JOURNAL OF SOLID STATE CHEMISTRY 2, 144–155 (1970)

Hydrides versus Fluorides: Structural Comparisons*†

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Received October 9, 1969

The closeness of the ionic radii of the hydride and fluoride ions results in close structural analogies between the corresponding binary and ternary compounds of the highly electronegative elements. The analogies are closest for the alkalis, the alkaline earths, and aluminum. For the binary lanthanide and actinide compounds, the structures are related, but modified for the hydrides by the nonstoichiometry. The relative difficulty so far encountered in attempts to prepare ternary hydrides involving these elements is probably also due to nonstoichiometry. For the transition metals, the hydride and fluoride structural patterns differ considerably, the metallic nature of the hydrides here being involved as well. On the basis of these analogies, the known structures of corresponding hydrides and fluorides are correlated and the possible new ternary hydride compounds may be predicted.

Introduction

The halide aspect of metal hydrides, by virtue of the He-like $(1s)^2$ structure of the hydride ion, was first pointed out by Lewis (*1*). Moers (*2*) first demonstrated the ionic conductivity of solid and molten lithium hydride.

The ionic nature of lithium hydride is brought out by the comparison with lithium fluoride shown in Table I.

Both are face-centered cubic in structure, with lattice constants differing by only 1.5%. The greatest difference is in the refractive index, as a result of the high polarizability of the hydride ion with its tenuous nature as compared with fluoride ion. Solid solutions are formed in all proportions above 300° (*3*) owing to the structural similarity. Tobolsky (*4*) has shown that for alkali-halide systems solid solutions in all proportions, stable at room temperature, should form when the lattice constants differ by less than 5%. However, the large difference in lattice energies between LiH and LiF is such that higher temperatures are required in this system. Since the lattice constants are so nearly the same, this difference is due to the lower repulsion exponent for the hydride in the Born lattice energy expression.

The Li–LiH system (*5*) closely resembles the alkali metal–metal halide systems. The mutual solubilities of Li and LiH at the melting point of LiH are 26 atom% H in Li and 1 mole% Li in LiH; at the melting point of LiF the solubility of Li in LiF is negligible, while that of LiF in Li is less than 5 mole% (*6*). The consolute temperature of Li and LiF is 1330°C (*6*) as compared with an estimated value of 1000° for Li and LiH (*7*). The greater nonstoichiometry of the hydrides as compared with the halides is to be expected from the much lower electron affinity of hydrogen as compared with the halogens; the greater solubility of hydrogen in metal is to be expected from atomic size.

The effective ionic radius of fluoride ion is given as 1.33 Å by Pauling (*8*) and 1.36 Å by Zachariasen (*9*), for coordination number 6. The effective ionic radius of hydride ion varies from 1.27 to 1.52 Å (*10*), being much more highly sensitive to the particular cation present and to the particular assumptions used in deriving the radius than the fluoride value. For the alkali metal hydrides other than lithium hydride, with the same face-centered cubic structure as the corresponding fluorides, the effective hydride radius is 1.47 Å for Na^+, and 1.52–1.54 Å for K^+, Rb^+, and Cs^+. For LiH, CaH_2, and BaH_2, the hydride ion radius is 1.34–1.36 Å. The closest similarities between hydrides and fluorides should thus appear here.

Gibb (*11*) has shown that for the alkali and alkaline earth compounds the Born–Haber lattice energies of the hydrides are of the order of 10% less

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* Contribution No. 409, Department of Chemistry, Tufts University, Medford, Mass.

† This work was sponsored by the U.S. Atomic Energy Commission, Contract AT (30-1) 1355.

TABLE I

COMPARISON OF LiH AND LiF

	mp°C	ΔS of Fusion e.u.	Lattice Energy kcal	Lattice Constant Å	Refractive Index n_D^{25}
LiH	691[a]	5.40[b]	218[c]	4.083[d]	1.985[c]
LiF	848[e]	5.77[e]	239[d]	4.027[f]	1.392[g]

[a] C. E. MESSER AND I. S. LEVY, *Inorg. Chem.* **4**, 543 (1965).

[b] J. W. VOGT, NASA Document N63-22167, 1962; Chem. Abstr. **61**, 11391e (1964).

[c] E. STARITZSKY AND D. J. WALKER, *Anal. Chem.* **28**, 1055 (1956).

[d] J. SHERMAN, *Chem. Rev.* **11**, 93 (1932).

[e] T. B. DOUGLAS AND J. J. DEVER, *J. Amer. Chem. Soc.* **76**, 4826 (1954).

[f] H. E. SWANSON AND E. TATGE, Natl. Bur. Stand. Circ. 539, U.S. Govt. Printing Office, Washington, D.C., Vol. I, 1953, pp. 61–62.

[g] K. SPANGENBERG, *Z. Kristallogr.* **57**, 494 (1923).

than the fluorides. With the combination of unfavorable lattice constant difference plus this factor, solid-solution formation between alkali metal hydrides and fluorides, other than lithium, is unlikely. For the alkaline earths, high temperature solubility is possible as in the case of lithium.

For the transition metal hydrides of Groups III A and IV A, and the actinides, Libowitz and Gibb (*12*) have shown that interatomic distances are most readily rationalized in terms of the ionic model. According to this model, these metallic hydrides may be considered to consist of metal core ions of high if not maximum oxidation number, hydride anions, and conduction electrons. The metal ion radius is taken as that in the high oxidation state, while that of the hydride ion is taken as 1.29 ± 0.05 Å throughout the series. Interatomic distances may also be rationalized according to a covalent bonding model (*13*).

