Electronic structure of lithium beryllium hydride

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Hartree-Fock band-structure and cluster calculations have been performed to study the electronic structure of $LiBeH_3$ in the cubic perovskite structure. The total energy, bulk modulus, band structure, density of states, charge densities, and x-ray structure factors are obtained. The energy minimum has been found for a lattice constant of 3.3 Å in the band calculation (3.2 Å in the cluster calculation), by far larger than the 2.545 Å proposed by Overhauser for a fcc superstructure of LiBeH₃ and used in a previous augmented-plane-wave calculation. The hydride is found to be an insulator. The essential features of the band structure can be understood in terms of the energy band of the BeH_2 planes present in the perovskite structure. A metal, and possible high-temperature superconductivity often envisioned for metallic hydrogen, could be obtained if beryllium is replaced by boron.

I. INTRODUCTION

In a recent paper[1] Overhauser suggested new research on incorporating hydrogen into metals as another avenue of enhancing superconductivity. In particular, attention was focused on light-metal hydrides, i.e., on ternary compounds such as $LiBeH_3$ or Li_2BeH_4. Based on an analysis of powder-diffraction data,[2] he proposed, instead of a simple perovskite structure having Li at cube corners, Be at cube centers, and H at the face centers, a modified perovskite structure for these compounds involving cubes with edges half the size of the lattice constant of 5.09 and 5.14 Å, respectively (cube size 2.545 and 2.57 Å). If metallic, these compounds could have superconducting properties similar to those predicted for metallic hydrogen[3−7] ($T_c \simeq 140-260$ K).

In view of the uncertainty about the crystal structure, we have studied the electronic properties of $LiBeH_3$, assuming for simplicity a cubic perovskite structure. In a recent band-structure investigation[8] using the augmented-plane-wave (APW) method, this hydride has been found to be a semiconductor with a small indirect band gap of 0.21 eV if a lattice constant of 2.545 Å is assumed. The purpose of our study is to optimize the geometry of the cubic perovskite structure, and then to calculate electronic-structure data such as binding energy, bulk modulus, band structure, density of states, and charge distributions for this optimized lattice constant. We will use the periodic linear combination of atomic orbitals crystal-orbital Hartree-Fock (LCAO-CO-HF) method[9−13] and the HF cluster approach.[14] Comparison of band structure and cluster results allows us to substantiate limits for the geometry optimization and to analyze limitations and merits of both approaches.

The all-electron LCAO HF band-structure calculations are performed employing the CRYSTAL program.[12,13] The program and the various truncation criteria are described in earlier applications.[12,13,15−18] By employing extended basis sets, the calculations on lithium nitride,[15] lithium hydride,[16] metallic lithium,[17] and beryllium[18] have

demonstrated that the HF approach is adequate for the study not only of insulating systems but also of metallic systems. The results prove that a number of ground-state properties, including binding energy, lattice constant, electron charge densities, x-ray structure factors, Compton profiles, band structures, and Fermi-surface shapes can be satisfactorily accounted for within the HF approximation.

Computational details including the basis sets for the band-structure and cluster calculations are discussed in Sec. II. The results are presented in Sec. III. First, we discuss the lattice-constant optimization in Sec. III A. After analyzing the band structure and total and projected density of states of $LiBeH_3$, the energy bands of planar BeH_2 and BH_2 are compared. Section III B ends with a discussion of the implications for achieving a metallic metal hydride. In Sec. III C the net charges, charge densities, and x-ray structure factors are described. Finally, in Sec. IV the conclusions are summarized.

II. COMPUTATIONAL DETAILS

A. Band-structure calculation

The HF LCAO program CRYSTAL (Refs. 12 and 13) required minor changes to run on a Floating Point Systems FPS 164 processor and small modifications to allow the calculation of an ABC_3 perovskite structure. A large series of computations was performed to define the basis set of 21 contracted Gaussians reported in Table I, which was finally used to calculate the crystal properties. As with all LCAO band-structure schemes employing extended basis sets, the problem of large overlaps of small-exponent Gaussian atomic orbitals (AO's) with neighboring atoms, leading to near singularities in the overlap matrix and the overcompleteness catastrophe, became particularly acute for a dense system like $LiBeH_3$ (see Fig. 1). The basis sets are based on sets used in the calculation of metallic lithium,[17] beryllium,[18] and, for H, of lithium hydride.[16] The uncontracted functions for the Be $1s$ func-

TABLE I. Exponents (in a.u.) and contraction coefficients of the s and p Gaussian functions used in the band-structure ($a_0 = 3.3$ Å) calculations.

