
9·4	490	450
18	974	915
37·6	1044	980

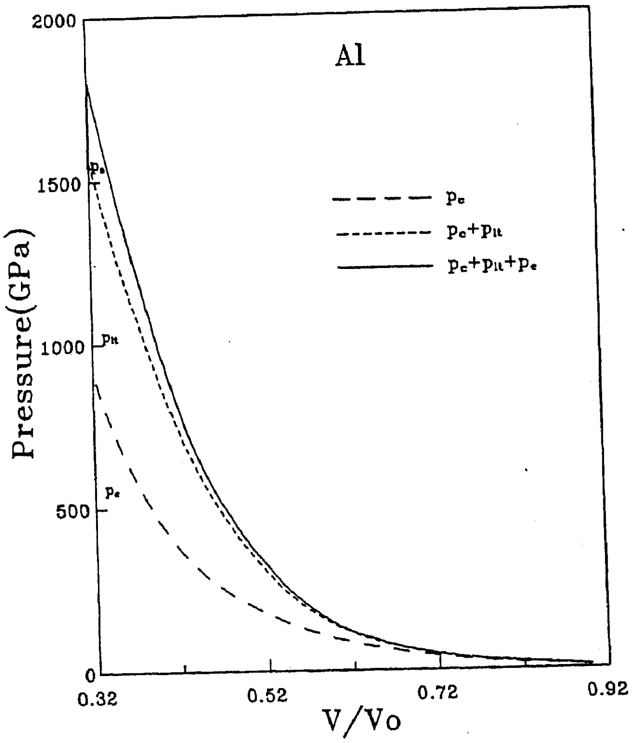

Figure 5. Computed pressure contributions from the Hugoniot of Al (Sikka *et al* 1997).

5. Phenomenology of PNE experiment

The first nuclear explosive test by India was conducted in the Rajasthan desert at Pokhran on May 18, 1974. This helped understanding of the explosion phenomenology, fracturing effects in rocks, ground motion and containment of radioactivity etc. In this experiment a plutonium device of yield 12 kt equivalent of TNT was emplaced in a shale medium at a depth of 107 m in a chamber at the end of a L-shaped hole. On detonation, the ground surface above the emplacement point rose with a velocity of 25–30 m/sec to form a dome—170 m in diameter and 34 m in height. There was no venting of radioactivity in this experiment. The resultant crater measured an average radius of 42 m and depth of 10 m with respect to the preshot ground surface.

Chidambaram *et al* (1985) explained the phenomenology of this experiment with a computer modelling of a one dimensional spherically symmetric rock mechanics. On a sudden release of explosive energy of a nuclear device, the surrounding geological medium is subjected to a variety of physico-mechanical processes. These are vaporization, melting, crushing, fracture and motion of the surrounding rock etc. The reflection of the stress wave at the free ground surface transfers additional kinetic energy to the rock medium. The final dimensions of the crater depend upon the total kinetic energy transferred to the region above the cavity produced by the explosion. Computer calculations showed that in the case of Pokhran-1, 640 tons of rock, extending up to 4·1 m radius around the device, vaporized. About 2000 tons of rock, upto a radial distance of 6·2 m, was shock melted. At the vapour–liquid interface the pressure is expected to be 160 GPa. Computed wave propagation and cavity growth is shown in figure 8. The final calculated cavity radius in the horizontal direction was 28–29 m compared to the post shot measured value of 30 m. More details of phenomenology have been presented elsewhere (Chidambaram and Ramanna 1975; Chidambaram *et al* 1985).

An important aspect of this computer simulation is to delineate the fracture system in the rock medium and to select a depth of emplacement to prevent connection of the ground surface with the cavity containing the hot radioactive gases. In the PNE test of 1974 and the five tests carried out in May 1998, such simulation calculations ensured that there is no residual radioactivity on the surface at the test sites.

