Compression and phase diagram of lithium hydrides at elevated pressures and temperatures by first-principles calculation

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Received 15 December 2015, revised 23 March 2016
Accepted for publication 30 March 2016
Published 4 August 2016

Abstract
High pressure and high temperature properties of AB (A = ⁶Li, ⁷Li; B = H, D, T) are comprehensively investigated with first-principles methods. It is found that H⁻ sublattice features in the low-pressure electronic structure near the Fermi level of LiH are shifted to that dominated by the Li⁺ sublattice under compression. The lattice dynamics are studied in quasi-harmonic approximation, from which the phonon contribution to the free energy and the isotopic effects are accurately modelled with the aid of a parameterized double-Debye model. The equation of state (EOS) obtained matches perfectly with available static experimental data. The calculated principal Hugoniot is also in accordance with that derived from shock wave experiments. Using the calculated principal Hugoniot and the previous theoretical melting curve, we predict a shock melting point at 56 GPa and 1923 K. In order to establish the phase diagram for LiH, the phase boundaries between the B1 and B2 solid phases are explored. The B1–B2-liquid triple point is determined at about 241 GPa and 2413 K. The remarkable shift in the phase boundaries with isotopic effect and temperature reveal the significant role played by lattice vibrations. Furthermore, the Hugoniot of the static-dynamic coupling compression is assessed. Our EOS suggests that a precompression of the sample to 50 GPa will allow the shock Hugoniot to pass through the triple point and enter the B2 solid phase. This transition leads to a discontinuity with 4.6% volume collapse—about four times greater than the same B1–B2 transition at zero temperature.

Keywords: equation of state, phase diagram, high pressure, high temperature

Online supplementary data available from stacks.iop.org/JPhysD/49/355305/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

As the lightest ionic compound, as well as the highest mass content of hydrogen and the highest melting point of 965 K at ambient pressure [1] in alkali metal hydrides, LiH has been widely studied and applied in the fields of hydrogen storage [2], thermonuclear fusion, and aviation and space industries [3–6]. Early static compression experiments using diamond anvil cells (DAC) showed that LiH occupies an FCC lattice and orders in NaCl (B1) structure under ambient conditions, and this structure is maintained up to at least 36 GPa (96 GPa for LiD) [7]. At this pressure, all other alkali hydrides were observed to transform into CsCl (B2) phase (NaH at 29.3 GPa, KH at 4.0 GPa, RbH at 2.2 GPa, CsH at 0.83 GPa) [8–10].
However, the same structural transition in LiH has yet to be observed, which continues to stimulate broad high pressure experimental and theoretical research. Recently, by analyzing the x-ray diffraction (XRD) data obtained in DAC experiment [11], it was shown that at room temperature LiH remains in the B1 structure under pressures up to 252 GPa, the highest pressure having been studied experimentally so far. In particular, the diffraction and Raman data indicated that the B1–B2 phase transition, as well as the accompanied metalization, may not be far beyond 252 GPa [11].

With theoretical methods, the pressure-induced B1–B2 structural transition and the insulator-metal transition in LiH at low temperatures [12–20] have been extensively investigated. The mechanism of the B1–B2 structural transition [14, 15, 21] is often interpreted using phonon softening and elastic instability. On the other hand, the insulator-metal transition was shown to occur prior to the B1–B2 transition by both the local density approximation (LDA) and semi-local generalized gradient approximation (GGA). This might be due to LDA and GGA usually tending to underestimate the energy gap. By using all-electron GW approximation, Lébegue et al [16] argued that the structural transition and metalization in LiH should occur simultaneously at a pressure of 329 GPa. This transition pressure is close to the 313 GPa transition pressure of 329 GPa. This transition pressure is close to the 313 GPa.

2. Computational methodology

Generally, the thermodynamics and the finite pressure-temperature phase diagram of a substance is determined by the Gibb's free energy, which consists of three parts in a solid: (i) the cold energy at zero temperature with nuclei at their equilibrium positions, (ii) the vibrational free energy contributed from lattice dynamics, and (iii) the free energy of thermal electrons [25]. In computer simulations, especially with first-principles total energy calculations, one usually obtains a set of discrete data of energy versus atomic volume, rather than a continuous curve of energy as an analytic function of density. To facilitate the practical application or post processing of the data, one would prefer to fit the discrete data to an analytical function or an equation of state, and then to derive a continuous and smooth curve. This not only endows the numerical data with physical implications, but also extends their application range greatly, if an adequate EOS model has been used. In this work, we fit the ab initio cold energies of the candidate solid phases to the Vinet EOS [26]

\[ E_c(V) = E_0 + \frac{4V_0K_0}{K_m} \left[ 1 - \left(1 - \frac{3}{2}\eta K_m\right) \exp\left(\frac{3}{2}\eta K_m\right) \right] \]

in which

\[ \eta = \left[1 - \left(\frac{V}{V_0}\right)^{1/3}\right], K_m = K'_0 - 1, K_0 = -V \frac{\partial P}{\partial V}, \]

\[ K'_0 = \frac{\partial K_0}{\partial P}. \]
their applicability to high pressures is restricted. Alternatively, the phonon spectra can be calculated directly using first-principles quasi-harmonic approximation (QHA). This approach does not rely on any empirical input, and has high accuracy and unlimited application range (in principle it can be applied as long as the solid phase is dynamically stable).

