

CONTRIBUTION FROM REACTOR CHEMISTRY DIVISION, OAK RIDGE
NATIONAL LABORATORY, OAK RIDGE, TENNESSEE¹

Cation Size Effects in Complex Fluoride Compound Formation

By R. E. THOMA

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The influence of cation sizes on the formation and character of complex compounds in binary systems of alkali fluorides with fluorides of metals in groups I-IV is discussed. Cation radius ratio limits are established prescribing binary combinations of these fluorides which can form systems with no intermediate compounds, with few or many intermediate compounds, or with solid solutions. Principal emphasis is given to systems of rare earth and actinide fluorides with the alkali fluorides. Stoichiometry and properties of complex fluoride compounds follow reproducible and systematic patterns which can be correlated with relative sizes of cations involved. From these patterns predictions can be made regarding the characteristic properties of nearly 200 complex fluoride compounds, not yet observed, between the alkali fluorides and the tri- and tetrafluorides of the rare earth and actinide elements.

Introduction

From a summary of the properties and phase behavior of complex compounds of binary fluoride systems, quantitative relationships may be derived to show that the number and type of complex fluoride compounds formed are functions of the relative cation sizes. For example in the binary systems alkali metal fluoride (MF)-metal fluoride (M^*F , M^*F_2 , M^*F_3 , M^*F_4) the properties of the system can be related to the value of the ratio of cation sizes, M^+/M^{*+n} . No previous discussion of relationships among the fluoride systems has been reported, though an increase in the number of compounds formed in binary systems with increasing difference in the cation sizes has been reported.^{2,3} The fluoride systems are distinguished from other halide systems by the much greater quality and detail of available information. Furthermore, the effects attributable to relative sizes are much more readily observed because of the small size of the fluoride ion. In a series of related systems of metal fluorides in which the cations have the same electronic outer shell, the only variations in effects are due to the sizes of the cations, since the fluoride ion is constant. But size effects as a variation, *e.g.*, as described by Goldschmidt⁴ for the perovskite structure tolerance factor

$$t = \frac{R_a + R_x}{2(R_b + R_x)}$$

where t = tolerance factor, R_a = ionic radius of larger cation, R_b = ionic radius of smaller cation, and R_x = ionic radius of anion, also involve the anions. The relative variation is greatest for the smallest sizes of anions, hence greatest for the fluorides. Evidence of the effects of variations in relative cation size, with special emphasis on systems containing alkali fluorides with the tri- and tetrafluorides of the rare earth and actinide elements, will be discussed in the following sections. The regular occurrence of certain complex compounds within sharply defined limits of relative cation size and the known structural relationships among the rare earth and actinide fluorides make it possible to predict some of the characteristics of many binary systems in reference to the numbers and properties of intermediate compounds formed in systems which have not been studied. The occurrence of compounds, or of complex ions discussed below does not imply the persistence of these substances in the molten liquid state.

Group Relationships among MF-MF, MF-MF₂, MF-MF₃, and MF-MF₄ Systems

Alkali Fluorides Only.—Binary phase diagrams of the alkali fluorides show that pairs of these substances form simple eutectic systems, solid solutions, and complex compounds. Several of the phase diagrams have not been investigated. Alkali fluorides form solid solutions in cases where the cation radii differ by less than 15%, the per-

(1) Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

(2) (a) S. D. Gromakov, *Zhur. Fiz. Khim.*, **24**, 641 (1950); (b) O. Schmitz-DuMont and G. Bergerhoff, *Z. anorg. Chem.*, **283**, 314 (1956).

(3) A. Reisman and F. Holtzberg, *J. Am. Chem. Soc.*, **80**, 6503 (1958).

(4) V. M. Goldschmidt, T. Barth, G. Lunde, and W. Zachariasen *Skrifter Norske Videnskaps-Akad. Oslo. I. Mat.-Naturv. Kl.*, No. 2 (1926).

missible limit described by Goldschmidt,⁵ and eutectic systems where the cation size differences are greater than 15%.^{6,7} When the larger cation radius is more than twice that of the smaller cation, intermediate compounds are formed. Thus, the system KF-RbF⁸ is observed to consist of a solid solution and the system RbF-CsF is expected to display miscibility; phase diagrams of the systems NaF-CsF and KF-CsF, not yet described in the literature, should display simple eutectic formation between the component pairs. The compounds LiF·RbF and LiF·CsF have been observed,^{7,9} though no structural data have been published.

Alkali Fluorides-Metal(II) Fluorides.—Of the fragmentary data reported concerning crystal symmetry relationships of intermediate compounds formed between alkali fluorides and metal(II) fluorides, a few examples indicate that there is wide variety within the series with respect to the existence of complex ions in the solid state. Evidence is reported for the existence in the solid state of the ions BeF_3^- and BeF_4^{2-} ,^{10,11} as well as evidence that no complex ions occur in the compounds NaF·MgF₂ and KF·MgF₂.^{12,13} It is not evident that the variation in compound formation within the series demonstrates differences in the stability of complex ions in the solid state. Table I lists the observed and predicted equilibrium solid state reaction products formed from the alkali fluorides and some metal(II) fluorides. A general trend is indicated in which MF-MF₂ main-group systems do not contain intermediate compounds for cation radius below 1.30, while for the MF-MF₂ sub-group systems, compound formation can occur with M^+/M^{++} radius ratios as low as 1.12, and as M^+/M^{++} increases the number of compounds formed in the systems increases. As in the binary systems of the alkali fluorides, a cation radius ratio of about one promotes formation of solid solutions, even though the component fluorides are not isostructural.

