

## Possibility of $\text{LiBeH}_3$ being metallic

Rici Yu and Pui K. Lam

*Department of Physics and Astronomy, University of Hawaii at Manoa, Honolulu, Hawaii 96822*

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Overhauser [Phys. Rev. B **35**, 411 (1987)] has recently proposed that  $\text{LiBeH}_3$  is a possible high- $T_c$  superconductor. A crucial question is whether  $\text{LiBeH}_3$  is metallic. To address this question, we have employed the pseudopotential total-energy method to investigate the properties of  $\text{LiBeH}_3$ . Two cubic perovskite structures are considered, one with Be at the cube center and Li at the cube corner and the other with their positions reversed. The former is a semiconductor with a calculated band gap of about 0.8 eV while the latter is a metal. The semiconductor structure is found to be more stable by 0.77 eV/atom. The equilibrium lattice constants of the two structures are almost the same,  $\sim 3.18 \text{ \AA}$ , yielding a density which is about half that of the structure proposed by Overhauser. Possible methods to achieve a metallic phase are explored. In particular, our results indicate that at high pressure ( $P \approx 0.7 \text{ Mbar}$ ) the semiconducting structure metallizes and remains more stable compared to the other structure.

The idea of metallic hydrogen being a high-temperature superconductor has attracted much interest.<sup>1</sup> The realization of metallic hydrogen via pressurization is not that promising at the present.<sup>2</sup> Extensive work has been done on incorporating hydrogen in transition-metal hydrides to achieve a high superconducting transition temperature. Thus far the highest superconducting transition temperature is below 20 K in these systems.<sup>3</sup> This is far below the anticipated superconducting transition temperature of solid atomic hydrogen (estimated to be about 250 K).<sup>1</sup> One of the reasons for the low value of  $T_c$  in the transition-metal hydrides could be that the electronic states at the Fermi level are not strongly tied to the hydrogen. This idea has led to the recent proposals<sup>4,5</sup> that light metal hydrides may be better candidates for superconductivity study, since the states at the Fermi energy interact strongly with the hydrogen in these materials.

However, the light metal hydrides are usually ionic or covalent in character and are insulators. Doping would be one way to induce metallic behavior.<sup>5</sup> There may also be light metal hydrides that are intrinsically metallic. In a recent paper,<sup>4</sup> Overhauser suggested that lithium beryllium hydride may be a metal with a high valence-electron density ( $3.64 \times 10^{23} \text{ cm}^{-3}$ ) and thus a good candidate for a high-temperature superconductor. By analyzing the x-ray-diffraction data of Bell and Coates,<sup>6</sup> Overhauser proposed tentative structures for  $\text{LiBeH}_3$  and  $\text{Li}_2\text{BeH}_4$ . We will concentrate only on  $\text{LiBeH}_3$ . From the powder-diffraction lines, Overhauser deduced that  $\text{LiBeH}_3$  has a face-centered cubic structure with a lattice constant of 5.09  $\text{\AA}$ . After unsuccessful attempt to come up with a cubic unit cell which contains four formula units, Overhauser proposed that the cubic unit cell contains eight formula units, specifically, eight small cubes of the perovskite type (H at face centers and Li and Be at cube center and corner). The Li and Be are, however, placed alternately at the corner sites and at the center sites. The rationalization of such a structure requires strong metallic bonding, as argued by Overhauser. This metallic behavior has not been examined experimentally because only a powder

sample has been prepared so far.<sup>7</sup> In taking the first step toward understanding this system, we have performed first-principles total-energy and electronic band-structure calculations on  $\text{LiBeH}_3$  in two structures of the perovskite type. In the first structure (see Fig. 1), the Be is located at the center site (with sixfold H coordination) and Li at the corner site (with 12-fold H coordination). In the second structure, the positions of Be and Li are interchanged. The hydrogens reside at the face centers in both cases. We shall refer to the first structure as I and the second as II. The structure proposed by Overhauser can be considered as a "mixture" of I and II. Our calculation indicates that at normal pressure I is a semiconductor and is more stable while II is a metal. We also found that the valence-electron density is half of that proposed by Overhauser. We will describe our results in detail and examine possible methods to achieve a metallic phase.