The variation in apparent radius of the hydride anion is then understood in terms of the sensitivity of the tenuous ion to the increasing electric field strength of the cation vertically from Cs^+ to Li^+, and horizontally from Group I to IV A.

Alkaline Earths

Calcium, strontium, and barium fluorides have the face-centered cubic fluorite structure at normal pressures and all temperatures up to their melting points. The corresponding dihydrides have an orthorhombic *pnma* structure closely resembling the lead chloride structure, in which the metal ions form a slightly distorted hexagonal close-packed structure. The corresponding compounds of europium (II) and ytterbium (II) have these same structures because of the peculiar stability of the inner $(4f)^7$ and $(4f)^{14}$ shells of these elements.

The fluorides of Ca, Sr, and Ba go over to the orthorhombic *pnma* structure at high pressures. The corresponding dihydrides undergo transitions at high temperatures to the presumed fcc structure. YbH_2 definitely undergoes a slow transition to two face-centered cubic forms, metastable at room temperature (*14*).

The crystal structure information on these compounds is shown in Table II. In this, and all subsequent Tables, structural information on hydrides is from Libowitz (*10*) and on fluorides from Wyckoff (*15*) unless otherwise stated.

The lattice constants of the *pnma* forms all agree within 3% for each hydride as compared with the corresponding fluoride.

The more polarizable hydrides take on the less symmetrical *pnma* structure at room temperature, but go over to a presumed more symmetrical form at higher temperatures where these forces are overcome by thermal energy. The fluorides, with the less polarizable anion, are cubic at ordinary pressures, but go over to the *pnma* structure at the higher pressures where the reduced interionic distances are able to produce the same effect.

Magnesium fluoride and hydride both have the tetragonal rutile structure with very similar parameters:

$$MgF_2\text{: } a_0 = 4.623\ \text{Å and } c_0 = 3.052\ \text{Å}\ (15),$$

and

$$MgH_2\text{: } a_0 = 4.517\ \text{Å and } c_0 = 3.021\ \text{Å}\ (16).$$

TABLE II

ALKALINE-EARTH HYDRIDES AND FLUORIDES: LATTICE CONSTANTS, Å

	Orthorhombic *pnma*					Cubic	
	a_0	b_0	c_0	Conditions	str	a_0	Conditions
CaH_2	6.851[a]	5.948	3.607	Normal	fcc?	—	>780°C[d]
SrH_2	7.358[a]	6.377	3.882	Normal	fcc?	—	>885°C[e]
BaH_2	7.845[a]	6.801	4.175	Normal	bcc[f]	—	>550°C[f]
YbH_2	6.794[b]	5.904	3.580	Normal	fcc[b]	5.19[b]	Metastable[b]
EuH_2	7.20[c]	6.26	3.78	Normal	—	—	—
CaF_2	7.03[g]	5.95	3.58	>100 kb[g]	fcc	5.463	Normal
SrF_2	7.43[g]	6.31	3.80	>50 kb[g]	fcc	5.800	Normal
BaF_2	7.91[g]	6.70	4.04	>50 kb[g]	fcc	6.200	Normal
EuF_2	—	—	—	—	fcc	5.796	Normal

[a] E. ZINTL AND A. HARDER, *Z. Elektrochem.* **41**, 33 (1935).
[b] J. C. WARF AND K. I. HARDCASTLE, *Inorg. Chem.* **5**, 1736 (1966).
[c] C. E. MESSER AND K. I. HARDCASTLE, *Inorg. Chem.* **3**, 1727 (1964).
[d] D. T. PETERSON AND V. G. FATTORE, *J. Phys. Chem.* **65**, 2062 (1961).
[e] D. T. PETERSON AND R. T. COLBURN, *J. Phys. Chem.* **70**, 468 (1966).
[f] D. T. PETERSON AND M. INDIG, *J. Amer. Chem. Soc.* **82**, 5645 (1960).
[g] K. F. SEIFERT, *Ber. Bunsenges. Phys. Chem.* **70**, 1041 (1966).

Beryllium hydride seems to be amorphous in all forms in which it has so far been synthesized. If the similarity to aluminum, so often noted in the chemistry of beryllium, is borne out, any crystalline form of BeH_2 should have one of the SiO_2 structures characteristic of BeF_2.

Lanthanides

The basic structural scheme for the hydrides and fluorides of these metals is given in Table III.

The hydrides of the lighter, larger lanthanide elements form continuous face-centered cubic solid solutions from $MH/_{\sim 1.9}$ to the closest feasible approach to MH_3. These phases are metallic conductors, shifting toward semiconductors as the trihydride limit is approached (*17*). The tetrahedral holes of the fluorite lattice are approximately filled at MH_2, the extra H going into the octahedral holes.

TABLE III

STRUCTURES OF LANTHANIDE HYDRIDES AND FLUORIDES

	La, Ce, Pr, Nd	Sm–Lu, Y, Sc[a]
Hydrides:	fcc MH_2–MH_3	fcc MH_2 miscibility gap trigonal MH_3
Fluorides: Low Temp	trigonal MF_3	Orthorhombic MF_3
Fluorides: High Temp	trigonal MF_3	Trigonal MF_3

[a] ScH_3 has not been prepared.

