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PREDICTED STRUCTURE AND DENSITY
OF BERYLLIUM HYDRIDE

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1. Introduction

The isotopes of hydrogen* are of great interest because of their importance in producing and influencing high energy nuclear reactions. As is to be expected, these effects are dependent on the concentration of the isotope and on the concentration and properties of other elements with which the hydrogen isotopes are associated. For most applications it is desirable to have as high a concentration of hydrogen as possible with a minimum of foreign particle dilution. At high temperatures where the atoms are completely ionized, it follows that elements of low atomic number are the least objectionable. This simplified picture may be altered in some cases due to special properties of the associated element, e.g., B^{10} has a large cross section for the absorption of thermal neutrons, beryllium is a good neutron reflector because of the high atomic density of the metal, and Li^6 can react with neutrons to give H^3 and He^4 .

In general, then, the properties of a hydride which determine its suitability with respect to other available compounds for applications at high energy are the apparent density or apparent atomic volume of hydrogen in the compound and the total number of electrons, or possibly the total number of particles (i.e., electrons plus nuclei), per hydrogen atom in the molecule. In Table I are presented such data for a selected list of compounds. Since it is desirable to have both the atomic volume and the total number of electrons as low as possible, it also follows that their product should be as low as possible; consequently, this product has also been recorded. It should be born in mind that since the relative importance of the two factors has not been specified for the various possible applications, one cannot unambiguously evaluate the importance of the compounds by comparing the atomic volume-to-1 electron product. The tabulated values do indicate that beryllium hydride will compete very favorably with the best compounds in the list if its density falls in the range 0.7 to 0.9 g/ml, and if its density should be considerably higher it becomes very attractive indeed. However, if the density is found to be 0.6 g/ml it will not be more favorable than NH_3 at low temperatures which has already been found to be very significantly inferior to liquid hydrogen for certain applications. The data would suggest that BeH_2 is not likely to be of interest for high temperature applications unless its density approaches 1.0 g/ml.

There are other compounds in the list worthy of careful consideration. If one looks at the figures for compounds at normal temperatures, it is seen that $LiBH_4$, $(C_2H_5)_4NBH_4$, $Be(BH_4)_2$, and $(CH_3)_4NBH_4$ are the best stable compounds on the list for which data are available. They are compounds with promising physical properties. $LiBH_4$ is a stable solid

*The term hydrogen will be used as a general name for all hydrogen isotopes.

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TABLE I
DENSITY-PARTICLE RELATIONS FOR LIGHT METAL HYDRIDES

Compound	State ⁽¹⁾	Density, g/ml	Atomic Volume Hydrogen, ml	η_e ⁽²⁾	$(N-Z)/N$ ⁽³⁾	Equivalent Ball ₂ Density, g/ml	(A. V. vol) ⁽⁴⁾	Equivalent ⁽⁷⁾ Ball ₂ Density, g/ml
H ₂	l	0.070	14.3	1	2	0.355	14.3	1.35
NH ₃	l	0.680	17.0	2.0	2.75	-	(14.7)	0.88
D ₂	l	0.31 (-100°)	9.0	2.7	4.0	0.61	26.2	0.89
*	*	0.377 (-100°)	9.0	-	-	0.64	21.9	0.78
LiH	*	0.812 ⁽⁵⁾	6.94	2.05	4.83	0.80	22.2	0.74
BaH ₂	*	0.398	6.1	2.75	4.1	0.64	22.2	0.74
CaH ₂	*	0.327 ⁽⁶⁾	6.32	2.5	4.32	0.65	22.2	0.73
NH ₂	l	0.85 (-10°)	6.7	2.2	4.7	0.63	26.7	0.82
*	*	0.72	7.40	-	-	0.71	25.7	0.64
*	*	0.817 (-75°)	6.94	-	-	0.79	22.9	0.72
BaH ₂	*	-	-	2.0	4.5	-	-	-
BaH ₂ ·2NH ₃	*	-	-	2.8	4.2	-	-	-
BaH ₂	*	-	-	2.8	4.2	-	-	-
LiOH	*	0.888	8.15	2.0	4.5	0.875	24.1	0.68
CaH ₂	l	0.415 (-100°)	6.7	2.5	3.75	0.57	24.2	0.68
CaH ₂ (Polymorph)	*	0.4	7.4	4.0	5.5	0.71	21.2	0.52
C ₂ H ₂	l	0.709	8.0	2.97	2.1	0.62	22.1	0.52
C ₂ H ₄	l	0.60 (0°)	8.7	2.4	4.8	0.51	22.0	0.56
NH ₂ F	*	1.313	7.5	2.0	6.5	0.74	22.0	0.47
Ba(OH) ₂	l	0.825 (-100°)	6.9	2.6	5.8	0.64	25.8	0.47
Al(OH) ₃	l	0.849	10.2	2.2	4.7	0.51	25.8	0.46
LiH	*	0.775	10.2	4.0	6.0	0.52	41.3	0.40
H ₂ O	l	1.00	8.0	2.0	6.5	0.61	45.0	0.38
H ₂ O ₂	l	1.01 (25°)	7.9	2.9	6.0	0.70	42.3	0.28
BaH ₂	l	0.888 (-100°)	11.2	4.5	5.5	0.47	22.0	0.31

(1) l - liquid, * - solid at room temperature unless other temperature specified.
 (2) Available above -20° - Armstrong, Am. Inst. Eng. Corp. Report 420 (1940). The density is a guess, assuming face-centered cubic type structure and the anion radius obtained from NH₄Cl and the tetrahydride radius obtained from BaH₂, using Pauling's radii for chloride and sodium.
 (3) Total electrons in the molecule per hydrogen atom.
 (4) Total particles, electrons plus nuclei, per hydrogen atom.
 (5) Hypothetical density of Ball₂ to give an apparent atomic volume for hydrogen equivalent to that for the specified compound.
 (6) Product of atomic volume and total number of electrons per hydrogen atom.
 (7) Hypothetical density of Ball₂ to give an atomic volume-atom electron product equivalent to the specified compound.
 (8) Data from Brown, Bragdon, and Gibb, J. Am. Chem. Soc., 75, 2247 (1953).

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which melts at 275° with slow decomposition. $\text{Be}(\text{BH}_4)_2$ melts at 123°, has a vapor pressure of 8 mm at 25° and sublimates above 90°. $(\text{CH}_3)_4\text{NBH}_4$ is a stable, hygroscopic, microcrystalline solid which decomposes slowly in vacuo at 150° and rapidly at 250°. $(\text{C}_2\text{H}_5)_4\text{NBH}_4$ has similar physical properties. Interesting possibilities might develop from a consideration of the compound $\text{Li}^6\text{B}^{11}\text{H}_4^2$ for high temperature reactions.

It is apparent from the data that BeH_2 cannot be of unique importance unless it has a density in excess of 0.74 g/ml, the value which gives an atomic volume-total electron product equivalent to that for $\text{Be}(\text{BH}_4)_2$ and $(\text{CH}_4)_4\text{NBH}_4$.

Light metal hydrides are also of interest because of the excellent neutron reflecting power of hydrogen and deuterium with respect to their masses. A high density beryllium hydride would be particularly attractive, but it must compete with beryllium metal which is also excellent due primarily to its high atomic density. A beryllium hydride with a density of 0.75 g/ml would be approximately equal to an equivalent volume of beryllium metal with respect to neutron reflecting ability. The transport cross sections are assumed to be equal for beryllium and hydrogen (actually deuterium) in making this estimate. The possibility of a somewhat higher density for the hydride makes the material of interest for applications of this type, but the advantages would not be spectacular unless the density were at least 1.0 g/ml. In applications of this type where the compound would be exposed to continuous radiation, i. e., in reactors, it is questionable whether the compound would have sufficient stability to be of practical importance. Since the compound will be largely covalent in nature it may not recover from radiation damage in the same way that a more ionic compound like lithium hydride does.

