

## Electronic structure of light metal hydrides

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The equilibrium lattice constant, cohesive energy, and electron density of states of light metal hydrides ( $\text{LiBeH}_3$ ,  $\text{LiMgH}_3$ ,  $\text{LiCaH}_3$ ,  $\text{NaMgH}_3$ , and  $\text{LiBH}_3$ ) are calculated using the linear combination of muffin-tin orbitals method on a perovskite lattice structure. Large gaps in the density of states appear at the Fermi energy of  $\text{LiBeH}_3$ ,  $\text{LiMgH}_3$ ,  $\text{LiCaH}_3$ , and  $\text{NaMgH}_3$  indicating that these classes of hydrides are insulators.  $\text{LiBH}_3$ , on the other hand, is metallic and could have interesting electronic properties. [S0163-1829(97)03404-8]

### I. INTRODUCTION

The motivation for this work was a search for light metal hydrides as a potential high- $T_c$  conventional (electron-phonon mediated) superconductor following the suggestions of Overhauser.<sup>1</sup> One possible benefit of these materials would be better mechanical properties than the standard cuprate-based ceramic high- $T_c$  materials. For the conventional superconductors, the simple BCS formula for the superconducting transition given by

$$T_c = 1.13 \frac{\hbar \omega_0}{k_B} e^{-1/N(0)V_{\text{BCS}}} \quad (1)$$

suggests that these superconductors should have three desirable properties. The phonon frequencies characterized by  $\omega_0$  should be made as high as possible. The electronic density of states at the Fermi energy,  $N(0)$ , should be high for the material. The electron-phonon coupling characterized by  $V_{\text{BCS}}$  should be strong. The simple BCS criterion [Eq. (1)] for  $T_c$  is somewhat naive, and extensive investigations<sup>2</sup> of criteria for higher  $T_c$  within Eliashberg strong coupling theory<sup>3-5</sup> have suggested some modifications to it. However, Overhauser's suggestion<sup>1</sup> of light metal hydrides as higher  $T_c$  conventional superconductors is easily rationalized even within the simple BCS formula.

Electronic properties of metal hydrides are expected to be particularly influenced by the light mass of hydrogen. The large vibrational amplitude of hydrogen can give rise to strong electron-phonon coupling effects especially if the hydride remains metallic with a high electronic density of states at the Fermi energy. It has been well established that the absorption of hydrogen by palladium and other heavy metals makes the material superconducting with a transition temperature that is much higher than in the bare metal. In some cases, this may even give rise to anomalous isotope effects on the transition temperature not only due to the anharmonicity in the phonon branches but also due to the quantum nature of hydrogen and its isotopes. Overhauser's suggestion was that a new class of light metal hydrides with a modified perovskite structure could exhibit unusual properties. He argued that the electron density in  $\text{LiBeH}_3$  could be high and this coupled with the large amplitude of the hydrogen vibration could make this class of light metal hydrides an ideal candidate for high-temperature superconductors. Since this

work, a large number of theoretical studies<sup>6-10</sup> of the electron band structure and density of states using a variety of methods and models have been carried out. All of these calculations reveal that  $\text{LiBeH}_3$  is not metallic and the band gap is large.

Attempts have been made to search for other light metal hydrides that could be metallic. Recently, calculations of the electronic structure of  $\text{LiMgH}_3$ ,  $\text{NaMgH}_3$ , and  $\text{LiCaH}_3$  have been carried out<sup>11</sup> using atomic clusters modeling the perovskite lattice. In this scheme<sup>12</sup> a small number of atoms forming a cluster with the local geometry of the lattice is assumed to mimic the electronic structure of the periodic solid qualitatively. Computational resources usually restrict the size of these clusters to about 50 atoms and one has to worry about finite-size effects on the electronic structure. This is particularly important when analyzing the density of states. In a cluster the energy levels are discrete and it is customary to broaden<sup>13</sup> these levels so that the cluster density of states can mimic the bulk density of states. The ambiguity lies in the fact that there is no fundamental way to choose the scale for this broadening. Electronic band-structure calculations are, therefore, necessary to unambiguously determine if  $\text{LiMgH}_3$ ,  $\text{NaMgH}_3$ , and  $\text{LiCaH}_3$  are metallic and to validate the results based on cluster calculations.

