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First-principles calculation of the shock-wave equation of state of isotopic lithium hydrides

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The equations of state (EOS) of solid LiH in the $B1$ (NaCl-type) and $B2$ (CsCl-type) structures have been calculated within the local-density approximation (LDA), using the augmented-plane-wave method with Ceperley-Alder's form for the exchange-correlation energy. Using the EOS obtained by the LDA, the volume dependencies of the Debye temperatures for both phases have been determined. The calculated Debye temperatures in the $B1$ phase at zero pressure and zero temperature are 1246 K for ^{7}LiH and 972 K for ^{7}LiD in agreement with the experimental values in the $T=0$ K limit at normal pressure which are 1190±80 K for ^{7}LiH and 1030±50 K for ^{7}LiD, respectively. The calculated lattice constants for isotopic LiH at zero pressure are in agreement with the experimental values at $T=83$ K by 1.9%. With these results the shock-wave equations of state (the Hugoniot) for both phases have been calculated. The Hugoniots for the $B1$ phase are in agreement with the experiment by Marsh.

I. INTRODUCTION

The properties of materials under high pressures and high temperatures have attracted much attention because of their relevance for understanding the compositions of the earth's interior and other planetary interiors.[1-3] Present-day shock-wave techniques can produce pressures of several hundred GPa and temperatures of ten or more thousand kelvins, which exceeds the conditions at the inner core of the earth. However, the two parameters of pressure and temperature in the shock-wave experiments are mutually related and cannot be controlled independently, so we need quantitative theoretical analysis to look into the properties of materials under high pressures and high temperatures using shock-wave data.

Solid LiH is a good candidate for investigating the shock-wave equation of state (Hugoniot) experimentally[4-8] and theoretically because it has large mass differences between different isotopic compositions and under normal conditions it is an insulator with the simple structure of $B1$ (NaCl-type[9]) and is expected to undergo a metallic transition to the $B2$ (CsCl-type) structure at an evaluated pressure.[10,11] Extensive experimental study on solid LiH under high pressures has been done by Marsh[8] using the shock-wave technique. There is no evidence of a transition for any of the isotopic combinations up to 45 GPa. So far the theoretical studies[10-15] have been done by a number of researchers laying a stress on the pressure-induced insulator-metal transition at zero temperature. Within the local-density approximation (LDA) Perrot[14] calculated the equation of state (EOS) of the $B1$ phase by using the augmented-plane-wave (APW) method with the Kohn-Sham (KS) exchange energy and took into account the correlation correction to the exchange energy by the first-order perturbation with Hedin-Lundqvist's form of the correlation energy. He predicted that the semimetallic and metallic transitions occur at about 200 GPa and 3 TPa, respectively. However, since the correlation energy is sizable in his results, it is not certain whether we can neglect the correction resulting from the modification of the electron density due to the correlation potential. Thus the self-consistent calculation inclusive of the correlation potential seems to be important. Using an empirical EOS Kulikov[10] predicted that the $B1$-$B2$ transition occurs at about 50–100 GPa accompanying the metallic transition before the band gap closing occurs in the $B1$ phase. However, his EOS of the $B2$ phase is not good, as will be shown in Sec. II. Hammerberg[11] discussed this problem from the electron-gas approach by using the Heine-Abarenkov–type pseudopotential with an empty core for the Li$^+$ ion. He predicted that the $B1$-$B2$ transition occurs at about 200 GPa. He used, however, an empirical EOS of the Born-Mayer type for the insulating $B1$ phase because his approach is not accurate at low densities. Rodriguez and Kunc[16] calculated the volume variation of the total energy in the $B1$ phase within the LDA using norm-conserving pseudopotentials.

A comparison of the theoretical values of the EOS under high pressures with those of the experiment has not been done yet. Thus, in addition to its high-temperature properties, the calculation of the Hugoniots of solid LiH is of interest from this point. In the present paper we have calculated the EOS for the isotopic LiH for the $B1$ and $B2$ structures within the LDA by using the APW method[15,17] and the Ceperley-Alder (CA) exchange-correlation energy.[18] With these results for rigid lattices we have determined the volume dependencies of the Debye temperature and thermodynamic Grüneisen parameters and have calculated the Hugoniots for both phases. Using the Lindemann relation, we have also estimated the pressure dependence of the melting temperatures. The preliminary results on the EOS and electronic band structure in the $B1$ phase under high pressures were reported elsewhere.[15]

II. EQUATION OF STATE AND ELECTRONIC BAND STRUCTURE OF A RIGID LATTICE

In the density-functional theory the total energy (per unit cell) of a crystal with rigid nuclei is a functional of the electron density n and is written as[19]

$$E_0[n]=T_s[n]+U[n]+E_{\mathrm{xc}}[n]\ , \tag{1}$$

where $T_s[n]$ is the kinetic energy of the noninteracting electron system with the same density n, $U[n]$ is the classical electrostatic energy, and $E_{\mathrm{xc}}[n]$ is the exchange-correlation (xc) energy, respectively. In the muffin-tin (MT) approximation the respective terms in Eq. (1) are written in atomic Rydberg units as

$$T_s[n]=\sum_i^{\mathrm{occ}}\varepsilon_i-\sum_\nu\int_0^{R_\nu}\sigma_\nu(\xi)v_\nu(\xi)d\xi\ , \tag{2}$$

$$\begin{aligned}U[n]=&-2\sum_\nu\int_0^{R_\nu}\frac{\sigma_\nu(\xi)}{\xi}d\xi\left[Z_\nu-\int_0^{\xi}\sigma_\nu(\xi')d\xi'\right]\\&+\sum_{\nu,\nu'}Q_\nu Q_{\nu'}\left[\sum_{\mathbf{R}}{}'\frac{1}{|\mathbf{R}-\mathbf{r}_{\nu\nu'}|}-\frac{1}{V}\int\frac{d\mathbf{r}}{r}\right]\\&+3n_I\sum_\nu\frac{Q_\nu V_\nu}{R_\nu}-\tfrac{6}{5}n_I^2\sum_\nu\frac{V_\nu^2}{R_\nu}\ ,\end{aligned} \tag{3}$$

$$E_{\mathrm{xc}}[n]=\sum_\nu\int_0^{R_\nu}\sigma_\nu(\xi)\varepsilon_{\mathrm{xc}}(n_\nu(\xi))d\xi+n_IV_I\varepsilon_{\mathrm{xc}}(n_I)\ , \tag{4}$$