It is worth pointing out, perhaps, that beryllium hydride with a density of 0.75 g/ml provides 40 per cent more hydrogen on a volume basis than does lithium hydride and 25 per cent more than beryllium borohydride or lithium borohydride. However, tetraethyl ammonium borohydride provides 13 per cent more hydrogen than beryllium hydride at this density. It is equivalent to beryllium hydride with a density of 0.85 g/ml.

The problem of the structure, stability, and density to be expected for beryllium hydride can be predicted with some degree of confidence on the basis of theoretical considerations and a study of analogous compounds of beryllium and other neighboring elements in the periodic system. The problem of preparing the material and actually measuring a density has been under investigation for some time and the progress of these investigations is reported in detail elsewhere.¹ A summary of recent data on the density of a beryllium hydride etherate is reported in the final section of this report.

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2. Predicted Properties of Beryllium Hydride Based on Properties of Neighboring Hydrides

If one examines the hydrides of elements in the region of the periodic table around beryllium, it is discovered that the alkali metals form hydrides with increasing heats of formation in the order of decreasing atomic number. Furthermore, the crystal lattice shrinks in size on the formation of the hydride for these elements. The same statements may be made concerning the alkaline earth hydrides.

Early in this investigation it was suggested that this might indicate that a very stable beryllium hydride should be found and furthermore, it might be expected to form interstitially without an expansion of the metal lattice. On this basis one calculates an atomic volume for hydrogen in beryllium hydride of 2.5 ml corresponding to a density of 2.27 g/ml. This assumption offers very exciting possibilities.

The preparation of the hydrides of zinc, cadmium, and mercury were reported by Schlesinger² and Wiberg³ and again the stability was observed to increase with decrease in atomic number.

The hydrides of aluminum, magnesium and beryllium had already been prepared by Schlesinger^{2,4} and Wiberg⁵ in ether solution in the form of etherates of variable composition. Subsequently, magnesium hydride was prepared in good yield at this laboratory* by direct synthesis** from the metal and hydrogen gas, and the crystal structure, dissociation pressures, and heat of formation were determined. The heat of formation was found to be less than for calcium hydride; however, it exhibited a different crystal structure. Unfortunately, the density of the hydride of magnesium was such as to indicate an expansion of the magnesium lattice. This strongly suggests that the density of a beryllium hydride cannot reasonably be expected to have the high value originally proposed. The density of magnesium hydride was found to be 1.419 g/ml which gives an atomic volume for hydrogen in magnesium hydride of 9.3 ml as compared with a value of 7.6 ml calculated on the assumption that the metal lattice does not expand on forming the hydride.

Aluminum hydride in pure form has been reported by Wiberg⁷ but no information on its density is available.

* This work was done by Potter and is reported in reference 1.

**Wiberg, Goeltzer and Bauer⁶ reported earlier than magnesium hydride could be prepared by direct synthesis, but their yield was 60 per cent and they did not determine the structure of the product.

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3. Stability of the Beryllium-Hydrogen Bond

The problem of the stability of the compound is, of course, of fundamental importance. It has already been demonstrated² rather convincingly that the compound exists at least in combination with ether; however, it is perhaps worth while to consider other evidence. The Be-H bond has been identified and studied rather extensively.⁸⁻²³ Also it can be shown in a qualitative manner, based on molecular orbital theory, that the BeH_2 molecule will be stable with respect to the beryllium and hydrogen atoms. Mulliken and others have contributed to this problem, which is further considered in some detail below.

If the formation of the beryllium hydride molecule from the isolated atoms is considered as a possible intermediate step in the process of going from beryllium metal and hydrogen gas to solid beryllium hydride, it is proper to inquire whether the interaction of free beryllium and hydrogen atoms will lead to a stable configuration of the resulting molecule. Although the binding energy of the most stable configuration can be computed rather closely by the molecular orbital method, the matrix elements for the secular determinant require the calculation of some sixty interaction integrals. Whether the result would be of sufficient value to warrant undertaking such an extensive investigation is questionable. Nevertheless, a qualitative examination of the molecular orbitals which can be formed by the union of beryllium and hydrogen atoms will be helpful in deciding whether a stable configuration can exist.

Without exhaustive calculations the molecular orbital method alone cannot decide which nuclear configuration is most stable, in this case the linear or the non-linear model. Structural information on other molecules seems to indicate, however, that the most stable atomic orbitals will be used as much as possible. In beryllium only two orbitals in the L shell are required, one 2s and one 2p, since there are only four outer shell electrons in the entire molecule and s orbitals are more stable than p orbitals. Linear combinations of beryllium s and p orbitals in a 1:1 ratio with hydrogen 1s orbitals can only lead to a linear nuclear configuration, so we shall not need to consider the non-linear arrangement.

If we neglect the molecular orbital arising from the beryllium 1s orbital which is essentially indistinguishable from the atomic orbital itself, there remain six atomic orbitals from which molecular orbitals can be constructed: 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals on beryllium and two 1s orbitals on the hydrogens. The molecular orbitals must have symmetry properties consistent with the nuclear arrangement, namely, axial symmetry, and symmetric or anti-symmetric character with respect to reflection in the plane through the center of the molecule perpendicular to its axis. If the z-axis is taken to coincide with the molecular axis, it will be seen that the $2p_z$ orbital is the only p orbital which will have significant overlap with the hydrogen 1s orbitals, or more precisely is the only p orbital with zero angular momentum

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about the molecular axis, and is thus the only p orbital which can combine with the hydrogen 1s orbitals.

Since combinations of atomic orbitals are possible only between those of like symmetry (symmetric or antisymmetric with respect to reflection in the xy plane), the molecular orbitals will be either symmetric or antisymmetric. From the two identical hydrogen 1s orbitals one symmetric orbital can be obtained, $1s + 1s'$, and one antisymmetric orbital, $1s - 1s'$. Beryllium similarly has one symmetric orbital, $2s$, and one antisymmetric orbital, $2p_x$. The resultant molecular orbitals will then be linear combinations of the above symmetric and of the antisymmetric orbitals obtained from the solutions of two quadratic secular determinants. The relative stability of these four orbitals can be determined by Slater's rule which states that the energies of the orbitals are arranged in the order of the number of nodes between the bonded nuclei. The nature of these molecular wave functions along the molecular axis can be shown diagrammatically in order of their stability in Fig. 1.

The most stable orbital of course is I with no nodes between nuclei, and the least stable is IV with three nodes. As there are only four electrons to be placed in pairs in these orbitals, only I and II will be occupied. Both of these are of the bonding type having no nodes between nuclei, so we may reasonably expect the BeH_2 molecule to be quite stable with respect to its isolated atoms.

This, of course, predicts nothing as to the thermodynamic stability of the compound with respect to beryllium metal and molecular hydrogen.

A further insight into the nature of beryllium hydride may be had by an estimation of its heat of formation on the assumption that the compound exists as an ionic crystal.

