to the presence of small amounts of adsorbed gases such as nitrosyl fluoride or dinitrogen tetroxide. The bands near 3500 and 1640 cm^{-1} in the spectrum of $(NO)_2PtF_6$ may be due to lattice water absorbed during the preparation of the mulls.

Other features of the spectra of these compounds were of lesser importance to the gross structural implications. That the stretching mode of the NO^+ ion appeared as a doublet in $NOPtF_6$ and $N_2O_3PtF_6$ should probably be interpreted as being due to coupling with lattice modes. A similar interpretation is reasonable for the splitting of the ν_3 and $\nu_1 + \nu_3$ bands of the NO_2^+ ion in $N_2O_3PtF_6$. However, in this case the splitting might be due to different interactions between randomly oriented NO^+ and NO_2^+ ions in the crystal. For example, if the NO^+ and NO_2^+ ions lie on the major threefold axis of a structure similar to that of O_2PtF_6,[2] then the three possible orientations of the ions NO^+—NO^+, NO_2^+—NO_2^+, and NO^+—NO_2^+ would result in two different crystal environments for both NO^+ and NO_2^+.

X-Ray Diffraction Results.—The crystal data indicate that $NOPtF_6$ is isostructural with O_2PtF_6[2] and $KSbF_6$.[29] These three compounds have nearly identical cell dimensions, and since the visually estimated relative intensities of $NOPtF_6$ are very nearly the same as those found for O_2PtF_6, the space groups for these two compounds are assumed to be identical, *i.e.*, $T_h{}^4$-$Ia3$. This similarity is to be expected since the NO^+ and O_2^+ ions are close in size.

It has been estimated that the NO^+ group, when rotating and acting as a sphere, has an effective radius of 1.40 A,[20] which is close to the radius of potassium ion (1.33 A). Since the molecular volume of SbF_6^- is nearly the same as that of the ions OsF_6^-, RuF_6^-, and PtF_6^-,[27] the isostructural relationship of $NOPtF_6$ and $KSbF_6$ is expected.

When the larger linear NO_2^+ ion is substituted for NO^+ in the crystal, the lattice expands a small amount (2.06%); this expansion is still more pronounced for $N_2O_3{}^{2+}PtF_6{}^{2-}$ (4.64%). Although $NOPtF_6$ and O_2PtF_6 are believed to be isostructural, it cannot be determined at present whether NO_2PtF_6 and $N_2O_3PtF_6$ are also isostructural to O_2PtF_6, since the corresponding relative intensities for some reflections differ considerably. However, since these compounds are cubic, and nearly isodimensional, they probably possess closely related packing features.

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The Sodium Fluoride–Lanthanide Trifluoride Systems[1]

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Phase diagrams are reported for the NaF–LnF_3 binary systems. Hexagonal phases of the formula NaF·LnF_3 are formed in all NaF–LnF_3 systems. Above 700° the hexagonal phases NaF·PrF_3 to NaF·LuF_3 become converted to disordered fluorite-like cubic phases of variable composition. The composition limits of the cubic phase region are extended in proportion to the difference in ion size between Na^+ and Ln^{3+} and vary in breadth ranging from 9 mole % (NaF–PrF_3) to 25 mole % (NaF–LuF_3). In each case, the LnF_3-rich phase boundary was found empirically to be 5NaF·9LnF_3 as the interstitial positions for anions become filled. Values of the fluorite unit-cell constants were calculated from ionic radii and found to be in good agreement with measured values. Unit-cube dimensions, a_0, range from a maximum value of 5.720 A for the LnF_3-rich phase in the system NaF–PrF_3 to 5.425 A for the NaF-rich phase in the system NaF–LuF_3. Lattice constants for the hexagonal phases NaF·LaF_3 to NaF·LuF_3 vary for a_0 from 6.157 to 5.967 A and for c_0 from 3.822 to 3.523 A. At high temperatures the 5NaF·9LnF_3 phase displays disordering characteristic of the fluorite-like solid solutions; at lower temperatures cationic ordering takes place in the 5NaF·9LnF_3 phases where Ln = Dy to Lu, transforming the cubic phase to an orthorhombic phase. Hexagonal NaF·LnF_3 and orthorhombic 5NaF·9LnF_3 compounds are partially miscible in the solid state. In the series Dy to Lu, the hexagonal phase is increasingly soluble in 5NaF·9LnF_3, stabilizing the 5:9 phase to the extent that the lutetium compound is stable at temperatures below 300°, the lower temperature limit of this study. Optical properties and refractive indices of the intermediate crystalline phases in the NaF–LnF_3 systems were determined as part of this investigation. Minimum liquidus temperatures in the NaF–LnF_3 systems are associated with an NaF–NaF·LnF_3 eutectic which varies in composition only from 25 to 29 mole % LnF_3 and in temperature from 733 to 595°.