In this paper we present results based on band-structure calculations of  $\text{LiBeH}_3$ ,  $\text{LiMgH}_3$ ,  $\text{LiCaH}_3$ ,  $\text{NaMgH}_3$ , and  $\text{LiBH}_3$  using the linear combination of muffin-tin orbitals (LMTO) method.<sup>14</sup> The crystal lattice was assumed to have the perovskite structure. We find that  $\text{LiBeH}_3$ ,  $\text{LiMgH}_3$ ,  $\text{LiCaH}_3$ , and  $\text{NaMgH}_3$  are all insulators while  $\text{LiBH}_3$  is metallic. We have also repeated the calculations on  $\text{LiBH}_3$  by interchanging the Li with B in the perovskite structure. The resultant  $\text{BLiH}_3$  was also found to be metallic. In Sec. II we outline the calculational procedure. The results are presented and discussed in Sec. III.

### II. METHOD OF CALCULATION

We have used the LMTO method<sup>14</sup> to study the electronic structure and total energies of the system. The space within the unit cell is divided into atomic or muffin-tin sphere regions and the interatomic (interstitial) region. The potential in any muffin-tin sphere (atomic region) is expressed as a sum of lattice harmonics. We generate muffin-tin potentials required for constructing the basis states at each iteration

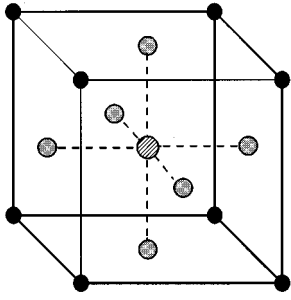


FIG. 1. The unit cell of the perovskite structure assumed for  $\text{LiBeH}_3$  class of compounds. The hydrogen atoms are at the face centers.

(successive solution of the Poisson and Schrödinger equations). These states are defined as the Bloch sums of muffin-tin orbitals,<sup>14</sup>

$$\Psi_{\kappa,\alpha,l,m}^{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \Phi_{\kappa,\alpha,l,m}(\mathbf{r} - \boldsymbol{\rho}_{\alpha} - \mathbf{R}), \quad (2)$$

where  $l$  and  $m$  represent quantum numbers and  $\boldsymbol{\rho}_{\alpha}$  is the position of the  $\alpha$ th atomic sphere in the unit cell, and  $\kappa$  is the interstitial kinetic energy. In the present case the basis states used are  $sp$  for Li and H whereas the  $d$  functions are also included for the other atoms. The core states are treated fully relativistically. Any core charge leaking from the muffin-tin spheres is added to the charge density in the interstitial region and other muffin-tin spheres as the tails extend beyond the sphere edge, thereby conserving the number of electrons.

The charge density is obtained by squaring the wave functions, and this is used to obtain the potential in the self-consistent iterative calculations. For the exchange and correlation potential a form due to Ceperly and Alder,<sup>15</sup> as parametrized by Perdew and Zunger,<sup>16</sup> is used. Within the muffin-tin spheres, the exchange and correlation potential is calculated using a simple numerical angular integration scheme. A Broyden's mixing scheme<sup>17</sup> is used to mix the input and output potentials for faster convergence.

The total energy is given by

$$E = T_S + E_H + E_{xc} = \sum_i \epsilon_i - \int \rho(\mathbf{r}) V_{\text{eff}}(\mathbf{r}) + E_H + E_{xc}, \quad (3)$$

where  $T_S$  is the kinetic energy,  $E_H$  is the electrostatic (Hartree) energy,  $V_{\text{eff}}(\mathbf{r})$  is the input value for the one-electron potential,  $\epsilon_i$  are the one-electron eigenvalues, and  $\rho(\mathbf{r})$  is the electron number density.  $E_{xc}$  is the net exchange and correlation energy, and is calculated in a manner similar to the construction of the exchange and correlation potentials.