The pseudopotential approach in the density-functional formalism<sup>8</sup> is employed in the present work. We use the Hedin-Lundqvist formula<sup>9</sup> for the correlation potential. The pseudopotentials are generated using the method of Hamann, Schlüter, and Chiang.<sup>10</sup> These potentials are

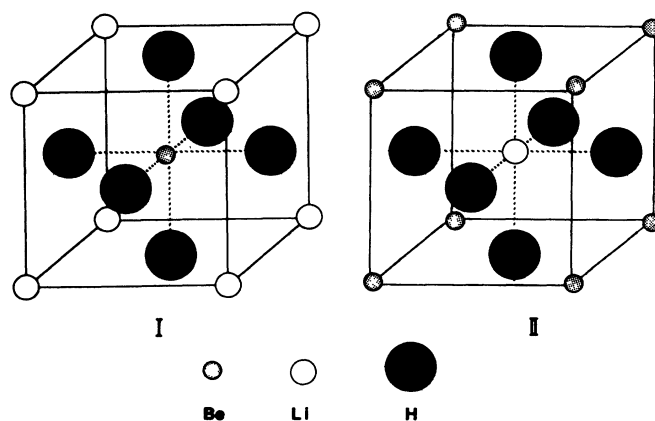


FIG. 1. Two assumed cubic perovskite structures of  $\text{LiBeH}_3$ .

tested against all-electron calculations for atoms and ions. The basis for solving the Schrödinger equation consists of plane waves within a sphere in the reciprocal space whose radius is determined by a cutoff energy  $E_{\max}$ . We chose  $E_{\max} = 30$  Ry. The dimension of the Hamiltonian matrices is approximately  $600 \times 600$ . Previous work<sup>5</sup> on magnesium hydride using the same  $E_{\max}$  yielded results which agree well with available experimental results. The four-special- $k$ -point scheme<sup>11</sup> is used in obtaining the self-consistent charge density in the calculation for both structures. The equilibrium lattice constant is determined by calculating the total energy of the crystal for various lattice constants.

The band structure of I at the equilibrium volume is shown in Fig. 2(a). The bands are labeled according to the notations of Bouckaert, Smoluchowski, and Wigner.<sup>12</sup> There is no overlap between the third and fourth bands; this system is insulating because the electrons fill up the three valence bands. The band structure has an indirect gap from valence-band edge  $X_2$  to the conduction-band edge  $R_1$ . This band gap is fairly small, it is 0.8 eV, indicating a low ionicity for the material. The density-functional theory, however, underestimates the energy gaps of semiconductors by about 50% (Ref. 13). We expect the actual energy gap to be  $\sim 1.6$  eV. The valence-bandwidth is found to be 11.2 eV.