In the QHA the vibrations are treated as a gas of 3N non-interacting phonons with frequencies $\omega_j$ depending on the atomic volume, where $N$ is the number of atoms per primitive cell. The vibrational free energy $F_{\text{vp}}$ in QHA is expressed as

$$F_{\text{vp}} = \sum_{j=1}^{3N} \left[ \frac{\hbar \omega_j}{2} + k_B T \ln(1 - e^{-\hbar \omega_j / k_B T}) \right],$$

where $k_B$ is the Boltzmann’s constant, and $T$ is the temperature. The thermal pressure is given by

$$P_{\text{th}} = -\left( \frac{\partial F_{\text{vp}}}{\partial V} \right)_T = \sum_{j=1}^{3N} \left[ \frac{\hbar \omega_j \gamma_j}{2V} + \frac{\hbar \omega_j \gamma_j / V}{e^{\hbar \omega_j / k_B T} - 1} \right],$$

where the mode Gruneisen ratio $\gamma_j = -\partial \ln \omega_j / \partial \ln V$ has been introduced. In practice, it is difficult to compute $\gamma_j$. Alternatively, the vibrational free energy can be formulated as

$$F_{\text{vp}} = \int_0^\infty \left[ \frac{\hbar \omega}{2} + k_B T \ln(1 - e^{-\hbar \omega / k_B T}) \right] g_{\text{ph}}(\omega) d\omega$$

by using the phonon density of states (phDOS) $g_{\text{ph}}(\omega)$. It is evident that $F_{\text{vp}}$ is completely determined by $g_{\text{ph}}(\omega)$.

The phDOS can usually be evaluated only on a discrete grid of volume. Therefore, direct application of QHA is limited. Especially, a very fine grid is required if one wishes to obtain an accurate thermal pressure from equation (4). Analogous to the first-principles cold energy $E_c$, it is desirable to represent the QHA results by an analytic model. A good model has the capability to both interpolate and extrapolate the discrete QHA data, thus only a few QHA calculations are required to derive accurate and wide-ranging thermodynamics. In addition to this benefit in computational efficiency, an accurate EOS model with fewer parameters is good to integrate into hydrodynamics code for macroscopic simulations. Furthermore, numeric values of QHA free energy inevitably contain artificial noise arising from computational precision. This noisy fluctuation is vital when calculating the phase boundaries from the intersection of free energies. Fitting the QHA data to a model can remove these fluctuations effectively. In contrast to cold energy, there are very few thermal EOS available for lattice vibrations. For an ionic compound such as LiH, the simple Debye model incorrectly treats the optical branches as acoustic modes. In this work, we will employ an improved variant of the Debye model, i.e. the double-Debye model, to tackle this problem. Parameters of this model are determined by fitting to first-principles QHA phonon spectra. As will be shown below, this double-Debye model accurately reproduces the free energy of QHA, and is a faithful representation of the latter.

In the double-Debye model, the total phDOS $g(\omega)$ is given by a linear combination of the density of states of two standard single-Debye model (1DM) (here we use ‘single’ to emphasize that it has just one Debye temperature), which is

$$g_D(\omega) = \xi_A^A g_A^A(\omega) + \xi_B^B g_B^B(\omega).$$

Here $g_D^{A,B}(\omega)$ is the standard DOS of a Debye model, and has nonzero value of $\omega^2 / (\omega^2 - \omega_D^2)$ only when $\omega \leq \omega_D^{A,B}$, where $\omega_D$ is the corresponding Debye frequency that relates to the Debye temperature by $k_B \theta_D = \hbar \omega_D$. The double-Debye is devised to reproduce the ZPE of QHA as $T \to 0$ K exactly and the high-temperature expansion of the harmonic free energy up to the 2nd order, all of them are dictated by the first-principles QHA phonon DOS $g_{\text{ph}}(\omega)$. These three equations for the phonon characteristic temperatures $\theta_A$, $\theta_B$, and $\theta_D$ as [25]:

$$k_B \theta_A = \hbar e^{(1/3)} \exp \left( \int_0^\infty (\omega) g_{\text{ph}}(\omega) d\omega \right),$$

$$k_B \theta_B = \frac{4}{3} \int \omega^2 g_{\text{ph}}(\omega) d\omega,$$

$$k_B \theta_D = \left( \frac{5}{3} \int (\omega)^2 g_{\text{ph}}(\omega) d\omega \right)^{1/2}.$$  