Center	Type	Exp.	Coeff.
Li	s	300.0	0.004 936
	s	60.0	0.024 37
	s	16.0	0.1038
	s	5.0	0.2412
	s	2.0	0.3859
	s	0.7	0.3834
	s	0.5	1.0
	sp	0.2858	1.0
Be	s	1154.7645	0.002 180 2
	s	172.767 87	0.016 707 2
	s	39.150 318	0.080 427 7
	s	11.023 330	0.254 978 7
	s	3.493 437 6	0.479 935 6
	s	1.169 072 6	0.320 053 2
	s	0.85	1.0
	sp	0.326	1.0
H	s	120.0	0.000 267
	s	40.0	0.002 249
	s	12.0	0.006 389
	s	4.0	0.032 906
	s	1.2	0.095 512
	s	0.5	1.0
	s	0.2037	1.0

tion are from Huzinaga.[19] The outermost exponents have been chosen so as to allow adequate variational freedom and to avoid the overcompleteness catastrophe over a large range of the lattice constant.

In the optimization of the lattice constant, the basis set was the same as in Table I, except for the exponents of the outermost s and p functions which were varied proportional to $1/a_0^2$ ($\alpha a_0^2 =$ const) following a suggestion by Surratt *et al.*[20] and used in previous HF studies.[15–18,21] This yields about the same level of description for all geometrical configurations and minimizes the effect of the approximations associated with the truncation of the
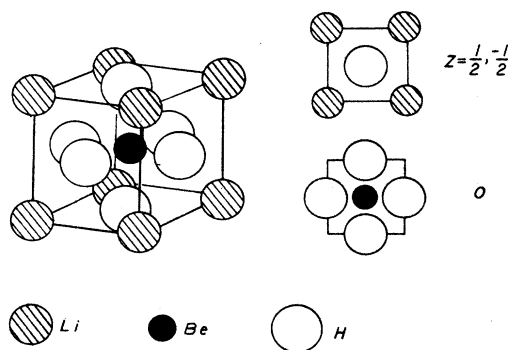

FIG. 1. Atom positions in the cubic perovskite structure of LiBeH$_3$. Horizontal layers are shown for different z values.

Coulomb and exchange series. Even so, small discontinuities in the energy-potential curve can be introduced.[21] This is clearly a disadvantage of the band-structure approach compared to a cluster calculation. The inclusion of p functions on the hydrogen atoms has been considered. However, the H p population was found to be only $0.002e$, and a larger decrease in total energy—at the same time avoiding near-linear–dependence problems at smaller distances—was obtained by using a basis of 3 s functions instead of a $2s/1p$ basis.

Apart from the choice of basis set, no problems were encountered in fixing the other computational parameters. A set similar to that used in previous calculations[12,13,15–18] was adapted. In particular, the t_2 parameter which defines the penetration threshold of two charge distributions, beyond which the Coulomb interactions are treated exactly, was taken to be 10^{-3}. Nine stars of lattice vectors have been included in the "quantum" zone which corresponds to a radius of 18.7 a.u., i.e., contributions from cells outside this radius are included as a classical Madelung term. Exchange sums have been limited to within three stars of neighboring cells. Multipole terms up to quadrupoles have been used in the evaluation of Coulomb interactions between separate charge distributions. The Madelung contribution amounts to only ~ 0.004 a.u., about a factor of 100 smaller than for ionic systems.[16] This is a clear indication that LiBeH$_3$ has little or no ionic character.

B. Cluster calculation

As a crosscheck on the band-structure calculations, and also incidentally to obtain a comparison between finite-cluster results and band theory for a proposed metallic system, a calculation for LiBeH$_3$ was made using the unrestricted-Hartree-Fock (UHF) –plus–many-body-correlation-theory ideas proposed by Boisvert and Kunz.[22] In this instance a finite cluster was constructed using 27 atoms in all. There was a Li atom at the cluster center surrounded by six other Li atom at the sites $(a,0,0)$. In addition, the eight nearest Be atoms at sites $(a/2, a/2, a/2)$ were included as well as the 12 hydrogens at $(a/2, a/2, 0)$.