$$Q_\nu=Z_\nu-\int_0^{R_\nu}\sigma_\nu(\xi)d\xi+n_IV_I\ , \tag{5}$$

where $\sigma_\nu(\xi)=4\pi\xi^2n_\nu(\xi)$ with $n_\nu(\xi)$ as the electron density in the νth MT sphere, $\boldsymbol{\xi}=\mathbf{r}-\mathbf{r}_\nu$ with $\mathbf{r}_\nu$ as the atomic position of the νth atom in the unit cell, Z_ν is the atomic number of the νth atom, $\mathbf{R}$ is the lattice translation vector, $\mathbf{r}_{\nu\nu'}=\mathbf{r}_\nu-\mathbf{r}_{\nu'}$, R_ν and V_ν are the radius and the volume of the νth MT sphere, and V is the volume of the unit cell. The average electron density in the interstitial region n_I is given by

$$n_I=\frac{1}{V_I}\sum_\nu\left[Z_\nu-\int_0^{R_\nu}\sigma_\nu(\xi)d\xi\right] \tag{6}$$

with V_I as the volume of the interstitial region in the unit cell. In Eq. (3) the last integral to be taken over all space cancels out the infinite part in the lattice sum. The electron density $n_\nu(\xi)$ is determined self-consistently by the one-particle Schrödinger-type equation:

$$[-\nabla^2+v_{\mathrm{eff}}(\mathbf{r})]\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r})\ , \tag{7}$$

$$n_\nu(\xi)=\sum_i^{\mathrm{occ}}\langle|\psi_i(\mathbf{r})|^2\rangle_\nu\ , \tag{8}$$

$$v_{\mathrm{eff}}(\mathbf{r})=\begin{cases}v_\nu(\xi) & \text{for } |\mathbf{r}-\mathbf{r}_\nu|\le R_\nu\\ 0 & \text{otherwise}\ ,\end{cases} \tag{9}$$

where in Eq. (8) the spherical average is taken over the νth MT sphere and the index i runs over the occupied states, and the effective potential inside the νth MT sphere is written as

$$\begin{aligned}v_\nu(\xi)=&-\frac{2Z_\nu}{\xi}+2\left[\frac{1}{\xi}\int_0^{\xi}\sigma_\nu(\xi')d\xi'+\int_\xi^{R_\nu}\frac{\sigma_\nu(\xi')}{\xi'}d\xi'\right]\\&-2\sum_{\nu'}Q_{\nu'}\left[\sum_{\mathbf{R}}{}'\frac{1}{|\mathbf{R}-\mathbf{r}_{\nu\nu'}|}-\frac{1}{V}\int\frac{d\mathbf{r}}{r}\right]\\&-4\pi n_IR_\nu^2+\mu_{\mathrm{xc}}(n_\nu(\xi))-v_0\ ,\end{aligned} \tag{10}$$

$$\begin{aligned}v_0=&\frac{2}{V_I}\sum_{\nu,\nu'}V_\nu Q_{\nu'}\left[\sum_{\mathbf{R}}{}'\frac{1}{|\mathbf{R}-\mathbf{r}_{\nu\nu'}|}-\frac{1}{V}\int\frac{d\mathbf{r}}{r}\right]\\&+\frac{2}{V_I}\sum_\nu 2\pi R_\nu^2(Q_\nu+\tfrac{1}{5}n_IV_\nu)+\mu_{\mathrm{xc}}(n_I)\ ,\end{aligned} \tag{11}$$

where $\mu_{\mathrm{xc}}(n)$ is the xc potential defined by $(d/dn)[n\varepsilon_{\mathrm{xc}}(n)]$. For the xc energy we used the LDA where we adopted the CA result parametrized by Perdew and Zunger.[20] In Eq. (9) the effective potential in the interstitial region is taken to be zero following the usual convention.

Using the scale transformation of the coordinates of electrons and nuclei $\mathbf{r}=\lambda\mathbf{r}'$ and $\mathbf{R}=\lambda\mathbf{R}'$, the pressure is calculated by

$$P=\frac{1}{3V}\frac{\partial}{\partial\lambda}E_0[n_\lambda]]|_{\lambda=1} \tag{12}$$

with $n_\lambda(\mathbf{r}')$ is the electron density of the transformed system. Since the wave function is transformed according to $\psi_{\lambda i}(\mathbf{r}')=\lambda^{2/3}\psi_i(\mathbf{r})$, the respective terms of $E_0[n_\lambda]$ are written as follows: $T_s[n_\lambda]=\lambda^2T_s[n]$, $U[n_\lambda]=\lambda U[n]$, and

$$E_{\mathrm{xc}}[n_\lambda]=\int_V n(\mathbf{r})\varepsilon_{\mathrm{xc}}(\lambda^3n(\mathbf{r}))d\mathbf{r}\ .$$

From Eq. (12) we readily get

$$\begin{aligned}3PV=&\,2T_s[n]+U[n]\\&-3\int_V n(\mathbf{r})[\varepsilon_{\mathrm{xc}}(n(\mathbf{r}))-\mu_{\mathrm{xc}}(n(\mathbf{r}))]d\mathbf{r}\ .\end{aligned} \tag{13}$$

For the MT approximation Eq. (13) is reduced to

$$\begin{aligned}3PV=&\,2T_s[n]+U[n]\\&-3\sum_\nu\int_0^{R_\nu}\sigma_\nu(\xi)[\varepsilon_{\mathrm{xc}}(n_\nu(\xi))-\mu_{\mathrm{xc}}(n_\nu(\xi))]d\xi\\&-3n_IV_I[\varepsilon_{\mathrm{xc}}(n_I)-\mu_{\mathrm{xc}}(n_I)]\ .\end{aligned} \tag{14}$$

Using the method mentioned above, we have calculated the total energies, pressures, and electronic band structures of solid LiH for the $B1$ and $B2$ structures. In the present calculation all electrons are treated as the Bloch electrons with wave vectors $\mathbf{k}$. The electron density has been calculated self-consistently by the APW method where the angular momenta are taken to be $l\le 12$, and for each $\mathbf{k}$ the reciprocal lattice vectors $\mathbf{G}$ are included up to $|\mathbf{k}+\mathbf{G}|^2\le 22(2\pi/a)^2$ for the $B1$ and $11(2\pi/a)^2$ for the $B2$ structures, respectively, with a as the lattice constants of the respective structures. For the sampling of $\mathbf{k}$ points in the Brillouin zone (BZ), we adopted the special-point technique for the insulating phase where we used 19 and 20 points for the $B1$ and $B2$ structures, respectively, and for the metallic phases we took a 256- and 216-point sampling for the $B1$ and $B2$ structures, respectively. The calculated equilibrium lattice constant of the rigid lattice for the $B1$ phase is 3.927 Å, which is independent of the isotopic compositions. The theoretical value is 3% smaller than the experimental ones.[9] The interpolated values of Perrot's results are 4.170 Å for the KS exchange energy and 4.045 Å for the KS exchange energy with the correlation correction, re-

TABLE I. Lattice constants of the isotopic LiH in the $B1$ phase at normal pressure.

	a (Å) (calc.)[a]			a (Å) (expt.)[b]		
T:	83 K	298 K	513 K	83 K	298 K	513 K
^{7}LiH	4.000	4.008	4.0296	4.0657	4.0829	4.1224
^{7}LiD	3.983	3.995	4.0215	4.0477	4.0693	4.1119
^{7}LiT	3.975	3.990	4.0042	4.0403	4.0633	
^{6}LiH	4.001	4.009	4.0302	4.0666	4.0851	4.1218
^{6}LiD	3.984	3.996	4.0221	4.0499	4.0708	4.1110

[a] a(rigid lattice) $=3.927$ Å.

