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Lithium Dihydrogen Fluoride—An Approach to Metallic Hydrogen

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The possibility of making a new form of hydrogen in the metallic state through preparation of the compound LiH$_2$F is discussed. A proposed structure is specified which is believed to be nearly stable under ambient conditions. The pressures needed to stabilize this compound and to convert it to a metal are estimated. It may have an exceptionally high hydrogen density, high electrical conductivity, high Debye temperatures in the hydrogen sublattice, and perhaps a high superconducting transition temperature.

The metallic form of hydrogen has been of interest for many years, at least since 1935 when Wigner and Huntington[1] made theoretical estimates of its properties and of the critical pressure needed to transform molecular hydrogen into it. It would be the simplest of all possible metals, and because of its low mass density and high elastic stiffness it might have an unusually high critical temperature for superconductivity, possibly above room temperature.[2] Also, at its theoretical density the number of hydrogen atoms per cubic centimeter is about 3.9×10^{23} compared with 8.5×10^{22} for liquid hydrogen. This makes it an attractive state in which to store hydrogen and in which to carry out nuclear-fusion reactions. The great disadvantage of the metallic state of hydrogen is that its critical pressure for stability is estimated to lie between 0.8 and 2.6 Mbar by some workers and as high as 20 Mbar by Alder and Christian.[3]

It is proposed here that a form of hydrogen in the metallic state might be achieved by changing the dielectric constant of the medium in which it exists. Since the equilibrium separation distance and the compressibility scale in proportion to the dielectric constant, this should substantially reduce the pressure needed to make the metallic state of hydrogen stable. It should affect the other properties as well, but they would still lie in ranges of interest. More specifically, it is proposed that the compound LiH$_2$F is nearly stable under ambient conditions and is a metal or will become a metal if moderate pressures are applied to it. Related compounds are LiHF and LiH$_6$F, but they will not be given attention here.

Structure.—A proposed structure for LiH$_2$F is sketched in Fig. 1. It consists of the LiF arrangement (*B*1 rock salt) with the pseudo-octahedral holes (tetrahedral holes in the fluorine sublattice) occupied by H atoms. Since the cell shown in the figure contains four lithium ions, four fluorine ions, and eight holes, this struc-

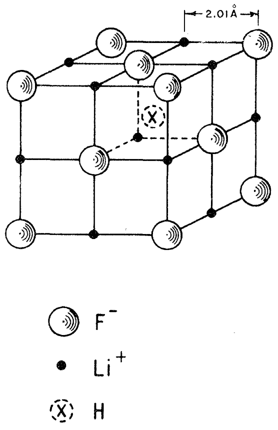

FIG. 1. Proposed structure for lithium dihydrogen fluoride. (For clarity of the diagram only one hole is shown to be occupied by hydrogen.)

ture yields the chemical formula LiH_2F. The hydrogen atoms might collect together as pairs which might then form an ordered array, but it is unlikely that this would be the favored arrangement at very high pressure levels because its density would be lower than an unpaired periodic array.

Stability. – Although lithium dihydrogen fluoride molecules are not known to exist in the gas or solution phases, there is some evidence that this compound is nearly stable. First, it is a mixed compound of LiH and HF, both of which are stable and which have stable dimers. Second, the lithium dihydrogen ion (LiH_2^+) is stable relative to Li^+ and H_2^- according to Ray[4]; and the HF_2^- ion is known to be stable. Third, it has been reported by Rase[5] that the etching behavior of dislocations in LiF is changed by an anneal in pure hydrogen at 260°C. This chemical evidence suggests a reaction between H_2 and LiF, either to form ionic complexes such as those mentioned above, or to form a molecular complex. It was the clue that led to the ideas expressed here.

Elementary theory suggests that a hydrogen sublattice might be stable within LiF. The interatomic distance in the H_2 molecule is $d(K=1) = 0.746$ Å where K is the dielectric constant. This distance scales in proportion to the dielectric constant which is 1.92 for LiF at optical frequencies. Thus the equilibrium distance for H_2 in LiF should be $d(K=1.92) = 1.43$ Å or considerably less than the normal hole spacing. The hole spacing of 2.01 Å as shown in Fig. 1 could be reduced to this value by a pressure of about 600 kbar as judged from the data of Drickamer *et al.*[6]

The paragraph above is based on the idea that H atoms would exist independently in LiF. However, they might form dimers. Then the crystal would not be expected to be a good conductor. In this case two critical pressures might exist: one to stabilize the composition LiH_2F, and another to transform it to the metallic state.

Now consider very approximately the stability of the metallic state. Energy scales as the inverse square of the dielectric constant, so the difference between the binding energy of molecular hydrogen (≃52 kcal/mol) and the binding energy of metallic hydrogen (≃11 kcal/mol according to Wigner and Huntington[1]) would be reduced by a factor of $K^2 = 3.7$ upon immersion in LiF. The new difference of ~10 kcal/mol corresponds to an internal pressure of ~40 kbar. This is more than an order of magnitude less than estimates of the critical pressure needed to form pure metallic hydrogen.

