Theoretical approach to predict the phase transition of NaH under pressure

Aayushi Jain[a] and R. C. Dixit[b]

Department of Physics, Government Holkar Science College, A. B. Road, Indore 452017, MP, India

E-mail: [a)]aayushijain2810@gmail.com, [b)]dixitrc@rediffmail.com

Abstract. This paper is dealing with the high pressure behavior of alkali halide (NaH) and a structural phase transition from NaCl to CsCl phase is predicted under high pressure. We have adopted an effective interionic interaction potential, which includes the long range Coulomb, van der Waals (vdW) interaction and the short-range repulsive interaction upto second-neighbor ions within the Hafemeister and Flygare approach. The thermodynamic requirement, for the equality of free energies, at a phase boundary, suggests that the transition pressure of NaH occur at 37 GPa. The transition involves the coordination number increasing from 6 for the NaCl-type structure to 8 for the CsCl-type structure.

1. Introduction

The alkali-metal hydrides (CsH, RbH, KH, NaH, and LiH) represent a series of partly ionic materials whose high-pressure behavior is expected to parallel that of the alkali-metal halides. The alkali metal hydrides are ionic compounds which can be treated as analogues to alkali metal halides. In alkali matal hydrides hydrogen considered as the first member of the halogen group of elements and formally it behaves as an H -ion. Support for this view can be obtained from the observed crystal structures of these compounds which are typical for ionic systems (NaCl and CsCl). But at normal condition alkali metal hydrides have NaCl or *B*1-type crystal structure, while the alkali metal halides can have both NaCl or *B*1-type structure or CsCl or *B*2 type crystal structure [1]. Pressure is most important thermodynamical quantity to bring out the mechanical properties of solids and alloys. The phase change in solids at high pressure usually involves a change in crystal structure. Co ordination number is important in phase transition due to high pressure. This is because thermodynamically the molar volume of high pressure phase must be smaller than low pressure phase. Hochheimer et al. [2] has reported the transition pressures for CsH, RbH, and KH, as well as the equation of state of NaH to 28 GPa. The change in volume can be estimated using known equation of state (EOS) [3]. Bashkin et al. [4] have pointed out, using a hard-sphere ion model, that the *B*1 to *B*2 transition is thermodynamically possible in NaH, KH, RbH, and CsH compounds. The Duclous *et al* determined the specific volumes of each phase by summing the metal and hydride ion radii, which depend on the structure and coordination number, to determine the *B*2 lattice constant [5].

In particular, NaH show a structural phase transition from NaCl to CsCl. For example, Ahuja et. al. [6] calculated transition pressure for NaH to be 37 GPa. In search of B1-B2 transition Duclous et al. [5] submitted sodium hydrides to pressure as high as 54 GPa which is in good agreement with the experiment value of around 51 GPa.

To estimate the possibility of the NaCl to CsCl transition in NaH under pressure, we consider the relationship of the Gibb's free energy of both phases. The phase transition pressures and the volume collapses were obtained from the effective interionic potential model (EIOP), which incorporates the long range Coulomb, the short-range vdW attraction and the overlap repulsive interactions operative up to the second neighbor ions within the Hafemeister and Flygare framework. The vander Waals coefficient are calculated by the Slater Kirkwood variation method as a first step. Then, we evaluate volume collapse.

2. Theory and method of computation

The effective interionic potential is expressed as

$$U(r) = \sum_{ij} \frac{Z_m e^2}{r_{ij}} + \sum_{ij} b\beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) + \sum_{ij} c_{ij} r_{ij}^{-6} + \sum_{ij} d_{ij} r_{ij}^{-8}. \tag{1}$$

Here, long-range Coulomb is represented by first term, second term correspond to Hafemeister and Flygare [7] form of short-range repulsive energies and van der Waals multipole are represented by third and fourth terms respectively. The symbols c_{ij} and d_{ij} represents the van der Waals coefficient and β_{ij} being the pauling coefficients, respectively. Z_m is the modified ionic charge and parametrically includes the effect of Coulomb screening effect, b and ρ are short-range parameters. Thus, the effective interionic potential contains only three free parameters (Z_m, b and ρ) which can be determined from the crystal properties [8]. Further, an isolated phase is stable only when its free energy is minimum for the specified thermodynamic conditions. As the pressure or any other variable acting on the systems is changed, the free energy of the system changes smoothly and continuously. A phase transition is said to occur when the changes in structural details of the phase are caused by such variations of free energy. The test materials transform from their initial $B1$ to $B2$ structure under pressure. The stability of a particular structure is decided by the minima of Gibbs's free energy, $G = U + PV - TS$. Here U is internal energy, which at 0 K corresponds to the cohesive energy, S is the vibrational entropy at absolute temperature T, pressure P and volume V.