(5) V. M. Goldschmidt, "Geochemistry," Clarendon Press, Oxford, 1954, p. 85.

(6) A. G. Bergman and E. P. Dergunov, *Compt. rend. acad. sci. U.R.S.S.*, **31**, 753 (1941).

(7) C. J. Barton, *et al.*, "Phase Diagrams of Nuclear Reactor Materials," ed. by R. E. Thoma, ORNL-2548, 1959, pp. 16-17.

(8) Reference 7, p. 20.

(9) Reference 7, p. 17.

(10) H. O'Daniel and L. Tscheischwill, *Naturwiss.*, **31**, 209 (1943).

(11) R. Hultgren, *Z. Krist.*, **88**, 233 (1934).

(12) J. H. Simons, "Fluorine Chemistry, Vol. II," Academic Press, New York, N. Y., 1954, p. 5.

(13) A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, 1950, p. 89.

The apparently anomalous case of the formation of the perovskite compound, LiBaF₃, is rationalized by Ludekens and Welch¹⁴ by the assumption that the crystal occurs as an "inverted perovskite," in which the lithium ion occupies the six-coördinated position. The cation radius ratio for $\text{Li}^+/\text{Pb}^{++}$ is sufficiently close to that of $\text{Li}^+/\text{Ba}^{++}$ that the possibility of perovskite formation exists, though no apparent attempt has been made to produce crystals of the perovskite LiPbF₃. Ludekens and Welch considered that each of the compounds they observed,¹⁴ for which tolerance factors ranged from 0.8 to 1.13, were modifications of the perovskite structure. Though tolerance factors in this range can be calculated for two MF·BeF₂ compounds, there is no evidence that either of these occurs as a perovskite structure.

The existence of intermediate compounds in the systems KF-CaF₂ ($M^+/M^{++} = 1.41$) and NaF-MgF₂ ($M^+/M^{++} = 1.51$) suggested that CsF-SrF₂, RbF-SrF₂, CsF-SrF₂, and possibly CsF-BaF₂ form complex compounds. Fusion experiments were conducted at this Laboratory in which molten mixtures of CsF-BaF₂, RbF-SrF₂, CsF-CaF₂, and CsF-SrF₂ were prepared. The cooling curve data, together with the results of optical and X-ray diffraction examinations of the cooled melts, lead to the conclusion that an intermediate compound, probably of 1MF:1MF₂ mole ratio, is formed in each of the systems.

Alkali Fluorides-Metal(III) Fluorides.—The occurrence of many metal(III) fluorides with similar structures in both the rare earth and transuranic series furnishes information for developing quantitative estimates regarding metal(III) fluoride systems not yet investigated. The similarities of chemical behavior throughout each series and between the two series have been widely discussed.^{15,16} Many similar properties of members within each of these series are attributed to the similarities in cation size of members at the same oxidation state. The established chemical similarity of such a large number of ions, having minor cation radii differences, enhances the usefulness of the available data in making predictions drawn from analogies.

An examination of the available phase diagrams and crystallographic data shows that

(14) W. L. W. Ludekens and A. J. E. Welch, *Acta Cryst.*, **5**, 841 (1952).

(15) S. Fried and W. H. Zachariasen, Proc. Intern. Conf. on the Peaceful Uses of Atomic Energy, Vol. VII, United Nations, New York, 1956, P/730, pp. 235-244.

(16) G. T. Seaborg and J. J. Katz, "The Actinide Elements," National Nuclear Energy Series IV-14A, McGraw-Hill, 1954.

TABLE I
COMPOUND FORMATION AMONG ALKALI FLUORIDES-METAL(II) FLUORIDES^a

M ⁺⁺ - F ₂	LiF			NaF			KF			RbF			CsF			
	M ⁺⁺ radius (Å.)	M ⁺ / M ⁺⁺	Tol. fact.	Comp. form.	M ⁺ / M ⁺⁺	Tol. fact.	Comp. form.	M ⁺ / M ⁺⁺	Tol. fact.	Comp. form.	M ⁺ / M ⁺⁺	Tol. fact.	Comp. form.	M ⁺ / M ⁺⁺	Tol. fact.	Comp. form.
BaF ₂	1.29	0.53	0.54	LiF·BaF ₂ ^{b,c}	0.71	0.62	None ^{b,c}	1.03	0.72	None ^{b,d,e}	1.15	0.76	None ^{b,f}	1.30	0.81	CsF·BaF ₂ ^g
SrF ₂	1.10	.62	.59	None ^b	.89	.67	None ^{b,d}	1.21	.77	None ^{b,d}	1.34	.82	RbF·SrF ₂ ^b	1.52	.87	CsF·SrF ₂ ^g
CaF ₂	0.94	.73	.63	None ^{b,h}	1.04	.72	None ^{b,i}	1.41	.83	KF·CaF ₂ ^{b,i,k}	1.57	.88	RbF·CaF ₂ ^{b,l}	1.78	.94	CsF·CaF ₂
MgF ₂	.65	1.05	.72	ss ^{b,m-p}	1.51	.83	2NaF·MgF ₂ ^{b,n}	2.02	.95	2KF·MgF ₂ ^{b,q,t}	2.28	1.00	2RbF·MgF ₂ ^{b,t}	2.57	1.06	CsF·MgF ₂ ^b
BeF ₂	.30	2.26	.90	2LiF·BeF ₂ ^w	3.26	1.03	2NaF·BeF ₂ ^y	4.43	1.18	3KF·BeF ₂ ^z	4.94	1.25	3RbF·BeF ₂ ^z	5.67	1.33	3CsF·BeF ₂ ^{aa}
				LiF·BeF ₂			NaF·BeF ₂			2KF·BeF ₂			2RbF·BeF ₂			2CsF·BeF ₂
PbF ₂	1.18	0.58	.57	None	0.83	0.65	None ^{bb}	1.12	0.75	4KF·PbF ₂ ^{cc}	1.25	0.79	ss ^m +	1.42	0.85	CsF·PbF ₂ ^{cc}
HgF ₂	1.08	.63	.59	None ^{dd}	.91	.68	None ^{dd}	1.23	.78	KF·HgF ₂ ^{dd}	1.37	.83	RbF·HgF ₂ ^{dd}	1.54	.88	CsF·HgF ₂ ^{dd}
CdF ₂	0.95	.72	.62	None	1.03	.72	None ^e	1.40	.82	KF·CdF ₂ ^{ee,ff,gg}	1.56	.87	RbF·CdF ₂ ^{ff}	1.76	.93	2CsF·CdF ₂
ZnF ₂	.74	.92	.69	ss ^{b,m,hh}	1.32	.79	NaF·ZnF ₂ ^{b,hh}	1.79	.91	2KF·ZnF ₂ ^{b,ff,ii}	2.00	.96	2RbF·ZnF ₂ ^{b,ff,hh}	2.26	1.02	2CsF·ZnF ₂ ⁿⁿ
										KF·ZnF ₂			RbF·ZnF ₂			CsF·ZnF ₂
																CsF·2ZnF ₂

