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Equilibrium Relations and Crystal Structure of Lithium Fluorolanthanate Phases

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Equilibrium phase diagrams of the LiF–LnF_3 condensed binary systems were established. For the members of the series with low atomic number only a simple eutectic is found; for the lanthanides europium to lutetium, the single intermediate compound, $LiLnF_4$, forms in each binary system. These compounds melt incongruently to LnF_3 and liquid when $Z = 63–68$, and congruently when $Z = 69–71$. The lithium tetrafluorolanthanates are isomorphous. A single-crystal study of $LiYbF_4$ established the space group as $I4_1/a$, with lattice constants $a_0 = 5.1335$ (2) and $c_0 = 10.588$ (2) Å. The existence of the tetrafluorolanthanates, conforming closely with earlier predictions, indicates the possibility of actinide analogs. Because of similar ionic sizes and charges of the lanthanides and the heavier actinides, it was anticipated that lithium fluoride–actinide trifluoride compound formation could begin at $Z \geq 96$ (curium). However, hydrogen reduction of the known $LiF \cdot AmF_4$ and $LiF \cdot CmF_4$ compounds gave only the trifluorides and LiF.

Introduction

The abundance of complex compounds formed by the lanthanide or actinide fluorides has attracted the interest of inorganic and structural chemists. Successful predictions of compound formation can be based on simple criteria such as cation radius ratios[2] and field strength ratios.[3,4] The two series of lanthanide and actinide fluoride complexes offer unique possibilities for further considerations of size and charge effects. They afford compound sequences in which adjacent members are differentiated by small but finite increments in ion size and field strengths.

The LiF–LnF_3 series of binary systems affords a good opportunity for examination of size–charge effects. Our previous investigation of the LiF–YF_3 binary system[5] had shown the occurrence of the single intermediate compound $LiYF_4$. In contrast, earlier investigations of the LiF–LaF_3 and LiF–CeF_3 systems, respectively,[6,7] had *not* indicated the occurrence of intermediate compounds. We expanded those initial studies to include the equilibrium behavior of all LiF–LnF_3 melts. We also determined the crystal structure of the $LiLnF_4$ compounds, using single crystals of $LiYbF_4$, produced in these investigations. Some preliminary data have already been noted in previous reviews.[8,9]

Experimental Procedures

Materials.—Standard techniques for preparation and purification of molten fluorides for high-temperature investigations have been reported previously.[9-11] Both commercial and laboratory prepared[12] single-crystal LiF samples were used.

Lanthanide oxides of 99.6–99.9% purity were converted to the trifluorides with ammonium bifluoride; this ensures that the oxide contamination of the product does not exceed ~300 ppm.[13] Purity of the trifluoride product was verified by X-ray diffraction analysis and by petrographic examination.

We have found from past experience that reaction between lithium fluoride and actinide fluorides at ~400° is not a satisfactory method of achieving compound formation. However, a preferred method involves conversion of a mixture of chlorides to fluoride with elemental fluorine. Thus, samples of LiCl and $AmCl_3$ and LiCl and $CmCl_3$ were equilibrated with F_2, yielding first the tetravalent actinide compounds $LiAmF_5$ and $LiCmF_5$.[14] Overnight equilibration in hydrogen reduced the tetravalent actinide to the trivalent state.

Methods.—Several methods were used for investigation of the equilibrium phase behavior in the LiF–LnF_3 binary systems. Preponderantly, phase-transition data were obtained by thermal analysis of crystallizing melts and subsequent thermal gradient quenching (a modification of classical quenching methods) and by direct visual observation techniques.

Single crystals of $LiYbF_4$ were isolated from quenched specimens of LiF–YbF_3 mixtures. Single-crystal fragments of $LiYbF_4$ were ground in an air race; an ellipsoid 0.184 × 0.184 × 0.292 mm was selected for single-crystal X-ray diffraction analysis. The ellipsoid was mounted on a computer-operated Picker four-circle goniostat and the diffraction intensities were measured with a scintillation-counter detector using unfiltered Mo $K\alpha$ radiation ($\lambda(K\alpha_1)$ 0.70926 Å, $\lambda(K\alpha_2)$ 0.713543 Å) out to 90° 2θ by the 2θ-scan technique. An angular range of 1.3° was step-scanned in increments of 0.01° with counts of 1 sec at each step. The background was counted for 100 sec at the beginning and end of each scan. The takeoff angle was 4°. A standard reflection (408) was used to check on intensity drift every 20 reflections. One measurement of the standard reflection was assigned unit value and the others are expressed as fractions of this value. The intensity measurements obtained between two successive measurements of the standard reflection are linearly interpolated. The intensities are thus referred to a single value of the (408) intensity. Each reflection was corrected for absorption ($\mu = 351.3\ \text{cm}^{-1}$). The lattice parameters were determined from 30 high-angle (45–80° 2θ) Mo $K\alpha_1$ reflections