By using $\theta_A$, $\theta_B$, and $\theta_D$, the Debye temperatures $\theta_A$ and $\theta_B$ ($\theta_A \leq \theta_B$) (which give rise to the respective density of state $g_A^A(\omega)$ and $g_B^B(\omega)$) must satisfy a set of nonlinear equations:

$$1 = \xi_A^A + \xi_B^B,$$

$$\ln(\theta_A) = \xi_A^A \ln(\theta_A) + \xi_B^B \ln(\theta_B),$$

$$\theta_1 = \xi_A^A \theta_A + \xi_B^B \theta_B,$$  

$$\theta_2 = \xi_A^A \theta_A^2 + \xi_B^B \theta_B^2.$$  

Solving these equations gives the solution for $\xi_A^A$, $\xi_B^B$, $\theta_A$, and $\theta_B$, which then determine the double-Debye model by equation (6). It is worth noting that all of these parameters are a function of the specific volume. The phonon DOS $g_D(\omega)$ obtained, though having features only qualitatively similar to the original $g_{\text{ph}}(\omega)$, can reproduce the vibrational free energy very accurately. In order to account for the variation of the phonon DOS with respect to compression, the Gruneisen parameters $\gamma_{(0,A,B)}$ are introduced and defined as

$$-\frac{d \ln \theta_{(0,A,B)}(V)}{d \ln V} \equiv \gamma_{(0,A,B)} = \alpha_{(0,A,B)} + \beta_{(0,A,B)} V.$$  

The solution of equation (14) is

$$\theta_{(0,A,B)}(V) = \theta_{(0,A,B)}^0 \left( \frac{V}{V_{\text{ref}}} \right)^{-\alpha_{(0,A,B)}} \exp \left[ \beta_{(0,A,B)} (V_{\text{ref}} - V) \right],$$  

where $\theta_{(0,A,B)}^0$ is the value of $\theta_{(0,A,B)}$ at the reference state with a volume of $V_{\text{ref}}$. In this way, the whole QHA free energy over a wide pressure and temperature range can be represented by a simple model with only nine parameters: $\theta_{(0,A,B)}^0$, $\alpha_{(0,A,B)}$, and $\beta_{(0,A,B)}$.

Finally, the phonon contribution to the total free energy is expressed as:

$$F_{\text{ph}}(V, T) \approx F_D(V, T) = \xi_A^A F_A(V, T) + \xi_B^B F_B(V, T),$$

with
\[ F_{AB}(V, T) = k_B T \left\{ \frac{9 \theta_{AB}}{8T} + 3 \ln \left[ 1 - e^{\frac{\theta_{AB}}{T}} \right] - D\left(\frac{\theta_{AB}}{T}\right) \right\}, \]

in which the Debye function is given by

\[ D(y) = \frac{3}{y^3} \int_0^y \frac{x^3}{\exp(x) - 1} \, dx. \]

In this work, the cold energy is calculated using DFT [30, 31] and plane-wave pseudopotential methods, as implemented in the Vienna ab initio simulation package (VASP) [32, 33]. The Perdew–Burke–Ernzerhof (PBE) parameterization of the electronic exchange-correlation energy function [34] is used. The interaction between ions and valence electrons is described by the projector augmented-wave (PAW) pseudopotentials [35, 36]. The kinetic energy cutoff for the plane-wave basis set is taken as 900 eV, a \(25 \times 25 \times 25\) Monkhorst–Pack grid for the \(k\)-points sampling is used for both B1 and B2 structures. The convergence of these parameters is well checked, with the uncertainty in the total energy less than 1 meV per atom.

Ignoring the effects of electron–phonon (e–p) coupling on electronic structure, the electronic structures of all isotopes are the same in ab initio calculations. Since the major contribution to isotopic effects comes from lattice dynamics, we imposed this approximation in our work. In this case we alter the atomic mass in the standard pseudopotential to obtain the imposed this approximation in our work. In this case we alter the atomic mass in the standard pseudopotential to obtain the isotopic effects. Lattice dynamics and phonon density of states are calculated by using the PHONOPY package [37], in which the force constants are approximated with the small displacement method. The required forces are evaluated using VASP, with a supercell containing 128 atoms in B1 phase and 250 atoms in B2 phase respectively. A \(4 \times 4 \times 4\) \(k\)-point mesh is used to sample the first Brillouin zone. The plane wave basis set cutoff is increased to 1000 eV. The convergence of the obtained forces is carefully checked to ensure that the uncertainty in the ZPE is less than 1 meV per atom. The phDOS are evaluated on a discrete volume grid. They are then fitted to the double-Debye model (2DM) as briefed above, which has been successfully applied to calculate the phonon free energy of dense hydrogen [38] and carbon [39]. For the purpose of comparison, the single-Debye model (1DM) is also evaluated in this work.

It should be noted that the contribution of thermoelectrons to the free energy in lithium hydrides is very small within our considered pressure and temperature range, and thus is neglected.

3. Results and discussion

3.1. Electronic structures

LiH is a large gap insulator under ambient conditions. The direct energy gap is about 4.94 eV by the reflectance measurement [40]. Our calculated band gaps at zero pressure with LDA and GGA are 2.65 and 2.95 eV respectively. As do other calculations reported in the literature [17, 18], this underestimates the band gap. Using GW approximation [41–44], we obtained a band gap of 4.80 eV, slightly smaller than the experimental value. It was reported that a simple self-interaction correction [45] is able to generate a band gap of 4.93 eV, in perfect agreement with the experimental result. Because of the good performance of the GW method for the band gap, all electronic structure calculations described below were carried out using this method.