A simple Gaussian basis set was employed using the sets of Huzinaga[19] for Be and Li and a set we developed for H. The Be and Li sets were those using four primitive Gaussians for the $1s$ orbital contracted to a single orbital and four primitives contracted into two functions, one of three Gaussians and a single Gaussian for the $2s$ level. In the case of H the basis set of five primitives was used contracted into two functions, one of four Gaussians and the other of a single Gaussian. This set has been used by us for many years and has proved satisfactory for hydrogen-bonding studies.

III. RESULTS AND DISCUSSION

A. Lattice-constant optimization

In Fig. 2 the total energy per unit cell of LiBeH$_3$ in the cubic perovskite structure is shown as a function of the
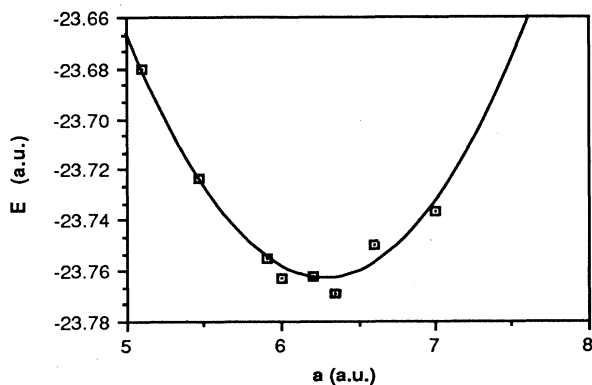
FIG. 2. Total energy per unit cell vs lattice constant a for LiBeH$_3$.

FIG. 3. Hartree-Fock energy bands for LiBeH$_3$ along symmetry lines in the sc Brillouin zone.

lattice constant. The approximations associated with the treatment of Coulomb and exchange series introduce discontinuities as observed before.[21] The energy minimum of -23.763 a.u. for the quadratic least-squares fit is obtained for a lattice constant of 6.28 a.u.$=3.3$ Å. A lower bound of 7 eV for the HF cohesive energy (5.3 eV for lithium nitride,[15] 9.2 eV for lithium hydride[16]) is calculated by subtracting the sum of the HF-limit energies of the constituent atoms (-23.505 a.u.) from the total crystal energy per cell. The lattice constant is $\sim 9\%$ larger than the Li-Li distance of 3.04 Å in lithium metal. The corresponding Be-H distance of 1.65 Å is larger than the bond distance of 1.4 Å in molecular BeH$_2$ or 1.55 Å found for planar BeH$_2$ (see below), and the corresponding Li-H distance of 2.33 Å is larger than the lattice constant of 2.05 Å for lithium hydride. Altogether, it does not seem unreasonable to expect for this highly dense packed system bond distances which are somewhat larger than those found in other crystal structures formed by the constituent atoms. Our lattice constant of 3.3 Å is by far larger than the 2.545 Å proposed by Overhauser[1] for a fcc superstructure of LiBeH$_3$ and used in a previous augmented-plane-wave (APW) calculation.[8]

From d^2E/dr^2 a force constant of 1.8 mdyn/Å and a bulk modulus of 6×10^{11} dyn/cm^2 or 60 GPa is obtained [experimental bulk modulus of LiH: $(2.3-3.5) \times 10^{11}$ dyn/cm^2 (Ref. 23)].

The net result of the cluster studies is that the cluster Li$_7$Be$_8$H$_{12}$ simulating the LiBeH$_3$ crystal is bound in the geometry given with internuclear separations corresponding to a lattice constant of 3.2 Å. This is 0.1 Å less than found in the band calculation. This lattice constant is found using the UHF+MBPT method and also using the UHF method alone. In these calculations the system is found to be strongly insulating with a band gap about twice that of the band calculation (see below). This exaggerated gap was determined using one-electron eigenvalues, rather than total-energy differences and is expected to be an overestimate due to the use of eigenvalues and also the finite size of the cluster.