### III. RESULTS AND DISCUSSIONS

#### A. $\text{LiBeH}_3$ , $\text{LiMgH}_3$ , $\text{LiCaH}_3$ , $\text{NaMgH}_3$

In Fig. 1 we give the unit cell of the perovskite structure used to construct the lattice of the above hydrides. Although extensive results are available<sup>6-10</sup> on  $\text{LiBeH}_3$ , not many studies have been done on the other hydrides where Li and/or Be atoms are replaced by their heavier species. Since the Na atom is larger than the Li atom as are Mg and Ca

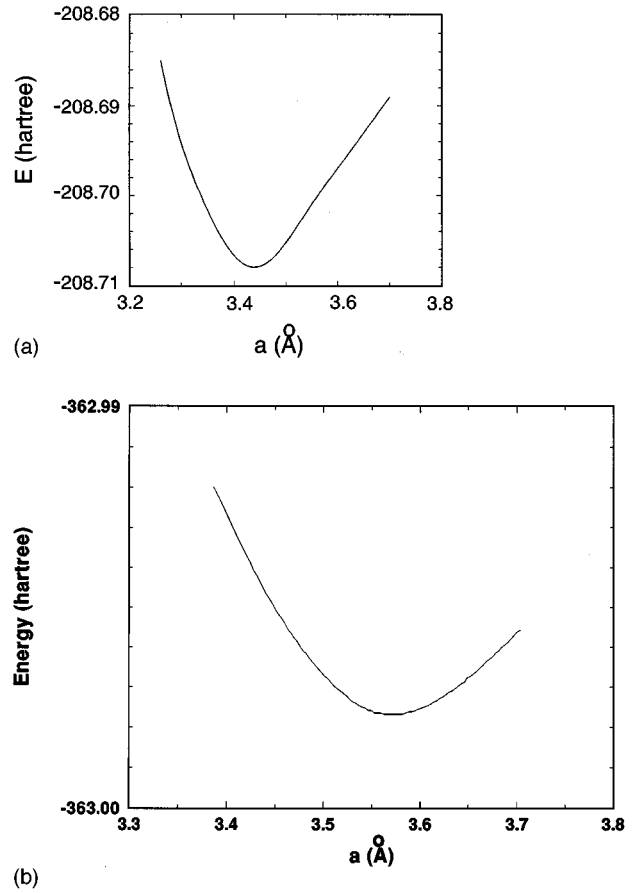


FIG. 2. Energy vs lattice constant of (a)  $\text{LiMgH}_3$  and (b)  $\text{NaMgH}_3$ .

compared to Be, one could expect that in a crystal where Li and/or Be atoms are replaced by larger atoms with the same chemistry, the larger overlap between the electron orbitals on neighboring atoms could give rise<sup>11</sup> to a narrowing of the band gap and possibly to metallicity. In order to determine the electronic structure of these hydrides, we first had to calculate the total energy as a function of lattice constant for the various hydrides. A few of the representative results are provided in Fig. 2. From the position of the minima in the total energy we derive the equilibrium lattice constants for the various hydrides and summarize the results in Table I. We also present in Table I the lattice constants derived from cluster calculations. Note that except for  $\text{LiBeH}_3$ , the lattice constants obtained using the band structure and cluster models are in very good agreement with each other. Our calculated lattice constant of 3.36 Å for  $\text{LiBeH}_3$  is in good agreement with previous band-structure results that range from 3.1 to 3.3 Å. As expected, the lattice constants increase as bigger atoms are used to replace either Li or Be.

In Figs. 3(a)–3(d) we plot the electron density of states in  $\text{LiBeH}_3$ ,  $\text{LiMgH}_3$ ,  $\text{LiCaH}_3$ , and  $\text{NaMgH}_3$ , respectively. The band gap in each case is given in Table I. It is easily seen that none of these hydrides can be metallic. In our earlier cluster calculation<sup>11</sup> we had indicated that  $\text{LiCaH}_3$  and  $\text{NaMgH}_3$  may exhibit metallic behavior. Although the density of states in the cluster calculation has the same qualitative features as reported here, the broadening of the energy levels used in the cluster model gave the impression that the

TABLE I. Comparison of lattice constants, electronic density of states  $N(0)$  at the Fermi energy, and the band gaps for various light metal hydrides. The results obtained for the lattice constants from the cluster calculations (Ref. 11) are also given.