[b] Reference 9.

spectively. The norm-conserving pseudopotential method[16] with the same CA xc energy as ours gives a rather smaller value of 3.34 Å. Owing to the light masses of the Li and H atoms the lattice vibration produces significant effects on the lattice constant even at low temperatures, as is seen in its large isotope dependence: In the $B1$ phase at normal pressure the extrapolated values of the experimental lattice constants to $T=0$ K are 4.0610, 4.0415, and 4.0340 Å for ^{7}LiH, ^{7}LiD, and ^{7}LiT, and are 4.0615 and 4.0425 Å for ^{6}LiH and ^{6}LiD, respectively. By using the Debye approximation, we estimated the pressure due to the lattice vibration with the Debye temperature theoretically determined by the method which will be mentioned in Sec. III. In Table I the calculated lattice constants for the isotopic LiH in the $B1$ phase at normal pressure are compared with the experimental ones.[9] The theoretical values are in agreement with the experimental ones at $T=83$, 298, and 513 K by (1.6–2.3)% for all isotopic combinations. In Table II we showed the calculated equilibrium lattice constant, bulk modulus, and its pressure derivative of normal LiH in the $B1$ phase at $T=0$ K and compared those with the values by the experiment and previous theories. Figure 1 shows the EOS for both phases, which are compared with the previous theoretical ones: Our pressures are lower than those by Perrot. Thus the modification of the electron density due to the correlation potential is important for a system with a small number of electrons like solid LiH. Since Kulikov's[10] EOS for the $B2$ phase is not good over all densities, his estimate of the transition pressure seems to be not accurate. We found that Hammerberg's[11] total energies are well represented up to the fourth significant figure for all densities in his Table I by $E(r_s)=a_0r_s^{-3}+a_1r_s^{-2}+a_2r_s^{-1}+a_3+a_4\ln r_s$ with $r_s=[3/(4\pi n)]^{1/3}$. According to this we estimated his pressures and Gibbs free energies for both phases. As shown in Fig. 1, the electron-gas results up to the third order of the electron-ion interaction are close to the pressures by the LDA at high densities. However, the $B1$-$B2$ transition occurs at $r_s=2.37$ and $P=2.8$ GPa, in contrast to the result of about 230 GPa by the LDA.

The volume variation of the characteristic excitation energies for the $B1$ and $B2$ phases are shown in Fig. 2. In the $B1$ phase the band gap is the direct gap with the X_1-X_4' symmetries up to the band closing at $V=3.35$ cm^3/mol which is 10% smaller than the value by Perrot. The pressure at the band-gap closing for normal LiH is estimated to be 226 GPa, which is 13% higher than that by Perrot. For further compressions after the band-gap closing the band crossing occurs on the Z line of the first Brillouin zone (BZ) between the state with the Z_1 symmetry and that with the Z_3 symmetry. Figure 3 shows the electronic band structures at normal pressure and at $V=2.83$ cm^3/mol. At lower compressions the valence band and at the bottom of the conduction band consist of the bonding and antibonding states of the H 1s and Li 2s, respectively. As the compression becomes higher, the states having s character shift upwards rapidly due to the symmetry. The bottom of the conduction band has p character of the Li 2p state and shifts downwards relatively to the valence band having s character and the band contact occurs at the X point in the BZ. In the $B2$ phase the band gap is the indirect gap with the R_2'-X_1 symmetries up to $V=7.05$ cm^3/mol. For further compressions the band gap becomes the indirect gap with the R_2'-M_5' symmetries and its closing occurs at $V=6.32$ cm^3/mol with the pressure of 26.6 GPa. In Fig. 4 the electronic band structures at normal pressure and at $V=6.18$ cm^3/mol are shown. Recently the pressure variation of the band gap for normal LiH in the $B1$ phase was measured up to 48 GPa by observing the optical reflectance spectra.[21] Despite the 60% compression of

TABLE II. Equilibrium lattice constant a, bulk modulus K_T, and its pressure derivative K_T' of normal LiH in the $B1$ phase at $T=0$ K. Parentheses denote the room-temperature values.

	a (Å)	K_T (GPa)	K_T'
Present	4.000	36.6	3.40
Perrot	4.170	25.5	
Rodriguez and Kunc	3.40–3.60	45–59	3.26–3.92
Expt.	4.061[a]	34.24 (32.35)[b]	(3.80±0.15)[b]

[a] Reference 37.

[b] Reference 33.

the volume at normal pressure the band gap decreases only slightly from 4.94 eV at normal pressure to 4.52 eV at 48 GPa. The corresponding values by the LDA are 2.57 and 1.70 eV, respectively. Since the LDA underestimates the band gaps of insulators, we estimate the band gaps at normal pressure and at 48 GPa by using the simplified self-interaction correction,[22] which are 4.93 and 3.93 eV, respectively. Though the LDA underestimates the band gaps it gives a reasonable value in the volume at the band closing.