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TABLE I

ATOMIC PARAMETERS AND INTERATOMIC DISTANCES FOR $LiYbF_4$

Atom	x	y	z	$\beta_{11}{}^{a}x10^3$	$\beta_{22}x10^3$	$\beta_{33}x10^3$	$\beta_{12}x10$	$\beta_{13}x10^3$	$\beta_{23}x10^3$
Yb	0.0	1/4	5/8	5.45(9)^b	c	0.51(2)	0	0	0
Li	0.0	1/4	1/8	15(5)	c	4(3)	0	0	0
F	0.2166(6)	0.4161(6)	0.4564(3)	9.7(8)	8.5(7)	1.4(2)	3.2(6)	1.2(3)	1.0(3)
		4(Yb-F)	2.217(3)Å			4(Li-F)		1.894(3)Å	
		4(Yb-F)	2.270(3)			4(Li-F)		2.871(4)	
		F - F	2.558(6)			2(F - F)		2.727(2)	
		2(F - F)	2.728(3)			F - F		2.803(4)	

^{a} Coefficients in the structure factor: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^{b} The standard error (in parentheses) is equivalent to the last digit as calculated from the variance–covariance matrix. ^{c} $\beta_{22} = \beta_{11}$.

which were automatically centered[15] in a reduced-slit system at 1.2° takeoff angle. The apparatus and techniques for handling the intensely radioactive actinide samples for X-ray studies have been described in an earlier publication.[16]

Results

The Structure of $LiYbF_4$.—The compounds of the $LiLnF_4$ class are all isostructural and isomorphous with $LiYF_4$.[5] Subsequent investigations by ourselves[17] and other workers[18] have confirmed this fact. A complete determination of the $LiLnF_4$ crystal was not made, however, prior to that of $LiYbF_4$ reported here. Lithium tetrafluoroytterbate was selected for this study because of the simplicity of preparation which it afforded. The compound $LiYbF_4$ was indexed initially from single-crystal data and found to conform to the space group $I4_1/a$, confirming that the $LiLnF_4$ compounds are isostructural with scheelite, $CaWO_4$.[5]

The observed conditions for diffraction (hkl, $h + k + l = 2n$; $hk0$, $h = 2n$; and $00l$, $l = 4n$) are consistent for space group $I4_1/a$ (88). The structure was refined by iterative least squares using a modification of the Busing, Martin, and Levy (1962) computer program.[19] An extinction correction was made on F_c by the method suggested by Zachariasen ($r^* = 0.011$ (2) Å).[20] The scattering factors for the ions were taken from Cromer and Waber[21] and the values of $\Delta f' = -0.6$ and $\Delta f'' = 6.4$ electrons were used for the anomalous dispersion of Mo Kα radiation by ytterbium.[22]

The quantity minimized by the least-squares program was $\Sigma w|s|F_o| - |F_c||^2$, where w is equal to the reciprocals of the variances which were estimated by the methods of Brown and Levy.[23] Anisotropic temperature factors were calculated for all atoms in Table I. Figure 1 shows a stereoscopic pair of drawings of the structure of $LiYbF_4$.

The discrepancy factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0310$ for 503 independent reflections. The standard deviation of an observation of unit weight is $[\Sigma w(F_o - F_c)^2/(m_o - m_v)]^{1/2} = 1.978$, where m_o is the number of observations and m_v is the number of variables. The interatomic distances are also listed in Table I. Observed and calculated structure factors are listed in Table II. A partial powder pattern of $LiYbF_4$ is given in Table III.

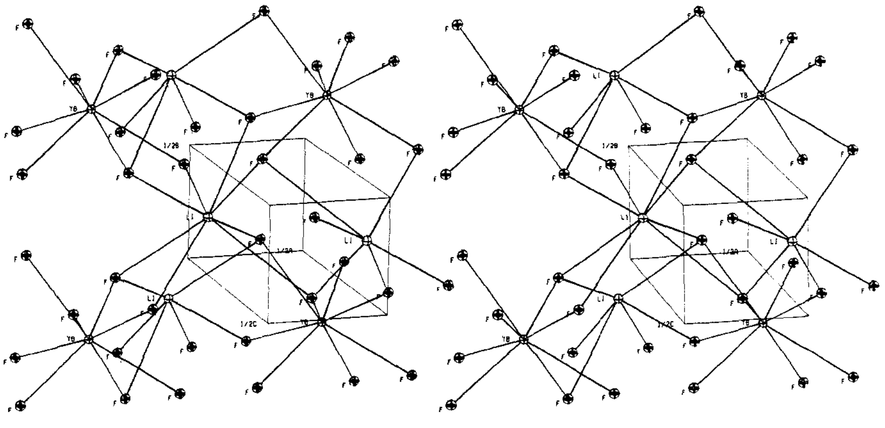

Figure 1.—Stereoscopic drawings of four nearest neighbor Li and Yb polyhedra. One-fourth unit cell outlined.