The hydrides of the heavier, smaller lanthanides form fcc nonstoichiometric MH_2 phases which are separated by a miscibility gap from the trigonal nonstoichiometric MH_3 phases. The alkaline earth nature of Eu (II) and Yb (II) hydrides has been discussed. EuH_3 has not been prepared; a $YbH_{2.5}$ phase, fcc, has been prepared at high pressure (Table II, Ref. *b*).

Catalano et al. (*18*) have recently reported behavior in the SmF_2–SmF_3 and EuF_2–EuF_3 systems analogous to that in the larger lanthanide MH_2–MH_3 systems. A face-centered cubic phase with interstitial F^- exists from MF_2 to $MF_{2.25}$, a phase of unresolved structure from $MF_{2.25}$ to $MF_{2.45}$, and two phases from $MF_{2.45}$ to virtually stoichiometric MF_3. These authors report but do not describe similar behavior for Yb and possibly Tm. This behavior is strongly suggestive of Warf's high-pressure Yb–H phases (Table II, Ref. *b*).

The trifluorides of La, Ce, Pr, and Nd were shown by Mansmann (*19*) and by Zalkin, Templeton, and Hopkins (*20*) to have a trigonal structure, space group $P\bar{3}\,c1$, rather than the previously proposed hexagonal Tysonite structure. Mansmann and Wallace (*19*) showed by neutron diffraction that holmium trideuteride has this same structure, and hence by implication all of the other trihydrides of the second half of the series. It may be described as a hexagonal close-packed metal lattice with the H^- or F^- ions in positions slightly displaced from the tetrahedral and octahedral interstices.

Azarkh and Gavrilov (*21*) report an orthorhombic structure for erbium trihydride.

The trifluorides of the heavier lanthanides have an orthorhombic *pnma* structure (*22*) at room temperature. The lattice constant ratios for this structure are quite different from those of Azarkh and Gavrilov for ErH_3.

These heavy lanthanide fluorides undergo high temperature phase transformations. For samarium through holmium, the high temperature form is the trigonal LaF_3 structure. For Er, Tm, Yb, Lu, and Y, the high temperature form is of a hexagonal type other than LaF_3, but not identifiable because of great instability of the phases at low temperatures (*23*).

The lattice constants for these compounds are shown in Table IV.

The lanthanide contraction is evident in both series. Each hydride lattice constant is smaller than that of the corresponding fluoride by 6–9 %. If both MH_2 and MH_3 phases (except YbH_2 and EuH_2) contain core M^{+++} ions, and $r_{H^-} = 1.27$ Å while $r_{F^-} = 1.36$ Å, this difference is largely accounted for.

For the heavier trifluorides, the stable form is orthorhombic; for the trihydrides, the trigonal. The trihydride phase is nonstoichiometric, and the trigonal structure is probably stabilized by the vacancies. The increasing effect of polarization with the lanthanide contraction possibly accounts for the shift to the orthorhombic trifluoride phase for the heavier lanthanides.

Stabilization by vacancies is also the probable reason why the earlier lanthanide trihydrides are face-centered cubic. Bismuth trifluoride has the LaH_3 structure, but admixture of a few percent of Bi_2O_3 shifts the structure over to the LaF_3 type (*24*). It is not impossible that, at compositions approaching MH_3 more closely than has yet been accomplished, there will be a shift to the LaF_3 structure for these hydrides also.

Actinides

The actinide trifluorides all have the LaF_3 structure (*25*). ThF_3 is not known. The actinide tetrafluorides of Th, U, Np, Pu, Am, and Cm (*25*, *26*), and also of Bk (*27*), have the monoclinic UF_4 structure (*28*). The unit cell description in (*26*) differs from that in Refs. (*25*, *27*, and *28*).

TABLE IV

LANTHANIDE TRIFLUORIDES AND TRIHYDRIDES: TRIGONAL LATTICE CONSTANTS, Å

M	MH_3		MF_3[a]		
	a_0	c_0	a_0	c_0	
La	fcc		7.190	7.367[a, b]	
Ce	fcc		7.112	7.279	
Pr	fcc		7.075	7.238	
Nd	fcc		7.030	7.200	
Sm	6.550	6.779	7.07	7.24	>555°
Eu	Nonexistent		7.04	7.26	>700°
Gd	6.47	6.71	7.06	7.20	>900°
Tb	6.408	6.658	7.03	7.10	>950°
Dy	6.358	6.615	7.01	7.05	>1030°
Ho	6.308	6.560	7.01	7.08	>1070°
Er	6.272	6.526	6.97	8.27	>1075°
Tm	6.233	6.489	7.03	8.35	>1030°
Yb	$YbH_{2.5}$ fcc high P		6.99	8.32	>985°
Lu	6.163	6.443	6.96	8.30	>945°
Y	6.360	6.659	7.13	8.45	>1052°

[a] R. E. THOMA AND G. D. BRUNTON, Ref. 23.

[b] M. MANSMANN, Ref. 19.

TABLE V

STRUCTURES OF THE ACTINIDE HYDRIDES

	MH_2	MH_3	MH_4
Ac	fcc	Not rep	—
Th	fc tet	—	Th_4H_{15} bcc
Pa	—	UH_3 cubic	—
U	—	UH_3 cubic	—
Np[a]	fcc	LaF_3	
Pu	fcc	LaF_3	
Am[b]	fcc	LaF_3	

[a] R. N. R. MULFORD AND T. A. WIEWANDT, *J. Phys. Chem.* **69**, 1641 (1965).

[b] W. M. OLSON AND R. N. R. MULFORD, *J. Phys. Chem.* **70**, 2934 (1966).

