Crystal structure of lithium beryllium hydride

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Analysis of powder diffraction data, published by Bell and Coates, reveals that $LiBeH_3$ and Li_2BeH_4 both have an fcc translation group with lattice constants 5.09 and 5.14 Å, respectively. The cubic cell of each contains eight formula units; so the total atomic concentrations, 3.03×10^{23} and 4.12×10^{23} cm^{-3}, exceed that of diamond by factors of 1.7 and 2.3. The computed densities are 1.91 and 2.63 g/cm^3. Both crystals have a modified perovskite structure involving cubes with edges half the size of the lattice constant. The (otherwise) sc lattice is broken by a chemical superstructure in $LiBeH_3$ and by an orientational superstructure in Li_2BeH_4. The "conduction"-electron density of the latter is 4.71×10^{23} cm^{-3}; so the equivalent-sphere-radius parameter is $r_s = 1.51$ bohr, a value in the range typically assumed for metallic hydrogen. Infrared absorption at 1600 cm^{-1} (≈ 2300 K) was reported. Consequently, these compounds, if metallic, may manifest the high-temperature superconductivity often envisioned for metallic hydrogen.

I. INTRODUCTION

Incorporation of hydrogen into metals as a means of enhancing superconductivity is an old idea. A noteworthy success is PdH, for which $T_c \sim 10$ K, compared to the absence of superconductivity in Pd. In alloys such as $Pd_{1-x}Cu_xH$, T_c can exceed 16 K. Impressive as this result is, the many predictions that metallic hydrogen should have T_c in the range 140–260 K,[1-6] suggest that the full potential of metal hydrides has not yet been achieved.

It seems worthwhile to propose that attention be focused on light-metal hydrides. In particular, a desirable goal might be insertion of hydrogen as a negative ion (rather than positive) so that coupling to the conduction electrons can be optimized. LiH is, unfortunately, a wide-band-gap insulator.[7] The H 1s band lies ~5 eV below the Li 2s conduction band (which is empty). Now the ionization potential of Be (9.32 eV) exceeds that of Li (5.39 eV) by almost the amount needed to provide overlap of a Be 2s band with an H 1s band. The fact that BeH_2 is a polymer,[8] and does not crystallize without ternary additions, suggests that 2s-1s hybridization is occurring. BeH_2 is an experimental rocket fuel, and seems not to have become a favorite object of study in solid-state laboratories.

Ternary compounds such as $LiBeH_3$ provide another possible avenue of invention. A perovskite structure having Li at cube corners, Be at cube centers, and H at the face centers would allow at least a relatively easy theoretical approach to questions of stability and electronic band structure. In due course investigation of the phonon spectrum and electron-phonon interaction might follow.

Fortunately there has been one, apparently successful, attempt to synthesize $LiBeH_3$ and Li_2BeH_4. Bell and Coates have reported preparation of these compounds and the Na analogs.[9] Little physical characterization was attempted. Debye-Scherrer powder patterns were obtained, but not interpreted, and the greyish-white precipitates were analyzed for chemical composition to confirm the synthesis. Since the work of Bell and Coates in 1968 there has not been another reference.

In the following sections I shall present my analysis of

the diffraction patterns of Bell and Coates. Naturally the crystal structures found are tentative suggestions, since there are only ten powder reflections for $LiBeH_3$ and thirteen for Li_2BeH_4. The intent is to stimulate new research on these very interesting compounds, and to suggest that their physical properties may turn out to be even more interesting.

II. $LiBeH_3$

The ten powder-diffraction lines obtained by Bell and Coates from $LiBeH_3$ are listed in Table I. The interplanar d spacings are given in angstroms, and the relative intensities are indicated by s, m, w, and v (strong, medium, weak, and very). Copper $K\alpha$ radiation was used. The diffraction lines were quite broad and were barely detectable. Each of the three ions, Li^+, Be^{2+}, and H^- has only two 1s electrons. (The material would seem more suitable as an x-ray window than as a sample.)