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TABLE II
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $LiYbF_4$ (×10)

L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL
0 0 L			5	839	-858	19	602	-601	16	136	-44	6	0	-17	13	439	450	11	532	-542	10	47	13	12	639	-618
4	1649	-1560	7	765	783	2 4 L			18	873	-852	8	1361	1352	4 8 L			13	503	-511	6 7 L			8 1 L		
8	1476	1424	9	628	628	0	1460	1482	20	76	-37	10	144	-154	0	758	786	5 7 L			1	405	-405	1	642	626
12	1725	-1658	11	641	-654	2	349	351	3 2 L			12	1145	-1129	2	67	-43	2	753	760	3	535	-538	3	498	491
16	1055	1000	13	551	-560	4	1452	-1481	1	1358	1379	14	93	-88	4	640	-651	4	91	-32	5	415	421	5	610	-585
20	742	-725	15	480	489	6	86	-32	3	819	-807	16	878	867	6	33	-1	6	662	-674	7	418	416	7	572	-554
1 0 L			1 7 L			8	1280	1292	5	1241	-1274	18	41	18	8	566	580	8	31	-15	9	477	-482	9	442	424
1	1352	-1380	2	1032	1053	10	227	-219	7	1134	1139	4 1 L			10	45	34	10	618	648	6 8 L			11	505	505
3	1155	1195	4	22	10	12	1039	-1032	9	733	726	1	835	827	4 9 L			5 8 L			0	544	542	13	460	-462
5	1444	1511	6	796	-807	14	123	-119	11	964	-959	3	1076	1085	1	393	406	1	386	-396	2	75	-15	8 2 L		
7	1328	-1359	8	50	8	16	858	851	13	823	-815	5	1232	-1260	3	437	435	3	430	427	4	563	-565	0	960	-927
9	1035	-1019	10	853	866	18	61	36	15	576	561	7	1160	-1172	5	382	-379	5	482	491	7 0 L			2	57	8
11	1054	1034	12	75	-1	2 5 L			17	673	674	9	913	914	5 0 L			7	467	-469	1	594	-590	4	763	725
13	919	883	14	722	-723	1	903	926	19	574	-563	11	694	679	1	1090	-1108	6 0 L			3	713	713	6	76	6
15	768	-728	1 8 L			3	892	905	3 3 L			13	615	-594	3	811	799	0	1287	1301	5	729	734	8	676	-651
17	770	-738	1	533	-528	5	839	-849	2	1406	1427	15	649	-632	5	957	970	2	158	-160	7	721	-704	10	71	-1
19	663	630	3	663	670	7	794	-807	4	45	7	17	664	656	7	876	-882	4	1130	-1122	9	648	-636	12	731	714
21	520	511	5	491	500	9	761	779	6	1569	-1613	19	585	595	9	676	-667	6	139	2	11	495	491	8 3 L		
1 1 L			7	495	-495	11	706	711	8	35	13	4 2 L			11	792	802	8	994	982	13	443	433	1	506	-492
2	1868	-1819	9	571	-581	13	607	-625	10	1164	1155	0	1597	-1613	13	729	720	10	122	111	15	469	-466	3	554	-535
4	731	-719	11	418	418	15	548	-561	12	100	11	2	115	-31	15	535	-540	12	947	-929	7 1 L			5	525	518
6	1872	1848	13	405	416	17	494	502	14	902	-893	4	1425	1434	17	570	-570	14	103	83	2	977	-961	7	513	504
8	408	-388	1 9 L			2 6 L			16	88	1	6	14	12	5 1 L			16	736	718	4	141	-124	9	502	-491
10	1532	-1485	2	688	-687	0	1125	-1162	18	841	844	8	1239	-1228	2	1437	-1444	6 1 L			6	994	980	11	437	-417
12	155	35	4	29	-23	2	203	207	3 4 L			10	91	25	4	374	128	1	901	881	8	101	-90	8 4 L		
14	1213	1159	6	653	646	4	1054	1089	1	918	-951	12	1110	1097	6	1156	1153	3	878	872	10	808	-782	0	613	590
16	177	161	8	46	-18	6	46	-9	3	1051	1098	14	102	5	8	77	75	5	862	-658	12	0	24	2	79	31
18	947	-927	1 10 L			8	945	-970	5	836	826	16	844	-856	10	1127	-1121	7	651	-639	14	683	678	4	762	-735
20	79	87	1	420	416	10	160	-151	7	774	-770	18	46	-12	12	0	-32	9	746	734	7 2 L			6	56	-5
1 2 L			3	354	-334	12	832	850	9	872	-879	4 3 L			14	916	921	11	670	662	1	741	720	8	700	682
1	1060	1029	2 0 L			14	141	-105	11	701	707	1	1175	-1197	16	61	-60	13	634	-621	3	654	-632	10	0	-28
3	1605	-1574	0	1408	1405	16	663	-692	13	637	650	3	896	-904	18	664	-667	15	554	-559	5	625	-606	8 5 L		
5	1318	-1292	2	244	-182	2 7 L			15	647	-687	5	785	789	5 2 L			6 2 L			7	605	591	1	478	459
7	1254	1226	4	1981	-2013	1	696	-726	17	500	-505	7	735	726	1	836	835	0	997	-942	9	547	548	3	478	469
9	1260	1224	6	0	14	3	869	-868	3 5 L			9	756	-750	3	1080	-1086	2	86	-44	11	578	-557	5	415	-394
11	855	-806	8	1735	1771	5	555	566	2	1300	-1357	11	852	-859	5	777	-772	4	1193	1174	13	547	-533	7	382	-380