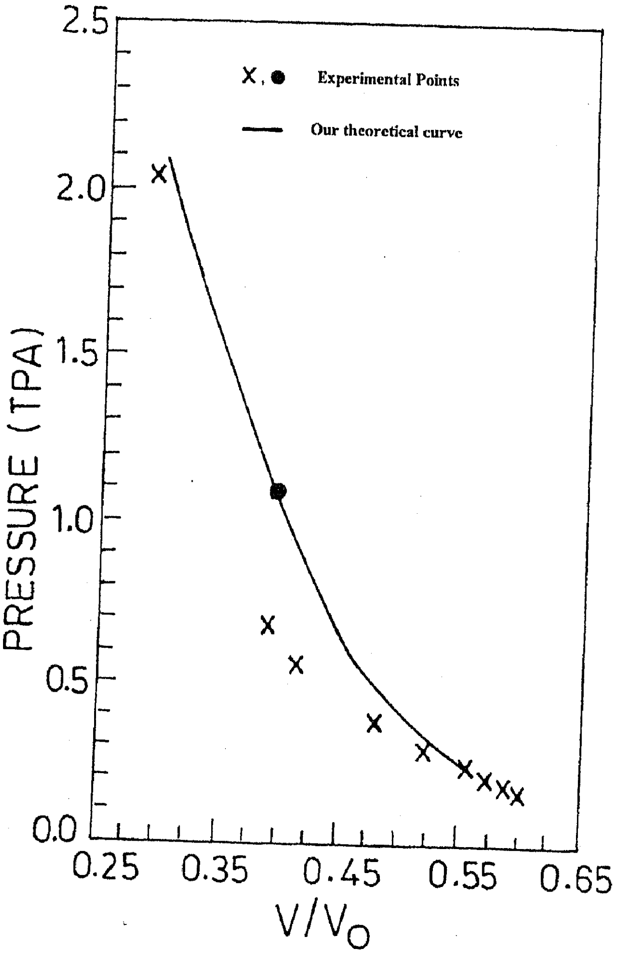

Figure 6. Comparison of calculated shock Hugoniot of Al ith experimental results up to 2 TPa i.e. covering the inter- ediate range (Godwal *et al* 1981). The experimental data shown as ● is due to Volkov *et al* (1980) and was ed after the completion of the calculation.

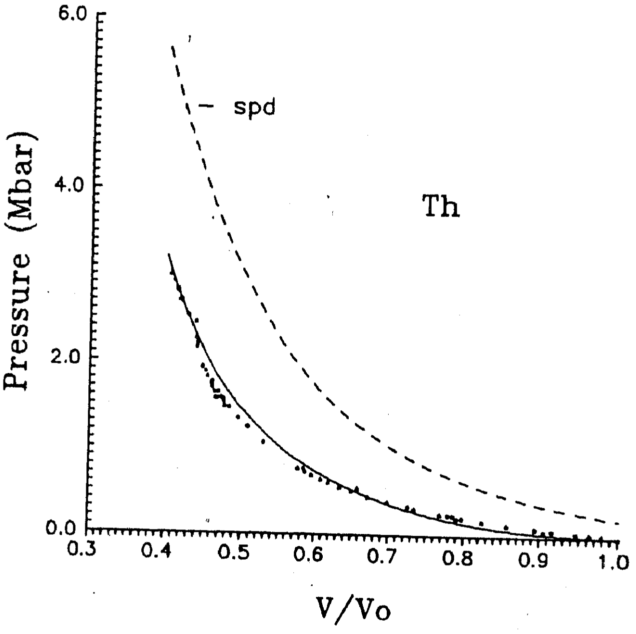

Figure 7. Computed isotherm of Th compared with experimental data (Rao *et al* 1992).