A pleasant surprise is that the ten lines reported are the first ten allowed reflections of an fcc translation group. The identifications are listed in the second column of Table I, and the expected d spacings for the lattice con-

TABLE I. Observed d spacings of $LiBeH_3$, their (hkl) indexing, and the calculated values for an fcc lattice with $a = 5.09$ Å. The data are from Bell and Coates, Ref. 9 (s, strong; m, medium; w, weak; v, very).

d spacing (Å)	(hkl)	Calculated (Å)
2.93 s	(111)	2.939
2.54 s	(200)	2.545
1.80 m	(220)	1.800
1.54 m	(311)	1.535
1.48 mw	(222)	1.469
1.29 vw	(400)	1.273
1.18 w	(331)	1.168
1.14 w	(420)	1.138
1.05 w	(422)	1.039
0.99 w	(333), (511)	0.980

stant,

$$a = 5.09 \text{ Å} \quad (\text{LiBeH}_3) \ , \tag{1}$$

are listed in the final column. Given that the lines were broad, a feature that I shall attribute to stacking faults, the agreement seems excellent. The interpretation requires (of course) further analysis, an exercise which would be difficult were it not for the high symmetry found.

The cubic cell must contain at least four formula units (on account of the fcc structure), but I have not succeeded in finding an atomic arrangement that would be consistent. The only reasonable alternative is eight. A (sc) perovskite structure with a lattice constant $a/2$ would fit, but then the h,k,l =odd reflections of Table I would be forbidden. This difficulty can be solved by introducing the chemical superstructure shown in Fig. 1. The cube corners (of the $a/2$-sized cubes) can be divided into two fcc sublattices. Let one have Li^+ ions and the other Be^{2+}. Similarly, the body centers (of the $a/2$-sized cubes) can be divided into two fcc sublattices, one of Li^+ and the other of Be^{2+}. All face centers (of the $a/2$-sized cubes) have H^- ions. The first three layers of this superstructure are shown in Fig. 1. The lattice has fcc symmetry with lattice constant a, Eq. (1); and all fcc Bragg reflections are allowed.

The Madelung energy of the perovskite structure strongly favors divalent (positive) ions at cube centers and monovalent (positive) ions at cube corners. The structure proposed in Fig. 1 violates this apparent requirement, and can be rationalized if the crystal is not strictly ionic. In other words the bonding must be predominantly metallic, so that the average charge of a Be ion is closer to one than two. This suggests (but does not prove) that metallic
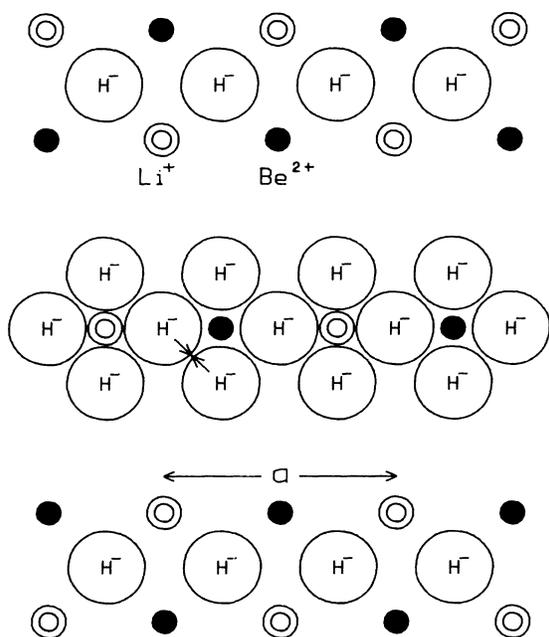
FIG. 1. First three atomic layers of the proposed structure for LiBeH₃. Displacements of the H^- ions are not shown (except by the arrows for two of them in the second layer). The layer spacing is $a/4$.