13	788	-737	10	126	77	7	516	531	4	123	5	13	764	760	7	738	740	6	51	-2	7 3 L			8 6 L		
15	845	807	12	1131	-1102	9	550	-570	6	913	914	15	577	584	9	891	885	8	1095	-1081	2	928	911	0	655	-630
17	676	654	14	76	37	11	542	-559	8	0	0	17	484	-493	11	627	-633	10	0	29	4	149	-153	2	87	59
19	604	-609	16	1078	1083	13	514	536	10	1020	-1044	4 4 L			13	590	-593	12	732	720	6	844	-816	4	544	528
1 3 L			18	79	-9	2 8 L			12	80	-4	0	1180	1195	15	657	660	14	73	26	8	148	-120	9 0 L		
2	1918	1922	20	848	-844	0	730	746	14	865	899	2	170	-180	17	473	474	16	704	-708	10	778	754	1	575	-555
4	225	-217	2 1 L			2	55	63	16	0	-1	4	1252	-1256	5 3 L			6 3 L			12	60	20	3	494	487
6	1365	-1335	1	1656	1695	4	787	-801	3 6 L			6	72	16	2	1234	1251	1	674	-662	14	646	-644	5	413	396
8	143	-142	3	1334	1368	6	23	7	1	654	671	8	1115	1125	4	178	158	3	790	-757	7 4 L			7	302	-380
10	1402	1397	5	981	-976	8	718	746	3	717	-736	10	105	117	6	1090	-1094	5	758	740	1	627	-610	9	430	-425
12	50	2	7	929	-912	10	15	-44	5	719	-737	12	884	-889	8	121	109	7	798	710	3	587	574	9 1 L		
14	1174	-1155	9	1049	1034	12	565	-585	7	705	724	14	96	69	10	1009	987	9	652	-640	5	550	531	2	697	-665
16	120	63	11	1085	1076	2 9 L			9	821	844	16	767	780	12	113	-26	11	515	-515	7	507	-490	4	65	46
18	773	756	13	989	-976	1	410	410	11	516	-526	4 5 L			14	828	-832	13	491	498	9	498	-493	6	691	672
20	46	43	15	802	-776	3	448	455	13	493	-500	1	678	675	16	102	-80	15	505	506	11	498	496	8	72	39
1 4 L			17	613	593	5	484	-498	15	470	482	3	647	672	5 4 L			6 4 L			13	462	452	9 2 L		
1	1281	-1303	19	523	511	7	479	-490	3 7 L			5	713	-726	1	738	-741	0	1151	1129	7 5 L			1	462	439
3	1014	1031	2 2 L			9	405	415	2	810	835	7	892	-707	3	859	868	2	0	2	2	741	-720	3	446	-422
5	944	938	0	2042	-2066	2 10 L			4	56	61	9	714	727	5	831	847	4	894	-872	4	98	-90	5	526	-512
7	897	-884	2	265	247	0	622	-607	6	911	-951	11	510	518	7	798	-814	6	47	3	6	747	743	7	496	478
9	835	-832	4	1633	1632	3 0 L			8	70	39	13	506	-513	9	598	-601	8	792	779	8	86	-79	9	397	380
11	890	887	6	70	-29	1	1193	-1194	10	678	699	15	556	-563	11	584	591	10	61	0	10	646	-627	9 3 L		
13	815	819	8	1435	-1425	3	1518	1575	12	74	-19	4 6 L			13	529	530	12	836	-838	7 6 L			2	659	630
15	635	-636	10	133	-123	5	953	945	14	579	-586	0	939	-995	15	438	-437	14	43	-5	1	418	411	4	75	68
17	543	-547	12	1358	1348	7	931	-938	3 8 L			2	137	-112	5 5 L			6 5 L			3	459	-452	6	607	-592
19	484	492	14	69	-53	9	1175	-1192	1	570	-583	4	913	943	2	939	-955	1	672	676	5	507	-500	9 4 L		
1 5 L			16	951	-932	11	846	831	3	466	474	6	48	4	4	67	64	3	510	505	7	485	486	1	415	-397
2	1205	-1220	18	73	24	13	797	792	5	485	503	8	865	-869	6	963	986	5	610	-605	9	425	414	3	475	457
4	74	12	20	718	725	15	841	-818	7	456	-473	10	106	88	8	111	56	7	571	-563	7 7 L			5	379	358
6	1470	1515	2 3 L			17	571	-548	9	421	-425	12	722	727	10	788	-787	9	464	453	2	615	609	10 0 L		
8	73	1	1	1029	-1019	19	539	528	11	459	487	14	95	65	12	0	2	11	553	555	4	50	-19	0	599	568
10	979	-1003	3	1082	-1079	3 1 L			3 9 L			4 7 L			14	662	666	13	484	-481	8 0 L			2	53	41
12	51	-10	5	1315	1322	2	1703	-1736	2	632	-640	1	597	-613	5 6 L			6 6 L			0	819	796	4	587	-559
14	792	796	7	1213	1212	4	176	161	4	64	79	3	478	-486	1	674	690	0	724	-723	2	76	30	10 1 L		
16	80	-6	9	912	-897	6	1640	1640	6	563	569	5	582	600	3	622	-627	2	41	-9	4	848	-834	1	373	354
18	790	-818	11	797	-774	8	133	113	4 0 L			7	556	570	5	470	-483	4	773	770	6	148	12	3	457	438
1 6 L			13	692	686	10	1340	-1319	0	1351	1352	9	437	-438	7	458	453	6	68	8	8	815	770	10 2 L		
1	805	825	15	651	645	12	136	7	2	264	271	11	493	-503	9	517	530	8	698	-697	10	199	-14	0	538	-519
3	716	-724	17	666	-678	14	1094	1061	4	1517	-1527															