4. Stability of an Ionic Lattice for Beryllium Hydride

The lattice energy of a crystal is the energy required to convert it to the gaseous ions. Starting with the familiar Born equation for the energy of ionic crystals, Kapustinsky²⁴ has developed a universal equation for the energy of the ionic lattice,

$$U = 287.2 \sum N \frac{e_1 e_2}{r_1 + r_2} \left(1 - \frac{0.345}{r_1 + r_2} \right)$$

where U is the ionic lattice energy per gram mole, 287.2 is a collected term involving one-half the product of the structure coefficient α ($\alpha = 1.745$ for a NaCl type lattice), Avogadro's number, and the square of the electron charge, $\sum N$ is the number of ions per molecule, e_1 and e_2 are the respective charges on the positive and negative ions, r_1 and r_2 are the corresponding radii and 0.345 is a universal constant. The equation is set up to give the correct

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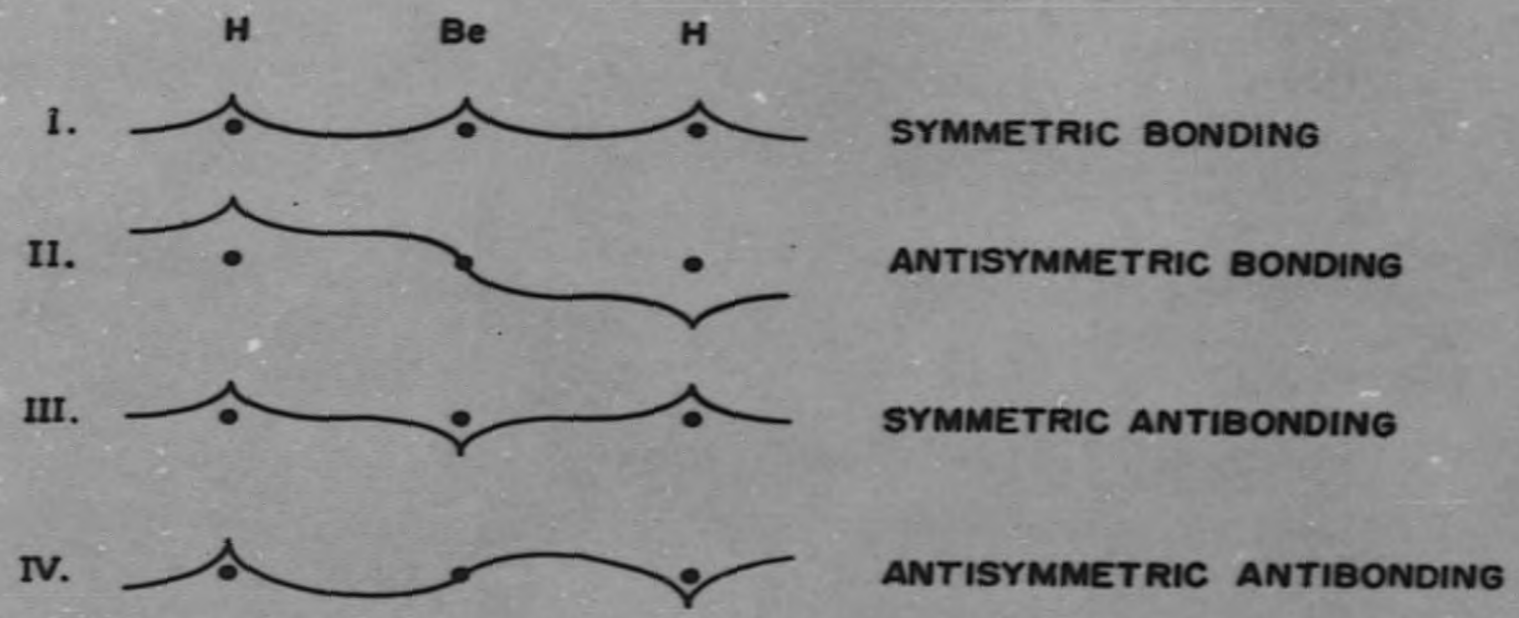


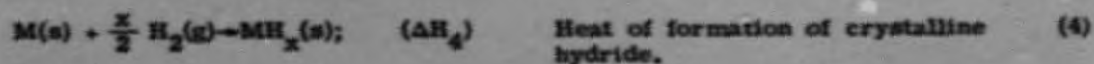
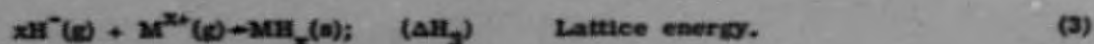
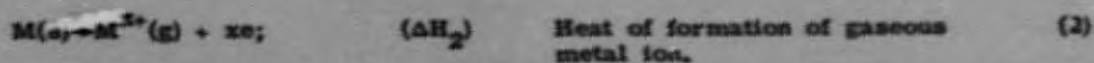
Fig. 1 Schematic Molecular Orbital Wave Functions for BeH_2

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energy using Goldschmidt type ionic radii (NaCl type lattice, coordination number 6) regardless of the actual crystal structure of the compound.

Use is made of this equation, along with certain available thermodynamic information, to calculate whether the projected compound BH_2 can exist as an ionic crystal. The lattice energy of hydrides may be combined with certain other thermodynamic information to obtain values for the heats of formation of these hydrides according to the following generalized equations:



In the equations, M represents any metal atom which is combined with the proper number of hydrogen atoms to form a molecule of the corresponding hydride. The heat of reaction, ΔH_3 , for Eq. 3 is an expression of the lattice energy, U, and for an ionic crystal may be calculated from Kapustinsky's expression.

In order to calculate the lattice energy for the hydrides it is necessary to know the ionic radii for the various ions. Pauling²⁵ has provided such values for the ions which are to be considered. However, his value for the radius of H^- , 2.08 A, does not give any reasonable value for the calculated ionic lattice energy of the alkali metal hydrides. In fact, this value is greater than the known interionic distance of 2.04 A for LiH. Emeleus and Anderson,²⁶ in a table listing a "self-consistent set of ionic radii", give a value for hydride ion of 1.53 A. Evidently Pauling's radius is not suitable for calculating the interionic distance for LiH. Since the sum of Pauling's radii check the experimentally determined values for a very large number of predominantly ionic crystals, it seems reasonable to use Pauling's radii for the metal ions and calculate a new value for the H^- radius from Kapustinsky's equation using LiH as the reference crystal.

If one uses the experimentally determined value of U for the ionic compound LiH, as determined by suitably combining the heats of formation²⁷ corresponding to Eqs. 1, 2, and 4 to give the heat of reaction for Eq. 3, and Pauling's radius for Li^+ , a value of 1.65 A is

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calculated for the radius of H^- by means of the expression for U . By making use of this value and Pauling's ionic radii for the alkali metals, the values of U for the alkali metal hydrides have been calculated. These values have been combined as shown in the above equations to give the heats of formation, ΔH_f , and are tabulated in Table II for comparison with the values arrived at experimentally. These compounds are accepted as being predominantly ionic in character, and the agreement between the experimentally determined values of U and those calculated is excellent. The corresponding heats of formation represent the small differences between relatively large numbers, and the precision is much less as is to be expected.

TABLE II

LATTICE ENERGY AND HEATS OF FORMATION FOR THE ALKALI METAL HYDRIDES

Compound	Lattice Energy, kcal/mole			ΔH_f , kcal/mole		
	Observed	Calculated	Difference, per cent	Observed	Calculated	Difference, per cent
LiH	216.5	216.5*	0	-21.61	-21.61*	0
NaH	193.8	191.8	1.01	-13.70	-11.7	-14.6
KH	170.7	171.3	0.35	-13.60	-14.2	4.4
RbH	164.4	163.4	0.55	-12.0 (?)	-11.0	- 8.3
CaH	156.1	154.3	1.15	-12.0 (?)	-10.2	-15.0

*Basis for calculation.

The choice of ionic radii is, of course, open to question. The method used can be defended mainly on the basis of the excellent agreement between the calculated and observed values for the lattice energy. It should be pointed out, however, that the calculated value for the radius of H^- , 1.65 Å, gives a Li - H distance of 2.25 Å. If one uses the observed interionic distance of 2.04 Å, the heat of formation is calculated to be -39 kcal/mole.