behavior is possible. Each *primitive* unit cell would contain 12 "conduction" electrons. (The Be and Li 1s electrons have not been counted.) The conduction-electron concentration, the r_s parameter, and the density are

$$n = 3.64 \times 10^{23} \text{ cm}^{-3} \ ,$$

$$r_s = 1.64 \text{ bohr} \ , \tag{2}$$

$$\rho = 1.91 \text{ g/cm}^3 \quad (\text{LiBeH}_3) \ .$$

The atomic concentration is $3.03 \times 10^{23} \text{ cm}^{-3}$, 72% larger than that of diamond. Since the volume of the Fermi surface is six times that of the Brillouin zone, it seems unlikely that LiBeH₃ could be a semiconductor or insulator. Band calculations[6] for metallic hydrogen, and for r_s values comparable to Eq. (2), lead to bandwidths of ~18 eV.

The alternation of Li and Be ions shown in the superstructure of Fig. 1 could not occur if the ($a/2$ sized) cube corners and centers were energetically disparate. Consequently a high density of stacking faults may occur during formation of the solid. Such faulting provides a plausible explanation of the unusual width of the powder-diffraction lines. A theory of this phenomenon was recently developed[10] and was applied to diffraction from stacking faults in the long-period ($9R$) low-temperature phase of Li.[11] The diffraction lines can be shifted slightly as well as broadened.

Be^{2+} ions are very small (~0.3 Å radius) so there is room for the six H^- ions surrounding each Be^{2+}, located at a (small) cube center, to relax together in pairs. The motion is illustrated for one such pair in the second layer of Fig. 1. There are eight ways to divide the six H^- ions into nearest-neighbor pairs. The resulting displacements (for a given pairing scheme) cause one of the $\langle 111 \rangle$ directions to differ from the other three. As a consequence the lattice will undergo a rhombohedral distortion. (A small distortion will cause additional broadening of the Debye-Scherrer lines.) However, the four $\langle 111 \rangle$ directions account for only half of the eight schemes. The other factor of 2 corresponds to a chirality along the unique axis. LiBeH₃ will be optically active parallel to that axis; and it can be either right- or left-handed. It is worthwhile to describe a particular case: The location of the ten ions of a primitive unit cell can be taken to be (in units of a)

$$\text{Be}^{2+}: (0,0,0) \text{ and } (\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4}) \ ;$$

$$\text{Li}^+: (\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) \text{ and } (\tfrac{3}{4},\tfrac{3}{4},\tfrac{3}{4}) \ ;$$

$$\text{H}^-: (\delta,\tfrac{1}{4}-\delta,\tfrac{1}{4}), \ (\tfrac{1}{4}-\delta,\delta,\tfrac{1}{4}) \ , \tag{3}$$

$$(\tfrac{1}{4}+\delta,\tfrac{1}{4},\delta), \ (\tfrac{1}{2}-\delta,\tfrac{1}{4},\tfrac{1}{4}-\delta) \ ,$$

$$(\tfrac{1}{4},\tfrac{1}{2}-\delta,\tfrac{1}{4}+\delta), \ (\tfrac{1}{4},\tfrac{1}{4}+\delta,\tfrac{1}{2}-\delta) \ .$$

The H^- ion displacement parameter is δ. Its determination will probably require neutron diffraction. The optic axis for the case described by (3) is $[1\bar{1}1]$ and it is right-handed. The proton separation of a pair is

$$d = \sqrt{2}[(a/4) - 2\delta] \ . \tag{4}$$

Bell and Coates reported that LiBeH₃ decomposed *in vacuo* at 300 °C with evolution of hydrogen. Infrared absorption was attempted by embedding the precipitate in

Nujol. In spite of excessive scattering (by the sample) they detected an absorption at 1540 cm^{-1}. The equivalent temperature is 2200 K.

III. Li$_2$BeH$_4$

Unlike the case described above the Debye-Scherrer lines of Li$_2$BeH$_4$ were sharp.[9] They are listed in Table II along with my (hkl) identifications and the calculated values for an fcc translation group with lattice constant,

$$a = 5.14 \text{ Å } (\text{Li}_2\text{BeH}_4) . \tag{5}$$

The fit is virtually perfect for the 13 identified lines. Noteworthy exceptions are the absence of the (400) and the (440) reflections. The missing (400) reflection is extremely important since, as I shall show, it essentially requires a unique atomic arrangement. The six unidentified lines and the missing (440) line will be discussed later.