^a Boldface entries indicate prediction concerning uninvestigated systems. ^b W. L. W. Luddeken and A. J. E. Welch, *Acta Cryst.*, **5**, 841 (1952). ^c N. A. Bychkova and A. G. Bergman, *Zhur. Obshchei Khim.*, **26**, 647 (1956). ^d E. I. Banashek and A. G. Bergman, *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei Neorg. Khim., Akad. Nauk S.S.S.R.*, **20**, 105 (1950). ^e N. A. Pushin and A. V. Baskov, *Z. anorg. u. allgem. Chem.*, **81**, 360 (1913). ^f E. I. Banashek and A. G. Bergman, *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei Neorg. Khim., Akad. Nauk S.S.S.R.*, **20**, 120 (1950). ^g Sh. T. Talipov and V. A. Khadzev, *Zhur. Obshchei Khim.*, **20**, 774 (1950). ^h G. A. Bukhalova and A. G. Bergman, *Doklady Akad. Nauk S.S.S.R.*, **66**, 69 (1949). ⁱ P. P. Fedotieff and W. P. Iljinski, *Z. anorg. u. allgem. Chem.*, **129**, 101 (1949). ^j G. A. Bukhalova and V. T. Berezhnaya, *Zhur. Neorg. Khim.*, **5**, 456 (1960). ^k M. Ishaque, *Bull. soc. chim. France*, **127** (1952). ^l C. J. Barton, *et al.*, "Phase Diagrams of Nuclear Reactor Materials," ed. by R. E. Thoma, ORNL-2548, 1959, p. 20. ^m Solid solution formation occurs. ⁿ A. G. Bergman and E. P. Dergunov, *Compt. rend. acad. sci. U.R.S.S.*, **31**, 753 (1941). ^o A. G. Bergman and E. P. Dergunov, *ibid.*, **31**, 755 (1941). ^p W. E. Counts, R. Roy, and E. F. Osborn, *J. Am. Chem. Soc.*, **75**, 2479 (1953). ^q A. G. Bergman and S. P. Pavlenko, *Compt. rend. acad. sci. U.R.S.S.*, **30**, 818 (1941). ^r R. C. DeVries and Rustum Roy, *J. Am. Chem. Soc.*, **75**, 2479 (1953). ^s I. Naray-Szabó, *Műegyetemi Közlemények*, **No. 1**, 36 (1947). ^t H. Remy and W. Seemann, *Rec. trav. chim.*, **59**, 516 (1940). ^u C. J. Barton, *et al.*, Reference I, p. 33. ^v A. V. Nuvoelova, Yu. P. Simanov, and E. I. Yarembach, *J. Phys. Chem.* (U.S.S.R.), **26**, 1244 (1952). ^w D. M. Roy, R. Roy, and E. F. Osborn, *J. Am. Ceram. Soc.*, **37**, 300 (1953). ^x D. M. Roy, R. Roy, and E. F. Osborn, *ibid.*, **36**, 185 (1953). ^y M. P. Borzenkova, A. V. Novoselova, Yu. P. Simanov, V. I. Chernikh, and E. I. Yarembach, *Zhur. Neorg. Khim.*, **1**, 2071 (1956). ^z R. C. Grebenshikov, *Doklady Akad. Nauk S.S.S.R.*, **114**, 316 (1957). ^{aa} O. N. Breusov, A. V. Novoselova, and Yu. P. Simanov, *Doklady Akad. Nauk S.S.S.R.*, **118**, 935 (1958). ^{ab} N. A. Pushin and A. V. Baskov, *Z. anorg. u. allgem. Chem.*, **81**, 354 (1913). ^{ac} O. Schmitz-DuMont and G. Bergerhoff, *ibid.*, **283**, 314 (1956). ^{ad} J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press, New York, N. Y., 1954, p. 6. ^{ae} C. Brisi, *Ann. Chim. (Rome)*, **42**, 356 (1952). ^{af} D. S. Crockett, III, "Preparation and Properties of Some Fluorometalates," *Dissertation Abstr.*, **20**, 3501 (1960). ^{ag} R. L. Martin, R. S. Nyholm, and N. C. Stephenson, *Chem. & Ind. (London)*, **83** (1956). ^{ah} O. Schmitz-DuMont and H. Bornfeld, *Z. anorg. u. allgem. Chem.*, **287**, 120 (1956). ^{ai} C. J. Barton, *et al.*, Reference I, p. 50.