In a similar manner values of the lattice energies and the heats of formation have been calculated for MgH_2 , CaH_2 , SrH_2 , and BaH_2 . The calculated values have been based on Pauling's radii using the H^- radius of 1.65 Å as calculated from LiH, and on Zachariasen's²⁸ radii (essentially Pauling's radii "reduced" to unit charge) using a value of 1.42 Å for H^- as calculated using CaH_2 as a standard. The calculated energies in both cases are in good agreement with the experimental values; however, the agreement is somewhat better using Pauling's radii. The data using Pauling's values are recorded in Table III along with the calculated values for the heats of formation.

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TABLE III
LATTICE ENERGY AND HEATS OF FORMATION FOR GROUP II HYDRIDES

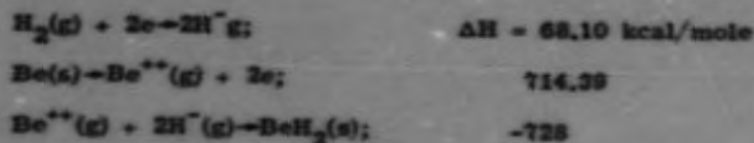
Compound	Lattice Energies, kcal/mole			ΔH_f , kcal/mole		
	Calculated*	Observed	Difference, per cent	Calculated	Observed	Error per cent
MgH ₂	637.	663.9	4.0	- 7	-34	-79.4
CaH ₂	567.	576.8	1.7	-35	-45.1	-22.4
SrH ₂	543.	534.4	1.6	-51	-42.3	+20.6
BaH ₂	508.5	504.7	0.8	-44	-40.9	+ 7.6

*Pauling's radii.

As was noted for the alkali hydrides, the calculated values for the heats of formation show considerable deviation as is to be expected. In all cases, however, the ΔH_f has a negative value which suggests a stable ionic crystalline form for the compound. In consideration of the large error in the ΔH_f for MgH₂ the evidence is perhaps less convincing. However, the interionic distance used in the calculation (1.65 + 0.65 = 2.30 Å) is quite large compared with the observed value, 1.95 Å. Here the difference is 0.35 Å as compared with the difference of 0.21 Å for LiH. If one uses an interatomic distance of 1.95 Å the calculated value for ΔH_f is -98 kcal/mole. The interionic distance for MgF₂ as calculated from Pauling's values is in excellent agreement with the X-ray value, yet the calculated heat of formation, making use of Kapustinsky's equation, is -210.7 as compared with the "selected value" of -250.8 kcal/mole. Perhaps the only conclusion to be drawn for MgH₂ is that the bonding probably is different from that exhibited in the other cases.

As a matter of general interest, and to give further evidence for the effectiveness of the method, the heats of formation, ΔH_f , for a number of other possible hydrides have been calculated and tabulated in Table IV. The results would indicate that the most of these compounds do not exist as ionic crystals.

The BeH₂ problem will now be considered. The lattice energy, U, for BeH₂ has been calculated using Pauling's values for the radius of Be⁺⁺, 0.31 Å, and the value 1.65 Å for the H⁻ radius. From this energy a value of $\Delta H_f = +54$ kcal/mole was obtained as follows:



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TABLE IV
PREDICTED HEATS OF FORMATION FOR CERTAIN HYDRIDES
ASSUMING AN IONIC CRYSTAL

Compound	ΔH_f , kcal/mole	Properties
CuH	+104	Unstable compound reported.
BeH ₂	+ 54	Existence established for complex etherate only.
ZnH ₂	+116	Compound decomposes at ~ 90°C.
CdH ₂	+174	Compound decomposes suddenly at 2°C.
HgH ₂	+219	Compound reported to decompose at -125°C.
LaH ₃	- 49	Exists as LaH ₂ and H in solid solution.
BH ₃	+333	Compound exists only as dimer with hydrogen bridge bonding.
AlH ₃	+ 63.6	Stable up to 100°C. Probably exists as the dimer.

This suggests that BeH₂ would not be expected to exist as an ionic crystal. No crystal structure for BeH₂ is known; however, the calculation for the lattice energy is adjusted for an assumed sodium chloride structure. Pauling points out that the interatomic distance is found to be the same in most cases whether the crystal exists with a sodium chloride structure or with the fluorite or rutile structure. In view of this it is perhaps significant that on the basis of geometric considerations alone an H⁻ radius of 1.65 Å with a sodium chloride lattice would require a Be⁺⁺ radius of 0.68 Å (Pauling's radius = 0.31 Å) for mutual contact between the ions, and thus would give rise to "double repulsion" and would be expected to have an effect on the lattice energy. Also it should be realized that since the ionic radius of Be⁺⁺ (0.31 Å) is so small in comparison with the selected H⁻ radius (1.65 Å), an error of only a few per cent in the H⁻ radius would have a very pronounced effect on the calculated lattice energy. In any case, the results should not prejudice one's views on the existence of BeH₂ as a coordination compound. Information is now available which permits a more detailed consideration of the stability of the molecule as a coordination compound.

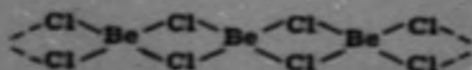
5. A Polymeric Structure and Predicted Density for Beryllium Hydride

In recent years there has been a rapid accumulation of detailed structural information on electron-deficient compounds largely through the work of Hundle and associates, although

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many individuals have contributed to the structural study of diborane, a problem of long standing. That beryllium hydride should be placed in this category was first suggested by Longuet-Higgins²⁹ in 1949 and is strongly implied by the structural analyses of beryllium chloride, beryllium dimethyl, and aluminum trimethyl dimer by Rundle.³⁰⁻³²

Both beryllium compounds are isostructural with SiSi_2 , forming long chains parallel to the crystallographic axis in which the configuration about the beryllium atom is approximately tetrahedral.



The space group in each case is the orthorhombic group D_{2h}^{26} - I_{h4m} with beryllium positions at

$$(0 \ 0 \ \frac{1}{4}, \ 0 \ 0 \ \frac{3}{4}) + 0 \ 0 \ 0, \ \frac{1}{2} \ \frac{1}{2} \ \frac{1}{2};$$

chlorine or carbon positions at

$$x(xy \ 0, \ xy \ \frac{1}{2}) + 0 \ 0 \ 0, \ \frac{1}{2} \ \frac{1}{2} \ \frac{1}{2};$$

and four molecules per unit cell. The cell dimensions for dimethyl beryllium are $a_0 = 11.53$, $b_0 = 5.65$ and $c_0 = 5.54 \text{ \AA}$ with a density of 0.9, and for the chloride $a_0 = 9.86$, $b_0 = 5.36$ and $c_0 = 5.26$ with a density of 1.91.

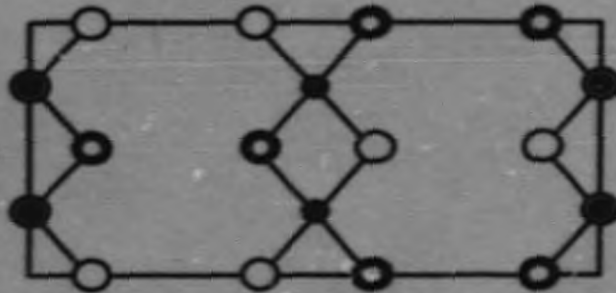
The unusual features of the structure of these compounds lie in the rather large bond lengths for Be - Cl and Be - C and the acute bond angle Be - C - Be. For the Be - Cl distance Rundle finds the value 2.02 \AA , which is to be compared with the value 1.88 for a normal single bond obtained by Pauling's rule and radii,³³ or the value 2.06 \AA for a half-bond (one-half electron pair per bond). Similarly, the observed Be - C distance is 1.92 \AA vs 1.66 \AA for a normal bond and 1.84 \AA for a half-bond. Although in the case of the chloride it appears that chlorine may contribute additional electrons to the bond, it is clear that in the methyl compound a deficiency of electrons must exist as only two pairs are available among the four bonds about each beryllium atom. This is consistent with the above comparisons based on Pauling's rule. The bond distance in SiSi_2 with one electron pair per bond, on the other hand, is normal.