TABLE III
PARTIAL POWDER PATTERN OF $LiYbF_4$

HKL	$d_{obs.}$	$d_{calc.}$	$I_{est.}$
011	4.627	4.619	8
112	2.996	2.994	10
013	2.905	2.908	3
004	2.650	2.647	1
020	2.569	2.566	2
121	2.242	2.243	7
015	1.956	1.957	4
123	1.923	1.924	7
024	1.841	1.842	7
220	1.815	1.815	4
116	1.588	1.587	5
132	1.554	1.522	9
033	1.540	1.540	3
017	1.452	1.451	2
231	1.412	1.411	3
127	1.264	1.263	2
141	1.237	1.236	2
136	1.196	1.195	4
235	1.182	1.181	3
028	1.176	1.176	3
415	1.073	1.073	2
228	1.070	1.069	2
244	1.053	1.053	4
219	1.047	1.047	2
341	1.022	1.022	4
11 10	1.017	1.016	2
152	0.989	0.989	4
343	0.987	0.986	3

The lattice constants of $LiYbF_4$ are $a_0 = 5.1335 \pm 0.0002$ and $c_0 = 10.588 \pm 0.002$ Å. The calculated density is 6.0928 g/cm^3, $Z = 4$.

Phase Equilibrium in the $LiF–LnF_3$ System.—The initial intent of this investigation was to determine the extent to which $LiLnF_4$ compounds occur in the lanthanide series and whether more than one equilibrium compound would form within a single $LiF–LnF_3$ system. However, the variations among the crystallization reactions of the $LiLnF_4$ compounds led to examination of their equilibrium phase behavior and to determination of the phase diagrams shown in Figure 2. A single intermediate compound is formed in $LiF–LnF_3$ systems over the range Eu–Lu only. In no case do the tetrafluorolanthanates exhibit dimorphism, nor do they appear to form solid solutions with either of their component fluorides. Invariant and singular equilibrium reactions are listed in Table IV. Experimental results are listed in Table V.

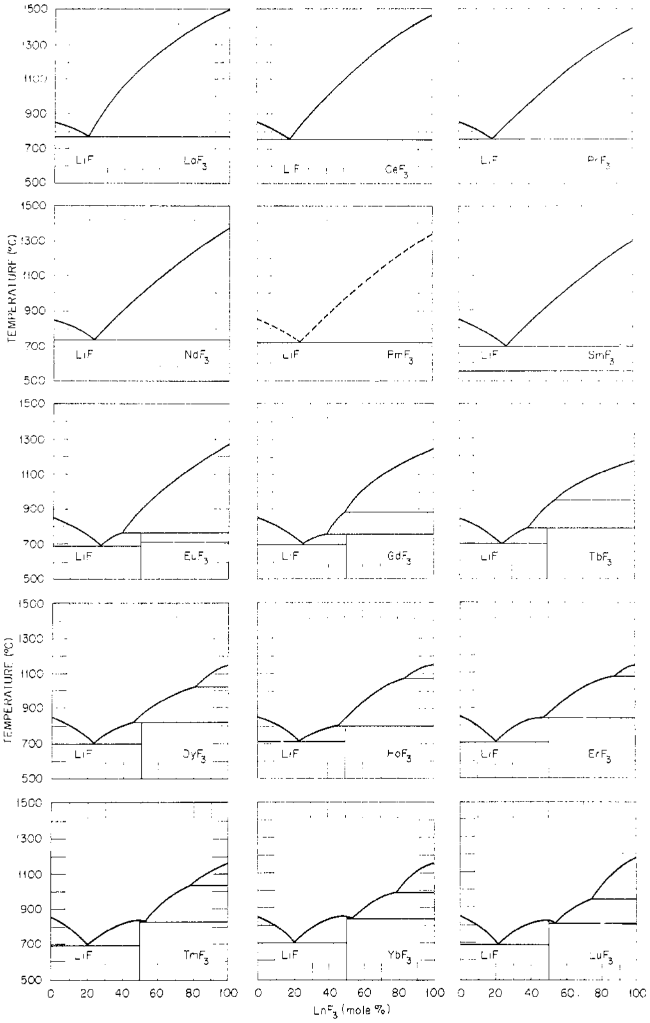

Figure 2.—Condensed-phase diagrams of the lithium fluoride–lanthanide trifluoride system.