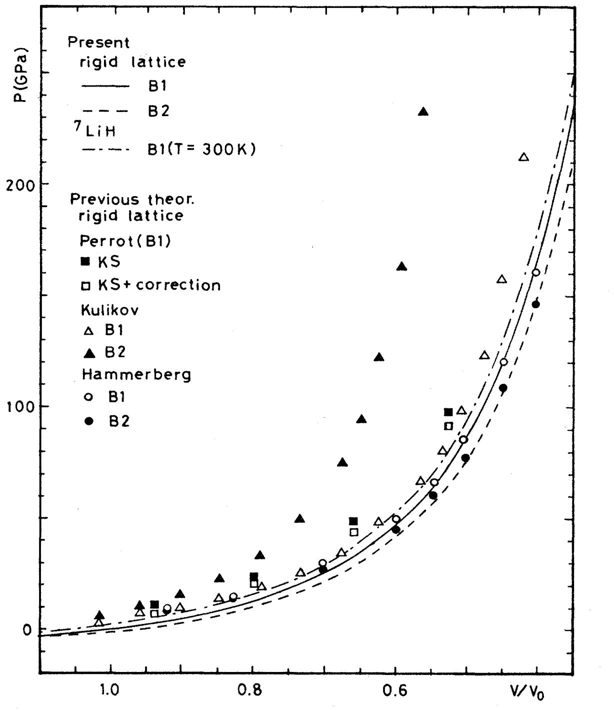

FIG. 1. Theoretical EOS for the $B1$ and $B2$ phases. The volume V is reduced by the calculated volume V_0 at $P=0$ for the rigid $B1$ phase which is given by $V_0=9.117$ cm^3/mol.

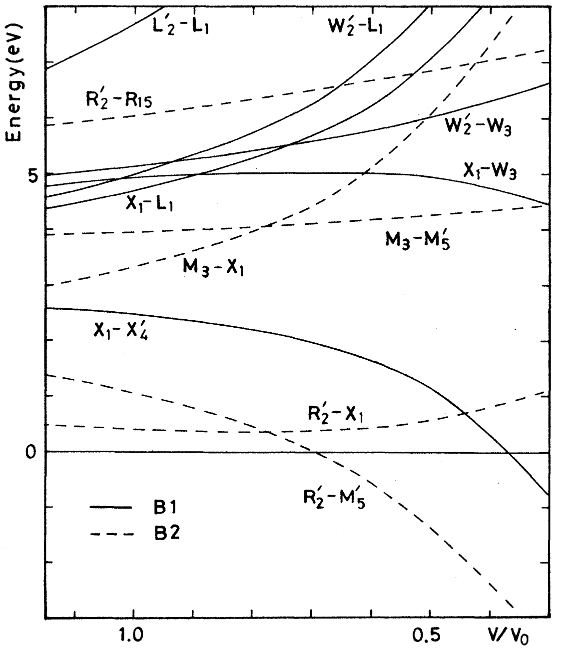

FIG. 2. Characteristic excitation energies of the $B1$ and $B2$ phases vs relative volume with $V_0=9.117$ cm^3/mol. The symbol attached to each curve (Γ-Γ') denotes the symmetry of the occupied state (Γ) and that of the unoccupied state (Γ'), respectively.

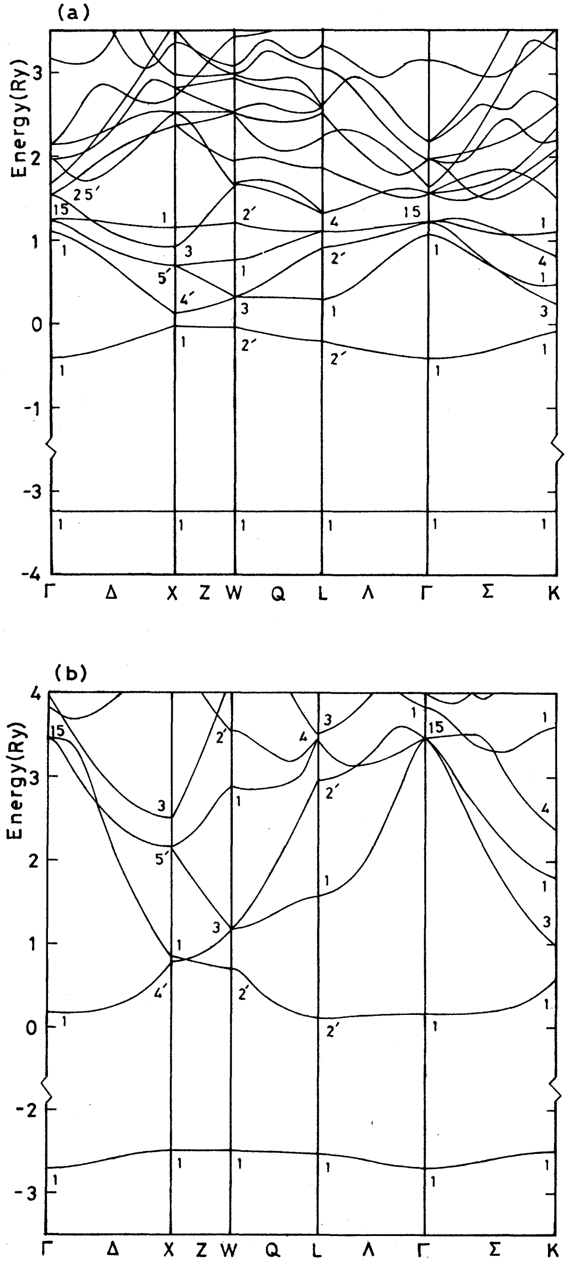

FIG. 3. Electronic band structures of the $B1$ phase (a) at normal pressure and (b) at $V=2.83$ cm^3/mol.