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Sc	Al	
LiF	0.64	0.66	<u>0.67</u>	0.69				0.73	<u>0.76</u>	<u>0.77</u>	<u>0.77</u>	<u>0.78</u>	<u>0.80</u>	<u>0.81</u>	<u>0.83</u>	<u>0.84</u>	<u>1.0</u>	<u>1.5</u>	
NaF	<u>0.93</u>	<u>0.95</u>	<u>0.96</u>	<u>0.99</u>	<u>1.00</u>	<u>1.02</u>	<u>1.04</u>	<u>1.05</u>	<u>1.09</u>	<u>1.11</u>	<u>1.11</u>	<u>1.12</u>	<u>1.15</u>	<u>1.16</u>	<u>1.18</u>	<u>1.21</u>	<u>1.44</u>	<u>2.18</u>	
KF	<u>1.26</u>	<u>1.29</u>	<u>1.32</u>	<u>1.34</u>	<u>1.36</u>	<u>1.38</u>	1.41	1.43	<u>1.48</u>	<u>1.51</u>	<u>1.51</u>	<u>1.53</u>	<u>1.56</u>	<u>1.58</u>	<u>1.62</u>	<u>1.64</u>	<u>1.95</u>	<u>2.86</u>	
RbF	<u>1.40</u>	<u>1.44</u>	<u>1.45</u>	<u>1.49</u>	<u>1.51</u>	<u>1.54</u>	<u>1.57</u>	<u>1.59</u>	<u>1.64</u>	<u>1.68</u>	<u>1.68</u>	<u>1.70</u>	<u>1.74</u>	<u>1.76</u>	<u>1.80</u>	<u>1.83</u>	<u>2.18</u>	<u>3.29</u>	
CsF	<u>1.57</u>	<u>1.62</u>	<u>1.64</u>	<u>1.67</u>	<u>1.70</u>	<u>1.74</u>	<u>1.77</u>	<u>1.79</u>	<u>1.86</u>	<u>1.90</u>	<u>1.90</u>	<u>1.92</u>	<u>1.96</u>	<u>1.99</u>	<u>2.04</u>	<u>2.06</u>	<u>2.46</u>	<u>3.71</u>	
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf		Es	Fm	Md	No	Lw			
LiF	<u>0.62</u>		<u>0.65</u>	0.66	<u>0.67</u>	<u>0.67</u>	0.69										0.73		
NaF	<u>0.89</u>		<u>0.93</u>	0.95	<u>0.97</u>	<u>0.97</u>	<u>0.99</u>	<u>1.00</u>	<u>1.01</u>	<u>1.02</u>		<u>1.03</u>	<u>1.04</u>	<u>1.04</u>	<u>1.05</u>	<u>1.05</u>			
KF	<u>1.21</u>		<u>1.27</u>	<u>1.29</u>	<u>1.32</u>	<u>1.32</u>	<u>1.34</u>	<u>1.36</u>	<u>1.37</u>	<u>1.38</u>		<u>1.40</u>	1.41				1.43		
RbF	<u>1.35</u>		1.41	<u>1.44</u>	<u>1.47</u>	<u>1.47</u>	<u>1.49</u>	<u>1.51</u>	<u>1.53</u>	<u>1.54</u>		<u>1.56</u>	<u>1.57</u>	<u>1.57</u>	<u>1.59</u>	<u>1.59</u>			
CsF	<u>1.52</u>		<u>1.59</u>	<u>1.62</u>	<u>1.65</u>	<u>1.65</u>	<u>1.67</u>	<u>1.70</u>	<u>1.72</u>	<u>1.74</u>		<u>1.76</u>	<u>1.77</u>	<u>1.77</u>	<u>1.79</u>	<u>1.79</u>			

NO COMPOUNDS IN SYSTEM
 AF-MF₃ COMPOUNDS
 3AF-MF₃ COMPOUNDS

UNDERLINED ENTRIES INDICATE PREDICTION CONCERNING UNINVESTIGATED SYSTEMS

Fig. 1.—Cation radius ratios of MF-MF₃ complex compounds.

binary mixtures of the alkali fluorides with the trifluorides of the rare earths and actinide elements will form: (1) simple eutectic systems without intermediate compounds where the cation radius, M^+/M^{3+} , lies below 0.67, (2) systems containing a single intermediate compound, $MF \cdot MF_3$, when M^+/M^{3+} lies between 0.77 and 1.40, (3) systems containing a congruently melting compound, $3MF \cdot MF_3$, when M^+/M^{3+} is greater than 1.43. A summary of MF-MF₃ systems¹⁷⁻³³ with respect to compound formation is shown in Fig. 1. Insufficient data are available presently

(17) E. P. Dergunov, *Doklady Akad. Nauk S.S.S.R.*, **60**, 1185 (1948).

(18) W. H. Zachariassen, *J. Am. Chem. Soc.*, **70**, 2147 (1948).

(19) Reference 7, p. 16.

(20) C. J. Barton, J. D. Redman, and R. A. Strehlow, *J. Inorg. & Nuclear Chem.*, **20**, 45 (1961).

(21) E. Rimbach and H. F. C. Kilian, *Annalen*, **368**, 101 (1909).

(22) H. Bode and E. Voss, *Z. anorg. u. allgem. Chem.*, **290**, 1 (1957).