Realizing the difficulties involved in applying rules relating bond length to bond order, Rundle was able to arrive at the same conclusion regarding the presence of an electron deficiency in the methyl derivative from a consideration of bond angles alone. The angles in the

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$a_0 = 9.86 \text{ \AA}$

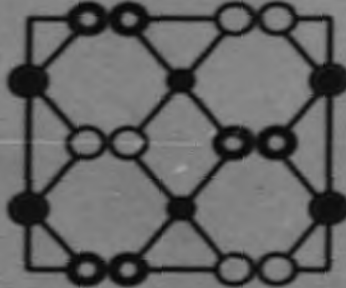
$c_0 = 5.26 \text{ \AA}$



PROJECTION ON XZ

$b_0 = 5.36 \text{ \AA}$

$c_0 = 5.26 \text{ \AA}$

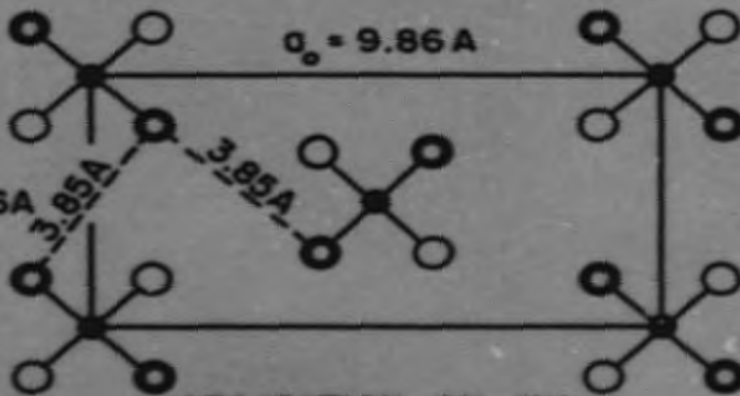


●● Be
○○ Cl

PROJECTION ON yz

$a_0 = 9.86 \text{ \AA}$

$b_0 = 5.36 \text{ \AA}$



PROJECTION ON xy

Fig. 2 Projections of the BeCl_2 Structure on the Principal Lattice Planes

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four-membered rings are significantly different in the two compounds. In dimethyl beryllium the angle C - Be - C is 114° , or greater than tetrahedral, while the corresponding angle Cl - Be - Cl is only 96° or less than tetrahedral. The narrow angle (see Fig. 3) Be - C - Be of 66° is believed to arise through the directing of one carbon tetrahedral orbital between two beryllium atoms, creating what has been called a three atom bond or orbital. The beryllium atoms tend to move together until a maximum overlap of orbitals is achieved. In the bonding orbital schematic in Fig. 3 it will be noted that the angle between the beryllium orbitals is rather less than the angle of the C - Be - C bond, and is probably close to the expected tetrahedral angle 109° . The beryllium atoms are sufficiently close, 2.09 A in this compound, to suggest that some mutual overlapping of their orbitals contributes to the stability of this structure also, but if so it seems to be a secondary effect since in the chloride the Be - Be distance is much larger.

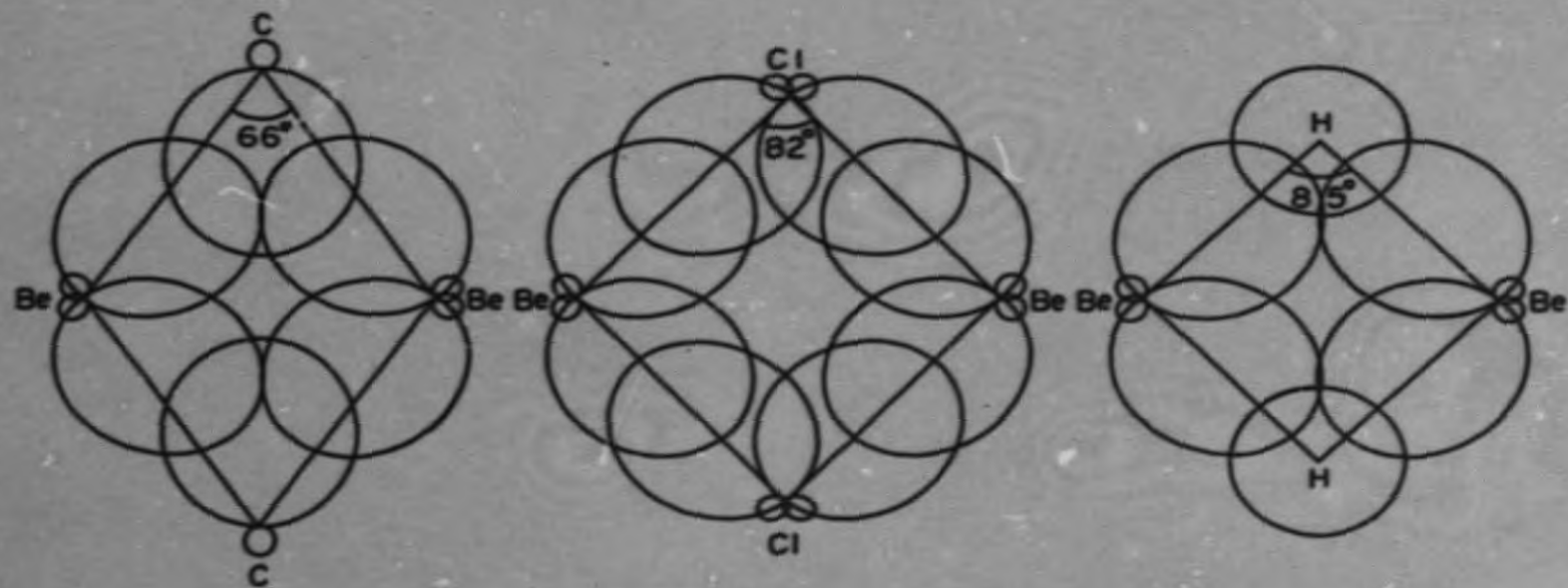
The greater Be - Cl - Be bond angle of 82° is required if chlorine brings into use one of its pair of unshared electrons. Normally two of the chlorine 3p orbitals (which are of comparable energy to the beryllium tetrahedral orbitals) would be directed at right angles to each other, but some compromise is necessary in order that the beryllium tetrahedral orbitals approach more nearly the preferred angle of 109° . Although the observed Be - Cl distance of 2.02 A is rather larger than 1.86 A estimated from Pauling's radii for a single electron pair bond, the corresponding bond in dimethyl beryllium is 0.08 A longer than a half-bond, so it is quite possible that Pauling's revised radius for beryllium is too small. His original tetrahedral radius was 1.06 A, or 0.17 A longer than the revised value.

Unfortunately, structural data on hydrides known to be electron deficient are available only for the boron hydrides and certain borohydrides, and then only from electron diffraction patterns which lack some of the precision obtained from X-ray measurements. The recent reinvestigation of the diborane structure by Hedberg and Schomaker,³⁴ however, leaves little doubt that a similar four-membered bridge structure occurs in that molecule also, as has been proposed independently by Pitzer³⁵ and by Longuet-Higgins.²⁹ The following dimensions for the diborane structure are quoted from the work of Schomaker.