In order to understand the electronic structure, the wave function is usually decomposed by projection onto atom-centered spherical orbitals with different angular momentum, and then construction of the differential charge density with respect to the atomic superposition to analyse the chemical bonding and charge transfer between atoms. It is a powerful tool in understanding how the quantum nature of electrons dictates material properties. Alternatively, for an ionic compound such as LiH, since one expects a complete charge transfer from Li\(-2\) to H\(-1\), it could be regarded as a pure ionic compound with nominal charge states of +1 and −1. In this case, the electronic structure of LiH should be more similar to its cation or anion sublattice, rather than the superposition of the atomic orbitals. Therefore we can compare its total DOS with that of the (artificial but heuristic) cation or anion sublattice, so as to understand profoundly the interaction between the sublattices and how it modifies the charge distribution and electronic structures. It is necessary to point out that this is just to view the same problem from an alternative perspective, and is complementary to the traditional decomposition of DOS into atom-centered spherical orbitals. For this reason, in the below we will analyse the electronic structures of LiH by both methods.

LiH at 0 GPa is assumed to be a pure ionic compound formed by sublattices of H\(^-\) and Li\(^+\). In terms of atomic orbitals, the 2\(s\) electron of a Li atom is transferred to the H\(-1\) state. The left 1\(s\) shell in Li\(^+\) is thus closed and tightly bound to the lithium nucleus, which is rigid and almost unresponsive to atomic environmental changes (see figure 1). Therefore the highest occupied valence band in LiH should be the 1\(s\) state contributed by the H\(^-\) sublattice, and the lowest unoccupied conduction band could be 2\(s\) or 2\(p\) states from the Li\(^+\) sublattice, depending on their relative shift by the local environment. However, since the electrons in H\(^-\) are spread out and not tightly bound, one may argue that at high pressures there might have some overlapping of the wavefunctions between neighboring H\(^-\) anions, leading to bonding \(\sigma\) and anti-bonding \(\sigma^*\) states. The latter might become the lowest unoccupied conduction band, and determine the size of the energy band gap. This simple picture seems qualitatively reasonable, but its validity needs further confirmation. Decomposing the LiH crystal into separate H\(^-\) and Li\(^+\) sublattices, and the interaction between them, our calculation predicts that the gap in the H\(^-\) sublattice of B1 structure is opened by 1\(s\) and 2\(p\) states from 0 to 300 GPa, rather than \(\sigma\) and \(\sigma^*\) states. The little hybridization observed in figures 2 and 3 indicates that the wavefunction overlapping in the H\(^-\) sublattice is very small. For the Li\(^+\) sublattice, we observe a stronger hybridization between 2\(s\) and 2\(p\) states, and results in a gap within the conduction band in the total DOS. It should be noted that
the 1s state of lithium lies at a much lower energy and thus is not shown in figures 2–4, in which the s state in the Li+ sublattice refers to Li-2s. In the real LiH crystal, the strong interaction between H− and Li+ sublattices transfers some electrons from the H− sublattice back to the Li+ sublattice, and leads to a significant hybridization among H-1s, Li-2s and Li-2p in the valence band. The band gap in LiH is almost the same size as in the (artificial) H− sublattice at low pressures. But there are two differences: (1) the sublattices’ interaction now leads to a strong hybridization of spd orbitals of H and Li atoms, and (2) the unoccupied p and d orbitals in the H− sublattice are greatly depressed by sublattice interactions, and the gap in LiH is opened between H-1s and Li-2p states. Specifically, our calculation at 0 GPa suggests that the top of the valence band of LiH is dominated by the anion 1s state, whereas the bottom of the conduction band is mainly the cation 2p state.

At higher pressures, taking the B1 and B2 phases at 300 GPa for example, though the sublattice interactions also transfer electrons back to the Li+ sublattice, the feature of DOS near the Fermi level is now mainly determined by the Li+ sublattice, rather than the H− sublattice as shown in figure 2. This is evident from figures 3 and 4, which provide the total and projected DOS of separate H− and Li+ sublattices, and LiH respectively. It can also be found that the stability of the B2 phase with respect to the B1 phase mainly comes from the larger valence band width of the former (18.91 eV versus 10.39 eV), i.e. the delocalization of the valence states. For the B1 phase at 300 GPa, GW pushes Li-2p orbital away from the Fermi level, and creates a gap of 2.05 eV, whereas in B2 phase GW broadens the valence band width to 18.91 eV.
as illustrated in figure 4. Therefore the band gap in the B1 phase at high pressures is opened between the cation 2p state and the hybridized spd state. By comparing the change of the total and projected DOS of LiH at around the B1 → B2 transition pressure of 300 GPa with that at 0 GPa calculated by GW method, it is evident that compression delocalizes H-1s, Li-2s and Li-2p states. This leads to a strong hybridization among them and broadens the valence band and conduction band width, thus reducing the band gap. The phase transition to the B2 phase at 300 GPa broadens the valence band width greatly, and for this reason the band gap closes up. At the same time the conduction band width is slightly narrowed, with unoccupied Li-2p state localized just above the Fermi level.

### 3.2. Vibrational free energy at high pressures and temperatures

Although the GW method provides a better description of the electronic structures, it is computationally demanding and does not lead to better values for total energy and forces. At the LDA or GGA level, the total energy and forces are usually well produced. For this reason, GGA is used to calculate the total energies in this work, which are then fitted to data in 0–100 GPa variation in the B1 phase, and the corresponding Grüneisen parameters thus cannot be derived. The exact cause of this abnormality is unclear, and requires further investigation in the future. Therefore, for the B1 phase of 7LiT we simply use the 1DM to reproduce the QHA results. This gives a slightly larger error at low temperatures, as shown in table 3.