System	$a_L$ (Å)		$N(0)$ (states/eV/spin/atom)	Band gap (eV)
	LMTO	Cluster		
LiBeH <sub>3</sub>	3.36	2.98	0	1.5
LiMgH <sub>3</sub>	3.44	3.47	0	1.8
LiCaH <sub>3</sub>	4.07	4.07	0	3.5
NaMgH <sub>3</sub>	3.56	3.53	0	2.0
LiBH <sub>3</sub>	3.11		0.042	
BLiH <sub>3</sub>	2.95		0.046	

density of states is finite at the Fermi energy. This is clearly not the case for LiCaH<sub>3</sub> and NaMgH<sub>3</sub> as shown in Figs. 3(c) and 3(d). Since the present band-structure study does not have the ambiguity associated with finite cluster size, we conclude that none of the above hydrides is metallic.

In order to test the effect of pressure on the electronic structure of these hydrides, we have repeated the band structure of LiMgH<sub>3</sub> by changing the lattice constant from the equilibrium value to simulate the effect of pressure and expansion. The resulting density of states are plotted in Figs. 4(a) and 4(b). Note that there is no significant change from the results in Fig. 3(b) and the Fermi energy still lies in the

gap. Thus it is unlikely that these hydrides can assume metallic behavior under moderate pressure or inverse pressure.

### B. LiBH<sub>3</sub> and BLiH<sub>3</sub>

To search for other possible light metal hydrides that could be metallic, we first describe an intuitive guide to positioning of the local density of states within the band. We note that bond polarity in diatomics is determined, at least to some extent, by the relative energies of the atomic orbitals involved in bonding. The electronegativity of an atom can similarly provide a guide to the positioning of the particular energy levels within the band. Moreover, hydrogen tends to exist in metallic environments as H<sup>-</sup>, which indicates that the hydrogen-related levels lie well below the Fermi energy near the bottom of the conduction band. Thus, the hydrogen-related bands in more electronegative host matrices should lie closer to  $\epsilon_F$ . Figure 5 shows the ionization potential (IP), electron affinity (EA), and electronegativity of a few light atoms. We have plotted the negative of the ionization potential, which is the minimum binding energy of an electron in the neutral atom. The energies shown are the enthalpy changes for adding an electron:

$$X^+(g) + e^- \rightleftharpoons X(g), \quad \Delta H = -IP \quad (4)$$

$$X(g) + e^- \rightleftharpoons X^-(g), \quad \Delta H = +EA. \quad (5)$$

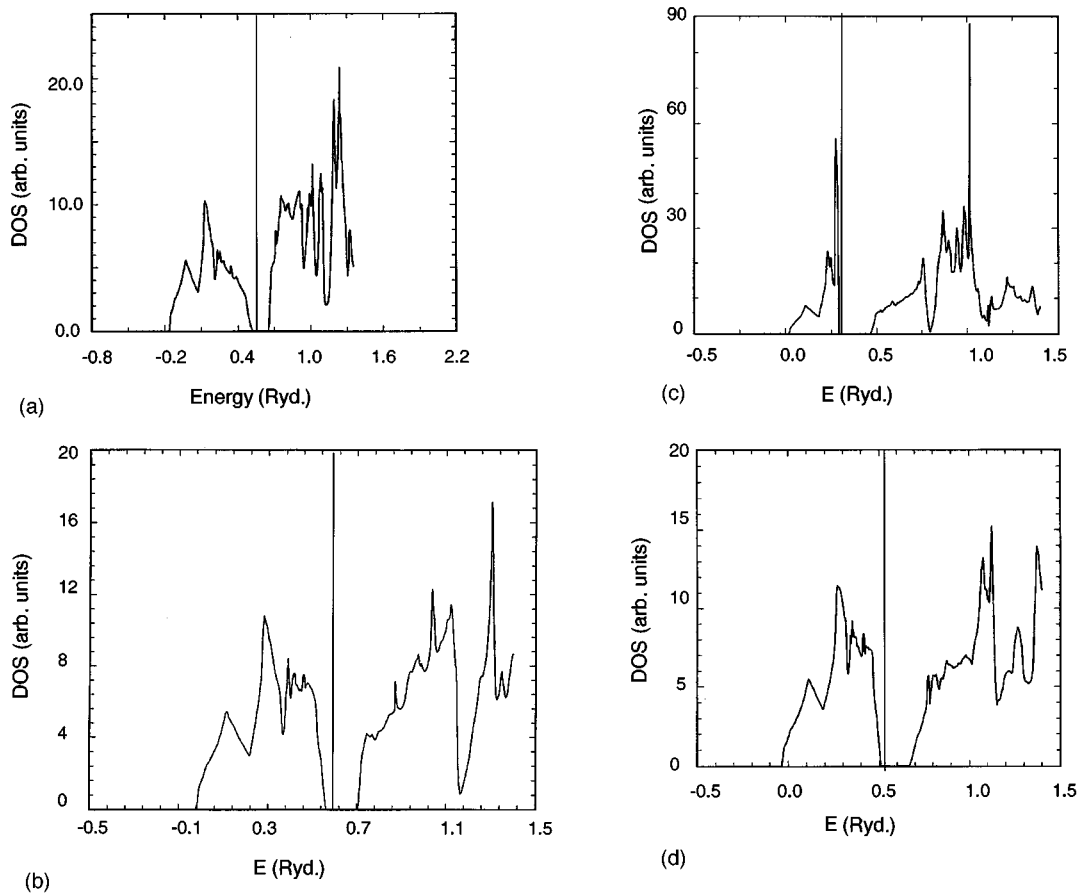


FIG. 3. Electron density of states of (a) LiBeH<sub>3</sub>, (b) LiMgH<sub>3</sub>, (c) LiCaH<sub>3</sub>, and (d) NaMgH<sub>3</sub>. The vertical line shows the position of the Fermi energy.