The actinide hydrides follow the pattern shown in Table V. As in the chemistry of these elements in general, the influence of the 6*d* electron state predominates for Th, Pa, and U, while for Np, Pu, and Am the dominance of the 5*f* shell produces behavior analogous to that of the lanthanides.

The UH_3 structure seems to be found only for U and Pa. The stability range of the fcc phases in the Np, Pu, and Am systems extends to a hydrogen to metal ratio of about 2.7, while for Gd through Lu the cubic phase limits are between 2.1 and 2.4.

The comparative lattice constants of the LaF_3-trigonal phases of the trifluorides and trihydrides are shown in Table VI, recalculated for the trigonal unit cell.

Although the data are relatively scarce, the contraction with increasing atomic number and the contraction on going from fluoride to hydride are as in the lanthanides.

The exceptional behavior of thorium is probably due to the special stability of the +4 oxidation state. Nonstoichiometric ThH_2 is body-centered tetragonal (*29*, *30*), which is suggestive of TiH_2, ZrH_2, and HfH_2. The higher hydride of thorium, Th_4H_{15}, has a complex structure with a body-centered cubic metal lattice (*31*), which apparently is more stable than a hypothetical nonstoichiometric ThH_4 with the UF_4 structure. A full knowledge of the hydrogen positions might elucidate any relation between the two structures.

TABLE VI

LaF_3-TRIGONAL LATTICE CONSTANTS, ACTINIDE COMPOUNDS, Å

	MH_3		MF_3[a]	
	a_0	c_0	a_0	c_0
U	Cubic		7.167	7.333
Np	6.531	6.713[b]	7.115	7.273
Pu	6.55	6.76[c]	7.079	7.240
Am	—		7.054	7.231

[a] W. H. ZACHARIASEN, Ref. (*25*).

[b] R. N. R. MULFORD AND T. A. WIEWANDT, Table V, Ref. *b*.

[c] R. N. R. MULFORD AND G. E. STURDY, *J. Amer. Chem. Soc.* **78**, 3897 (1956).

Aluminum and Copper

Although the bonding in cuprous hydride, CuH, seems to be covalent and that in aluminum hydride, AlH_3, is of the polymeric Al–H–Al bridge type, the comparisons are close here also, as shown in Table VII.

The more stable or α forms of the aluminum compounds have the same structure and six-coordination despite the differences in bonding. The β form of AlF_3, stable above 460°, is a pseudo-perovskite with half of the cation sites vacant.

Appel and Frankel (*31*) prepared a so-called aluminum deuteride by bombardment of Al metal with deuterons. This material gave a hexagonal diffraction pattern with $a_0 = 2.90$ Å and $c_0 = 4.55$ Å. Since the entire sample was only about 4.5% deuterated, and the molar volume corresponding to these constants is very close to that of Al metal, it is not certain that a true deuteride phase was formed.

TABLE VII

COPPER AND ALUMINUM FLUORIDES AND HYDRIDES: STRUCTURES; LATTICE CONSTANTS, Å

Compound	Structure	a_0	c_0
$AlH_3\alpha$	Trigonal[a]	4.449	11.804
$AlF_3\alpha$	Trigonal[b]	4.914	12.43
$AlF_3\beta$	Cubic[c]	3.58	
CuH[d]	Hexagonal ZnO	2.893	4.614
CuF[e]	Cubic ZnS	4.255	

[a] J. W. TURLEY AND H. W. RIAN, *Inorg. Chem.* **8**, 18 (1969).

[b] R. G. WYCKOFF, Ref. 15.

[c] R. ROY, *J. Amer. Ceram. Soc.* **37**, 581 (1954).

[d] J. A. GOEDKOOP AND A. F. ANDRESEN, *Acta Crystallogr.* **8**, 118 (1955).

[e] F. EBERT AND H. WOITINEK, *Z. Anorg. Allg. Chem.* **210**, 269 (1933).

The structure of cuprous hydride is the same as that of the high temperature forms of cuprous chloride and iodide, the hexagonal zincite structure. The structure of cuprous fluoride, and also that of the other cuprous halides, is reported as cubic Wurtzite. Wyckoff (*15*) points out that the energies of the two four-coordinated structures are not very different. A hypothetical Wurtzite form of CuH of the same molar volume as the normal hexagonal form would have a lattice constant of about 4.05 Å. Hence, in all cases the lattice constants of the hydrides are 5–10% below those of the fluorides, as for the lanthanides and actinides.

Sharpe (*33*) questions the evidence for the existence of cuprous fluoride at room temperature, but the similarity between cuprous hydride and the other three cuprous halides remains.

Transition Metals

The structures of the known hydrides of the transition metals from Groups IV A through VIII A are given in Table VIII, along with those of the difluorides.

The hydrides, especially in Groups V–VIII, are strongly nonstoichiometric as well as decidedly metallic in character. In most of the systems there are phase transformation phenomena, and some of the phases are distorted from the cubic form. The dihydrides of V, Nb, and Cr are stable only at high pressures. The low oxidation states of the metals are stabilized by the delocalization energy of the conduction electrons as well as by the nonstoichiometry, relative to, say, a covalent or saline TiH_4.