### 3.3. Equation of state and B1–B2 solid phase boundary

Due to the high accuracy of 2DM in reproducing the vibrational free energy, it can be used to calculate the EOS of lithium hydrides. The vibrational free energy of 6LiH reproduced by 1DM has the largest relative errors ranging from 7.27% to 10.98% for both B1 and B2 phases, at 100 and 450 GPa respectively. Note that the relative errors at 3000 K are greatly reduced. Heavier hydrogen isotopes have lesser relative errors. This is because the larger mass of these hydrogen isotopes reduces their vibrational frequencies, and the phonon spectrum becomes more similar to that of a single-Debye model. When the 2DM is employed to represent the QHA results, all of the relative errors in 6LiH, 6LiD, and 7LiT are reduced by one or two orders of magnitude. Note that for the B2 structure at 100 GPa and 3000 K, the relative error of 2DM is slightly smaller than that of 1DM, and both are less than 3.97%. This indicates that 1DM and 2DM have similar precision to reproduce the QHA data under this condition, but 2DM is much better in all other cases. The good performance of 2DM is attributed to the multiple peaks in the phonon spectrum of lithium hydrides, which more easily captured by 2DM than 1DM. Figure 5 displays the phDOS of the first-principles QHA and that of 2DM in B1 and B2 structures of 6LiH at 100 and 450 GPa respectively. It is evident that the shape of $\text{U}_G(\omega)$ is closer to 2DM than 1DM, the latter having just one peak.

For the standard single-Debye model, the thermal pressure is given by:

$$P_0 = \frac{\gamma_0}{V} \left( -\frac{9}{8} k_B \theta_0 + 3 k_B T \frac{\theta_B}{T} \right).$$

Here the Grüneisen parameter $\gamma_0$ is a smooth function of volume, and can usually be described approximately by equation (14). The Grüneisen parameters $\gamma_{A,B}$ in 2DM also have a similar behavior to $\gamma_0$, and equation (14) works well for most cases, except for 7LiT. In supplementary figures S1 and S2, we plot the variation of $\theta_A$ and $\theta_B$ of 7LiT in B1 and B2 phases as a function of volume. It can be seen that both $\theta_A$ and $\theta_B$ are well-behaved in the B2 phase, and can be described by equation (14) very well. However, $\theta_A$ and $\theta_B$ show irregular variation in the B1 phase, and the corresponding Grüneisen parameters thus cannot be derived. The exact cause of this abnormality is unclear, and requires further investigation in the future. Therefore, for the B1 phase of 7LiT we simply use the 1DM to reproduce the QHA results. This gives a slightly larger error at low temperatures, as shown in table 3.
Table 2. Parameters of the double-Debye model obtained by fitting to first-principles phDOS of both B1 and B2 phases of $^6$LiH, $^6$LiD, $^7$LiT and $^7$LiH within a pressure range from 100 to 450 GPa.

|         | $\theta_0^0$ (K) | $\alpha_0$ | $\beta_0$ (Å$^{-3}$) | $\theta_A^0$ (K) | $\alpha_A$ | $\beta_A$ (Å$^{-3}$) | $\theta_B^0$ (K) | $\alpha_B$ | $\beta_B$ (Å$^{-3}$) |
|---------|------------------|------------|-----------------------|------------------|------------|-----------------------|------------------|------------|-----------------------|
| $^6$LiH(B1) | 3036.65 | 0.326 | 0.053 | 1474.33 | -0.462 | 0.138 | 4383.04 | 0.506 | 0.037 |
| $^6$LiD(B1) | 2553.45 | 0.318 | 0.057 | 1316.22 | -0.606 | 0.125 | 3229.39 | 0.593 | 0.027 |
| $^6$LiT(B1) | 2307.49 | 0.319 | 0.057 | 1222.27 | -0.098 | -0.005 | 2809.79 | 0.807 | -0.010 |
| $^7$LiT(B1) | 2220.26 | 0.320 | 0.057 | — | — | — | — | — | — |
| $^6$LiH(B2) | 2995.69 | -0.286 | 0.218 | 1844.87 | 0.298 | 0.118 | 4205.52 | 0.802 | -0.004 |
| $^6$LiD(B2) | 2518.94 | 0.249 | 0.112 | 1974.72 | -0.887 | 0.405 | 3139.34 | 0.844 | 0.010 |
| $^6$LiT(B2) | 2276.23 | 0.252 | 0.111 | 2153.76 | -3.779 | 1.024 | 3245.11 | 1.351 | -0.004 |
| $^7$LiT(B2) | 2423.82 | 0.249 | 0.112 | 1718.53 | -2.396 | 0.737 | 3066.68 | 1.023 | 0.007 |
| $^7$LiH(B1) | 2038.74 | 0.420 | 0.039 | 1137.90 | 0.096 | 0.057 | 2926.23 | 0.714 | 0.008 |
| $^7$LiD(B1) | 1714.40 | 0.420 | 0.039 | 1146.12 | -0.388 | 0.087 | 2103.34 | 0.855 | -0.010 |
| $^6$LiH(B1)$^a$ | 3036.65 | 0.404 | 0.041 | 1474.33 | -0.116 | 0.076 | 4383.04 | 0.616 | 0.018 |

$a$ Fitting to the B1 phase of $^6$LiH from 0 to 450 GPa.