We experienced considerable difficulty in determining liquid–solid transitions involving the $LiLnF_4$ compounds by thermal gradient quenching methods because of a pronounced tendency of $LiF–LnF_3$ mixtures to nucleate in even the most rapidly quenched melts. As a result, microscopic examination of quenched specimens was often ineffective as a means of distinguishing crystals of equilibrium primary phases from the accompanying nucleated flux. This behavior may result

TABLE IV

INVARIANT EQUILIBRIA AND SINGULAR POINTS IN THE $LiF-LnF_3$ SYSTEMS

Ln	Composition (Mole % LnF_3)	Temp. (°C)	Type of Equilibrium at Invariant Temps.	Equilibrium Reaction
La	20[a]	770	Eutectic	$L \rightleftarrows LiF + LaF_3$
Ce	19[b]	755	Eutectic	$L \rightleftarrows LiF + CeF_3$
Pr	19	750	Eutectic	$L \rightleftarrows LiF + PrF_3$
Nd	23	738	Eutectic	$L \rightleftarrows LiF + NdF_3$
Sm	27	698	Eutectic	$L \rightleftarrows LiF + SmF_3$
Eu	27	688	Eutectic	$L \rightleftarrows LiF + LiEuF_4$
	30	710	Peritectic	$L + \text{Hex. } EuF_3 \rightleftarrows L + \text{Orth. } EuF_3$
	40	760	Peritectic	$L + \text{Orth. } EuF_3 \rightleftarrows L + LiEuF_4$
Gd	26	700	Eutectic	$L \rightleftarrows LiF + LiGdF_4$
	39	755	Peritectic	$L + \text{Orth. } GdF_3 \rightleftarrows L + LiGdF_4$
	50	875	Peritectic	$L + \text{Hex. } GdF_3 \rightleftarrows L + \text{Orth. } GdF_3$
Tb	24	700	Eutectic	$L \rightleftarrows LiF + LiTbF_4$
	39	790	Peritectic	$L + \text{Orth. } TbF_3 \rightleftarrows L + LiTbF_4$
	(54)[c]	950	Peritectic	$L + \text{Hex. } TbF_3 \rightleftarrows L + \text{Orth. } TbF_3$
Dy	(24)	700	Eutectic	$L \rightleftarrows LiF + LiDyF_4$
	46	820	Peritectic	$L + \text{Orth. } DyF_3 \rightleftarrows L + LiDyF_4$
	(81)	1030	Peritectic	$L + \text{Hex. } DyF_3 \rightleftarrows L + \text{Orth. } DyF_3$
Ho	(24)	(710)	Eutectic	$L \rightleftarrows LiF + LiHoF_4$
	46	798	Peritectic	$L + \text{Orth. } HoF_3 \rightleftarrows L + LiHoF_4$
	(84)	1070	Peritectic	$L + \text{Hex. } HoF_3 \rightleftarrows L + \text{Orth. } HoF_3$
Er	21	700	Eutectic	$L \rightleftarrows LiF + LiErF_4$
	48	840	Peritectic	$L + \text{Orth. } ErF_3 \rightleftarrows L + LiErF_4$
	(88)	1075	Peritectic	$L + \text{Hex. } ErF_3 \rightleftarrows L + \text{Orth. } ErF_3$
Tm	21	692	Eutectic	$L \rightleftarrows LiF + LiTmF_4$
	50	(835)	Congruent m.p.	$L \rightleftarrows LiTmF_4$
	53	824	Eutectic	$L \rightleftarrows LiTmF_4 + \text{Hex. } TmF_3$
	(78)	1030	Peritectic	$L + \text{Hex. } TmF_3 \rightleftarrows L + \text{Orth. } TmF_3$
Tb	21	700	Eutectic	$L \rightleftarrows LiF + LiYbF_4$
	50	850	Congruent m.p.	$L \rightleftarrows LiYbF_4$
	53.5	840	Eutectic	$L \rightleftarrows LiYbF_4 + \text{Orth. } YbF_3$
	(79)	985	Peritectic	$L + \text{Hex. } YbF_3 \rightleftarrows L + \text{Hex. } YbF_3$
Lu	22	695	Eutectic	$L \rightleftarrows LiF + LiLuF_4$
	50	(825)	Congruent m.p.	$L \rightleftarrows LiLuF_4$
	54	810	Eutectic	$L \rightleftarrows LiLuF_4 + \text{Orth. } LuF_3$
	74	945	Peritectic	$L + \text{Hex. } LuF_3 \rightleftarrows L + \text{Orth. } LuF_3$

[a] Reported as $LiF-LaF_3$ (86–14 mol %), 758°, by G. A. Bukhalova and E. P. Babaev, *Zh. Neorgan. Khim.*, **10,** 1883 (1965). [b] From C. J. Barton and R. A. Strehlow, *J. Inorg. Nucl. Chem.*, **20,** 45 (1961). [c] Estimated value.

from the relatively high lattice energy of the $LiLnF_4$ compounds, compared with other complex fluorides. This is supported qualitatively since values of the corresponding temperatures, $0.5(T_{m\text{LiF}} + T_{m\text{LnF}_3}) - T_{m\text{LiLnF}_4}$, fall in the range 150–300°, while those for the hexagonal $NaLnF_4$ phases are greater, 250–480°. Direct determination of liquid–solid transition temperatures in melts was achieved by recording temperatures of visually observed phase changes taking place in melts which were protected by dry inert atmospheres. Although this method afforded the greatest reliability and reproducibility, it was of limited use because of the quantities of materials required. Therefore the phase diagrams of the $LiF-LnF_3$ systems were deduced from a variety of experimental methods. In some cases, redundancy of transition temperature determination was achieved by use of more than one method for at least part of the system.

The diagrams shown in Figure 2 were constructed using the transition temperature data for a specific system, as well as data interpolated from adjacent systems. The relationship introduced by the dimorphism of the lanthanide trifluorides is assumed. The possible occurrence of solid solutions involving the high-temperature forms of the lanthanide trifluorides was not examined.