B. Band structure

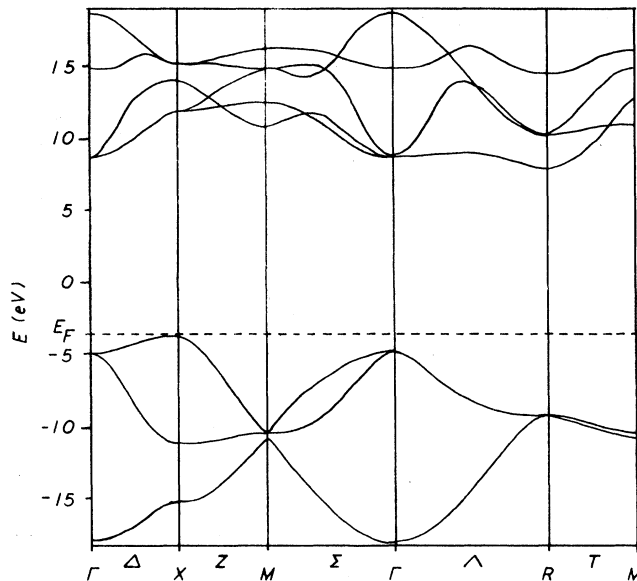The band structure of lithium beryllium hydride is shown in Fig. 3 for $a_0 = 3.3$ Å. It agrees qualitatively with the APW band structure for $a_0 = 2.545$ Å, except that the indirect band gap between X and R is very large, 11 eV. Using the $2s/1p$ basis for hydrogen, the gap is reduced to ~ 6.5 eV. Even allowing for 50% overestimation of the gap in HF, the present calculation still leads to the result that cubic perovskite LiBeH$_3$, at the optimized lattice geometry, is an insulator with a large indirect band gap. To reach a semiconducting or a metallic phase, found for $a = 2.545$ and 2.459 Å in the APW calculation, would require an unrealistic decrease in lattice constant from the HF equilibrium value by 25%.

The three valence bands have a total width of 14.2 eV between Γ and X; they result from the metal s, metal p, hydrogen s, and hydrogen-hydrogen interactions. The lowest valence band has Li s, Be s, and H s contributions. The other two arise mainly from strong nearest-neighbor Be-H interactions (the Be-H distance of 1.65 Å is much smaller than the Li-H distance of 2.33 Å) and antibonding combinations of the three H s states present in the unit cell. The general features of this picture are illustrated by the results for the total and projected densities of states (DOS's) shown in Fig. 4. As expected, the contributions from hydrogen states (solid line) dominate the total DOS (heavy black line) in the valence-band region. The importance and large participation of the Be p states in the occupied portion ($\times \times \times$), known from metallic beryllium, is evident from Fig. 4.

The essential features of the lower two valence bands can be understood in terms of the band structure of planar BeH$_2$ (the $z = 0$ plane in Fig. 1)—in close analogy to the strong Cu-O in-plane interactions in La$_2$CuO$_4$ (Refs. 24 and 25). The energy bands of planar BeH$_2$ are shown in Fig. 5(a). This two-dimensional model (the optimized lattice constant is 1.55 Å) provides a quite accurate description of the dispersion of the lower two LiBeH$_3$ valence bands. If one replaces Be by B, then the band la-
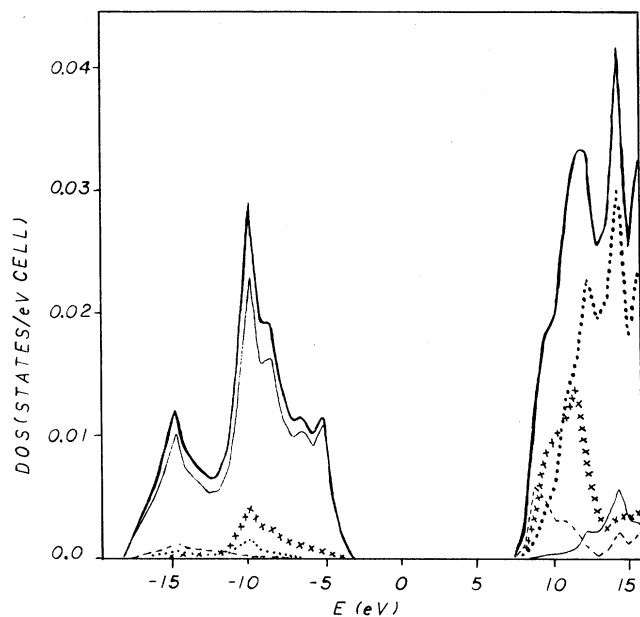
FIG. 4. Total and projected density of states results for Li-BeH$_3$ in the cubic perovskite structure. ..., Li; — — —, Be s; × × ×, Be p; ——, H; ——, total DOS.