(23) Reference 7, p. 84.

(24) Reference 7, p. 86.

(25) C. J. Barton and R. A. Strehlow, *J. Inorg. & Nuclear Chem.*, **18**, 143 (1961).

(26) R. E. Thoma, *et al.*, *J. Phys. Chem.*, **65**, 1096 (1961).

(27) F. Hund, *Z. anorg. Chem.*, **261**, 109 (1950).

(28) W. Nowacki, *Z. Krist.*, **101**, 273 (1939).

(29) A. A. Grinberg, "Einführung in die Chemie der Komplexverbindungen," Veb Verlag Technik, Berlin, 1955, p. 356.

(30) P. P. Fedotieff and K. Timofeef, *Z. anorg. u. allgem. Chem.*, **206**, 266 (1932).

(31) P. P. Fedotieff and W. P. Iljinskii, *ibid.*, **80**, 212 (1913).

(32) C. Brossset, *ibid.*, **239**, 303 (1938).

(33) Dow Chemical Co., ASTM Card 3-0622.

to fix the exact radius ratios for the transitions in system type described above. Except for the systems NaF-AlF₃, KF-AlF₃, RbF-AlF₃, and KF-ScF₃, ($M^+/M^{3+} > 1.90$ in each case) no more than one intermediate compound has been observed in any MF-MF₃ system. Further investigations of MF-MF₃ systems for which the cation radius ratio M^+/M^{3+} is large should prove to be particularly useful in extending generalizations concerning these systems to the cases where several intermediate compounds may occur.

A remarkable variation among the phase diagrams of the MF-MF₃ systems is observed which is associated with the presence or absence of the $3MF \cdot MF_3$ compound. When formed, $3MF \cdot MF_3$ compounds are associated with liquidus maxima, *i.e.*, they melt congruently. For this reason MF₃ should, in general, display lower solubility in MF if the system MF-MF₃ contains the equilibrium phase $3MF \cdot MF_3$. From correlations of complex compound occurrence as a function of cation radius ratio it becomes evident that there are predictable differences among the phase diagrams of the rare earth trifluorides with the alkali fluorides. Fission products formed during the operation of molten salt reactors using fluorides as fuels and as breeder blankets are principally rare earths. From the observations discussed

above, fission products can be expected to differ significantly in their high-temperature solubilities depending on the concentration of alkali fluoride in the fuel solution and whether they form $\text{MF}\cdot\text{MF}_3$ or $3\text{MF}\cdot\text{MF}_3$ compounds.

Alkali Fluorides-Metal(IV) Fluorides.—Many intermediate compounds are formed in the systems of the alkali fluorides with the metal(IV) fluorides. Phase equilibrium diagrams of the systems of the alkali fluorides with ZrF_4 , ThF_4 , UF_4 , and to some extent HfF_4 , are known. Each of these systems contains four to eight intermediate compounds. Limited data are available for the other tetravalent rare earth and actinide metal fluoride systems. Only a few compound types, such as $3\text{MF}\cdot\text{MF}_4$, $2\text{MF}\cdot\text{MF}_4$, $7\text{MF}\cdot 6\text{MF}_4$, and $\text{MF}\cdot\text{MF}_4$, persist with regularity in the $\text{MF}\text{--}\text{MF}_4$ systems. The variety in stoichiometry of the many other intermediate compounds formed indicates only that $\text{MF}\text{--}\text{MF}_4$ systems not yet investigated can be expected to contain other compounds in addition to some of the regular group. The tetrafluorides of the rare earth metals and the heavy metals Th, Pa, U, Np, Pu, Am, and Cm have monoclinic symmetry and are isostructural with ZrF_4 .³⁴ The range of cation radius ratios, M^+/M^{4+} , where $M^{4+} = \text{Zr}^{4+}$, Hf^{4+} , Th^{4+} , or U^{4+} , includes those of the transuranic metal 4+ cations as well as those of Ce^{4+} and Tb^{4+} . Therefore, data from the similar binary systems of the alkali fluorides with ZrF_4 , HfF_4 , ThF_4 , and UF_4 should be useful in predicting the character of the systems of the alkali fluorides with CeF_4 , PrF_4 , NdF_4 , TbF_4 , PaF_4 , NpF_4 , PuF_4 , AmF_4 , and CmF_4 . Table II summarizes the information available with regard to the regularly occurring $\text{MF}\text{--}\text{MF}_4$ compounds and lists many of the compounds expected to be observed in future investigations.

There are few series of complex fluoride compounds which have been described as isomorphous. One such series includes the rhombohedral $7\text{MF}\cdot 6\text{MF}_4$ compounds. The compounds crystallizing with this structure, space group $R\bar{3}$, do not display polymorphism, and may be formed when M^+/M^{4+} cation radius ratios lie between 0.99 and 1.68. Reporting the results of a recent investigation of the system $\text{KF}\text{--}\text{ZrF}_4$, Novoselova, *et al.*,³⁵ indicate the occurrence of $7\text{KF}\cdot 6\text{ZrF}_4$, although they infer the stoichiometry of the sub-

solidus phase from thermal data and do not claim to have isolated rhombohedral crystals of the compound. Systems in which rhombohedral $7\text{MF}\cdot 6\text{MF}_4$ compounds may occur are shown in Table II and Fig. 2. Rhombohedral $7\text{MF}\cdot 6\text{MF}_4$ compounds have not been observed for M^+/M^{4+} values lower than 0.99. In the system $\text{LiF}\text{--}\text{ZrF}_4$, no mid-composition compound occurs, though in the systems $\text{LiF}\text{--}\text{UF}_4$ and $\text{LiF}\text{--}\text{ThF}_4$, $7\text{MF}\cdot 6\text{MF}_4$ compounds having tetragonal symmetry do occur. Several rhombohedral complex fluoride structures observed earlier and reported to have the formula $\text{MF}\cdot\text{MF}_4$ ³⁶⁻³⁸ are deduced by analogy with $7\text{NaF}\cdot 6\text{ZrF}_4$ ³⁹ to be $7\text{MF}\cdot 6\text{MF}_4$.

