Prediction of Equation of state for LiH at high pressure volume

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Abstract

Analysis of high pressure-volume equation of state has been performed for LiH solid in compression range from v/v_0 =1.0 down to v/v_0 =0.20. Values of pressure, isothermal bulk modulus and pressure derivative of bulk modulus corresponding to different compression have been obtain using the Born-Mie Equation of state. The result have been discussed and compared with best curve fitting.

Introduction

Lithium hydride, LiH, is the most elementary ionic compound in terms of electronic structure, having only four electrons per unit cell, and has the highest hydrogen content, in mass percentage, of any saline hydride. Its volumetric and gravimetric hydrogen contents are also very competitive among other hydrides; electing LiH a prospective candidate for hydrogen storage.[1] Hydrogen is a propitious alternative energy source that could be the primary facilitator in the transition from fossil fuels to clean sources of energy. There is, however, a challenge to produce a material capable of both reacting with hydrogen to form a stable state and release a significant quantity on demand, at minimum energy expense. LiH is an industrially versatile compound with applications in hydrogen generators, in the manufacturing of ceramics, and in both the shielding and cooling of nuclear reactors. Because of its high reactivity, LiH is an excellent desiccant and chemical reducing agent, as well as the precursor for the synthesis of binary intermetallic hydrides such as lithium aluminum hydride, another potential candidate for hydrogen storage.[2] There are various industrial methods in producing pure LiH, all of which involve the hydrogenation of the constituent materials, often in the presence of a catalyst, at elevated temperatures.[3,4] At ambient pressure, hydrogen is absorbed into molten lithium at temperatures ranging between 700 and 1000 K; the melting point of lithium at ambient pressure is 453.7 K while LiH itself melts at 961 K.[5] The synthesis temperatures of NaH and KH also occur above the melting temperature of pure Na and K, motivating investigations into alternative, energy economical, synthesis routes. Surprisingly no synthesis method has been reported involving cold (room temperature) synthesis of LiH from its pure constituents. Pressure can have a profound effect on chemical reactivity,

inducing changes in atomic and electronic structure. Two different elements that do not react at ambient conditions can form novel compounds if statically compressed, even without additional heating. Pressure alone was sufficient enough to form novel compounds such as PtH, silicon dehydrate or rhenium hydride,[6–9] showing that the kinetics of the solid-state reactions could be greatly influenced by the application of high densities. LiH does not decompose into pure elements until heated to above its melting point (>1000 K) at atmospheric pressure, however it easily reacts with water to the corresponding hydroxide liberating hydrogen from water.[10] The decomposition of LiH at high pressures and temperatures has yet to be investigated, which would have direct consequences for the viability of LiH as a hydrogen storage material.

Review

The equation of compressed solids is fundamentally important in many fields such as condensed matter physics and geographic. The derivation of EOS of a thermodynamic system is based on a fundamental theorem which equates the negative of pressure to the isothermal volume derivative of a Hoimholtz of a free energy function F. The function F consists of two terms in the case of solid, the first of which represents yhe potential energy of a non vibrating lattice, while the second its origin to the thermal vibration.

An extensive study of the equation of state and other thermodynamic properties of solid was first made by Gruneisen[11] who used a simple power law for the potential energy expression. However the best known EOS for solids credited to Murnaghan [12] and is based on empirical observation that the isothermal bulk modulus is a linear function of pressure .A modification and improvement of the Murnaghan by Brich EOS[13,14] based on the finite strain theory has been widely used in geophysics.

Recently, Shankar et al[13] have obtained three set of Equation s each for pressure isothermal bulk modulus and its pressure derivative corresponding to three functions showing the dependence of short range force constant on volume . The first function is represented by the inverse power form, which leads to the Equation of state given by Born and Mie 14,15. The second function is represented by an exponential form, which is identical to that obtained by

Method of Formulation and Analysis Brenan and Stacey 15,17 using the thermodynamic formulation for the Gruneisen parameter. The third function is represented by a modified exponential form which leads to a new equation of state known as the Shankar equation of state. Shankar et al 18 have applied the derived EOS in case of NaCl crystal.