TABEL VIII

TRANSITION METAL HYDRIDES AND FLUORIDES

TiH_2	VH	CrH				NiH
fcc	bc	hex				fc
	VH_2	CrH_2				
	fcc	fcc				
ZrH_2	NbH					PdH
fc	bc					fcc
	NbH_2					
	fcc					
HfH_2	TaH					
fc	bc					
		CrF_2	MnF_2	FeF_2	CoF_2	NiF_2
		(rut)	rut	rut	rut	rut
						PdF_2
						rut

fc = face centered, bc = body centered, fcc = face-centered cubic, hex = hexagonal, rut = rutile, (rut) = distorted rutile,

The difluorides of these metals all have the normal or distorted rutile structure, resulting from the small cation size relative to the fluoride ion.

The known dihydride phases are all normal or distorted fluorite. The cation to anion radius ratios of the fluorides are all within the range expected for the rutile structure, less than 0.732 (*8*). However, for all of the dihydrides the radius ratios are far less than 0.732, even if the radii of the +2 cations were to be used rather than those of the highest oxidation state. With the exception of CrH_2, the dihydrides follow the Libowitz and Gibb additivity principle (*12*) (*34*).

The dioxides of the metals in Table VIII are all of the rutile type or rutile-based, with the exception of fluorite-based ZrO_2 and HfO_2. The dioxides of the lanthanides and actinides, with larger cations, have the fluorite structure (*15*). Thus the dioxides, with O^{--} radius 1.40 Å (*8*), follow the same pattern as the difluorides in the effect of radius ratio on choice of structure.

The results for hydride–fluoride comparisons beyond the alkali and alkaline earth metals may be summarized in terms of the preference of a hydride for a more symmetrical structure, often of higher coordination number, than the corresponding fluoride, chiefly resulting from the nonstoichiometry. The cubic phases in the Zr–H and Hf–H systems, for example, appear when hydrogen is removed from the nonstoichiometric tetragonal ZrH_2 and HfH_2. The shielding of polarization effects by the conduction electrons must also play a role, because for Ca, Sr, Ba, Yb, and Eu the hydride structure is less symmetrical than the fluoride.

Ternary Compounds: Introduction

It might be expected in general that a ternary hydride would exist, of a formula and structure corresponding to a given ternary fluoride, in those cases where both binary hydride–fluoride pairs had similar compositions and structures. In some borderline cases the energetics of formation of the ternary compound from the two binaries might differ enough between the corresponding hydride and fluoride to modify the correlation. For the decidedly saline systems containing the alkali and alkaline earths only, the correspondence would be closest. For systems containing lanthanides and actinides, the correspondence would be less, and for the transition and B-subgroup metals, least.

Thoma (*35*) has surveyed those fluoride systems in which one of the components is an alkali fluoride, in terms of the effect of relative cation–anion size effects on complex compound formation. All references to systems containing alkali fluorides are from this paper unless otherwise noted.

Lithium Systems

The complex compounds reported in systems of LiF and LiH with the respective fluorides and hydrides of Groups I A, II A, III A, the lanthanides, and Group IV A, are shown in Table IX.

The appropriate systems have not been investigated, but from crystallographic considerations the compounds LiH·RbH and LiH·CsH should also exist.

TABLE IX

COMPLEX LITHIUM HYDRIDES AND FLUORIDES

LiF·RbF, LiF·CsF[a]	
$LiBaF_3$	$LiBaH_3$,[f] $LiSrH_3$,[f] $LiEuH_3$[g]
Li_2BeF_4, $LiBeF_3$, $Li_3Be_2F_4$[b]	Li_2BeH_4[h]
$LiAlF_4$,[c] Li_3AlF_6	$LiAlH_4$, Li_3AlH_6,[i] $LiAl_4H_{13}$[j]
$LiScF_4$ (also Y, Gd–Lu)	LiH + LnH_{2+}: no interaction 690°[k]
3LiF·ThF_4 (Th–Bk, Ce, Pr, Tb)	
7LiF·6ThF_4 (Th, Pa, U)	
LiF·4ThF_4(Th–Bk, Ce, Pr, Tb)	
Li_2TiF_6[d]	LiH + TiH_2: no interaction 690°[l]
Li_2ZrH_6,[e] 3LiF·ZrF_6, LiF·4ZrF_4	LiH + ZrH_2 = no interaction 690°[l]

[a] J. H. BURNS AND W. R. BUSING, *Inorg. Chem.* **4**, 1510 (1965).

[b] E. THILO AND H. A. LEHMANN, *Z. Anorg. Allg. Chem.* **258**, 332 (1949).

[c] G. GARTON AND B. M. WANKLYN, *J. Inorg. Nucl. Chem.* **27**, 2461 (1965).

[d] G. J. JANZ, M. R. LORENZ, AND C. T. BROWN, *J. Amer. Chem. Soc.* **80**, 4126 (1958).

[e] R. HOPPE AND W. DÄHNE, *Naturwissenschaften* **47**, 397 (1960).

[f] C. E. MESSER, J. C. EASTMAN, R. G. MERS, AND A. J. MAELAND, *Inorg. Chem.* **3**, 776 (1964).

[g] C. E. MESSER AND K. HARDCASTLE, *Inorg. Chem.* **3**, 1327 (1964).

[h] N. A. BELL AND G. E. COATES, *J. Chem. Soc.* **A1968**, 628.

[i] R. EHRLICH, A. R. YOUNG II, G. RICE, J. DVORAK, P. SHAPIRO, AND H. F. SMITH, *J. Amer. Chem. Soc.* **88**, 858 (1966).

[j] J. BOUSQUET, J. J. CHOURY, AND P. CLAUDY, *Bull. Soc. Chim. France*, 3852 (1967).

[k] C. E. MESSER AND I. S. LEVY, *Inorg. Chem.* **4**, 543 (1965).