B - B	1.770 ± 0.013 A
B - H (terminal)	1.187 ± 0.030 A
B - H (bridge)	1.334 ± 0.027 A
H - B - H (terminal)	$121.5 \pm 7.5^\circ$
H - B - H (bridge)	97°

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Fig. 3 Schematic Representation of Bonding Atomic Orbitals in Some Electron-Deficient Beryllium Compounds

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We find here also the characteristic long B - H bonds in the bridge relative to the normal terminal ones. The angles in the bridge resemble most closely those in beryllium chloride, but the interpretation in this case differs greatly as a result of the electron deficiency in diborane. In order to use four orbitals formed by sp^3 hybridization rather than three as in the isolated BH_3 molecule (sp^2 hybrid), it becomes necessary to supply additional energy to the electrons because of the greater relative stability of an s orbital to a p orbital. Less promotional energy will be required, however, if the s orbital is used largely to form the normal external B - H bond, and the bridge half-bonds are made up primarily of p orbitals, since there are twice as many electrons in the former. This accounts for an external H - B - H angle larger than tetrahedral and a bridge angle smaller than tetrahedral. Due to the spherical symmetry of the lowest hydrogen orbital (1s), the hydrogen atoms exercise no influence on the bridge bond angle, in contrast to the two beryllium compounds discussed above, except indirectly through their bonding radius. In addition to the B - H bonds there appears to be a significant amount of overlapping of the boron orbitals with each other if one compares the B - B distance with the normal value 1.60 A.

The early electron diffraction investigation of diborane and aluminum and beryllium borohydrides by Bauer and Beach³⁶ led them to propose structures for these molecules which were more consistent with the normal coordination and bond distances, but in the face of spectral evidence for bridge structures Bauer and Silbga have reexamined the data on the basis of unsymmetrical bridge models not considered in the work of Bauer and Beach and admit that such structures are not inconsistent with data.³⁷ The infrared spectra of several borohydrides have been analyzed by Price³⁸, who interprets them in terms of bridge type models. Using interatomic distances for the heavy atoms from electron diffraction studies by others and semi-empirical rules for estimating bond distances from force constants, he has proposed the following distances and angles:

A. Diborane

B - B	1.79 A
B - H (terminal)	1.18 A
B - H (bridge)	1.39 A
H - B - H (terminal)	120°
H - B - H (bridge)	97°

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B. Aluminum Borohydride

Al - B	2.19 A	
B - H (terminal)	1.20 A	
B - H (bridge)	1.31 A	
Al - H	1.75 A	
H - B - H (bridge)	106°	
H - Al - H	73°	35'

C. Beryllium Borohydride

Be - B	1.73 A	
B - H (terminal)	1.19 A	
B - H (bridge)	1.31 A	
Be - H	1.43 A	
H - B - H (bridge)	108°	
H - Be - H	95°	36'

D. Sodium Borohydride

Na - B	3.07 A	
B - H (terminal)	1.26 A	
B - H (bridge)	1.26 A	
Na - H	2.50	
H - B - H (bridge)	110°	
H - Na - H	47°	

The information of particular interest is the data on beryllium borohydride where the distorted tetrahedral arrangement of hydrogen atoms expected in beryllium hydride presumably exists (electron diffraction data are unable to differentiate between quasi-square and quasi-tetrahedral configurations).

To arrive at a reasonable structure for beryllium hydride it is first essential to consider the electronegativity differences of these elements in order to eliminate the consideration of ionic structures. From Pauling's table²⁵ we find the value 1.5 for beryllium and 2.1 for hydrogen. It is clear then that the degree of ionic character will be relatively low, hardly greater for example than in C - H or C - N bonds. Even the two beryllium compounds discussed above should have greater degrees of ionic character in their beryllium bonds than the hydrides, yet the peculiarities of their structure can only be understood in terms of an essentially covalent model.

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If the bridge bond structure is accepted as characteristic of electron deficient molecules and crystals, and it is assumed that such bonds will be formed wherever it is possible, it follows logically that beryllium hydride will choose to form a long chain-like polymer such as has been observed in beryllium chloride and dimethyl beryllium. That the D_{2h}^{26} - Ih_{am} space group is particularly stable for the packing of such chain like polymers seems reasonable when molecules as different in composition as these two compounds are found to exhibit it. It remains then to determine what bond lengths and angles and packing distances will be expected for the hydride. For this purpose the diborane structure will probably serve as our best guide.

Since the Be - H bonds are necessarily equivalent in the above structure, they will all contain the same combination of s and p orbitals and will prefer to be directed tetrahedrally. For maximum overlap between 1s hydrogen orbitals and sp^3 beryllium orbitals, however, neighboring beryllium atoms will be brought too close to each other so that repulsive forces are likely to become important. It may reasonably be assumed that the Be - Be distance will not be less than 1.78 Å, Pauling's value³² for a single bond, and may be greater than 1.96 Å corresponding to a half-bond (the shortest metal-metal bonds observed in bridge structures are at least as long as a half-bond). Its actual value is relatively unimportant in estimating the unit cell volume in any case. As an approximation to the Be - H bond length, the observed B - H distance will be increased by the difference between Pauling's beryllium and boron radii³³ to obtain 1.42 Å, in close agreement with Price's estimate of 1.43 Å. This value probably represents a lower limit since it has been noted above that observed bond lengths in beryllium bridge bonds are usually larger than those calculated from Pauling's radii. For an upper limit this may be increased to 1.52 Å.

The greatest uncertainty in this beryllium hydride structure lies in the packing distance between hydrogen atoms of adjacent chains. Observed van der Waal radii for hydrogen fall generally in the range 1.05 - 1.35 Å which will be used here for upper and lower limits.* The van der Waal radius of chlorine in the beryllium chloride structure is about as large as in any other chlorine compound, but in view of the unusual nature of the bridge structure it is not safe to assume that there will be a parallel tendency in the hydride, especially since less evidence already has been noted for electron deficiency in the chloride.

If the arrangement of beryllium hydride chains is similar to those in the chloride and dimethyl derivatives, limits have been fixed on a sufficient number of parameters to determine

*Since this report was written the crystal structure of tetraborane has been reported by Nordman and Lipscomb.³⁹ They give for the smallest intermolecular hydrogen distance 2.61 Å, which corresponds to a van der Waal radius of 1.32 Å.

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the most probable range of the unit cell volume and density of the hydride. A simple calculation shows that the hydride unit cell volume will probably fall in the range 81 - 110 A.³ The corresponding density range is 0.66 - 0.90 g/cc.

By recognition of beryllium hydride as an electron deficient compound, a great deal of insight into its chemistry is revealed as well. It is not difficult now to understand the stability of its etherate. With a deficiency of two electron pairs per beryllium atom it can easily accommodate two ether molecules at the ends of a BeH₂ chain polymer, and it has a counterpart in diborane in the reaction



In fact, its reactivity towards various reagents can be expected to parallel that of diborane, whose chemistry is now well known, and possibly aluminum hydride which has already been prepared.

6. Considerations Relative to the Structure of Magnesium Hydride

The question which is often raised regarding the various hydrides is where one should place the dividing line between ionic and covalent types. If there is any basis in Pauling's estimation of bond polarities from his empirical electronegativity scale,²⁵ it will be realized that completely ionic or covalent types are only extremes and that the vast majority of hydrides lie in between. The molecular orbital description of bonding, however, aids in understanding the smooth transition from one extreme bond type to the other, for it is merely necessary to make the proper choice of coefficients in the linear combination of atomic orbitals. These coefficients are related, though not in a straight-forward manner, to Pauling's electronegativity values which can be used to obtain rough estimates of bond polarities.

In the case of MgH₂ the Mg - H bond would be expected to have only about 18 per cent ionic character, a surprising result in view of the rutile structure assigned to it recently by Zachariasen.⁴⁰ The rutile lattice is generally associated with the relatively ionic fluorides and oxides. Nevertheless, the importance of covalent bonding in MgH₂ can be seen from a closer analysis of the interatomic distances in this and the more ionic hydrides. If the Pauling ionic radii for the metallic ions is subtracted from the interatomic distances in magnesium and alkali hydrides, an abnormally low value for the hydride radius in MgH₂ is found as shown in Table V.