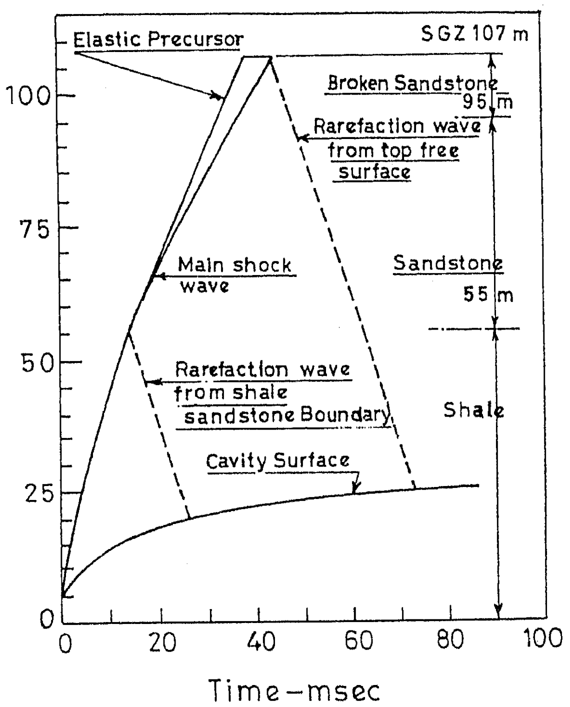

Figure 8. Calculated wave propagation and cavity growth in vertical direction for the Pokhran-I experiment (Chidambaram *et al* 1985).

6. Future directions

Many of the earlier high pressure X-ray measurements suffered from the fact that collimation of the X-ray beam was not fine enough. Therefore the pressure was not uniform over the sampled region. Now with more powerful synchrotron sources one could get very good intensity with a very fine collimation (Mao *et al* 1998) ($3 \times 5\ \mu^2$). Thus it is likely that many of the important materials may be reinvestigated in the ranges of higher pressures (~ a Mbar or higher). This is more likely to be so, where the issues of interest are the phases at high pressure and high temperatures. In this context, simultaneous development of double hotplate method of heating the sample will prove to be very useful (Mao *et al* 1997). Both these developments together are likely to provide useful information about high pressure, high temperature behaviour of materials under static pressures. Also several controversial issues, such as phase diagram of iron will be more reliably resolved. In addition recent advances in the usage of diffraction data under non-hydrostatic stresses may provide a better understanding of the strength of materials under large compression (Singh *et al* 1998). While many new materials are being investigated and will continue to interest the high pressure community, still the metallization of hydrogen under static pressures continues to be of immense interest. Though there is reasonable acceptance for the metallic conductivity observed by Weir *et al* (1996) under shock conditions, there are still nagging doubts whether this is due to complex plasma state arising from partial molecular dissociation and ionization. Under static pressures metallic hydrogen continues to be elusive. Recent electronic structure calculations show that at nine-fold compression (compared to specific volume at 0·1 MPa) the hydrogen system develops a spontaneous polarization making the vibron IR active and increasing the otherwise reducing band gap (Nellis *et al* 1984; Edwards and Hensel 1997). Therefore this apparently simple quantum solid continues to fascinate the high pressure community world over (Mao and Hemley 1994). On the theoretical side, the enormous increase in the computational resources now permit one to investigate subtle crystallographic changes computationally and also from the first principles. A few examples of this kind investigated by our group include Zn (Meenakshi *et al* 1992), Cd (Godwal *et al* 1998), and $AlPO_4$ (Garg and Sharma 1999) etc. It is also hoped that there will be increase in the reliable first principles molecular dynamical simulations.

In the field of shock response of materials, re-emergence of interest and consequent recent progress in the X-ray diffraction under shocks may provide a fundamental understanding of shock response in materials (Rigg and Gupta 1998). It will also be interesting to compare the accuracy of pyrometric technique to measure shock induced temperature in materials with that of the Raman scattering (Panglinan and Gupta 1997). As most of the studies of materials under shocks have been of continuum kind, usage of techniques which provide microscopic information about materials is likely to help understand the shock response of materials at a fundamental level. Laser-induced shocks have been used to obtain equation of state of materials for a long time. However, there have always been doubts regarding the accuracy of data obtained. These concerns were due to lack of planarity of shock front, lack of proof of steadiness of the shock wave front, preheating of material ahead of shock front, etc. But various experimental developments have improved the quality of propagating shock waves (Balani *et al* 1996). Recent measurements employing these improvements have provided reliable absolute equation of state data using laser shocks from NOVA (Da Silva 1997), for example. Availability of so called National Ignition Facility at Lawrence Livermore Laboratory may provide useful data upto ~ 40 Mbar (Cambel *et al* 1998).

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