Discussion

Our initial prediction that $LiLnF_4$ compounds having the scheelite structure would exist throughout the lanthanides from $LiF-TbF_3$ to $LiF-LuF_3$[2] was based on the occurrence of $LiYF_4$ and early indications that no intermediate compounds were formed in the $LiF-NdF_3$ system. In tests of this prediction, Vorres and Riviello[24] found that the system sequence is somewhat more extensive than was originally predicted, in that it includes the systems $LiF-EuF_3$ and $LiF-GdF_3$ as well. Subsequently, Keller and Schmutz[18] prepared each of the $LiLnF_4$ compounds and obtained precise values for their lattice constants. The results of our present investigation confirm the previous findings and, in addition, report the equilibrium behavior of the tetrafluorolanthanates as well as the detailed crystal structure of $LiYbF_4$.

The first member of the $LiLnF_4$ series is the pure compound $LiEuF_4$ which crystallizes from the melt between 27 and 30 mol % as a primary phase and melts incongruently at 710° to EuF_3 and liquid. Thereafter the melting temperatures of the intermediate compounds show a general increase with increasing atomic number of the lanthanide. Further, the liquidus of the

[24] K. S. Vorres and R. Riviello, *Proc. Conf. Rare Earth Res., 4th, Phoenix, Ariz., 1964,* 521 (1965).

Table V

Liquid–Solid Phase Transition Data for the LiF–LnF$_3$ Systems[a]

LnF_3 Conc. (mole %)	LaF_3	PrF_3	NdF_3	SmF_3	EuF_3	GdF_3	TbF_3	DyF_3	HoF_3	ErF_3	TmF_3	YbF_3	LuF_3
10			815T[b]										
15			785T	775T 698T	685Q[c]	770Q 695V 692Q	775V[d] 703V			737Q 699Q	740Q 695Q		747Q 699Q
20		758T 750T	755T	745T	745V 690V	710V 694Q 690V	738V 702V	699Q	710V	710V		715Q 699Q	
25	865T 770T			710T 698T	703V 690V		708V 702V			740V 736Q 698Q		738V 699Q 695V	722Q 695Q
30		875T 750T	790T 738T	735T 698T	710V 690V	728Q 725V 700V 694Q	748V 702V			780V		780V 700V	
35			760T 738T	698T	745V 720Q 710V 690Q	735V 726Q 702V	775V 702V	699Q		810V		810V 700V	
40		942T 750T		830T	780V 755V 710V 685V	775V 755V 695V	807V 792V 703V			829V 818T 699Q 698V	795Q 694Q	828V 700V	803Q 696Q
45				885T	835V 755V 710V 683V	840V 755V 695V	858V 792V 790Q 702V			835V		840V	
50		1035T 750T	980T 738T	910T 698T	890Q 888V 770Q 769V 720Q 712V 690V	880V 755V 748Q 695V	908V 792V	846Q 818Q	837Q 798Q	845V 820Q		848V	798Q
55					945V	953V 875V 755V	955V 792V			905V		850V 840V	
60					980V 760V 690V	1010V 875V	990V 792V			940V 822Q 830Q		895V 840V	
65							1030V 790V					1020V 840V	902Q 836Q
67.5										975V			
70							1065V 780V					960V 840V	
75								815Q		1004Q	>1005Q 824Q	990V 983Q 840V	955Q 811Q

[a] The phase transitions represented by these data are evident in Figure 2. [b] Thermal analysis data. [c] Data from thermal gradient quenching experiments. [d] Data from direct visual observation of crystallizing melts.

trifluoride component deviates increasingly from ideality with increasing atomic number of the lanthanide so that, beginning with LiF–ErF$_3$, the remaining lanthanide systems exhibit congruent melting of the LiLnF$_4$ compound. As in the LiF–YF$_3$ system, only one compound forms in the LiF–LnF$_3$ systems and is never found to undergo solid-state transitions within the temperature range of this investigation.

As noted previously,[10] BiF$_3$ serves as a proxy for lanthanide trifluorides since the radius of Bi^{3+} is nearly equal to those of mid-Ln^{3+} ions. The compound LiBiF$_4$ is known and has the scheelite structure.[18] The absence of compounds with the scheelite structure in the NaF–LaF$_3$ and NaF–UF$_3$ systems, with cation radium ratios $r(M^+)/r(M^{3+}) = 0.93$ and 0.95, respectively, suggests that although the compound LiScF$_4$ should be formed in the LiF–ScF$_3$ system where $r(Li^+)/r(Sc^{3+}) = 1.0$ it will not have the scheelite structure.