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TABLE V
INTERATOMIC DISTANCES IN HYDRIDES

	X - H	H ⁻ radius
MgH ₂	1.95 A	1.30 A
LiH	2.04	1.44
NaH	2.44	1.49
KH	2.85	1.52
RbH	3.02	1.54
CsH	3.19	1.50

Let us now consider MgH₂ as an electron deficient covalent structure. In the rutile structure magnesium has octahedral coordination or 6 bonds, and hydrogen has trigonal planar coordination or 3 bonds. This requires on the average a distribution of one-third electron pair to each bond. The sum of the normal single bond radii is 1.70 A, which corrected for bond order by Pauling's rule leads to a value of 1.99 A, in fair agreement with the observed distance 1.95 A. It has already been seen that a similar application of Pauling's rule to diborane predicts a B - H distance in the bridge bond of 1.36 A compared to the observed value of 1.33 A.

One may object to such an interpretation in the case of magnesium on the grounds that the normal crystal coordination number of magnesium is four in more covalent compounds, corresponding to the presence of tetrahedral sp³ hybrid orbitals. But coordination higher than four is not altogether uncommon among elements of the second row, even when bonded to elements whose electronegativity is not much more than one unit larger; for example, Al(BH₄)₃, PCl₅, PBr₅, AlCl₃ (crystalline), MgI₂, various silicides, and possibly AlH₃. To account for octahedral coordination at least two combinations of orbitals are possible. By promoting one-third of an s electron to a p orbital, magnesium can form four bonds at right angles, two linear sp_x bonds and p_y and p_z bonds at right angles which may alternate among the remaining four bond directions. The other alternative is to promote two-thirds of an s electron to a 3d orbital to form six d²sp³ octahedral bonds. The extra strength of such bonds may be sufficient to compensate for the considerable excitational energy required to use a 3d orbital. The trigonal bipyramidal coordination in PCl₅ and PBr₅ lends some support to the latter possibility, since dsp³ hybridization results in exactly this type of coordination. Also, the similarity between FeCl₃ and AlCl₃ (dimerization to Fe₂Cl₆ molecules with tetrahedral coordination or crystallization to give octahedral coordination) suggests the availability of d orbitals.

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The coordination of hydrogen is not restricted to certain directions due to the use of the $1s$ orbital exclusively, and probably it forms bonds of the bridge type in MgH_2 as in diborane but linked to three magnesium neighbors rather than two.

Thus, we find in MgH_2 a hydride which already appears to be intermediate between extreme ionic and covalent types, and it is only reasonable to conclude that in BeH_2 the covalent character will predominate as in the chloride and dimethyl beryllium. However, if one admits the unlikely possibility that BeH_2 also can exhibit the rutile structure, a density of 1.37 g/ml is calculated on the assumption that the Be - H interatomic distance is 1.48 Å. This value was obtained by reducing the corresponding value for MgH_2 , i. e., 1.95 Å, by the difference between Pauling's single bond (metallic) radii for Mg and Be.

7. A Density for Beryllium Hydride Based on Optical Properties of Related Hydrides

If it is assumed that beryllium hydride will exhibit a type of bonding which is not radically different from that found in magnesium hydride and the hydrides of other second group elements, then it is possible to arrive at a different estimated density⁴¹ for beryllium hydride by means of the Lorentz-Lorentz formula

$$d = \frac{M(n^2 - 1)}{R(n^2 + 2)}$$

where d is the density of the compound, M is the molecular weight, R is the molar refractivity and n is the refractive index. In order to make use of the formula one must arrive at reasonable values for the molar refractivity and the refractive index.

Reliable data for the optical properties of some Group I and Group II hydrides are summarized in Table VI.

TABLE VI
OPTICAL PROPERTIES OF SOME HYDRIDES

Compound	Molecular Weight	X-ray Density	Refractive Indices (5893Å)	Mean Index	Molar Refractivity (5893)
LiH	7.948	0.7751	1.9847	1.9847	5.074
NaH	24.005	1.36	1.72 ₅	1.72 ₅	7.0
MgH ₂	26.34	1.419	1.95, 1.95, 1.96	1.95 ₃	8.98
BaH ₂	139.38	4.15	2.02, 2.03, 2.08	2.03 ₇	17.2

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In order to estimate a value for the molar refractivity of beryllium hydride it is necessary to evaluate the ionic refractivity of the hydride ion. Values for the refractivity of the hydride ion in other Group II hydrides can be obtained by subtracting the refractivity of the respective cations from the values for the molar refractivity given in Table VI. Sets of values for the refractivity of cations have been proposed by Pauling⁴² and Fajans and Jona,⁴³ and they are reproduced in part in Table VII.

TABLE VII
THE REFRACTIVITY OF CATIONS FOR GROUP II ELEMENTS

Ion	Pauling (1927)	Fajans (1924)
Be ⁺⁺	0.020	0.09
Mg ⁺⁺	0.238	0.28
Ca ⁺⁺	1.19	1.33
Sr ⁺⁺	2.18	2.34
Ba ⁺⁺	3.94	4.28

Pauling derived his values from theoretical considerations and some experimental data. Fajans values are based on measurements of molar refractivities of gases and of solutions extrapolated to infinite dilution and these values have been used in the present calculations. All the values were derived on the assumption of mutual independence of ions. The total refractivity for a molecule can be expected to be lower than the value obtained by adding the figures for the individual ions on the assumption of mutual independence. This discrepancy can be expected to be more significant for a solid than for the gases and solutions for which the data were derived. The magnitude of this effect in a crystal will vary as the polarizing power of the cation and the polarizability of the anion. The polarizing power will be greater the smaller the cation and will increase with increasing charge of the cation.

Values for the refractivity of the hydrogen ion have been obtained for magnesium hydride and barium hydride by the above method. A value for beryllium hydride can be obtained by an extrapolation as shown in Fig. 4. In order to demonstrate the probable validity of such an extrapolation, values for the ionic refractivity of oxide, fluoride, and chloride ions for the second group elements have also been calculated in a similar manner. The data are tabulated in Table VIII and plotted in Fig. 4.