Note: Also given are the B1 phase of $^7$LiH and $^7$LiD from 0 to 100 GPa. The reference state of $\theta_{0,A,B}^0$ is at the highest pressure end for each pressure range considered.

Table 3. Relative error of the vibrational free energy calculated by single-Debye model and double-Debye model with respect to the first-principles QHA in lithium hydrides at about 100 and 450 GPa respectively.

|       | Single-Debye model | Double-Debye model |
|-------|-------------------|--------------------|
|       | $^6$LiH | $^6$LiD | $^6$LiT | $^7$LiT | $^6$LiH | $^6$LiD | $^6$LiT | $^7$LiT |
| B1 100 GPa | 7.33 | 2.75 | 1.33 | 5.21 | 0.05 | 0.02 | 0.09 | — |
| 300 K   | 6.00 | 1.89 | 0.09 | 0.45 | 0.009 | 0.004 | 0.04 | — |
| 450 GPa | 10.60 | 6.18 | 4.92 | 1.71 | 0.02 | 0.01 | 0.003 | — |
| 300 K   | 4.04 | 0.94 | 0.48 | 0.05 | 0.01 | 0.003 | 0.02 | — |
| B2 100 GPa | 10.98 | 3.95 | 2.51 | 2.87 | 2.60 | 0.14 | 0.61 | 0.26 |
| 300 K   | 3.97 | 0.23 | 0.14 | 0.15 | 3.50 | 0.11 | 0.10 | 0.09 |
| 450 GPa | 7.27 | 2.56 | 1.08 | 1.52 | 0.03 | 0.03 | 0.03 | 0.03 |
| 300 K   | 2.40 | 0.31 | 0.05 | 0.09 | 0.14 | 0.07 | 0.07 | 0.05 |

Figure 5. Phonon density of state (phDOS) of $^6$LiH in B1 and B2 structures at 100 and 450 GPa respectively. The black lines denote the first-principles QHA data, and red lines are for 2DM.
experimental data, especially at high pressures. The vibrational contribution softens the EOS greatly. In particular, the 300 K isotherm is in good agreement with the experimental data, whereas the 0 K isotherm is still less compressible. This reveals that zero-point motion and temperature play a significant role in the EOS of lithium hydrides. The change of the lattice constant with temperature for the B1 phase in 7LiH at ambient pressure is shown in the inset of figure 6. It can be seen that our EOS is in good agreement with other theoretical [19] and experimental data [49]. It should be noted that both 2DM and 1DM give a similar static compression curve across the whole pressure range under consideration.

The isotopic shift in the pressure between 7LiH and 7LiD at 300 K has been measured experimentally [7]. Previous DFPT results [23] revealed the important role of ZPE in this isotopic shift at low pressures. Here we employ the 2DM and 1DM to calculate the isotopic shift for the whole pressure range considered in the experiment. As shown in figure 7, our 1DM results are in good agreement with the previous results that also used the standard single-Debye approximation. Both results underestimate the isotopic shift. On the other hand, the mixed Debye-Einstein approach (with the transverse optical phonons represented by the Einstein model) overestimates this isotopic shift. However, when 2DM is used to represent the QHA data, the isotopic shift in pressure is accurately reproduced. This suggests that it is the function form of the single-Debye model that deteriorates the QHA results.

Moreover, we also investigate the isotopic effects on the B1–B2 solid phase boundaries of lithium hydrides. Previous theoretical studies mainly focused on this transition of 7LiH at 0 and 300 K, and estimated a transition pressure spanning from 200 to 500 GPa [9–16]. The finite temperature phase transition and isotopic effects, however, are not explored. The calculated B1–B2 solid phase boundaries of 6LiH, 6LiD, 6LiT, and 7LiT are displayed in figure 8. Those of 7LiH and 7LiD are not listed because their isotopic effect is very close to 6LiH and 6LiD respectively. 2DM is employed to calculate the phase boundaries for 6LiH, 6LiD, and 6LiT, whereas 1DM is used for 7LiT because the double-Debye cannot be well defined for this isotope when in the B1 phase. The inset of figure 8 demonstrates the relative errors of 1DM with respect to that of 2DM in the B1–B2 phase transition pressures of 6LiH, 6LiD, and 6LiT with temperature varying from 0 to 300 K. It can be seen that the relative errors decrease with increasing temperature, and the largest relative error is about 5% in 6LiH at 0 K. The magnitude of these errors cannot be ignored when describing the B1–B2 solid phase boundary.