The fcc translation symmetry of Li$_2$BeH$_4$ suggests a spinel structure with the Be^{2+} ions occupying the tetrahedral sites. I computed the structure factors for the spinel by employing the ion scattering factors of Cromer and Waber.[12] The results eliminated this possibility. For example, the (200), (420), (442), and (600) reflections are forbidden, the (111) and (331) reflections though allowed are extremely weak, and the (400) reflection should have medium intensity. All of these features are contradicted by the data.

The only way I found to "get rid" of the (400) reflection is to locate two Li$^+$ ions at (vector) separations ($\pm \frac{1}{8}, \pm \frac{1}{8}, \pm \frac{1}{8}$) from each corner of the cubic lattice with periodicity $a/2$. (400) scattering from the Li$^+$ ions then almost cancels the amplitude from Be^{2+} ions (located at the small-cube centers) and that from the H$^-$ ions (located at the corners and face centers of the small cubes). One should visualize at this point a perovskitelike structure (cube edge $= a/2$) having a linear trimer (Li$^+$H$^-$Li$^+$) at each corner, with the trimer axis along (say) [111], Be^{2+} at each body center, and the three other H$^-$ at the face centers. This "perovskite," (LiHLi)BeH$_3$, would have an sc translation group and would cause the h,k,l odd reflections of Table II to be absent.

The foregoing dilemma is easily solved by incorporating an *orientational* superstructure. Divide the sc lattice of trimers into two fcc sublattices and let the trimer axis be, for example, [111] on one sublattice and [$\bar{1}$11] on the other. This structure is shown in Fig. 2. The calculated powder-pattern lines are consistent with the identified lines of Table II. The (400) reflection, though present, is so weak that one should observe it only in an experiment of much higher sensitivity. The foregoing solution does not require the Li ions of each trimer to be exactly at a distance $\sqrt{3}a/8$ away from the central H$^-$ of the trimer. This separation can be (and would be expected to be) somewhat smaller on account of Coulombic repulsion from the Be^{2+} ions. A 10% decrease can be tolerated before the (400) intensity recovers significantly.

It is obvious that the structure shown in Fig. 2 does not have cubic symmetry (on account of the lower symmetry of the trimers). This broken symmetry is particularly apparent in reciprocal space where some reflections of a family, say $\langle 111 \rangle$, have large intensity and others have none.

TABLE II. Observed d spacings of Li$_2$BeH$_4$, their (hkl) indexing, and the calculated values for an fcc lattice with $a = 5.14$ Å. The data are from Bell and Coates, Ref. 9 (s, strong; m, medium; w, weak; v, very).

d spacing (Å)	(hkl)		Calculated (Å)
2.96 s	(111)		2.968
2.57 s	(200)		2.570
1.81 s	(220)		1.817
1.55 ms	(311)		1.550
1.48 mw	(222)		1.484
· · ·	(400)		1.285
1.18 mw	(331)		1.179
1.15 mw	(420)		1.149
1.05 mw	(422)		1.049
0.99 w	(333),	(511)	0.989
· · ·	(440)		0.909
0.87 mw	(531)		0.869
0.86 w	(600),	(442)	0.857
0.81 w	(620)		0.813
0.78 w	(533)		0.784
Unidentified			
3.54 m	a		
2.78 m	b		
2.43 w	c		
2.32 w	d		
2.05 w	e		
1.39 w	f		

FIG. 2. First three atomic layers of the proposed structure for Li$_2$BeH$_4$. The (LiHLi)$^+$ trimers have axes oriented along [111] and [$\bar{1}$11] directions (which do not lie in the plane of the figure). The layer spacing is $a/4$.