[l] C. E. MESSER, J. MELLOR, J. A. KROL, AND I. S. LEVY, *J. Chem. Eng. Data* **6**, 328 (1961).

The known alkali-alkaline earth ternary hydrides are cubic, of the inverse perovskite structure. The lattice constants and effective hydride ion radii along the M^{++}–X^- line are given in Table X.

The barium addition compounds have radius ratios within the limits of the Goldschmidt tolerance factor for the cubic perovskite structure (0.90–1.00), and the metal to nonmetal distances are the same as in LiF or LiH. However, the metal–hydrogen distances are considerably shortened in the strontium and europium compounds, and the Goldschmidt tolerance factors are reduced into the range to be expected for a distorted perovskite. $LiBaH_3$ only has been positively demonstrated to be cubic by neutron diffraction (*36*).

The compound $LiBaF_3$ exists as an incongruently melting compound at high temperatures (*37*). The system LiF–SrF_2 seems to show only simple eutectic behavior at high temperatures (*38*). Roy (Table VII, Ref. *c*) attempted without success to prepare $LiSrF_3$, but it might exist at low temperatures. $LiBaH_3$ is still solid at 800°; $LiSrH_3$ melts congruently, or nearly so, at 745°C (Table IX, Ref. *f*). These perovskite hydrides are definitely more stable than the fluorides. The polarizability of the hydride ion enables it to adapt to less favorable radius ratio requirements to form compounds which the more rigid fluoride ion cannot form.

For the lanthanides, compounds of the type $LiMF_4$ exist for the smaller +3 ions Sc Y, and Gd through Lu, with the Scheelite tetragonal structure (*39*). Messer and Levy (Table IX, Ref. *k*) showed that lithium hydride at its melting point of 691° was unable to dissolve significant amounts of any of several lanthanide hydrides. At this temperature,

TABLE X

LITHIUM INVERSE PEROVSKITES

		d_{Li-X}		
	a_0 Å	$LiMX_3$	LiX	$t_{Goldsch}$
$LiBaF_3$	3.988[a]	2.99	2.01[c]	0.92
$LiBaH_3$	4.023[b]	2.01	2.04	0.92
$LiSrH_3$	3.833[b]	1.92	2.04	0.85
$LiEuH_3$	3.796[b]	1.90	2.04	0.86

[a] W. L. W. LUDEKENS AND A. J. E. WELCH, *Acta Crystallogr.* **5**, 841 (1952).

[b] Table IX, Refs. *f*, *g*.

[c] Table I.

however, the lanthanide hydrides are highly nonstoichiometric, varying in composition from $MH_{2.0}$ to $MH_{2.5}$. It is possible that at lower temperatures and higher hydrogen contents the $LiMH_4$ compounds might form, possibly in LiCl–KCl eutectic.

LiF forms only simple eutectics with UF_3 and and PuF_3 (*40*), so that it is unfavorable from the purely crystallographic viewpoint that any compounds of LiH with the actinide trihydrides might be found.

LiF forms several series of ternary fluorides with the tetrafluorides of the actinides (and also of certain lanthanides), the most important of which are shown in Table IX. For all of the actinides except thorium, MH_3 is the limiting stoichiometric composition, and these phases are highly nonstoichiometric above 300–400°. Hence, it is unlikely that the hydride analog of any of these fluorides would exist. However, the stability of Th_4H_{15}, the only solid approaching a "tetrahydride," is such that the corresponding thorium ternary compounds might exist at lower temperatures.

The addition of TiH_2 and ZrH_2 did not significantly lower the mp of LiH (Table IX, Ref. *l*), even though here the M/H ratio for Ti and Zr at the experimental temperature varied only from 1.75 to 1.90. Interaction was not tested at lower temperatures. In the LiF–TiF_4 system, only the octahedral complex-type Li_2TiF_6 was found. For the LiF–ZrF_4 system, in addition to this complex, others of the type found with thorium are also found (see Table IX).

Li_2BeH_4 and Li_2BeF_4 are both known, but the structure has been deduced for the latter only. The close structural analogies for the aluminum compounds are separately discussed.

Graefe and Robinson (*41*) and Magee and coworkers (*42*) have shown that LiH is able to form adducts with Rh, In, Pd, and Pt, and possibly with Ag and Cd. For Rh, a series ranging in composition from Li_4RhH_4 to Li_4RhH_5 has been demonstrated; Li_3InH_6, Li_4PdH_4, and Li_5PtH_3 have been postulated from hydrogen losses on heating LiH plus metal. These adducts are metallic in nature, and the type of bonding suggested is possible only in this part of the periodic table.

For lithium fluoride–metal fluoride systems in this part of the periodic table, Li_2MF_6 octahedral complexes are most characteristic, as shown for Pd and Pt (*43*).

The intermetallic compounds of Li, and also of other alkali and alkaline earth metals, with the palladium metals, the platinum metals, and the B-subgroup metals are very stable. It is possible to decompose most saline hydrides quantitatively, for example, by fusion in tin at 600–700°C. This factor militates against ternary hydrides in this part of the periodic table, the exceptions being of a type where the hydrogen can fit into the metallic bonding of an intermetallic compound.

Systems with Other Alkali Metals

Attempts to synthesize ternary hydrides including alkali metals other than lithium would be rendered difficult by the relative instability of the hydrides, the dissociation pressures over the two-phase metal–hydride systems reaching 1 atm at 400–450° (*44*). The number of such compounds reported, other than Na_2BeH_4 (Table IX, Ref. *h*) and the aluminohydrides, is small, yet the stabilities of the Na and K compounds relative to the Li compounds in the Be and Al series is sufficient to indicate that other complexes might be found.