The propensity of the heavier lanthanides to form the compound LiLnF$_4$ suggests that such complex fluoride scheelites will probably be formed by other fluoride systems as well. Most important of these are the heavier actinide trifluorides CmF$_3$, BkF$_3$, CfF$_3$, and EsF$_3$ which offer possibilities for evaluation of effects related to complex compound formation. Derived radii for the trivalent and tetravalent actinides[25,26] of atomic numbers 89–98 reflect the contraction anticipated from the development of the 5f shell. Plots of these radii clearly suggest that as Z increases, the radii of the trivalent actinides are decreasing to a minimum value and have nearly reached the radius of europium at californium. If trivalent ionic radius were the only consideration, compound formation would not be expected with Cm^{3+} (0.979 Å) but might occur with Bk^{3+} (0.954 Å) and certainly with Cf^{3+} (0.949 Å); recall that LiF·LnF$_3$ is formed with Eu^{3+} (0.950 Å) but not with Sm^{3+} (0.964 Å). These trivalent radii are derived from oxides; the corresponding ones from fluorides are: Cm, 0.946 Å; Bk, 0.93 Å; Cf, 0.915 Å; Eu, 0.909 Å; Sm 0.921 Å.[25] Experimental tests of the predicted compound formation can be made when sufficient amounts of Bk and Cf are available. In the case of berkelium, which has both 3+ and 4+ oxidation states, hydrogen reduction of the expected compound of tetravalent berkelium, LiBkF$_5$, should yield LiBkF$_4$. This should be a more definitive test than the reaction LiF + BkF$_3$ on a micro scale. If greater

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(25) J. R. Peterson and B. B. Cunningham, *J. Inorg. Nucl. Chem.*, **30**, 1775 (1968); *Inorg. Nucl. Chem. Letters*, **3**, 327 (1967).

(26) R. D. Shannon and C. T. Prewitt, *Acta Cryst.*, **B25**, 925 (1969).

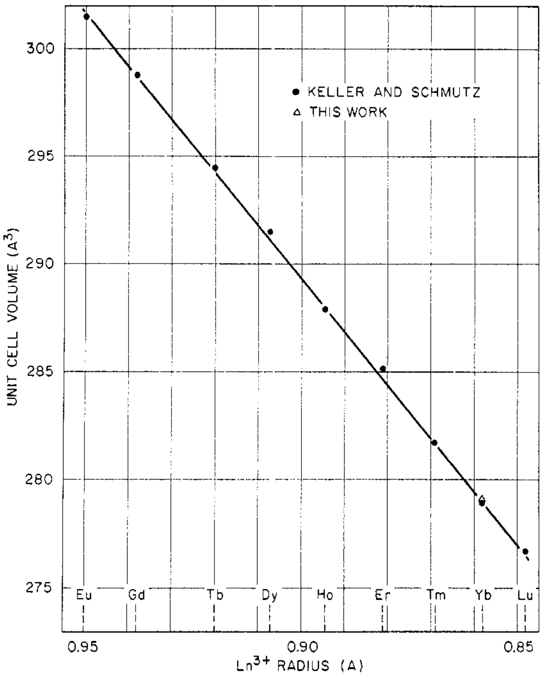

Figure 3.—Unit cell volumes of the $LiLnF_4$ compounds.

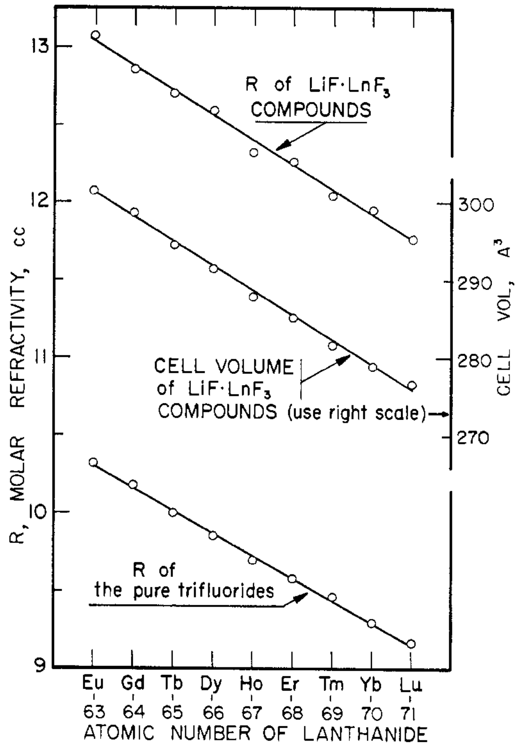

Figure 4.—Molar refractivities of $LiF \cdot LnF_3$ and LnF_3 and the cell volumes of $LiF \cdot LnF_3$ *vs.* atomic number of the lanthanide.

5f-orbital participation in bonding played a significant role, we might have found that the lithium fluoride–actinide trifluoride compound formation occurred at a slightly larger trivalent ion radius than in the case of the lanthanides. However, the effect was insufficient to hold the compound $LiF \cdot CmF_3$ even when the correct lithium:curium ratio was already established (in $LiF \cdot CmF_4$ which was hydrogen reduced).

The unit cell volume of $LiYbF_4$ obtained from our single-crystal studies is in excellent agreement with the value obtained by Keller and Schmutz[18] and attests to the accuracy and precision of their measurements. It is evident in Figure 3 that the volumes of the $LiLnF_4$ unit cells decrease linearly with decreasing radius of the Ln^{3+} ion. No such trend is followed by the refractive indices themselves of either the $LiLnF_4$ compounds or the lanthanide trifluorides. However, the Lorentz–Lorenz molar refractivities of both do indeed obey a linear relationship. This is shown in Figure 4 and confirms that the molar refractivities of these compounds are additive as shown to be generally true of fluoride complexes.[27]

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[27] R. A. Penneman, *Inorg. Chem.*, **8**, 1379 (1969).