When the positions of Li and Be atoms are switched, we

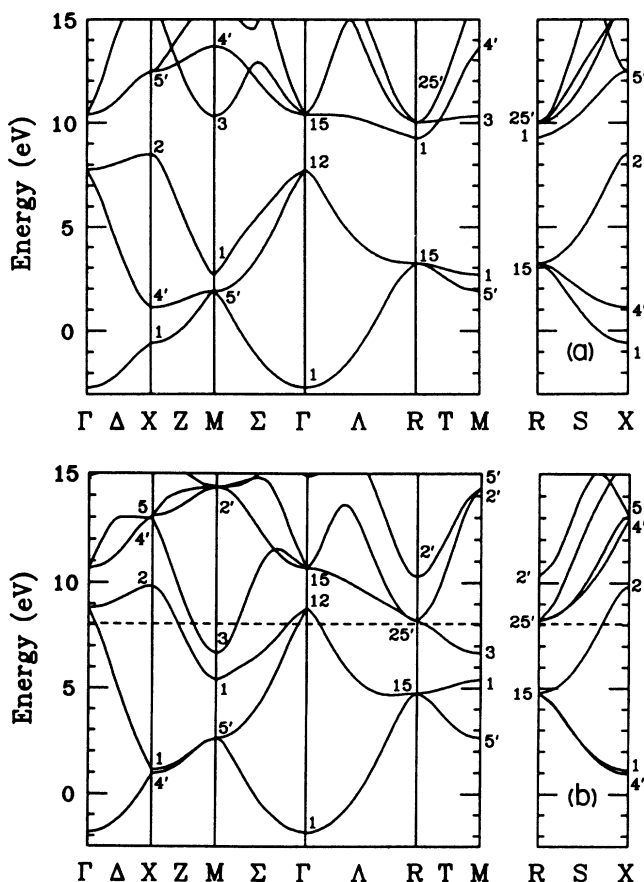


FIG. 2. Calculated band structure of (a) I for  $a = 3.19$  Å and (b) II for  $a = 3.18$  Å. The dashed line indicates the Fermi level.

find a metallic phase. The electronic band structure of II is shown in Fig. 2(b). Comparing with the band structure of I [Fig. 2(a)], it is seen that the metallic behavior comes from the lowering of the conduction-band state  $M_3$ . The energy overlap from  $M_3$  to  $X_2$  is 3.2 eV. The Fermi level is at about 8.06 eV which corresponds to an occupied bandwidth of 9.9 eV. The Fermi surface intersects with the second, third, and fourth band. Except for a small and nearly spherical hole pocket around the zone center  $\Gamma$ , the second band is completely filled; thus, this band will contribute little to the metallic property. The metallic behavior will be determined mainly by the third and fourth band. We note that the triply degenerate  $R'_{25}$  state is very close to the Fermi energy. It is 0.14 eV above the Fermi energy, although the exact value should not be taken too seriously since our calculation uses the four special  $k$ -point summation for the charge density. In Fig. 3, we plot the density of states for II. A dip is observed at  $\sim 5.0$  eV which corresponds to an occupancy of about four electrons per unit cell. The density of states at the Fermi energy is approximately 0.75 states/eV per unit cell.

It is important to understand the character of the states at  $M$  and  $R$  since they are responsible for the conversion from an insulator (I) to a metal (II). We have performed angular momentum decompositions of the wave functions<sup>14</sup> around the different atoms. We find that the wave function of the  $M_3$  state is mainly  $s$  character at the corner site, viz., Li in I and Be in II, and  $p$  character around the hydrogens. This explains why the band overlap occurs in II. Since the Be pseudopotential is much more attractive than the Li pseudopotential, the energy of the  $M_3$  states is lowered when Be is moved to the cube corner. The triply degenerate  $R'_{25}$  state is mainly  $p$  character at the corner and face-center sites. Again, the energy is lower when Be is located at the corner.

Although the I structure is an ionic insulator, there is still a fair amount of hybridization of the Be  $2s$  states with the hydrogen states. The hybridization is illustrated by the  $M_1$  state. Angular momentum decomposition shows a large  $s$  component around the center site in this state. The change of the occupation of the center site by Be to that

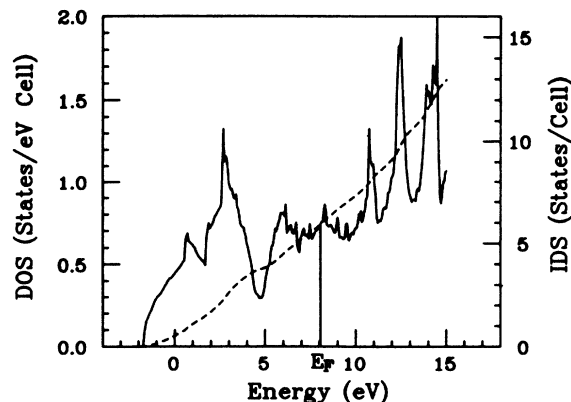


FIG. 3. The calculated density of states per unit cell (solid line, left scale) and the integrated density of states (IDS) (dashed line, right scale) of II. The vertical line indicates the Fermi energy.

by Li results in the upward shift of the energy [Figs. 2(a) and 2(b)]. This shift is actually responsible for the dip in the density of states of II slightly below 5.0 eV, which is absent in the density of states of I. Another example is offered by the lowest two states at  $X$ . The difference in the energy splitting of  $X_1$  and  $X'_4$  in the two structures is direct evidence of the involvement of the metal states.