From figure 8, it is evident that the isotopic effects on the B1–B2 phase boundaries are striking. At high temperatures (above 2000 K), there are remarkable isotopic shifts between 6LiH and 6LiD. When temperature decreases, the isotopic effect between 6LiT and 7LiT also becomes large. But this
might be due to the errors in $^7$LiT, because its phase boundary is calculated with 1DM. At 0 K, the transition pressure difference between $^6$LiH and $^7$LiT is about 15 GPa. With increasing temperature this difference reduces, and finally overlaps at 1490 K and 280 GPa. Beyond that temperature, $^6$LiH has higher B1–B2 transition pressure than $^7$LiT. Note that $^6$LiH also reverses the relative position of its boundary with respect to $^6$LiD and $^7$LiT. At very high temperatures (close to 3000 K), the isotopic shift diminishes. It is necessary to point out that except $^7$LiT, all of $^6$LiX (X = H, D, T) show a weak reentrant feature in their B1–B2 phase boundary. Specifically, within a narrow pressure range just above the 0 K transition pressure, increasing temperature will transform the compound back to the B1 phase, and further increasing temperature will bring it back to the B2 phase again. It is highly unclear whether this is a unique property of lithium hydrides or also shared by other alkali hydrides.

3.4. Phase diagram

With the above comprehensive calculations and analysis, we finally reach the stage of constructing a finite temperature phase diagram for LiH. This phase diagram is fundamental to understanding the high-pressure and high-temperature thermodynamics of lithium hydrides. Combining our calculated B1–B2 finite temperature phase boundary of $^6$LiH, and the previously calculated melting curve of B1 phase for $^7$LiH reported by Ogitsu et al [50], as well as its extrapolation using the Kechin equation [51]

$$ T_m(P) = 790[1 + 0.3911(P + 0.28)]^{0.5221} e^{-0.001373P + 0.28} $$

where $T_m(P)$ is the melting temperature at a given pressure $P$. We obtain a first-principles phase diagram of LiH, and show it in figure 9. The B1–B2-liquid triple point is determined at 241 GPa and 2413 K. Here we note that the isotopic effect on the melting curves between $^6$LiH and $^7$LiH is negligible, because of the small relative mass difference between them.

Besides static experiments such as DAC, dynamical compression is also an important method to explore the high pressure physics. The principal shock Hugoniot of $^6$LiH calculated by 2DM is shown in figure 9, and is compared with the deduced data of the shock-wave experiment reported by Marsh [52] (the details of calculating shock Hugoniots from first-principles calculations are referenced to [53]). It can be seen that our results are in good accordance with the deduced data of shock wave experiments. Only when the shock pressure is higher than 25 GPa does our 2DM predict a slightly higher shock temperature. However, the slight deviation in shock temperature might not be due to the QHA data or the fitting error in 2DM. It should be noted that the samples of the shock wave experiment in [52] contained minor impurities (4.5% $^7$Li). This might modify the phonon spectra and lattice specific heat, and thus reduce the lattice dynamics contributions.

Our calculation predicts that the shock melting occurs at 1923 K and 56 GPa, which is far from the stable region of B2 solid phase. As shown in figure 9, a direct shock of LiH cannot cross the B1–B2 phase boundary. Besides isentropic or multiple shock compression techniques, precompression of the sample at low pressure is an alternative route to enter the B2 solid phase. We find that in order to pass through the triple point and enter the B2 phase requires a precompression of at least 50 GPa at 293 K. The resultant precompression plus shock Hugoniot is also shown in figure 9. When entering the B2 phase along this path, there is a temperature drop of 230 K. The corresponding volume collapse is about 4.6% (see figure S3 in the supplemental material). By comparison, the same B1 → B2 transition at 0 K has only 1.2% volume collapse.

4. Conclusions

In summary, we have performed comprehensive first-principles calculations to understand the electronic structures, thermodynamic properties, and phase diagram of lithium hydrides. By investigating the electronic structures, we found that LiH is not a pure ionic compound with nominal charge state. There is a strong interaction between Li$^+$ and H$^-$ sublattices of the assumed pure ionic compound, which leads to a charge transfer from the latter back to the former, and results in a strong spd hybridization in the real LiH. At low pressures, the electronic structure near the Fermi level is determined by the H$^-$ sublattice, whereas it is dominated by the Li$^+$ sublattice at high pressures. The first-principles QHA was used to describe the lattice dynamics. The discrete phonon data were then fitted to a double-Debye model with only nine parameters, which accurately reproduces the first-principles vibrational free energy. The isotopic effects on the equation of states and the B1–B2 solid phase boundaries of lithium hydrides are also well modelled. Furthermore, the phase diagram of LiH was amended and completed by first-principles methods, which predicted a triple point at 241 GPa and 2413 K.
analysis revealed that a precompression of the sample to 50 GPa will make the shock Hugoniot go through the B1–B2 boundary and enter the B2 solid phase with a discontinuity having large volume collapse. Considering that lithium hydrides are applied widely in industry and nuclear power engineering, our results will be practical, helpful and stimulate further theoretical and experimental investigations.

Acknowledgments

This work is supported by the National Natural Science Foundation of China under Grant Nos. 11274281 and 11174214, the CAEP Research Projects under Grant Nos. 2012A0101001 and 2015B0101005, and the NSAF under Grant No. U1430117.