The purpose of the present study is to find a best Equation of State which explain the behavior of LiH using Born Mie EOS. The reason for choosing this solid is thatit is not show any phase transition up to ultra high compressions, whereas the NaCl crystal considered by Shankar et al. shows structural phase transition at 30 GPa and v/v_0 nearly equal to 0.65. thus in case of ranger LiH it is possible to present the test of EOSs corresponding to much wider range of compressions 8,15.

The three forms of isothermal equation of state is derived from the lattice potential theory[13] are as follows:

$$P = \frac{3B0}{(3B0'-8)}[(\frac{V}{V0})^{4/3B0'}-(\frac{V}{V0})^{-4/3}] \quad (1)$$

$$P = \frac{3B0-(\frac{V}{V0})^{-\frac{4}{3}}}{(3B0'-5)}[\exp\{\frac{(3B0,-5)}{3}X(1-\frac{V}{V0})\}-1] \quad (2)$$

$$P= \frac{3B0-(\frac{V}{V0})^{-\frac{4}{3}}}{(3B0'-8)}\left[\left(1-\frac{1}{t}+\frac{2}{t^2}\right)\{\exp(ty)-1\}+y(1+y-\frac{2}{t})\exp(ty)\right] \quad (3)$$

Where $y = (1-\frac{V}{V0})$ and $t= (B_0'-\frac{8}{3})$

V is the volume at pressure P and V0 is the volume at zero pressure.B0 (=39.1 GPa) and B0'(3.51GPa) are the isothermal bulk modulus and its first pressure derivative at zero pressure respectively. Eq. (1) is the Born Mie Eos based on an inverse power form for short range repulsive potential energy 15,18.Eq.(2) is the Brennan-Stacey EOS derived using thermodynamic formulation for the Grunician parameter 16,17. Eq. (3) is the Shanker EOS derived using modified exponential dependence for the short range force constant on volume.13I used experimental data by above Eq. which is below in Table 1 and try to give best fit graph or Eq . for this data.

v/v0	P
1	0
0.9	4.96
0.8	12.93
0.7	26.18
0.6	49.33
0.5	92.78
0.4	183
0.3	406
0.2	1144

Table 1

First pressure P versus v/v_0 for LiH have been plotted by MATLAB and fitted best curve than give the best equation of state for above data given in Table 1. Basic graph for given data is –