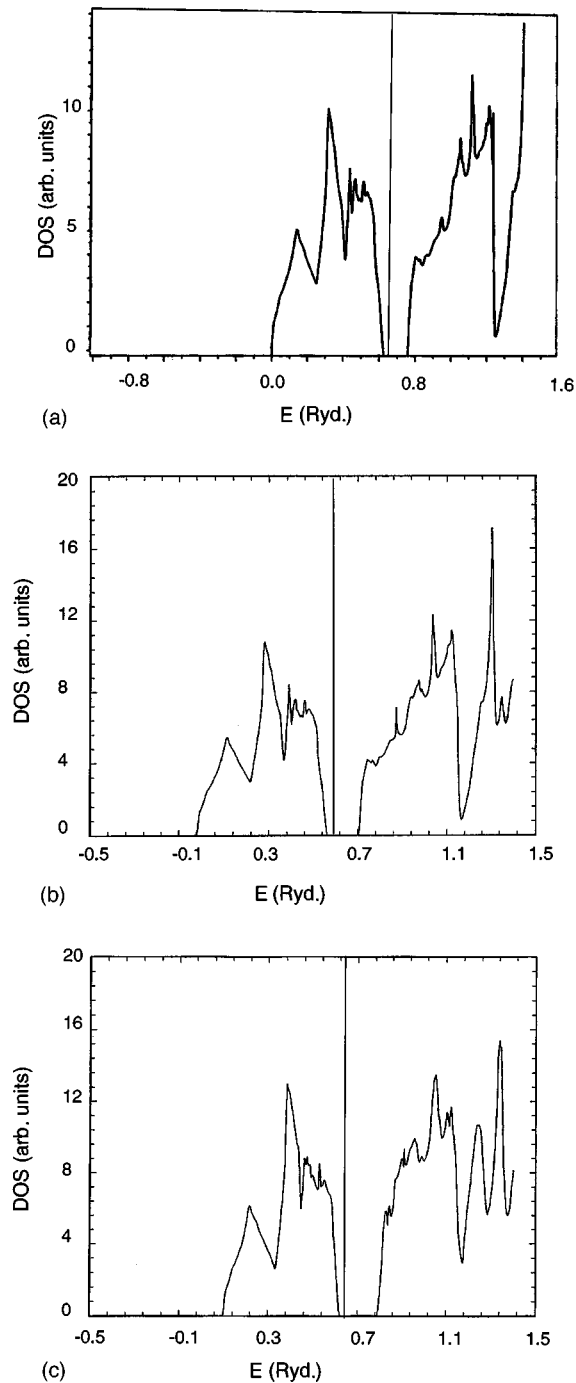


FIG. 4. Electron density of states of  $\text{LiMgH}_3$  with lattice constant that differ from the equilibrium value. The values of the lattice constants are (a) 3.33 Å, (b) 3.44 Å (equilibrium value), and (c) 3.70 Å.

Both of these indicate the relative stabilities of the neutral atoms or negative ions against electron loss in the gas phase. The Pauling electronegativity is also an indication of charge transfer, or more precisely the ionic character of a bond. It is defined by taking the excess binding energy  $\delta H_{AB}$  of the heteronuclear diatomic molecule over the geometric mean  $[\Delta H_{A_2} \Delta H_{B_2}]^{1/2}$  of the binding energy of the homonuclear diatomics. So  $\delta H_{AB} \equiv \Delta H_{AB} - [\Delta H_{A_2} \Delta H_{B_2}]^{1/2}$ , and choosing the electronegativities  $x$  to be the most consistent set of values giving  $\delta H_{AB} = |x_A - x_B|^2$  with energies expressed in

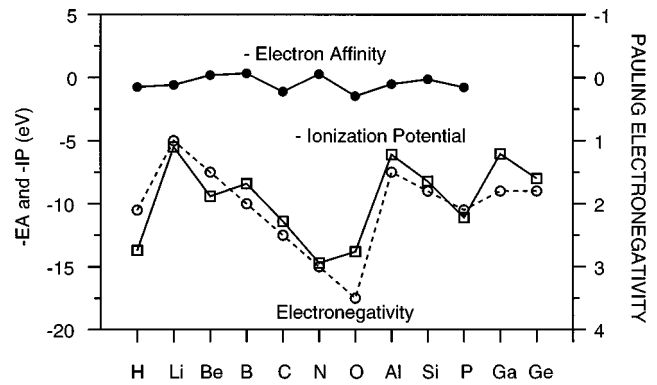


FIG. 5. Negative of the ionization potential, electron affinity, and Pauling electronegativity of some light elements.

eV per molecule.  $\delta H_{AB}$  is, in this sense, the ionic resonance energy stabilizing the bond. Thus, it is this energy that drops the hydrogen level below the host Fermi energy in a more electropositive host, and is the energy we wish to avoid.

Figure 5 suggests that if the hydrogen-related bands do lie too far below the Fermi energy in the series  $\text{XYH}_3$  with  $X = \text{Li, Na}$  and  $Y = \text{Be, Mg, Ca}$ , a more electronegative host might prove interesting. Boron, for example, has an electronegativity close to that of hydrogen. It forms interesting covalent hydrides, such as diborane ( $\text{B}_2\text{H}_6$ ), which has three-center bonds. Also, one of the rough criteria emerging from the studies of  $T_c$  optimizations within Eliashberg strong-coupling theory is that the optimal phonon frequency to enhance  $T_c$  is  $\approx 7k_B T_c$ . This suggests a mass somewhat heavier than hydrogen, perhaps in the neighborhood of B or C.

We have, therefore, studied the electronic structure of a new class of hydrides, namely,  $\text{LiBH}_3$ . For easy comparison with the hydrides discussed above and to study the effect of replacing the alkaline earth elements by B, we have used the simple perovskite structure shown in Fig. 1 for  $\text{LiBH}_3$ . We have also repeated the calculations for  $\text{BLiH}_3$  where the Li and B sites are interchanged (see Fig. 1).