beled A in Fig. 5(a) is pulled down below the Fermi level, i.e., planar BH$_2$ is a metal [see Fig. 5(b)]. This leads to the suggestion that LiBH$_3$ in the cubic perovskite structure could be the compound which might have the properties envisioned for metallic hydrogens. Investigations along these lines are in progress.

C. Electron population and charge distribution

The Mulliken charges on Li, Be, and H for $a_0 = 3.3$ Å are 2.22, 2.73, and 1.68, respectively. The cluster calculation and another band-structure computation using a $2s/1p$ basis for hydrogen instead of $3s$ and a different lat-
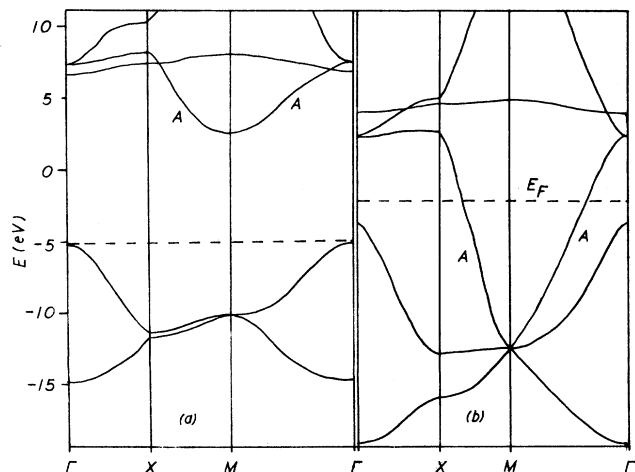
tice constant (3.5 Å) gave similar results. Independent of the approach or the type of basis set, H picks up $(0.6-0.7)e$, Li loses $(0.7-0.8)e$, and Be $(1.1-1.3)e$, i.e., most of the electronic charge is located on the hydrogen atom. The corresponding charge densities are shown in Fig. 6 for the $z = 0$ (BeH), $z = \frac{1}{2}a_0$ (LiH), and (110) planes (LiHBe). Despite the large charge transfer, the crystal is not ionic. As mentioned before, the Madelung contribution to the total energy per unit cell is ~ 100 times smaller than for a typical ionic system like LiH. Moreover the overlap population for the Be—H bond is $0.162e$, for Li—H still $0.053e$, indicating covalent character especially for the six nearest-neighbor Be—H bonds.

For completeness we report in Table II the calculated x-ray structure factors since experimental x-ray structure factors provide the possibility of testing the calculated charge densities. They would also provide a means of checking whether the cubic perovskite structure is realized in a particular LiBeH$_3$ sample. The f_{hkl} values are uncorrected for thermal motion, which is particularly important for high-index reflections from light atoms such as lithium, hydrogen, or beryllium. If a Debye-Waller correction is included, then the calculated HF structure factors, in general, agree quite well with experimental ones.[15]