The normal perovskite compounds of the $KMgF_3$ type should have hydride analogs capable of synthesis under conditions suitable for the synthesis of the binary alkali hydride. These fluoride complexes are given in Table XI.

The polarizability of the hydride ion could again, as in the case of the lithium inverse perovskites, enable it to form other compounds of the series beyond those listed.

Thoma (*35*) also reports ternary compounds of the type $2MF \cdot M'F_2$, but the instability of the alkali hydride makes it less likely that these compounds of higher alkali content would form. However, the recently reported orthorhombic $Cs_4Mg_5F_{10}$ does show the existence of structures other than the perovskites in these systems (*45*).

For systems of the alkali fluorides with the lanthanide and actinide trifluorides, Thoma predicts: for Na, $NaMF_4$ for all except Th; KMF_4 for La–Sm and K_3MF_6 for Tb–Lu and the actinides; Rb_3MF_6 and Cs_3MF_6 for most lanthanides and actinides. The $NaMH_4$ and KMH_4 compounds are possible at low temperatures; the MH_6 complexes

TABLE XI

FLUORIDE PEROVSKITE COMPOUNDS[a]

Cubic = $CsCaF_3$, $RbCaF_3$
Tetragonal = $CsMgF_3$, $NaMgF_3$
Monoclinic = $KCaF_3$, $KMgF_3$, $RbMgF_3$

[a] Ref. *a*, Table X.

may be less likely because of the high alkali hydride content. Of the possible ternary hydrides with metal (IV), only the thorium compounds would be likely.

The unusual complexes K_2ReH_9 (*46*, *47*) and K_2TcH_9 (*48*) have been investigated carefully. The nine hydrogens are equidistant from the Re at the corners and in the directions of the face centers of a triangular prism. The compounds are white, and the rhenium compound is only slowly reactive to water. The structures are hexagonal, and the same for both.

The closest corresponding fluoride complex seems to be K_2ReF_8, orthorhombic with no assigned atomic positions (*49*). Since the hydride complex seems quite ionic, it would not seem impossible to make K_2ReF_9 by further fluorination.

Alkali Aluminohydrides and Aluminofluorides

The alkali metals all form with aluminum ternary hydrides of the types $MAlX_4$ and M_3AlX_6, of considerable stability. The compounds containing the higher alkali metals are very little less stable than those containing lithium, despite the considerably lower stability of NaH to CsH as compared with LiH.

The structures of the compounds containing lithium, sodium, and potassium are given in Table XII. In the $MAlX_4$ series the hydrides do not resemble the fluorides in the external crystal structures. In the M_3AlX_6 series the structures are very similar for the sodium and potassium compounds.

Li_3AlF_6 undergoes several crystalline transformations on warming (*50*). Na_3AlF_6 and K_3AlF_6 go over to cubic forms at high temperatures. The thermal instability of the aluminohydrides might cause them to decompose at temperatures below any possible crystalline transition.

The remarkable stability of the aluminohydrides may result from the covalent nature of the aluminum–hydrogen bond, or possibly from greatly reduced nonstoichiometry in M_3AlH_6 as compared with MH. The high stability of the sodium and potassium compounds increases the likelihood of the existence of other ternary hydrides containing the heavier alkalis.

TABLE XII

ALUMINOFLUORIDES AND ALUMINOHYDRIDES: STRUCTURES AND LATTICE CONSTANTS, Å

	a_0	b_0	c_0	β
	$MAlX_4$			
$LiAlH_4$[a] Monoclinic	4.845	7.826	7.917	112.5°
$LiAlF_4$[b] Tetragonal	3.50		5.84	
$NaAlH_4$[c] Tetragonal	5.02		11.31	
$NaAlF_4$[b] Tetragonal	3.50		6.00	
$KAlF_4$[b] Tetragonal	3.56		6.15	
	M_3AlX_6			
Li_3AlH_6[d] Monoclinic	5.72	5.39	5.69	91°20′
Li_3AlF_6[e] Orthorhombic	8.39	11.92	7.82	
Na_3AlH_6[d] Monoclinic	5.40	5.60	7.78	90°11′
Na_3AlF_6[f] Monoclinic	5.46	5.61	7.80	90°11′
K_3AlH_6[d] Tetragonal	8.45		8.58	
K_3AlF_6[g] Tetragonal	8.40		8.48	

[a] N. Sklar and B. Post, *Inorg. Chem.* **6**, 668 (1967).

[b] G. Garton and B. M. Wanklyn, *J. Inorg. Nucl. Chem.* **27**, 2461 (1965).

[c] I. V. Seidl, *Sb. Vys. Sk. chem. technol. v Praze Odil Fak. Anorg. org. technol.* 5–9 (1958); *Chem. Abstr.* **55**, 6095g (1961).

[d] P. Chini, A. Barodel and C. Vacca, *Chim. Ind. (Milan)* **48**, 596 (1966); *Chem. Abstr.* **65**, 11746d (1966).

[e] J. L. Holm, *Acta Chem. Scand.* **20**, 1167 (1966).

[f] S. Naray-Szabo and C. W. Wolfe, *Z. Krist.* **A99**, 27 (1938).

[g] E. G. Stewart and H. P. Rooksby, *Acta Cryst.* **6**, 49 (1953); J. L. Holm, *Acta Chem. Scand.* **19**, 261 (1965).