In Figs. 6(a) and 6(b) we plot the energy versus lattice spacing of  $\text{LiBH}_3$  and  $\text{BLiH}_3$ . From the positions of the minima in the energy, the equilibrium lattice constants for  $\text{LiBH}_3$  and  $\text{BLiH}_3$  are those given in Table I. The electron density of states for these two hydrides calculated at their equilibrium lattice constant values are presented in Figs. 7(a) and 7(b). The electronic densities of states at the Fermi energy,  $N(0)$ , are also given in Table I. For comparison,  $N(0)$  is in the range of 0.1–1.0 states/eV/spin/atom in conventional metallic superconductors. Both of these hydrides, unlike those discussed earlier, are metallic even though their  $N(0)$  is somewhat lower than the range mentioned. This is in keeping with the intuitive picture discussed above and in agreement with conclusions of a cluster calculation by Seel, Kunz, and Hill.<sup>7</sup> We should, however, caution the reader that for the Li-B-H solids we have studied neither other lattice structures nor other relative compositions. This is an enormous task since many crystal structures are possible and the calculation of equilibrium lattice constant, energies, and energy band structure is a laborious process. We hope that our results on the Li-B-H system would provide some room for

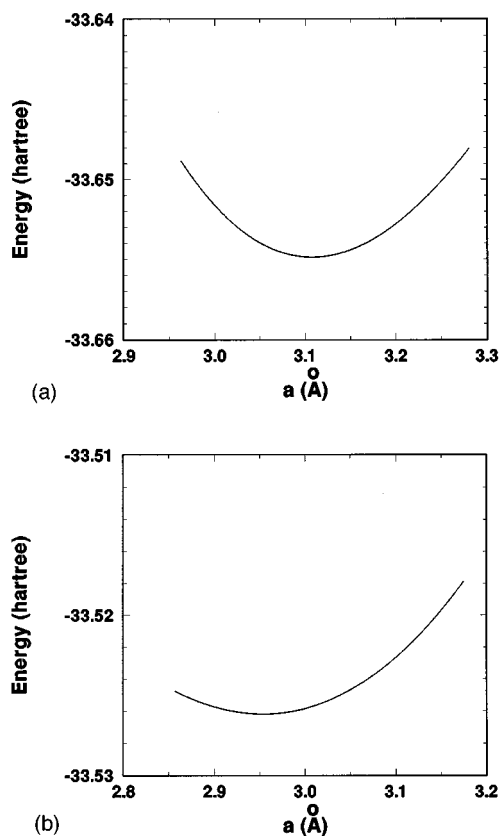


FIG. 6. Energy vs lattice spacing of (a)  $\text{LiBH}_3$  and (b)  $\text{BLiH}_3$ .

optimism that light metal hydrides could become metallic. It will be very interesting if experimentalists could synthesize the Li-B-H class of compounds, determine their preferred compositions and structures, and study their electronic properties.

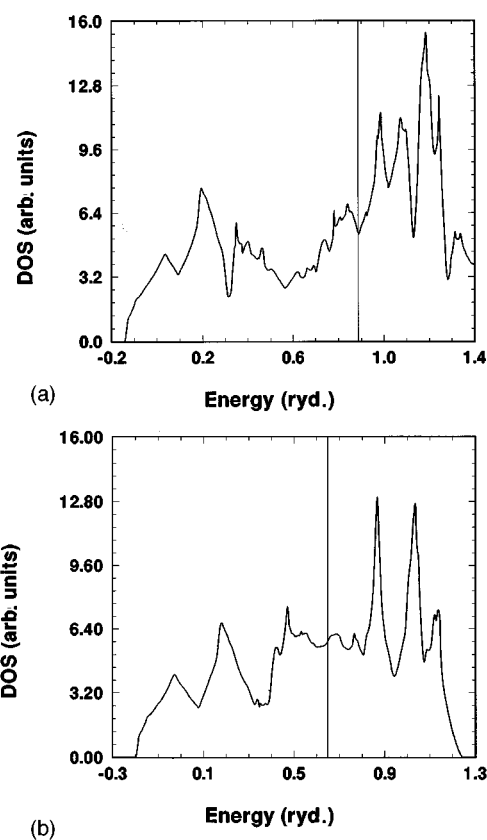


FIG. 7. Electronic density of states of (a)  $\text{LiBH}_3$  and (b)  $\text{BLiH}_3$ . The vertical line shows the position of the Fermi energy.

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