The Gibbs's free energies $G_{B1}(r) = U_{B1}(r) + 2Pr^3$ for NaCl ($B1$) phase and $G_{B2}(r') = U_{B2}(r') + [8/3\sqrt{3}]Pr'^3$ for CsCl ($B2$) phase become equal at the phase-transition pressure P and at zero temperature i. e., $\Delta G (= G_{B1} - G_{B2})$. Here, U_{B2} and U_{B1} represent cohesive energies for $B1$ and $B2$ phases, and are

$$U_{B1}(r) = -1.7475 \frac{e^2 Z_m^2}{r} + 6V_{ij}(r) + 6V_{ii}(r) + 6V_{jj}(r), \tag{2}$$

$$U_{B2}(r') = -1.7627 \frac{e^2 Z_m^2}{r'} + 8V_{ij}(r') + 3V_{ii}(r') + 3V_{jj}(r'). \tag{3}$$

Here r and r' are nearest-neighbor (nn) separations corresponding to NaCl and CsCl phases, respectively.

$$V_{ij}(r) = b\beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) - c_{ij} r_{ij}^{-6} - d_{ij} r_{ij}^{-8}; \quad i,j = 1,2. \tag{4}$$

Here, c_{ij} and d_{ij} being the vdW coefficients due to dipole-dipole (d-d) and dipole-quadrupole (d-q) interactions. We follow SKV method [9] to derive c_{ij} and d_{ij} as

$$c_{ij} = \frac{3}{2} \frac{e\hbar}{\sqrt{m_e}} \alpha_i \alpha_j \left[\left(\frac{\alpha_i}{N_i}\right)^{1/2} + \left(\frac{\alpha_j}{N_j}\right)^{1/2}\right]^{-1}, \tag{5}$$

and

$$d_{ij} = \frac{27}{8} \frac{\hbar^2}{m_e} \alpha_i \alpha_j \left[\left(\frac{\alpha_i}{N_i}\right)^{1/2} + \left(\frac{\alpha_j}{N_j}\right)^{1/2}\right]^2 \alpha_i \alpha_j \left[\left(\frac{\alpha_i}{N_i}\right) + \frac{20}{3}\left(\frac{\alpha_i \alpha_j}{N_i N_j}\right)^{1/2} + \left(\frac{\alpha_j}{N_j}\right)\right]^{-1}. \tag{6}$$

Here, m_e being the electron mass. α_i is the electronic polarizability and N_i denotes the effective number of electrons of the ith ion, respectively. The values of the overall vdW coefficients (C and D) are obtained following Tosi approach [10] in terms of appropriate lattice sums [S6(0), S6(r), S8(0) and S8(r)].

Table 1. Van der Waals coefficients c_{ij} ($i, j = 1,2$) [in units of 10^{-60} erg cm^6], d_{ij} ($i, j = 1,2$) [in units of 10^{-76} erg cm^8] and overall van der Waals coefficients (C, D) for NaH compound.

	c_{11}	c_{12}	c_{22}	C	d_{11}	d_{12}	d_{22}	D
NaH	9.236	8.482	9.632	72.982	3.142	5.717	8.31	39.742

Table 2. Crystal data and model parameters for NaH compound.

Solid	Material Parameters					Model Parameters		
	r_i (Å)	r_j (Å)	a (Å)	B_T (GPa)		Z_m^2	ρ (10^{-1} Å)	$b(10^{12}$ erg)
NaH	0.9	1.28	4.88	23		0.81	2.41	3.089

Table 3. Calculated (reported) transition pressures and volume collapses in NaH compound.