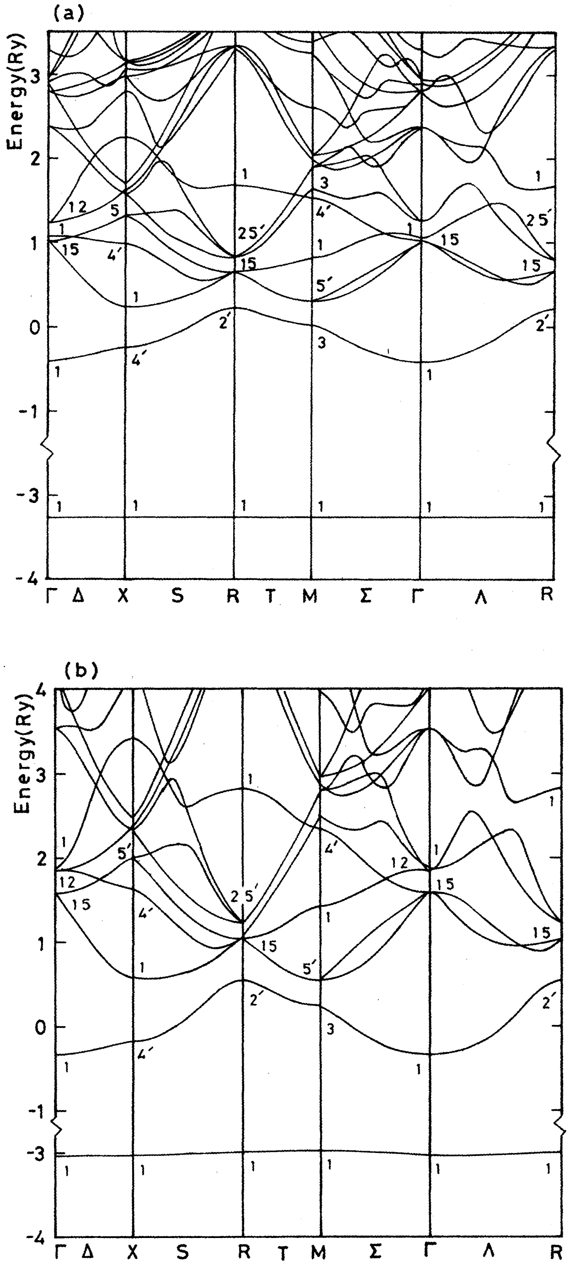

FIG. 4. Electronic band structures of the $B2$ phase (a) at normal pressure and (b) at $V=6.18\ \mathrm{cm}^3/\mathrm{mol}$.

III. VOLUME VARIATION OF THE DEBYE TEMPERATURE

For an insulator having relatively large energy band gap the thermal excitation of electrons is very small and has negligible effects on the total energy and pressure. Thus we take the following approximation:

$$E(V,T)=E_0(V)+E_{\mathrm{vib}}(V,T)\ , \tag{15}$$

$$P(V,T)=P_0(V)+P_{\mathrm{vib}}(V,T) \tag{16}$$

where E_0 and P_0 denote the total energy and pressure for a rigid lattice calculated by the LDA, as was mentioned in Sec. II, and E_{vib} and P_{vib} denote those for the lattice vibration. In the Debye approximation for the lattice vibration we can write

$$\begin{aligned} E_{\mathrm{vib}}&=\tfrac{9}{8}nk_B\Theta+3nk_BTD\left[\frac{\Theta}{T}\right]\ ,\\ P_{\mathrm{vib}}&=\tfrac{9}{8}nk_B\frac{\gamma\Theta}{V}+3nk_BT\frac{\gamma}{V}D\left[\frac{\Theta}{T}\right]\ , \end{aligned} \tag{17}$$

where n denotes the number of atoms in the unit cell, k_B is the Boltzmann constant, Θ is the Debye temperature, and $D(x)$ is the well-known Debye function. The thermodynamic Grüneisen parameter γ defined by $-(\partial\ln T/\partial\ln V)_S$ is expressed as $-(\partial\ln\Theta/\partial\ln V)_T$. The Debye temperature is related to the mean-squared vibration frequency as

$$\Theta=\frac{\hbar}{k_B}(\tfrac{5}{3}\langle\omega^2\rangle)^{1/2}\ , \tag{18}$$

where $\hbar=h/(2\pi)$ and h is Planck's constant. According to the lattice dynamics,[23] $\langle\omega^2\rangle$ can be expressed by the trace of the dynamic matrix $D^{\nu\nu}_{\alpha\alpha}(\mathbf{k})$ divided by the number of normal modes $3nN$ as follows:

$$\begin{aligned} \langle\omega^2\rangle&=\frac{1}{3nN}\sum_{\nu,\alpha}\sum_{\mathbf{k}}D^{\nu\nu}_{\alpha\alpha}(\mathbf{k})\\ &=\frac{1}{3n}\sum_{\nu}\frac{1}{M_\nu}\sum_{\nu',\mathbf{R}}{}'[\nabla^2\phi_{\nu\nu'}(r)]_{r=|\mathbf{R}+\mathbf{r}_{\nu\nu'}|}\ , \end{aligned} \tag{19}$$

where M_ν is the mass of the νth atom located at $\mathbf{r}_\nu$ in the unit cell, and $\phi_{\nu\nu'}(r)$ is the pair potential between the νth and ν'th atoms which is assumed to be centrally symmetric. In the following we assume that there are two atoms in the unit cell, as is the case for the $B1$ and $B2$ structures. Though the force constant $\nabla^2\phi_{\nu\nu'}$ in Eq. (19) may be calculated from first principles by using the LDA,[24] it is laborious and is not appropriate for the simple Debye model. In the present paper we use the following approximation to calculate $\langle\omega^2\rangle$: According to the lattice dynamics of diatomic solids[25] we can express approximately $[\omega(\text{acoustic})]^2\propto 1/M$ and $[\omega(\text{optic})]^2\propto 1/\mu$, with M and μ the total and reduced masses of the two atoms, respectively. In order to take into account the acoustic and optic frequencies in the average manner, we replace $1/M_\nu$ in Eq. (19) by $\frac{1}{2}(1/\mu+1/M)$. Thus we can write Eq. (19) as

$$\langle\omega^2\rangle=\frac{1}{12}\left[\frac{1}{\mu}+\frac{1}{M}\right]\sum_{\nu,\nu'}\sum_{\mathbf{R}}{}'[\nabla^2\phi_{\nu\nu'}(r)]_{r=|\mathbf{R}+\mathbf{r}_{\nu\nu'}|}\ . \tag{20}$$

We estimate the average force constant at the nearest-neighbor distance d and write Eq. (20) as

$$\begin{aligned} \langle\omega^2\rangle&=\frac{1}{6}\left[\frac{1}{\mu}+\frac{1}{M}\right][\nabla^2\Phi(r)]_{r=d}\\ &=\frac{3}{2}\left[\frac{1}{\mu}+\frac{1}{M}\right]\left[\frac{V}{d}\right]^2\left[\frac{d^2}{dV^2}+\frac{4}{3V}\frac{d}{dV}\right]\Phi(V)\ , \end{aligned} \tag{21}$$

where $\Phi(r)$ denotes the lattice energy per unit cell for the system having the nearest-neighbor distance equal to r, and V is the volume of the unit cell. Inserting Eq. (21) into Eq. (18), we get

$$\Theta=\frac{\hbar V}{k_B d}\left[\frac{5}{2}\left[\frac{1}{\mu}+\frac{1}{M}\right]\left[\frac{d^2}{dV^2}+\frac{4}{3V}\frac{d}{dV}\right]\Phi(V)\right]^{1/2} . \tag{22}$$