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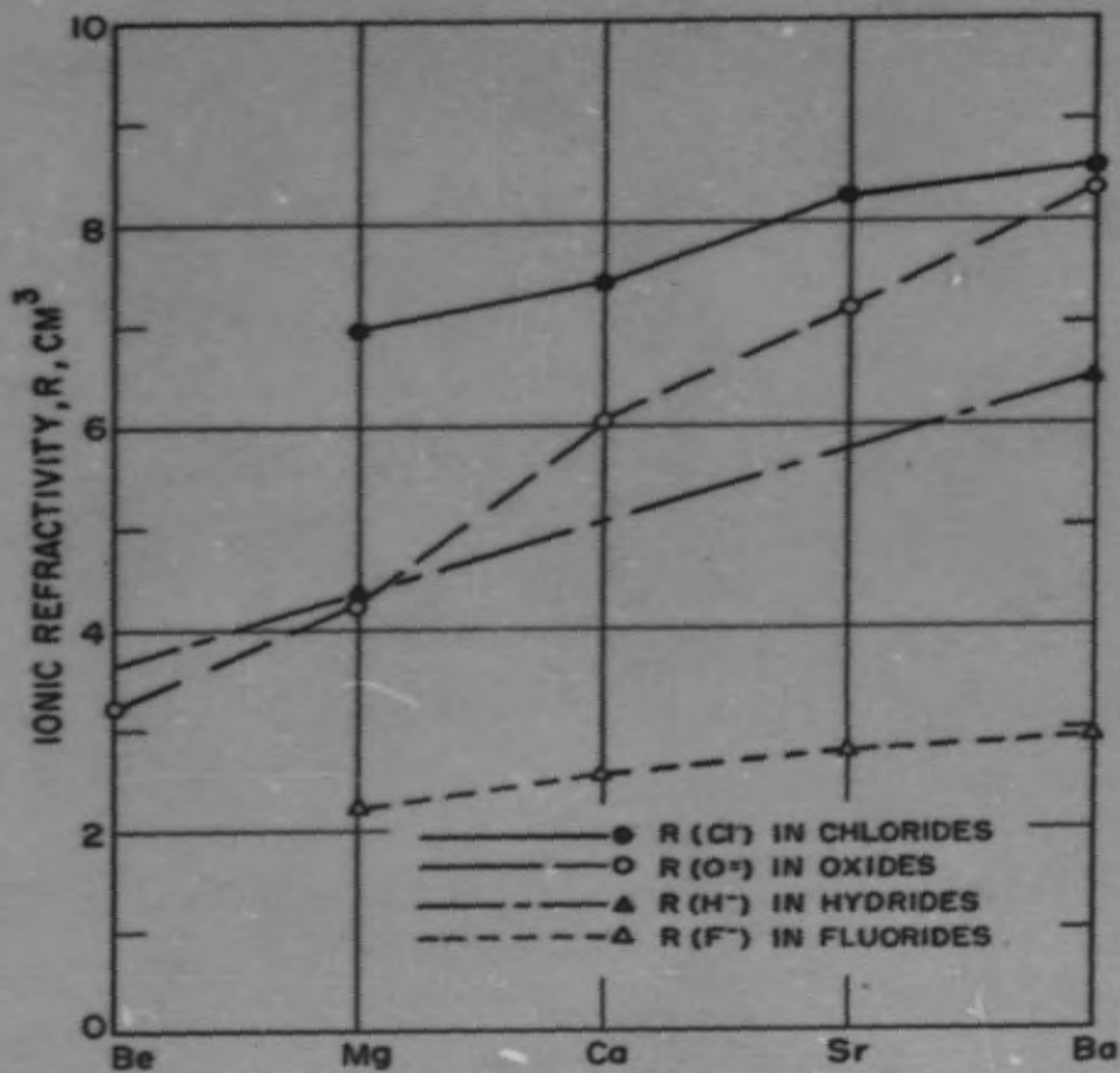


Fig. 4 Ionic Refractivity of the Chloride, Oxide, Hydride, and Fluoride Ions of Group II Elements

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TABLE VIII
 IONIC REFRACTIVITY VALUES FOR CERTAIN IONS

<u>R(H⁻)</u>	<u>R(O²⁻)</u>	<u>R(F⁻)</u>	<u>R(Cl⁻)</u>
	in BeO : 3.23	in BeF ₂ : 7	in BeCl ₂ : 7
in MgH ₂ : 4.35	in MgO : 4.24	in MgF ₂ : 2.21	in MgCl ₂ : 6.96
in CaH ₂ : 7	in CaO : 6.06	in CaF ₂ : 2.53	in CaCl ₂ : 7.4
in SrH ₂ : 7	in SrO : 7.13	in SrF ₂ : 2.76	in SrCl ₂ : 8.25
in BaH ₂ : 6.45	in BaO : 8.31	in BaF ₂ : 2.90	in BaCl ₂ : 8.54

It may be seen from the plot that the polarizability for the hydride ion, as indicated by the slopes of the curves, appears to be less than that of oxide ion, greater than for the fluoride ion, and about equal to that for the chloride ion. The data for beryllium are very limited, but for the oxides there is no serious discontinuity in the value of the ionic refractivity for oxide ion in going from barium to beryllium. If it is assumed that there is no sudden change in the character of the bonding in going from magnesium hydride to beryllium hydride, then the extrapolated hydride curve may be expected to give a reasonable value for the refractivity of the hydrogen ion. The value 3.65 is obtained from the curve for hydrogen. A value for the molar refractivity of BeH₂ of 7.4 is calculated from the ionic refractivities.

If one assumes that the refractive index for beryllium hydride is 2.0, in agreement with the values for various other hydrides recorded in Table VI, then the density of beryllium hydride as calculated from the Lorentz-Lorentz formula is 0.75 g/ml. It is very unlikely that the refractive index could exceed 3.0 (very few compounds, tellurides and sulfosalts, have higher refringences) which would give a figure for the maximum density of 1.1 g/ml. Of course, these values could have no significance if the bonding in beryllium hydride is radically different from that in magnesium hydride.

8. Experimental Estimate of the Density of Beryllium Hydride Etherate

Recently the experimental determination of the density for the products from five different preparations of beryllium hydride etherate has been completed.¹ These samples analyzed between 50 and 59 per cent by weight beryllium hydride as estimated from beryllium and hydrogen analyses. One of these samples (55 per cent BeH₂) was found to contain 18 per cent diethyl ether. Other samples prepared in a similar manner, but for which no density has been determined, were found to contain from 14 to 29 per cent ether depending on the particular preparation and to a limited extent, whether it was heated and pumped on intensively in an

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attempt to remove ether. The samples contained appreciable amounts, possibly as much as 10 to 25 per cent, lithium and aluminum, presumably as hydrides, and small amounts of other compounds. The densities were determined by flotation in benzene, ether, or 3-methylpentane. Although the densities as determined are believed to be correct, it is not possible to exclude the possibility of error due to gas pockets, convection currents, solvation and surface tension effects. The densities ranged in value from 0.65 to 0.72 g/ml with a precision of ± 0.01 g/ml. Because of the heterogeneous nature of the samples and the lack of complete analytical data it is not possible to infer the density of BeH_2 from these values. However, since the observed density is less than that of ether and since all of the impurities have a density greater than ether, except the ether impurity itself, it seems plausible that these values can be considered as an upper limit for the density of BeH_2 , and it is not unlikely that the true value is considerably less than these values.

9. Conclusions

It can be concluded from the foregoing theoretical considerations that beryllium hydride can be expected to exist as a chain polymer with hydrogen bridging. It is most likely to have a density less than 1.0 g/ml whether its structure is polymeric or crystalline. It would not seem reasonable to expect that the density could possibly exceed 1.4 g/ml, and this high value is most unlikely. Furthermore, the experimental evidence to date confirms the theoretical predictions quite closely.

Despite the apparent excellent agreement between theoretical prediction and the limited experimental results available, it must be borne in mind that in all of the calculations on structure and density included in this report it has been necessary to resort to certain assumptions. In each case the assumptions are thought to be conservative and reasonable in light of present knowledge. However, in each case it may be seen that the resulting density estimates are quite sensitive to factors which involve assumptions with rather wide uncertainties. Consequently, experimental confirmation of theory seems desirable.

It is unfortunate that the structure, and resulting density, cannot be calculated with sufficient certainty to obviate the necessity for experimental confirmation. Indeed, it is only recently that sufficient structural information on electron-deficient compounds has accumulated to make it possible to predict the structure with any degree of certainty. Even now structural data on hydrides known to be electron deficient are available only for the boron hydrides and some of the borohydrides. The fact that the structure and properties of magnesium hydride were not available at an earlier date made an early guess at the density of beryllium hydride difficult, and the fact that it is now known that magnesium hydride does not fit into the

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predicted structure pattern for electron-deficient compound in a straightforward, simple manner also points to the necessity to resort to experimental confirmation.

The theoretical treatment predicts a stable beryllium hydride having a density much less than the maximum density anticipated on the basis of simple analogy with the hydrides of the alkali and alkaline earth elements. However, it will be noted that the predicted values for the density bracket the minimum value for the density, i.e., about 0.75 g/ml, which appears to be of interest for nuclear application. Thus, had this theoretical treatment been available before experimental work was undertaken, it still would have been necessary to attempt the preparation of the pure compound. Furthermore, the remote possibility of an unpredictably high density for beryllium hydride makes an experimental investigation mandatory because of the great potential usefulness of the compound.

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