Compound	Transition pressure P_t (GPa)	Volume collapses (%)
NaH	37(28-32 [4], 37 [6], 30.7 [13], 29.3 [14], 32 [15])	4.3

3. Results and discussions

The effective interionic potential is constructed in a hierarchical and easy generalizable manner. We have undertaken such structural and elastic properties in an ordered way. For such purposes we have then three free parameters, namely, modified ionic charge, range and hardness parameters (Z_m, ρ and b). To estimate the free parameters, we first deduce the vdW coefficients from the Slater-Kirkwood variational method [11] and are listed in table 1. It is perhaps worth to remark that we have deduced the values of free parameters modified ionic charge (Z_m), range (ρ) and hardness (b) from the knowledge of equilibrium distance and the bulk modulus following the equlibrium conditions [12]. The input data along with their relevant references and the model parameters for NaH compounds are given in table 2.
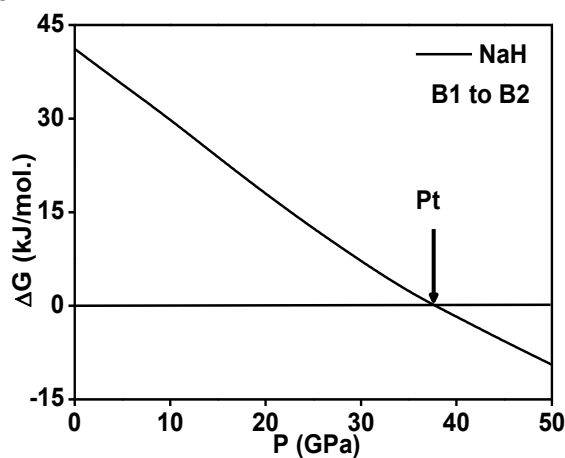

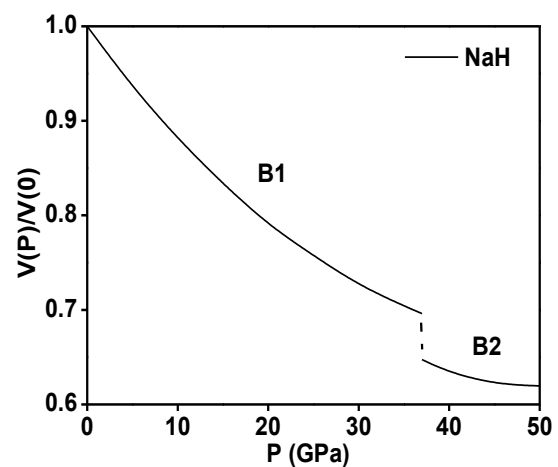**Figure 1.** Variation of Gibb's Free energy with pressure

Figure 2. Variation in relative volume with pressure

In an attempt to reveal the structural phase transition of the test materials, we minimise the Gibbs's free energies $G_{B1}(r)$ and $G_{B2}(r')$ for the equilibrium interatomic spacing (r) and (r'). The Gibbs's free energy difference ΔG [$= G_{B2}(r) - G_{B1}(r')$] have been plotted as functions of pressure (P) in figure 1 using the interionic potential discussed above for NaH.

Let us now estimate the values of relative volumes associated with various compressions following Murnaghan equation of state.

$$\frac{V}{V_0} = \left(1 + \frac{B'}{B_0} P\right)^{-\frac{1}{B'}}, \tag{7}$$

V_0 being the cell volume at ambient conditions. The estimated value of pressure dependent radius for both structures, the curve of volume collapse with pressure to describe the phase diagram is exemplified in figure 2 for NaH. It is noticed from the graph that our access has predicted correctly the relative stability of competitive crystal structures, as the values of ΔG are positive. The magnitude of the discontinuity in volume at the transition pressure is obtained from the phase diagram and their values are tabulated in table 3, which is in fair good agreement with those revealed from experiments [4, 6, 13] and other theoretical works [14, 15].

3. Conclusions

A high pressure structural phase transition from NaCl ($B1$) to CsCl ($B2$) in alkali metal hydride (NaH) was predicted following the developed EIOP model. It has been found that the $B1$ type structure of NaH is unstable at after pressure 37 GPa. This was established by calculating the Gibb's free energies in both the structures under consideration. Further, the associated volume collapses at the phase transitions have been found to be 4.3% for sodium hydride.

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