In the low-temperature region where the excitation of phonons is small, we can take the total lattice energy to be equal to the total energy of the rigid lattice E_0 in Eq. (15), where we neglect the zero point energy. Thus we can express the Debye temperature as[26]

$$\Theta_0=\frac{\hbar}{k_B d}\left[\frac{5}{2}\left[\frac{1}{\mu}+\frac{1}{M}\right]V\right]^{1/2}(K_T^0-\tfrac{4}{3}P_0)^{1/2} , \tag{23}$$

where $K_T^0=-V(\partial P_0/\partial V)_T$. The thermodynamic Grüneisen parameter γ is given by $[\frac{1}{2}(\partial K_T^0/\partial P_0)_T-\frac{2}{3}]/[1-\frac{4}{3}(P_0/K_T^0]-\frac{1}{6}$. If we neglect the $-\frac{4}{3}P_0$ term in Eq. (23), our γ is reduced to the Slater γ.[27] At high temperature the force constant itself depends upon temperature due to lattice vibrations. We consider in the present model that the phonon contribution of the total lattice energy is equal to the thermal mean of the harmonic potential energy. Thus we can express

$$\Theta=\Theta_0(1+\Theta_1)^{1/2},\quad \Theta_1=\frac{1}{2}\left[\tilde{K}_T-\tfrac{4}{3}P_{\text{vib}}-T\left[\frac{\partial}{\partial T}(\tilde{K}_T-\tfrac{4}{3}P_{\text{vib}})\right]_V\right]\Big/(K_T^0-\tfrac{4}{3}P_0) , \tag{24}$$

where $\tilde{K}_T=-V(\partial P_{\text{vib}}/\partial V)_T$. Since Θ_1 in Eq. (24) depends upon Θ, we have to determine Θ self-consistently. To look into the accuracy of our model we applied it to calculate the Grüneisen parameters for solid Ar and Ne, using the Lennard-Jones potential. The results are in reasonable agreement with those by self-consistent phonon calculation[28] where we assumed that

$$\gamma=\sum_{q,s}\omega_{qs}^2\gamma_{qs}\Big/\sum_{q,s}\omega_{qs}^2\sim(1/3N)\sum_{q,s}\gamma_{qs}$$

with γ_{qs} the mode Grüneisen parameter and ω_{qs} the normal-mode frequency. From the result we found that the $-\frac{4}{3}P_0$ term in Eq. (23) is important to obtain reasonable agreement and produces a pronounced effect at high pressures.

Table III shows the calculated Debye temperatures in the $B1$ phase at $T=0$ K and $P=0$. The theoretical values of 1246 K for ^{7}LiH and 972 K for ^{7}LiD are in good agreement with the experimental values in the $T=0$ K limit, which are 1190±80 K for ^{7}LiH and 1030±50 K for ^{7}LiD, respectively.[29] In Fig. 5 the volume variations of the Debye temperatures and thermodynamic Grüneisen parameters are shown. The pressure variation of the melting temperature T_m can be estimated by using the Lindemann relation[30]

$$T_m=\frac{mk_B}{9\hbar^2}(\delta d)^2\Theta^2 , \tag{25}$$

where $\delta=(\langle u^2\rangle)^{1/2}/d$ with $\langle u^2\rangle$ as the mean-square displacement of thermal vibrations. Due to the light mass of the hydrogen atom we assume that T_m is determined by the temperature at which the melting of the Li sublattice occurs. Thus m in Eq. (25) is the mass of the Li atom. According to Shapiro[30] the Lindemann relation holds well for each structure separately where the critical fraction δ for fcc is estimated to be 0.071. The melting

TABLE III. Debye temperatures Θ at $T=0$ K and the melting temperatures T_m in the $B1$ phase at normal pressure.

	Θ (K)		T_m (K)	
	Calc.	Expt.[a]	Calc.	Expt.[b]
^{7}LiH	1246	1190±80	959	961
^{7}LiD	972	1030±50	588	
^{6}LiH	1266		849	
^{6}LiD	995		529	

[a] Reference 29.

[b] Reference 31.

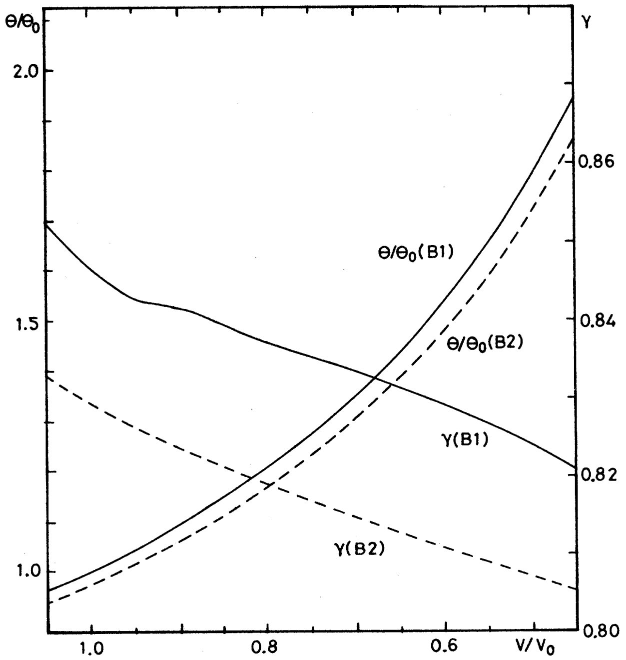

FIG. 5. Debye temperatures Θ and the thermodynamic Grüneisen parameters γ of the $B1$ and $B2$ phases at $T=0$ K vs relative volume with $V_0=9.117$ cm^3/mol. The Debye temperatures are reduced by $\Theta_0=\Theta(V_0)$, which are given by 1308, 1009, 1330, and 953 K (1164, 897, 1182, and 847 K) for ^{7}LiH, ^{7}LiD, ^{6}LiH, and ^{6}LiD for the $B1$ ($B2$) phase, respectively.

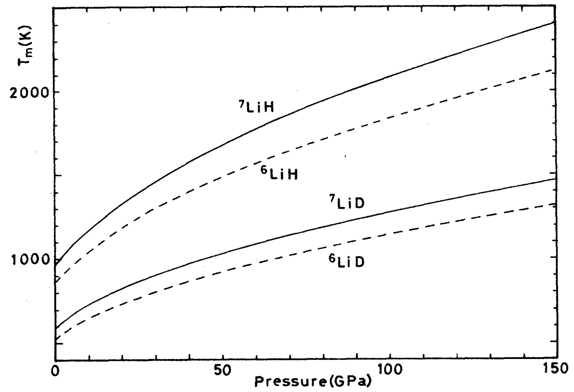

FIG. 6. Pressure variation of the melting temperatures T_m for the $B1$ phase.

temperatures for isotopic LiH at $P=0$ are listed in Table III. The calculated T_m for ^{7}LiH of 959 K is in agreement with the experimental one of 961 K.[31] Figure 6 shows the pressure variation of T_m for isotopic LiH.