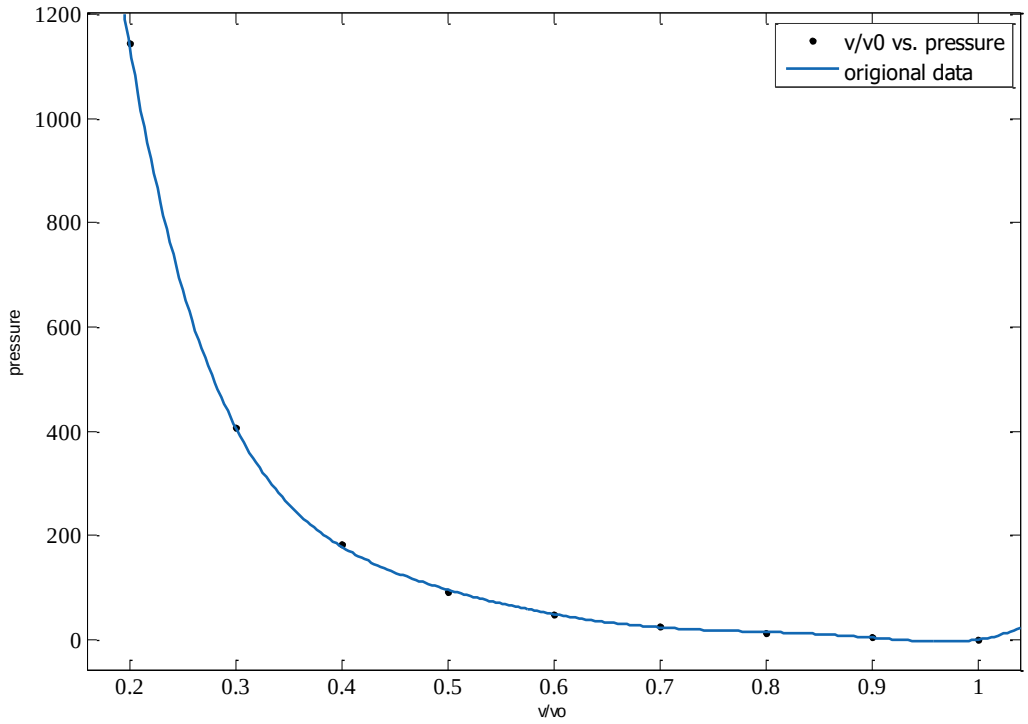

Figure 1:Original curve from table 1

Further find the best fit graph showing in following:

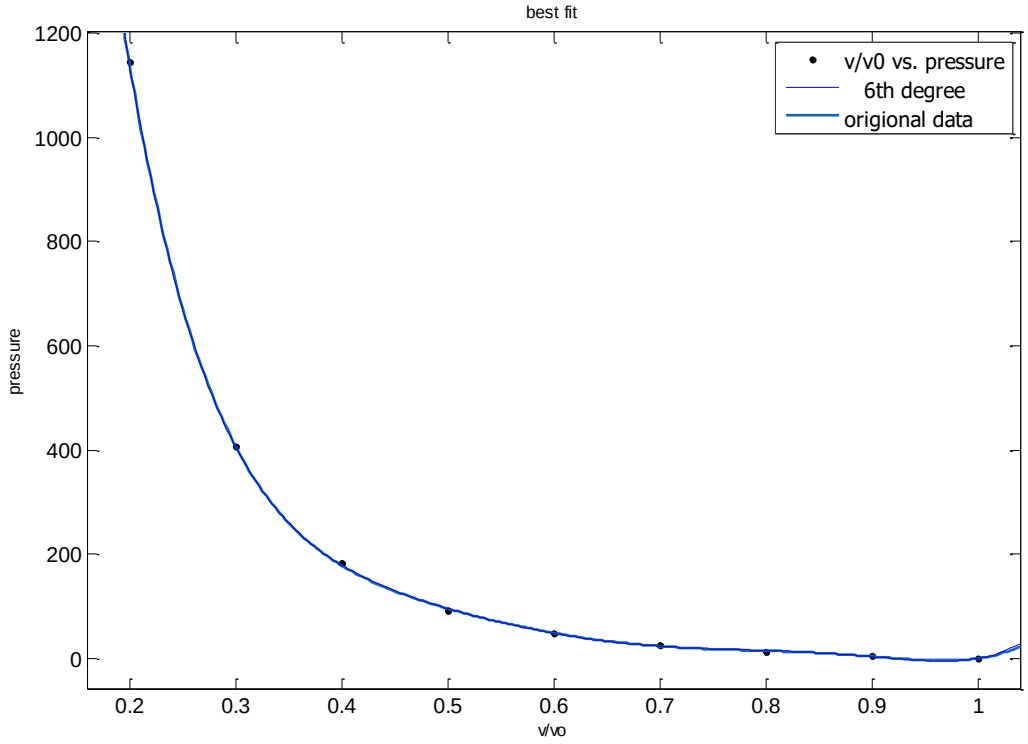

Figure 2: Sixth order fitted curve

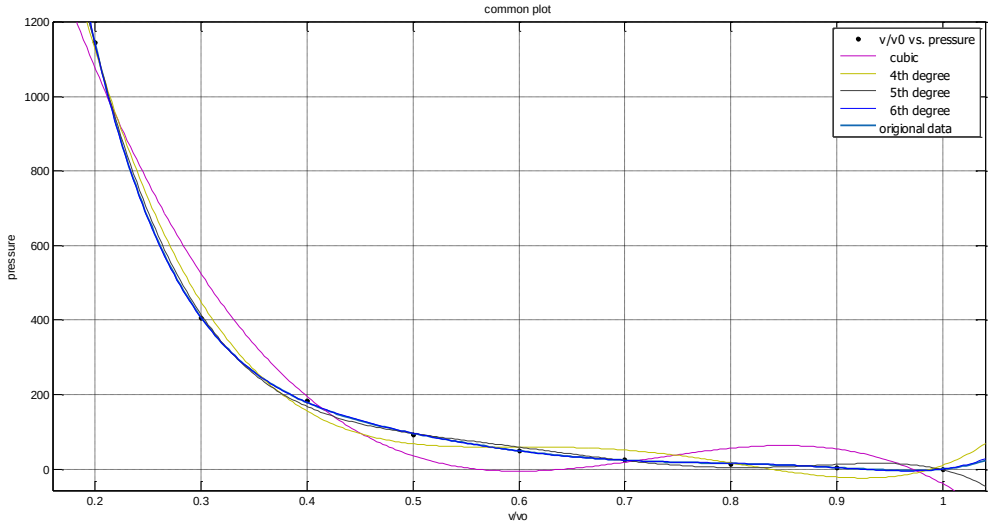

Figure 3: All fitted curve

Corresponding Equation of states are given below:

$P3 = - 8.8e+3(\frac{V}{V_0})^3 + 1.9e+(\frac{V}{V_0})^2 - 1.3e+4(\frac{V}{V_0}) + 3.1e+3$

$P4= 2.1e+4(\frac{V}{V_0})^4 - 5.9e+4(\frac{V}{V_0})^3 + 6.1e+4(\frac{V}{V_0})^2 - 2.7e+4(\frac{V}{V_0}) + 4.6e+3$

$P5 = - 4.6e+4(\frac{V}{V_0})^5 + 1.6e+5(\frac{V}{V_0})^4 - 2.2e+5(\frac{V}{V_0})^3 + 1.4e+5(\frac{V}{V_0})^2 - 4.7e+4(\frac{V}{V_0}) + 6.4e+3$

$P6= 9.6e+4(\frac{V}{V_0})^6 - 3.9e+5(\frac{V}{V_0})^5 + 6.5e+5(\frac{V}{V_0})^4 - 5.7e+5(\frac{V}{V_0})^3 + 2.8e+5(\frac{V}{V_0})^2 - 7.4e+4(\frac{V}{V_0}) + 8.3e+3$

And the table for successive order of pressure is follow:

v/v0	pressure	3rd order	4th order	5th order	6th order
1	0	-37.93	12.3	-3.106	0.8
0.9	4.96	53.4	-21.66	12.82	3.452
0.8	12.93	56.47	15.84	4.15	15.57
0.7	26.18	19.27	50.65	21.81	23.92
0.6	49.33	-5.596	59.03	58.49	47.01
0.5	92.78	34.51	67067	95.3	97.32
0.4	183	192.2	153.7	170.2	181.7
0.3	406	520.1	444.5	410.9	402.5
0.2	1144	1071	1118	1128	1129

Table 2:

Result and Discussion

On analyzing the equation of state for LiH solid and the variation of the volume corresponding to diffrerent pressure have been using the obtain Born Mie equation of state.The curve fitting done on available experimental data. On calculating the values obtain from available. The best fitted curve and most suitable value are obtained. We have seen the best fitted curve obtained for sixth order and corresponding equation is also mentioned maybe quite useful for studying the high pressure elastic behavior of solids.

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