References

[1] Messer C E and Levy I S 1965 Inorg. Chem. 4 543
[2] George L and Saxena S K 2010 Int. J. Hydrog. Energy 35 5454
[3] Van Houten R 1974 Nucl. Eng. Des. 31 434
[4] Tyutyunnik V 1992 Phys. Status Solidi B 172 539
[5] Bradtke C, Dutz H, Gehring R, Meyer W, Plickthun M, Reicherz G, Runkel K and Thomas A 1995 Nucl. Instrum. Methods Phys. Res. A 356 20
[6] Mueller W, Blackledge J and Libowitz G 1968 Metal Hydrides (New York: Academic)
[7] Loubeyre P, Le Toullec R, Hamel M, Ulivi L, Datchi F and Hausermann D 1998 Phys. Rev. B 57 10403
[8] Duclos S J, Vohra Y K, Ruoff A L, Filipek S and Baranowski B 1987 Phys. Rev. B 36 7664
[9] Hochheimer H, Strössner K, Hönle W, Baranowski B and Filipek F 1985 Z. Phys. Chem. 143 139
[10] Ghandehari K, Luo H, Ruoff A L, Trail S S and DiSalvo F J 1995 Phys. Rev. Lett. 74 2264
[11] Laziczi A, Loubeyre P, Occelli F, Hemley R J and Mezouar M 2012 Phys. Rev. B 85 054103
[12] Hammerberg J 1978 J. Phys. Chem. Solids 39 617
[13] Martins J L 1990 Phys. Rev. B 41 7883
[14] Zhang J, Zhang L, Cui T, Li Y, He Z, Ma Y and Zou G 2007 Phys. Rev. B 75 104115
[15] Mukherjee D, Sahoo B, Joshi K and Gupta S C 2011 J. Appl. Phys. 109 103515
[16] Wang Y, Ahuja R and Johansson B 2003 Phys. Status Solidi B 235 470
[17] Lebegue S, Alouani M, Arnaud B and Pickett W 2003 Europhys. Lett. 63 562
[18] Zurek E, Hoffmann R, Ashcroft N, Oganov A R and Lyakhov A O 2009 Proc. Natl Acad. Sci. USA 106 17640
[19] Yu W, Jin C and Kohlmeyer A 2007 J. Phys.: Condens. Matter 19 086209
[20] Hama J and Kawakami N 1988 Phys. Lett. A 126 348
[21] Xie Y, Ma Y, Cui T, Li Y, Qiu J and Zou G 2008 New J. Phys. 10 063022
[22] Zhang H, Yu Y, Zhao Y, Xue W and Gao T 2010 J. Phys. Chem. Solids 71 976
[23] Roma G, Bertoni C M and Baroni S 1996 Solid State Commun. 98 203
[24] Dammak H, Antoshchenkova E, Hayoun M and Finocchi F 2012 J. Phys.: Condens. Matter 24 435402
[25] Chiscolm E D, Crockett S D and Wallace D C 2003 Phys. Rev. B 68 104103
[26] Vinet P, Rose J H, Ferrante J and Smith J R 1989 J. Phys.: Condens. Matter 1 1941
[27] Murnaghan F D 1937 Am. J. Math. 59 235
[28] Birch F 1947 Phys. Rev. 71 809
[29] Poizat J P and Taramola A 1998 Phys. Earth. Planet. Inter. 109 1
[30] Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864
[31] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
[32] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[33] Kresse G and Furthmüller J 1996 Comput. Mater. Sci. 6 15
[34] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[35] Blöchl P E 1994 Phys. Rev. B 50 17953
[36] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[37] Togo A, Oba F and Tanaka I 2008 Phys. Rev. B 78 134106
[38] Caillabet L, Mazevet S and Loubeyre P 2011 Phys. Rev. B 83 094101
[39] Correa A A, Benedict L X, Young D A, Schweger E and Bonev S A 2008 Phys. Rev. B 78 024101
[40] Kondo Y and Asaumi K 1988 J. Phys. Soc. Japan 57 367
[41] Shishkin M and Kresse G 2006 Phys. Rev. B 74 035101
[42] Shishkin M and Kresse G 2007 Phys. Rev. B 75 235102
[43] Fuchs F, Furthmüller J, Bechstedt F, Shishkin M and Kresse G 2007 Phys. Rev. B 76 115109
[44] Shishkin M, Marsman M and Kresse G 2007 Phys. Rev. Lett. 99 246403
[45] Baroni S, Parravicini G P and Pezzica G 1985 Phys. Rev. B 32 4077
[46] Vidal J P and Vidal-Valat G 1986 Acta Crystallogr. B
[47] Gerlich D and Smith C 1974 J. Phys. Chem. Solids 35 1587
[48] Mukherjee D, Sahoo B, Joshi K and Gupta S C 2013 Proc. of Int. Conf. on Recent Trends in Applied Physics and Material Science: RAM 2013 vol 1536 (Melville, NY: AIP Publishing) pp 403–4
[49] Smith D K and Leider H 1968 J. Appl. Crystallogr. 1 246–9
[50] Ogitsu T, Schweger E, Gyyi F and Galli G 2003 Phys. Rev. Lett. 91 175502
[51] Kechin V V 2001 Phys. Rev. B 65 052102
[52] Marsh S Technical Report No. LA–4942, Los Alamos Scientific Lab., NM, USA
[53] Geng H, Chen N and Sluiter M 2005 Phys. Rev. B 71 012105