IV. SHOCK-WAVE EQUATION OF STATE

Let us consider the shock-wave compression of a material from the initial state (V_0, P_0, T_0) to the Hugoniot state (V_H, P_H, T_H). The Hugoniot state is determined by the Rankine-Hugoniot conservation relation[32]

$$E_H - E_0 = \tfrac{1}{2}(V_0 - V_H)(P_0 + P_H) , \tag{26}$$

where E_H and E_0 denote the internal energy of the Hugoniot state and the initial state, respectively. We now consider the case that a phase transition occurs under the compression. The increase of the internal energy can be calculated by thermodynamic consideration as[32]

$$\begin{aligned} E_H - E_0 = {} & E^h(V_0^h, T_0) - E^l(V_0, T_0) \\ & + \int_{V_0^h}^{V_H} \left[\frac{T_0}{V} \gamma^h(V, T_0) C_V^h(V, T_0) \right. \\ & \qquad \left. - P^h(V, T_0) \right] dV \\ & + \int_{T_0}^{T_H} C_V^h(V_H, T) dT , \end{aligned} \tag{27}$$

where the superscripts l and h denote the low- and high-pressure phases, respectively, C_V is the heat capacity at constant volume, and V_0^h and V_0^l $(=V_0)$ are the volumes of the unit cell for the respective phases at $P=P_0$ and $T=T_0$. Inserting Eq. (27) into Eq. (26) we get the Hugoniot equation of state. Where there is no phase transition under the compression we must replace h by l in Eq. (27). The Hugoniot temperatures in the respective phases are determined by solving

$$P_H = P^\alpha(V_H, T_0) + \frac{1}{V_H} \int_{T_0}^{T_H} \gamma^\alpha(V_H, T) C_V^\alpha(V_H, T) dT \tag{28}$$

with $\alpha = l$ and h. If the temperature variation of the Grüneisen parameter is neglected, Eq. (28) is written as

$$\int_{T_0}^{T_H} C_V^\alpha(V_H, T) dT = \frac{V_H}{\gamma^\alpha(V_H)} [P_H - P^\alpha(V_H, T_0)] . \tag{29}$$

Inserting Eq. (29) into Eq. (27) with Eq. (26), we have

$$\begin{aligned} P_H = {} & \left[P^h(V_H, T_0) + P_0 - \frac{\gamma^h(V_H)}{V_H} \Delta E_{h-l} \right. \\ & \left. - \frac{\gamma^h(V_H)}{V_H} \int_{V_0^h}^{V_H} \left[\frac{T_0}{V} \gamma^h(V) C_V^h(V, T_0) - P^h(V, T_0) \right] dV \right] \Big/ \left[1 - \tfrac{1}{2} \gamma^h(V_H) \left[\frac{V_0}{V_H} - 1 \right] \right] - P_0 , \end{aligned} \tag{30}$$

where $\Delta E_{h-l} = E^h(V_0^h, T_0) - E^l(V_0, T_0)$.

Using Eq. (30), we have calculated the Hugoniot pressures and temperatures for isotopic LiH for the $B1$ and $B2$ structures and have compared these with the experiments in Fig. 7 where the initial temperature is taken to be $T_0 = 293$ K according to Marsh's experiment.[8] Solid lines represent the Hugoniots with the densities calculated at $P=0$ and $T=293$ K in the $B1$ phase as the initial densities ρ_0, where we used the values of V_0^l, V_0^h, and ΔE_{h-l} tabulated in Table IV. In order to treat porous samples or those with lower densities than the calculated crystal densities, we consider these as expanded crystals with the pressure given by $P_0(V_0, T_0)$. Using Eqs. (26), (27), and (29), we have calculated the Hugoniots for lower-density samples in the $B1$ phase, where we replace $P_H - P(V_H, T_0)$ in Eq. (29) by $P_H + P_0 - P(V_0, T_0)$ in order to take $P_H = 0$ at $V_H = V_0$ and $T_H = T_0$. In Fig. 7(a), Burton and Landeen's data, which are estimated by $P_H = \rho_0 u_p u_s$ obtained from u_p and u_s values cited in Ref. 8, where we assumed ρ_0 to be the crystal density at normal conditions[33] of 0.783 g/cm^3, seem to show a phase transition at $P = 70$–90 GPa. We estimated the Gibbs free energies of both phases at the temperature $T = 2000$ K corresponding to their Hugoniot data for ^{n}LiH within the present model and found that the $B1$-$B2$ transition occurs at $P = 130$–140 GPa. Since the energy difference between the $B1$ and $B2$ phases is small and pressures increase rapidly at high densities, a more detailed treatment with regard to the precise determination of the Fermi surfaces and the phonon energy beyond the Debye approximation is required. Thus we cannot deny the possibility of a phase transition at $P = 70$–90 GPa within the present model. Here we note that we did not consider the thermal excitation of electrons. As is shown in Fig. 2,