A single-crystal experiment would reveal this asymmetry dramatically. A Debye-Scherrer pattern tends to conceal such features, and is sensitive primarily to lattice distortions of the translation group. Apparently in Li_2BeH_4, these distortions (created by the trimers) are too small to be seen in the data of Bell and Coates. The small radius of Li^+ may possibly be the explanation. The powder pattern of Na_2BeH_4 is more complex, a likely consequence of the larger Na^+ ions.

The six unidentified lines, a–f in Table II, are probably caused by a second phase. They have no discernable relationship with the fcc reflections. Possibly Li_2BeH_4 exhibits several alternative orientational superlattices. Versions other than the one shown in Fig. 2 might occur at different temperatures or with states of strain created by impurities. Related compounds of different stoichiometry may also arise during synthesis. Obviously five independent powder lines (since $b = 2f$) are insufficient to resolve such a problem.

Finally, the question of the missing (440) reflection must be addressed. I have found it impossible to suppress all {440} reflections. Some of them always have very large structure factors. A reasonable surmise is the following. Powder-diffraction samples are frequently enclosed in fused-silica capillaries which, however, contribute a continuous background from amorphous scattering. Such a background is usually tolerable, but perhaps not when the sample has only two electrons per atom. An experimental solution could involve use of a crystalline sample holder of Cu or Al. The amorphous scattering is then eliminated, but one must contend with the Debye-Scherrer lines of the Cu or Al. These may cover up some of the lines from the sample. Repeating the experiment with both Cu and Al containers provides a complete spectral range since the Cu and Al lattice constants differ. However, the Li_2BeH_4 (440) reflection would be obscured by *both* the Cu (400) and the Al (420) reflection. If such a technique had been used, a Li_2BeH_4 (440) reflection could not have been reported. Nevertheless, this problem remains open and can be clarified in future experiments.

The number of "conduction" electrons per primitive cell is 16, so the Fermi surface encloses a volume of eight Brillouin zones. The "conduction-electron" concentration, r_s parameter, and density are

$$n = 4.71 \times 10^{23}\, cm^{-1}, \quad r_s = 1.51\ bohr\ ,$$
$$\rho = 2.63\ g/cm^3\ (Li_2BeH_4)\ . \tag{6}$$

The atomic concentration, $4.12 \times 10^{23}\ cm^{-3}$, is 2.34 times that of diamond! Clearly Li_2BeH_4 is an unusual material. It decomposes *in vacuo* at $340\,°C$.[9] An infrared absorption centered at $1600\ cm^{-1}$ was reported. The temperature equivalent, 2300 K, is likely indicative of the Debye temperature.

IV. DISCUSSION

It is clear that the structure determinations of the foregoing sections are tentative and are subject to confirmation or modification following more extensive diffraction studies. Nevertheless, I believe that these two materials and their complementary deuterides should be the focus of a comprehensive experimental and theoretical program.

Bell and Coates suggested that they might have failed to synthesize $LiBeH_3$ on account of the one-to-one correspondence of nine diffraction lines in the two materials. Instead they regarded the "$LiBeH_3$" product as an equal molar mixture of Li_2BeH_4 and BeH_2. This conclusion was reached in spite of the facts that the low-index d spacings differed by $\sim 1\%$, that the 1.29 Å spacing in $LiBeH_3$ had no equivalent in the (sharper) spectrum of Li_2BeH_4, that a BeH_2 infrared absorption at $1760\ cm^{-1}$ was not observed in the $LiBeH_3$ product, and that the $1600\ cm^{-1}$ absorption peak in Li_2BeH_4 was not observed in $LiBeH_3$.

Since the fcc structures shown in Figs. 1 and 2 are primarily determined by close-packing of large H^- ions, the one-to-one correspondence mentioned above may not seem too surprising. My conclusion is that Bell and Coates were successful in the synthesis of both compounds.

Despite the high n's and small r_s's of Eqs. (2) and (6), it remains undetermined whether or not these compounds are metallic. There is always the possibility that long-period superstructures will develop and create energy gaps covering the entire Fermi surface. Until this important issue is decided, one will not know whether lithium beryllium hydride is a substitute for metallic hydrogen.

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