Predictions regarding the occurrence of the complex fluorides of elements 98-103 in the tetravalent oxidation state could be made, though there is little evidence that this oxidation state is stable enough to permit chemical investigation.

Predicted Crystal Properties of Complex Fluorides.—Sufficient data have been accumulated on the fluoride binary systems to make possible some predictions regarding occurrence of many unknown complex fluoride compounds and estimates of their optical properties and lattice dimensions. For example, the lattice dimension, a_0 , measured for eleven $7\text{MF}\cdot 6\text{MF}_4$ compounds is proportional to the M^{4+} cation radius (Fig. 3). The nearly linear relationship between the rhombohedral lattice parameters, a_0 , and the radius of M^{4+} allows an estimate of this dimension for each of the remaining twenty-one $7\text{MF}\cdot 6\text{MF}_4$ compounds not yet described. On the other hand, the angle α for these crystals does not appear to be a regular function.

The present lack of optical data concerning the fluoride complex compounds of the higher atomic number elements in the rare earth and actinide series makes it impossible to predict with accuracy the optical properties of the complex fluorides formed in these series. However, linear increases in refractive index of the tetrafluorides thorium-uranium-amerium can be extrapolated and compared with those of the uranium-thorium complex fluorides to gain a rough estimate of the refractive index of other transuranic complex fluorides. Such extrapolations indicate, for example, that the refractive indexes of the com-

(36) W. H. Zachariasen, *J. Am. Chem. Soc.*, **70**, 2147 (1948).

(37) L. B. Asprey, *ibid.*, **76**, 2019 (1954).

(38) L. B. Asprey and T. K. Keenan, *J. Inorg. & Nuclear Chem.*, **16**, 260 (1961).

(39) P. A. Agron and R. D. Ellison, *J. Phys. Chem.*, **63**, 2026 (1959).

(34) R. D. Burbank and F. N. Bensey, USAEC Report K-1280, 1956.

(35) A. V. Novoselova, Yu. M. Kovenev, and Yu. P. Simanov, *Doklady Akad. Nauk. S.S.S.R.*, **139**, 892 (1961).

TABLE II
 COMPOUND FORMATION AMONG ALKALI FLUORIDE-METAL(IV) FLUORIDES^a

Alkali fluoride	Cation radius ratio	ThF ₄	PaF ₄	UF ₄	NpF ₄	CeF ₄	PrF ₄	PuF ₄	AmF ₄	CmF ₄	BkF ₄	TbF ₄	ZrF ₄	HfF ₄	
LiF	M ⁺ /M ⁴⁺	0.69	0.71	0.73	0.74	0.74	0.76	0.76	0.76	0.77	0.77	0.86	0.88	0.89	
		3:1 ^{b,c}	3:1	3:1 ^e	3:1	3:1	3:1	3:1	3:1	3:1	3:1	3:1	3:1 ^{f,g}	3:1	
		7:6	7:6	7:6 ^d											
		1:4	1:4	1:4	1:4	1:4	1:4	1:4	1:4	1:4	1:4	1:4	1:4 ^o	1:4	
NaF	M ⁺ /M ⁴⁺	0.99	1.02	1.05	1.06	1.06	1.09	1.09	1.10	1.11	1.11	1.24	1.27	1.29	
				3:1 ^{i,d}	3:1	3:1 ^j	3:1	3:1	3:1	3:1	3:1	3:1	3:1 ^{k,l}	3:1 ^{t,m}	
		2:1 ^{b,h,i}	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	
		7:6	7:6	7:6	7:6	7:6	7:6 ^{i,n}	7:6	7:6	7:6	7:6	7:6	7:6	7:6	
		1:1 ^e											1:1 ^e	1:1	
		1:2	1:2	1:2											
KF	M ⁺ /M ⁴⁺	1.34	1.38	1.43	1.44	1.44	1.48	1.48	1.49	1.51	1.51	1.68	1.73	1.75	
		3:1 ^{t,h,o,p}	3:1	3:1 ^q	3:1	3:1	3:1	3:1	3:1	3:1	3:1	3:1	3:1 ^{r,s,t,u}	3:1 ^{s,v}	
		2:1	2:1	2:1	2:1	2:1 ^j	2:1 ^j	2:1	2:1	2:1	2:1	2:1	2:1	2:1	
		7:6	7:6	7:6	7:6	7:6	7:6	7:6 ^t	7:6 ^w	7:6	7:6				
												1:1	1:1	1:1	
		1:2	1:2	1:2											
RbF	M ⁺ /M ⁴⁺	1.49	1.54	1.59	1.61	1.61	1.64	1.64	1.66	1.68	1.68	1.68	1.92	1.95	
		3:1 ^{x,y,p}	3:1	3:1 ^q	3:1	3:1	3:1	3:1	3:1	3:1	3:1	3:1	3:1 ^z	3:1	
		2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1 ^{aa}	2:1	2:1	2:1	2:1	2:1	
		7:6	7:6	7:6	7:6	7:6	7:6	7:6 ^t	7:6	7:6	7:6	7:6			
CsF	M ⁺ /M ⁴⁺	1.69	1.74	1.80	1.82	1.82	1.86	1.86	1.88	1.90	1.90	2.12	2.16	2.20	
		3:1 ^p	3:1	3:1 ^{bb}	3:1	3:1	3:1	3:1	3:1	3:1	3:1	3:1	3:1 ^{cc}	3:1	
		2:1	2:1	2:1	2:1	2:1 ^j	2:1 ^j	2:1	2:1	2:1	2:1	2:1	2:1	2:1	
		1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	
	1:6	1:6	1:6												