IV. CONCLUSIONS

LiBeH$_3$ in the cubic perovskite structure is found to be an insulator with a large indirect band gap between X and R (HF value 11 eV). The maximum for the cohesive en-
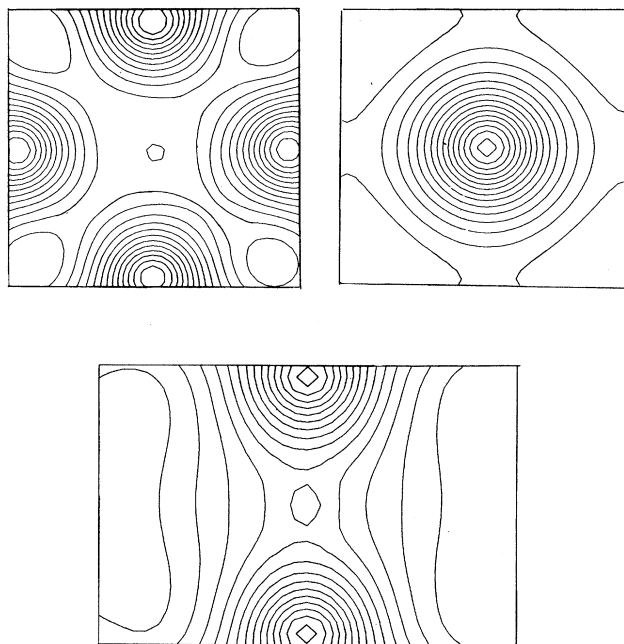

FIG. 5. Hartree-Fock energy bands for planar (a) BeH$_2$ and (b) BH$_2$ along symmetry lines in the two-dimensional square-lattice Brillouin zone. Band A is pulled below the Fermi energy if beryllium is replaced by boron.

FIG. 6. Valence-electron equal-density contours of LiBeH$_3$ in the cubic perovskite structure for the $z = 0$, $z = \frac{1}{2}$, and diagonal (110) planes. The electron-density spacing is $0.002e^-$ bohr^{-3}.

TABLE II. (hkl) Miller indices, corresponding d spacings (in Å) for a cubic perovskite structure with $a_0 = 3.3$ Å, and x-ray structure factors f_{hkl}. The third and fourth columns report the core and valence contributions, and the last column the total $|f_{hkl}|$ without any thermal corrections.

(hkl)	d (Å)	Core	Val.	Tot.
000		4.0	6.0	10.0
100	3.300	0.067	1.339	1.406
110	2.333	3.580	−0.617	2.963
111	1.905	0.168	−1.522	1.354
200	1.650	3.231	1.063	4.294
210	1.476	0.238	0.241	0.479
211	1.347	2.937	−0.280	2.657
220	1.167	2.686	0.416	3.102
300	1.100	0.320	0.131	0.451
221	1.100	0.320	0.094	0.414
310	1.046	2.469	−0.099	2.370
311	0.995	0.341	−0.283	0.058
222	0.953	2.280	0.247	2.527
320	0.915	0.355	0.078	0.433
321	0.882	2.114	−0.055	2.059
330	0.778	1.836	−0.028	1.808
331	0.757	0.365	−0.113	0.252
332	0.738	1.612	−0.017	1.595
333	0.635	0.347	−0.060	0.287

ergy (7 eV) is found for a lattice constant of 3.3 Å (3.2 Å in the cluster calculation), which corresponds to somewhat larger Li-Li, Li-H, and Be-H distances than those found in other compounds formed by these atoms. This is not surprising in view of the close packing of large H^- ions. Band-structure and cluster calculations with different basis sets lead to similar results for geometry

and charge distributions. It is undetermined whether the superstructure proposed by Overhauser[1] would lead to a metallic state, but it does not seem to be very likely. Carefully executed Hartree-Fock calculations have proven to give reliable results with respect to geometry and metal-insulator characteristics. The truncation of the outermost exponents is not unusually large for a LCAO band-structure calculation. The only consideration in the choice of basis sets was the problem with near singularities, not computer time. For cluster calculations these problems arise only for much smaller exponents; therefore standard molecular-type basis functions could be used, i.e., their range is larger than the range of the basis functions for the band-structure calculations. It is a clear indication for the near independence of the result on the basis sets that both approaches yield very similar results. In the meantime two more papers have appeared.[26,27] The lithium beryllium hydride was also found to be nonmetallic with a lattice constant around or above 3 Å (the pseudopotential calculation[27] gives 3.18 Å).

It was found that the main features of the valence-band structure can be understood in terms of the bands of two-dimensional BeH_2 planes. Since we could show that the substitution of Be by B leads to a metal, it seems probable that a cubic perovskite $LiBH_3$ might be a metallic compound. Further theoretical investigations on $LiBeH_3$ using Overhauser's fcc superstructure and on the boron substitution are in progress.

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