Other Alkaline Earth Systems

The phase behavior to be expected in binary systems of alkaline earth fluorides with each other might be expected to resemble that found in systems of alkaline earth hydrides with each other, without compound formation.

A related interesting structural analogy is found regarding the congruently melting alkaline earth hydride halides, MHX, known for Ca, Sr, Ba, Cl, Br, I (*51*). These all have the tetragonal lead fluochloride PbFCl structure, which is related to fluorite.

CaFCl, SrFCl, BaFCl, and BaFI also have the PbFCl structure (*52*). The lattice constants again compare closely: $a_0 = 3.85$, $c_0 = 6.86$ for CaHCl; $a_0 = 3.89$, $c_0 = 6.83$ for CaFCl. CaFCl is known to melt incongruently (*53*). The ternary hydride halides may thus be more stable than the corresponding fluoride halides.

Extensive compound formation and solid solution formation are found in the systems of CaF_2, SrF_2, and BaF_2 with the lanthanide trifluorides. Knowledge of the extensive solid solubility of YF_3 in CaF_2 dates back to the early days of systematic chemical mineralogy (Vogt in 1914, Goldschmidt in 1926). In these, the extra F of the dissolving YF_3 goes into the octahedral interstices of the CaF_2 lattice (*54*).

The phase equilibria in these systems have been most systematically investigated by Ippolitov, Garashina, and coworkers (*55*), and are systematized in Table XIII. The structures given are for quenched samples. Despite the large number of systems, the quantitative trends in phase stability regions and miscibility gaps are such that the general results can be described in this remarkably compact qualitative way. The differences among the Ca, Sr, and Ba systems are also small.

In the fluorite phases, solubilities increase from Ca^{++} to Ba^{++}, and decrease from La^{+++} to Lu^{+++}.

TABLE XIII

ALKALINE EARTH-LANTHANIDE FLUORIDE SYSTEMS

Single-Phase Regions (from Ippolitov et al.)		
	La to Nd	
0–45% LnF_3 fcc fluorite		80–100% LnF_3 LaF_3 Tysonite
	Y (and Sm to Lu)	
0–35% LnF_3 fcc fluorite	66–72% LnF_3 $MF_2 \cdot 2LnF_3$	80–100% LnF_3 LaF_3 Tysonite

The $MF_2 \cdot 2LnF_3$ single-phase region is found only for the smaller lanthanides. It is to be noted that no orthorhombic-phase regions were found at the highest MF_3 concentrations. Roy (*54*) questioned whether the phase existing at high LnF_3 concentrations was really the Tysonite (trigonal) LaF_3 structure stabilized by the defects introduced by the dissolved CaF_2, or whether there might be a new nonstoichiometric 1:3 or 1:4 compound of hexagonal structure.

Some research of the author and his coworkers has given preliminary evidence that analogous phase behavior might be found in the calcium–lanthanum–hydrogen system. From X-ray diffraction studies (*56*) on quenched and annealed samples, the amounts of face-centered cubic phase present were well in excess of the amounts expected in mechanical mixtures, and the lattice constants were also different. Corresponding calcium–yttrium–hydrogen mixtures gave the diffraction patterns to be expected of mechanical mixtures.

A calcium–lanthaum–hydrogen mixture of metal mole ratio 1 : 1 was found to show hydrogen dissociation pressure behavior at 400° similar to that shown by the La–H system at corresponding hydrogen contents at much higher temperatures (*57*). Such high dissociation pressures indicate a chemical potential of hydrogen in this phase higher than in a mechanical mixture of CaH_2 and LaH_x of the same composition. A stable ternary phase could then exist only if there were a strong Ca–La attractive interaction to compensate.

The alkaline earth fluorides form with the actinide tetrafluorides compounds of the type $M^{+2}M^{+4}F_6$, with the LaF_3 structure (*58*). However, $CaUF_6$ is also reported as having the Na_3As structure (*59*). The existence of this type of compound in the hydride case seems possible only with thorium, as previously discussed for the alkali metals.

A series of ternary metallic compounds, of which Sr_2IrH_4 is an example, have been investigated (*60*). The Sr and Ir atoms form a fluorite lattice. The bonding is similar to that in the Li–Rh–H phases. A fluoride analog is unlikely because of the metallic nature of the bonding.

The solid–liquid phase diagram of the system CaF_2–AlF_3 was reported to show simple eutectic behavior only (*53*). However, more recent work indicated the presence of $CaAlF_5$, melting incongruently at 740° (*61*). Crystallographic studies on quenched samples further indicated α-$CaAlF_5$ at room temperature and β-$CaAlF_5$ above 840°, both orthorhombic, and, in the SrF_2–AlF_3 system, tetragonal $SrAlF_5$ and Sr_2AlF_7 (*62*). A corresponding magnesium compound $MgAlF_5$ has been reported as a hydrate only (*63*). In the hydride series, the structures of the aluminohydrides $Mg(AlH_4)_2$ and $Ca(AlH_4)_2$ have not yet been reported.

Summary of Ternary Phases

When only metals of the alkali, alkaline earth, lanthanide, and actinide series, and aluminum, are involved, ternary hydrides analogous to known ternary fluorides are likely to form. When lanthanide and actinide metals are involved, the large degree of nonstoichiometry may stabilize a different structure in the hydride system. For the true transition metals, any hydride phases are apt to be strongly metallic and the metals therefore in a low oxidation state relative to the normal, so that any ternary phases are different in structure from those expected in the fluoride systems.

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