^a Italic entries indicate prediction concerning uninvestigated systems. ^b R. E. Thoma, *et al.*, *J. Phys. Chem.*, **63**, 1266 (1959). ^c L. A. Harris, G. D. White, and R. E. Thoma, *ibid.*, **63**, 1974 (1959). ^d C. J. Barton, *et al.*, *J. Am. Ceram. Soc.*, **41**, 63 (1958). ^e Metastable phase. ^f R. Hoppe and W. Dahne, *Naturwiss.*, **47**, 397 (1960). ^g R. E. Moore, *et al.*, "Phase Diagrams of Nuclear Reactor Materials," ed. by R. E. Thoma, ORNL-2548, 1959, p. 16. ^h V. S. Emelyanov and A. I. Evstuykhin, *J. Nuclear Energy (II)*, **5**, 108 (1957). ⁱ W. H. Zachariasen, *J. Am. Chem. Soc.*, **70**, 2147 (1948). ^j R. Hoppe, *Angew. Chem.*, **71**, 457 (1959). ^k C. J. Barton, *et al.*, *J. Phys. Chem.*, **62**, 665 (1958). ^l L. A. Harris, *Acta Cryst.*, **12**, 172 (1959). ^m R. E. Thoma, *et al.*, Reference g, p. 70. ⁿ L. P. Asprey and T. K. Keenan, *J. Inorg. & Nuclear Chem.*, **16**, 260 (1961). ^o W. J. Asker, E. R. Segnit, and A. W. Wylie, *J. Chem. Soc.*, 4470 (1952). ^p R. E. Thoma and T. S. Carlton, *J. Inorg. & Nuclear Chem.*, **17**, 88 (1961). ^q R. E. Thoma, *et al.*, *J. Am. Ceram. Soc.*, **41**, 538 (1958). ^r C. J. Barton, *et al.*, Reference g, p. 56. ^s H. Bode and G. Teufer, *Acta Cryst.*, **9**, 929 (1956). ^t G. C. Hampson and L. Pauling, *J. Am. Chem. Soc.*, **60**, 2702 (1938). ^u A. V. Novoselova, Yu. M. Kovenev, and Yu. P. Simanov, *Doklady Akad. Nauk S.S.S.R.*, **139**, 892 (1961). ^v G. Hevesy, *Chem. Revs.*, **2**, 1 (1926). ^w L. B. Asprey, *J. Am. Chem. Soc.*, **76**, 2019 (1954). ^x E. P. Dergunov and A. G. Bergman, *Doklady Akad. Nauk S.S.S.R.*, **60**, 391 (1948). ^y L. A. Harris, *Acta Cryst.*, **13**, 502 (1960). ^z R. E. Moore, *et al.*, Reference g, p. 57. ^{aa} F. H. Kruse and L. B. Asprey, *Inorg. Chem.*, **1**, 137 (1962). ^{bb} C. J. Barton, *et al.*, Reference g, p. 92. ^{cc} C. J. Barton, *et al.*, *ibid.*, p. 58.

pounds 3CsF·MF₄ (M = Np-Bk) will fall in the range 1.47-1.48, while those of 3RbF·MF₄ (M = Np-BK) will fall in the range 1.43-1.44.

Compound Occurrence in Chloride Systems.—Relationships of cation radius ratio or similar correlating factors to systematic occurrence of intermediate compounds in halide systems MX-MX₁₋₄ should become less distinct as the size of X increases. A survey of the reported data concerning intermediate compound formation in the alkali chloride-metal(II) chloride systems⁴⁰⁻⁶⁹

- (40) C. Sandonnini, *Atti reale accad. Lincei*, **22** [1], 629 (1913).
 (41) I. N. Belyaev and M. L. Sholokhovich, *Sbornik Statei Obshchei Khim., Akad. Nauk S.S.S.R.*, **1**, 141 (1953).
 (42) E. Elchardus and P. Laffitte, *Bull. soc. chim. France*, **51**, 1577 (1932).
 (43) E. I. Banashek, *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei Neorg. Khim. Akad. Nauk S.S.S.R.*, **20**, 120 (1950).
 (44) I. I. Il'yasov and A. K. Bostandzhian, *Zhur. Obshchei Khim.*, **26**, 2396 (1956).
 (45) Ya. A. Ugal, *Doklady Akad. Nauk S.S.S.R.*, **70**, 653 (1950).
 (46) I. I. Il'yasov, A. K. Bostandzhian, and A. G. Bergman, *Zhur. Neorg. Khim.*, **1**, 2549 (1956).
 (47) E. I. Banashek and A. G. Bergman, *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei Neorg. Khim., Akad. Nauk S.S.S.R.*, **25**, 252 (1954).
 (48) G. A. Bukhalova, *ibid.*, **26**, 142 (1955).

shows that this is the case. Although the effects of relative cation size are less pronounced