Also, it may be noted that the estimated interatomic distance in pure metallic hydrogen[2] is 1.5 Å, so this distance in a medium with $K = 1.92$ should be 2.86 Å which is considerably greater than the hole spacing in LiF in the (100) directions. It is close to the hole spacing in the (110) directions, however, and if half the holes were occupied, the compound LiHF could form. The corresponding distance based on the work of Alder and Christian[3] is 1.72 Å, and compressibility data[6] indicate that LiF could be compressed to this by a pressure of about 140 kbar.

The above considerations are quite rough but they suggest that LiH_2F might be stable at some moderate pressure level, say 100 kbar.

Another approach to the stability of the compound can be made from data on heats of formation.[7] Consider the following reaction:

$$\mathrm{LiH(sol)} + \mathrm{HF(liq\ or\ gas)} \rightarrow \mathrm{LiH_2F(sol)}, \qquad (1)$$

but the product might decompose:

$$\mathrm{LiH_2F(s)} \rightarrow \mathrm{LiF(s)} + \mathrm{H_2(g)}, \qquad (2)$$

so the overall equilibrium is

$$\mathrm{LiH(s)} + \mathrm{HF(l/g)} \rightleftharpoons \mathrm{LiH_2F(s)} \rightleftharpoons \mathrm{LiF(s)} + \mathrm{H_2(g)}. \qquad (3)$$

The pertinent heats and free energies of formation are as follows:

Substance	H_f^0 (kcal/g mole)	G_f^0 (kcal/g mole)
H_2(g)	0	0
HF(g)	−64.2	−64.7
HF(l)	−94.9	• • •
LiH(s)	−21.6	−16.7
LiF(s)	−146.3	−139.5

Then at 298°K, and one atmosphere,

$$\Delta G_f^0 = (0-139.5) + (16.7+64.7)$$
$$= -58.1 \text{ kcal/g mole}$$

which is the free energy tending to drive the reaction all the way to the right. This could be stopped by putting pressure on the gaseous hydrogen. At equilibrium,

$$\Delta G_f^0 = -RT \ln(P_{\mathrm{H}_2}/P_{\mathrm{HF}}),$$

$$\log(P_{\mathrm{H}_2}/P_{\mathrm{HF}}) = \frac{-58\,100}{-1.987\times 298 \times 2.3} = 42.8, \qquad (4)$$

and the required pressure (or activity) ratio is

$$P_{\mathrm{H}_2}/P_{\mathrm{HF}} \simeq 10^{43}, \qquad (5)$$

which is very high indeed, but it can be reduced by lowering the temperature.

Extrapolation of available vapor pressure data to low temperatures yields the following pressure needed for stability:

Temp. (°K)	Pressure needed (atm)
100	3420
74	1000
46	100

Thus the compound might be stable at the boiling point of N_2 under a pressure of a few kilobars.

Properties. – The simplest property of interest is the number density of hydrogen atoms. Assuming that the lattice parameter of LiH_2F is nearly the same as that of LiF, a value for the hydrogen density is obtained which may be compared with values for H metal and LiH:

Substance	H atoms/cm^3
H, liquid	8.5×10^{22}
metal (high *P*)	39.2×10^{22} (est.)
LiH_2F	12.3×10^{22} (est.)
LiH	5.8×10^{22}

It may be seen that the hydrogen density in LiH_2F is less than for the hypothetical pure metal, but greater than for liquid H, and more than twice that of LiH. This makes the compound attractive as a means for storing hydrogen, and as a nuclear-fusion fuel.

The electrical conductivity of the cubic form of LiH_2F should be metallic and might be very large because of the periodic arrangement of the protons. The Debye temperature of the hydrogen sublattice should be high (perhaps 2500°K), so there is some possibility that the superconducting transition temperature will be high, according to the arguments of Ashcroft.[2]

At the estimated spacing of the atoms, the bulk modulus B of the hydrogen sublattice can be estimated:

$$B \simeq (5.5\times10^{11})r_0^{-4}\ \mathrm{dyn/cm^2},$$

where r_0 is the atomic radius in angstroms. Based on the 1.72-Å distance given above, $r_0 = 0.86$ Å and the estimated bulk modulus becomes 10.1×10^{11} dyn/cm^2 which is less than twice the bulk modulus of pure LiF (6.7×10^{11} dyn/cm^2). It thus appears that the two sublattices are mechanically compatible, and that the elastic stiffness of LiH_2F will be substantially greater than that of LiF.

Preparation. –Equation (3) indicates two means for preparing LiH_2F. One consists of dissolving LiH in liquid HF. It is unattractive at first sight because of the hygroscopy of LiH, and the high reactivity of HF. The other would consist of dissolving H_2 into LiF. It has more amenable reactants but it might be a relatively slow process. In both cases it would be necessary to carry out the reactions at high pressure levels.

Another technique might consist of making dissociated hydrogen react at low temperatures with cold LiF. This might be a simple gas-solid reaction or the reactants might be isolated in a matrix such as condensed argon or neon.[8] A proton beam might also be used to inject H into LiF at low temperatures; sputtering into a cold substrate is another approach.

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