Next, we examine the structural properties. The calculated equilibrium lattice constants, cohesive energy, the bulk modulus, and its pressure derivative for both structures are listed in Table I. These parameters are determined by fitting the calculated total energies with the Murnaghan equation of state.<sup>15</sup> The cohesive energy is defined as the difference between the total energy of the crystal and that of the individual atoms. The energies of H and Li atoms are obtained from the spin-polarized calculations using the Ceperly-Alder correlation potential with Perdew-Zunger parametrization.<sup>16</sup> Comparison of the cohesive energy shows that I is more stable. The energy difference between the two structures is 0.77 eV/atom from our total-energy calculation. We may attempt to interpret this energy difference in terms of the difference in Madelung energy. Assuming full ionic charges at the sites, the difference in Madelung energy is 1.1 eV/atom, which is comparable to our calculated energy difference. In the proposed structure of Overhauser, the Li and Be are alternately placed at the body centers and at the corners of the cubes. The present calculation indicates that such an arrangement is probably not stable compared to I.

The calculated equilibrium lattice constants of I and II are approximately the same ( $\sim 3.18$  Å). This gives a valence-electron density of  $1.85 \times 10^{23}$  cm<sup>-3</sup>, which is about half that of the structure proposed by Overhauser<sup>4</sup> ( $3.64 \times 10^{23}$  cm<sup>-3</sup>). Since the proposed structure of Overhauser is a "mixture" of I and II, it is reasonable to conclude that its density is too high, and hence it is not the correct structure. An fcc lattice with four formula units (instead of eight) would have the same density as our theoretical one. The determination of the atomic arrangement of the real structure awaits further experiments.

Assuming that the two perovskite structures of Fig. 1 still have some relevance to the real crystal, it is of practical interest to investigate the effects of pressure on the crystal. From our structural parameters listed in Table I, a pressure-induced phase transition between I and II does not seem likely at any available pressure. We examine instead the possibility of pressure-induced metallization of the insulating I structure. Band structure has been determined at  $a = 3.07$  Å, which corresponds to about 100 kbar according to the Murnaghan equation of state<sup>15</sup> and the parameters listed in Table I. The band gap in I is found to increase to 1.1 eV. If this trend continues at higher pressure, I would not metallize. The calculations at 100 kbar, however, do not apply to higher pressure. The increase in the band gap at low pressure is because the  $R_1$  state, which is the conduction-band edge at zero pressure [Fig.

TABLE I. The calculated equilibrium lattice constant, cohesive energy, bulk modulus, and its pressure derivative for the two perovskite structures.

	$a$ (Å)	Cohesive energy (eV/atom)	$B_0$ (100 kbar)	$B'_0$
I	3.19	2.84	6.9	2.8
II	3.18	2.07	6.0	3.2

2(a)], moves up. On the other hand, the  $R'_{25}$  state comes down with the increase of pressure. At a lattice constant of 2.72 Å (62% of equilibrium volume), which corresponds to a pressure of about 0.7 Mbar, we find that band-overlap occurs. The  $R'_{25}$  state is lowered in energy to  $\sim 0.2$  eV below that of the  $X_2$  state. Another calculation is done for the unit-cell volume being half of the normal value (which corresponds to a fairly high pressure of  $\sim 1.5$  Mbar). The band overlap increases from 0.2 to 1.4 eV. The density of states at the Fermi level is on the order of 0.1 states/eV cell. In view of the low density of states at the Fermi level at such a high pressure, other mechanisms may be preferred to induce a metallic phase. For example, it might be possible to put in an unequal amount of Li and Be in the crystal, that is, to make  $\text{Li}_{1-x}\text{Be}_{1-x}\text{H}_3$  with  $x > 0$ . This may force some of the Be to occupy the corner sites and thus bring down the  $M_3$  state. We should mention that the calculated pressure at small volumes using the Murnaghan equation of state depends strongly on the value of  $B'_0$ . An increase in  $B'_0$  by 20% could change the pressure to 0.8 Mbar at 62% of equilibrium volume and to 1.9 Mbar at 50% of the equilibrium volume.