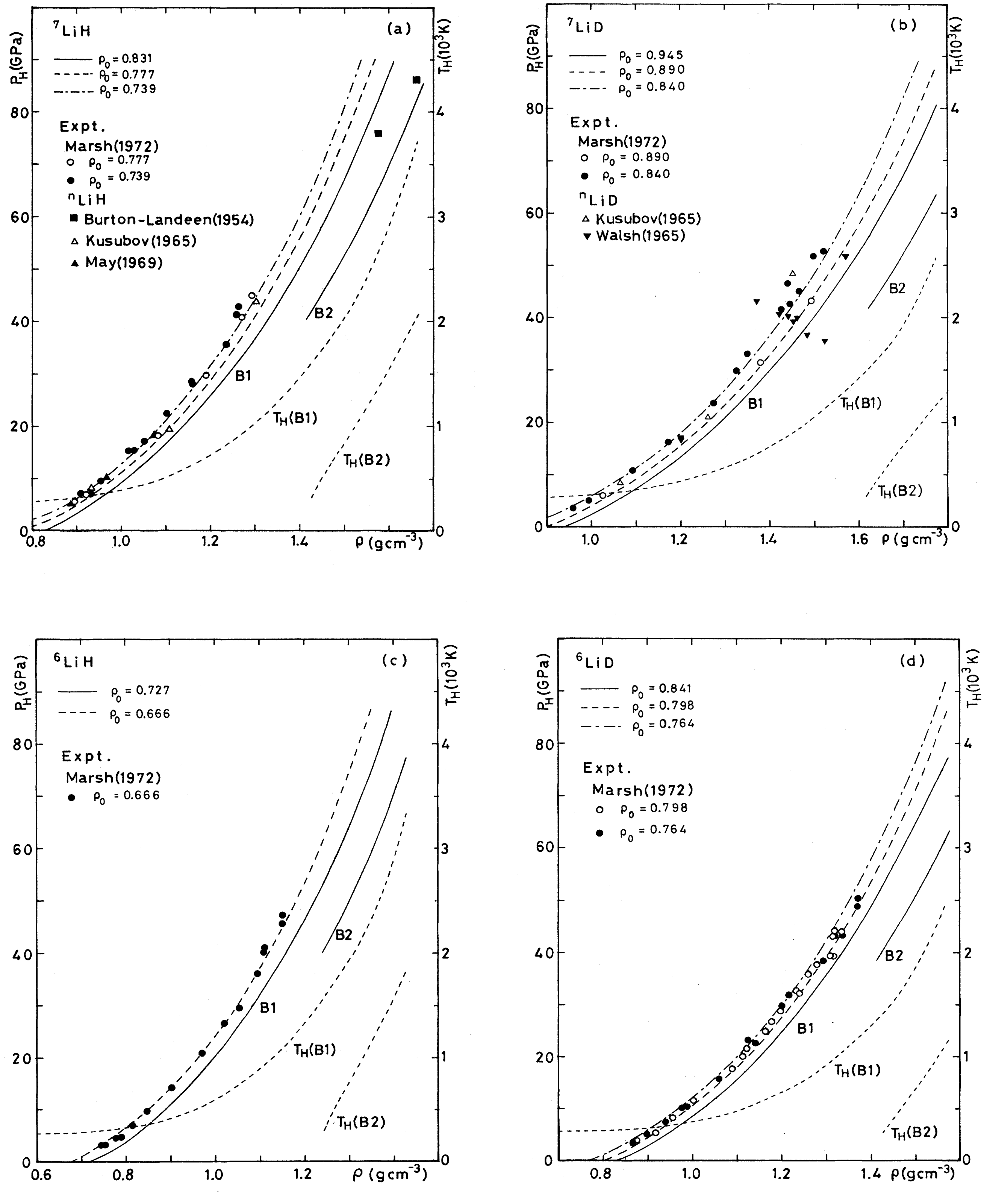

FIG. 7. Hugoniot pressures P_H and temperatures T_H vs density ρ where ρ_0 denotes the initial density in units of g cm^{-3}. (a) ^{7}LiH, (b) ^{7}LiD, (c) ^{6}LiH, and (d) ^{6}LiD.

TABLE IV. Parameters used to calculate the Hugoniots.

	V_0^l (cm^3/mol)	V_0^h (cm^3/mol)	ΔE_{h-l} (mRy)
^{7}LiH	9.692	9.367	25.18
^{7}LiD	9.598	9.285	25.59
^{6}LiH	9.699	9.373	25.16
^{6}LiD	9.605	9.292	25.56

the band gaps close at $V=3.35$ cm^3/mol and 6.32 cm^3/mol for the $B1$ and $B2$ phases, respectively. Thus for the pressure range considered in Fig. 7 this effect is negligible in the $B1$ phase and it may give an effect in the $B2$ phase at high pressures. Though the electronic thermal effect can be treated by using the electronic excitation spectra calculated by the LDA,[34] we will not consider it further at present.

V. DISCUSSION

In this paper we have shown that the equilibrium lattice constant and Debye temperature at normal pressure are well described by the LDA. As for the thermodynamic Grüneisen parameter which is written in the present model as

$$\gamma=-\frac{4P+24VP'+9V^2P''}{6(P+3VP')} \tag{31}$$

with the primes P' and P'' denoting the volume derivatives, it is very sensitive to the P-V curve near zero pressure and increases rapidly when the volume increases from the calculated zero-pressure volume. The calculated γ at zero pressure of 0.85 deviates from the experimental value[33] of 1.21 but it becomes 1.31 when estimated at the experimental volume 10.3 cm^3/mol at normal conditions.[33] After confirmation that the properties at normal pressure are in agreement with the experiment, we have calculated the Hugoniot and have shown that the high-pressure and high-temperature properties are also well described by the LDA with the Debye approximation for the lattice vibration.

The two-point Hugoniot data by Burton and Landeen[5] in Fig. 7(a) seems to show a phase transition at 70–90 GPa with volume decrease of about 10%. Judging from the fact that the higher-pressure datum is near the calculated Hugoniot and from the large volume decrease, the high-pressure phase is expected to be the $B2$ phase if these data represent a true transition. This pressure is close to the pressure for the $B1$-$B2$ transition predicted by Kulikov.[10] However, the empirical EOS used in his theory is not accurate enough to predict the phase transition. Using the electron-gas theory, Hammerberg[11] calculated the total energies of the $B1$ and $B2$ phases at $T=0$ K. His pressures are in excellent agreement with those by the LDA above 70 GPa but his theory predicts that the $B2$ phase is stable above 2.8 GPa, according to our estimation of the pressures and Gibbs free energies with the use of his results. In fact, he used an empirical potential instead of the electron-gas theory in order to calculate the Gibbs free energies for the insulating $B1$ phase and estimated the transition pressure to be about 200 GPa. The empirical potential whose parameters are determined at normal pressure does not seem to be accurate up to the compression of $0.3V_0$–$0.4V_0$, with V_0 as the volume at normal conditions. Considering the excellent agreement of the pressures by the electron-gas theory and those of the LDA for both phases above 70 GPa, the electron-gas theory is also applicable to the $B1$ phase as well as to the $B2$ phase in this pressure range. Thus the total energies seem to be correct at high densities except for some nearly constant shifts in energy, presumably resulting from the core region of the pseudopotential neglected in his calculation. However, the estimated pressure for the transition is in agreement with that by the LDA of about 230 GPa. Within the present model we also estimated the pressure for the $B1$-$B2$ transition of ^{n}LiH to be 130–140 GPa at $T=2000$ K, which corresponds approximately to the calculated Hugoniot temperature for Burton and Landeen's data.

In the present paper we have used the MT approximation to calculate the total energy and pressure. For solids with a small number of electrons such as solid He and LiH the MT approximation is expected to be good:[35] The MT approximation gives only a small correction to the pressure.[36] And for the total energy it gives a small and nearly-constant shift in energy especially for the $B1$ phase because of the larger volume of the interstitial region in the unit cell than that of the $B2$ phase, which is in a direction reducing the transition pressure.[36] However, since the difference of the Gibbs free energies between both phases is small and the pressure increases rapidly at high densities, the structure-dependent contributions of the lattice vibration to the Gibbs free energies are also important for solid LiH to predict the phase transition as is inferred from the large zero-point energy.[14,15] This problem is beyond the scope of the present paper, so we will not consider it further at present.

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