	Ce	Pr	Nd	Gd	Tb	Dy	Lu	Zr	Hf
LiF	0.74	0.76			0.86			0.88	0.89
NaF	1.06	1.09			1.24			1.27	1.29
KF	1.44	1.48			1.68			1.73	1.75
RbF	1.54	1.64			1.87			1.92	1.95
CsF	1.82	1.86			2.12			2.16	2.20
	Th	Pa	U	Np	Pu	Am	Cm	Bk	
LiF	0.69	0.71	0.73	0.74	0.74	0.76	0.77	0.77	
NaF	0.99	1.02	1.05	1.06	1.09	1.10	1.11	1.11	
KF	1.34	1.38	1.43	1.44	1.48	1.49	1.51	1.53	
RbF	1.49	1.54	1.59	1.61	1.64	1.66	1.68	1.68	
CsF	1.69	1.74	1.80	1.82	1.86	1.88	1.90	1.90	

0.00 7 MF·6 MF₄ COMPOUND OBSERVED
0.00 7 MF·6 MF₄ COMPOUND PREDICTED
 0.00 7 MF·6 MF₄ COMPOUND NEITHER OBSERVED NOR PREDICTED

Fig. 2.—Cation radius ratios of rhombohedral 7MF·6MF₄ complex compounds.

- (49) S. M. Aslanov and V. P. Blidin, *Zhur. Neorg. Khim.*, **4**, 748 (1959).
 (50) W. Herz and W. Paul, *Z. anorg. Chem.*, **82**, 431 (1913).
 (51) I. N. Velyaev and K. E. Mironov, *Zhur. Obshchei Khim.*, **22** 1480 (1952).
 (52) J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press Inc., New York, N. Y., 1954, p. 21.
 (53) D. S. Lesnykh, A. G. Bergman, and N. G. Bukun, *Zhur. Obshchei Khim.*, **26**, 2676 (1956).
 (54) A. G. Bergman and E. L. Bakumskaya, *ibid.*, **25**, 2412 (1955).
 (55) C. Brand, *Neues Jahrb. Mineral. Geol. u. Paläontol.*, **32**, 627 (1911).
 (56) G. Grube and W. Rudel, *Z. anorg. u. allgem. Chem.*, **133**, 375 (1924).
 (57) V. E. Plyushchev, F. V. Kovalev, and I. V. Shakhno, *Zhur. Obshchei Khim.*, **25**, 857 (1955).
 (58) M. Ishaque, *Bull. soc. chim. France*, 127 (1952).
 (59) Ya. A. Ugai, *Doklady Akad. Nauk. S.S.S.R.*, **70**, 653 (1950).
 (60) V. E. Plyushchev, L. N. Komissarova, L. V. Meshchaninova, and L. M. Akulkina, *Zhur. Neorg. Khim.*, **1**, 830 (1956).
 (61) N. N. Evseeva and A. G. Bergman, *Zhur. Obshchei Khim.*, **21**, 1767 (1951).
 (62) F. R. Duke and R. A. Fleming, *J. Electrochem. Soc.*, **104**, 253 (1957).
 (63) B. K. Markov, I. D. Panchenko, and T. G. Kostenko, *Ukrain. Khim. Zhur.*, **22**, 290 (1956).
 (64) W. Klemm and P. Weiss, *Z. anorg. u. allgem. Chem.*, **245**, 281 (1940).
 (65) A. I. Ivanov, *Sbornik Statei Obshchei Khim., Akad. Nauk S.S.S.R.*, **1**, 758 (1953).
 (66) B. F. Markov and I. D. Panchenko, *Zhur. Obshchei Khim.*, **25**, 2039 (1955).
 (67) B. F. Markov and I. D. Panchenko, *ibid.*, **25**, 2042 (1955).
 (68) E. Furby and K. L. Wilkinson, *J. Inorg. & Nuclear Chem.*, **14**, 123 (1960).
 (69) W. Klemm and P. Weiss, *Z. anorg. u. allgem. Chem.*, **245**, 279 (1940).

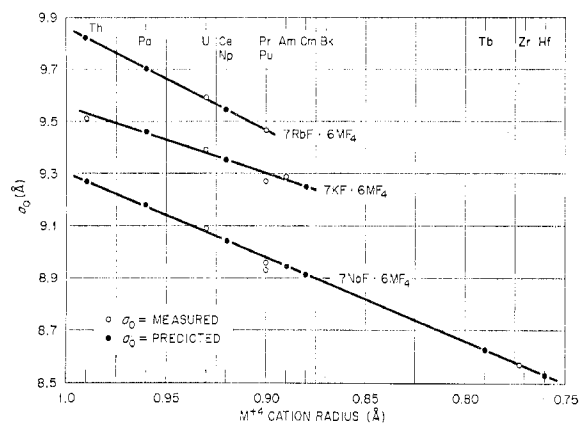


Fig. 3.—Rhombohedral unit cell dimensions (a_0) of 7MF·6MF₄ compounds.

than in the comparable fluoride systems, the trend evident in the chloride systems toward the formation of increasing numbers of intermediate compounds as M^+/M^{++} cation radius ratios increase illustrates the prevailing influence of relative cation size on compound formation.

Conclusions

It is possible to make very useful predictions regarding the nature of the alkali fluoride systems with the trifluorides and tetrafluorides of the rare earth and actinide elements from correlations of observed properties with cation radius ratios. Future investigations designed to further characterize the chemical behavior of the rare earth and actinide elements can be simplified by application of the kinds of estimates discussed above. In those cases where characterization of a chemical species will be difficult either because there is only a small amount of material available, or because, in addition, the half-life of the heavy metal limits the time available for accumulating measurements, experiments can be planned, using the data discussed here to facilitate definitive characterization in the shortest time.

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