In conclusion, we have performed first-principles calculations to study the properties of  $\text{LiBeH}_3$ . Our calculation indicates that the valence-electron density is  $1.85 \times 10^{23}$  cm<sup>-3</sup>, half of that of the structure proposed by Overhauser. To determine the real structure of  $\text{LiBeH}_3$  requires further experiments and calculations. Although the electronic properties of the actual structure will not be known before the structure is determined, our calculations do suggest that the stable structure is likely to be a semiconductor at ambient pressure if the structure consists of units of the perovskite type. The semiconducting structure could become metallic under high pressure,  $P \approx 0.7$  Mbar.

After this work was completed, we learned that Martins<sup>17</sup> has performed *ab initio* calculations on the structure proposed by Overhauser and found that it is an insulator.

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- <sup>1</sup>N. W. Ashcroft, Phys. Rev. Lett. **21**, 1748 (1968); T. Schneider, Helv. Phys. Acta **42**, 957 (1969); A. C. Switendick, in *Superconductivity in d- and f-Band Metals*, edited by D. H. Douglass (Plenum, New York, 1976), p. 593; D. A. Papaconstantopoulos and B. M. Klein, Ferroelectrics **16**, 307 (1977); A. K. McMahan, in *High-Pressure and Low Temperature Physics*, edited by C. W. Chu and J. A. Woollam (Plenum, New York, 1978), p. 21; B. I. Min, H. J. F. Jansen, and A. J. Freeman, Phys. Rev. B **33**, 6383 (1986).
- <sup>2</sup>Attempts have been made to achieve metallic hydrogen using pressure in excess of 1 Mbar. See, for example, H. Shimizu, E. M. Brady, E. K. Mao, and P. M. Bell, Phys. Rev. Lett. **47**, 128 (1981); K. H. Weil and V. Nardi, Int. J. Hydrogen Energy **10**, 859 (1985).
- <sup>3</sup>B. Stritzker, in *Electronic Structure and Properties of Hydrogen in Metals*, edited by P. Jena and C. B. Satterthwaite (Plenum, New York, 1983), p. 309. A  $T_c \sim 17$  K can be achieved in hydrides of Pd-Cu alloys.
- <sup>4</sup>A. W. Overhauser, Phys. Rev. B **35**, 411 (1987).
- <sup>5</sup>R. Yu and P. K. Lam, Phys. Rev. B **37**, 8730 (1988).
- <sup>6</sup>N. A. Bell and G. E. Coates, J. Chem. Soc. A **1968**, 628 (1968).
- <sup>7</sup>A. W. Overhauser, Int. J. Mod. Phys. B **1**, 279 (1987).
- <sup>8</sup>P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965); J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).
- <sup>9</sup>L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).
- <sup>10</sup>D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).
- <sup>11</sup>D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).
- <sup>12</sup>L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).
- <sup>13</sup>M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985).
- <sup>14</sup>P. K. Lam and M. L. Cohen, Phys. Rev. B **27**, 5986 (1983).
- <sup>15</sup>F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944); O. L. Anderson, J. Phys. Chem. Solids **27**, 547 (1966).
- <sup>16</sup>J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- <sup>17</sup>J. L. Martins, Bull. Am. Phys. Soc. **33**, 709 (1988); and (private communication).

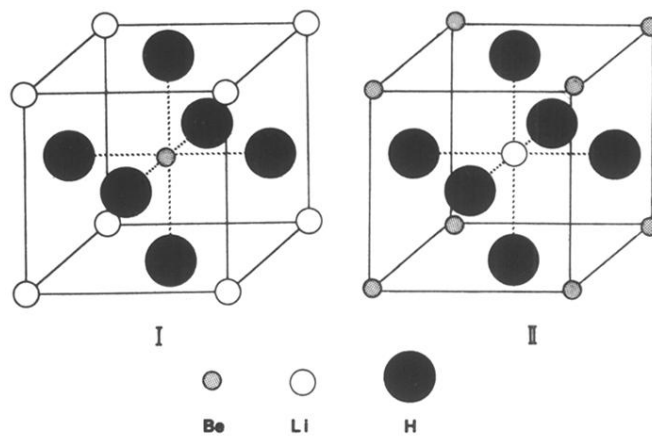


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