Introduction

We proposed some time ago[2] that the system NaF–YF_3 would serve as a model for the binary systems NaF–SmF_3, –EuF_3, –GdF_3, –TbF_3, –DyF_3, –HoF_3, –ErF_3, –TmF_3, –YbF_3, and –LuF_3. This hypothesis was based

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(2) (a) R. E. Thoma, G. M. Hebert, H. Insley, and C. F. Weaver, *Inorg. Chem.*, **2**, 1005 (1963); (b) R. E. Thoma, "Complex Compounds in the Sodium Fluoride–Rare Earth Trifluoride Systems," Proceedings of the Fourth Rare Earth Research Conference, Phoenix, Ariz., April 22–25, 1964.

on the fact that the trifluorides of the rare earths, SmF_3 to LuF_3, were believed to occur in an orthorhombic form which is isomorphous with YF_3, as well as in the hexagonal form,[3] and that phase equilibria in the NaF–LnF_3 binary systems of these lanthanides would correspond to those in NaF–YF_3, but in the systems NaF–LaF_3 to NaF–PmF_3 would be described qualitatively by NaF–CeF_3.[4] The present report records the results of attempts to test this hypothesis.

Experimental Procedures

Materials.—Commercial reagent grade NaF was used for preparing all of the mixtures used in the investigation of the NaF–LnF_3 systems. The lanthanide trifluorides used in this study were prepared by conversion of the appropriate oxides by ammonium bifluoride at elevated temperatures. That complete conversion to the trifluorides took place was verified by X-ray, petrographic, and chemical analysis. As previously noted,[5] this fluorinating agent is also effective in purifying nonvolatile fluorides and accordingly was used to ensure that fused mixtures of NaF and the lanthanide trifluorides were free of contamination by small amounts of oxides. Rare earth oxides were obtained from several vendors. With the exception of La_2O_3, Ce_2O_3, and Ho_2O_3, the oxides were normally at least 99.99% pure with respect to the specified rare earth. All lanthanide trifluorides prepared from these oxides were analyzed at this laboratory by spectrochemical methods. The results of these analyses indicate that, although the starting materials were not as pure as claimed by the manufacturers, the concentration of contaminant cations did not exceed 0.2 atom %.

Methods.—Investigation of high-temperature behavior in the fluoride systems studied at this laboratory have ordinarily employed a group of standardized methods[6] which entail thermal analysis of crystallizing melts and subsequent thermal gradient quenching, a modification of classical quenching methods, to provide a large number of samples at a time. In the present work, very few thermal analysis data were obtained because of the ineffectiveness of this technique for the investigation of the model system NaF–YF_3.

Reactions of the NaF–YF_3 cubic solid solutions could not be determined by cooling curves because little or no heat was evolved as the cubic phases nucleated; neither was their decomposition *via* solid-state reactions evident from cooling-curve data. Consequently, NaF–LnF_3 equilibrium data were obtained principally from specimens which were equilibrated in a thermal gradient at temperatures ranging from 300 to 1200° (2 days to 1 month) and then quenched. The equilibration periods were varied according to the transition investigated; *e.g.*, specimens were equilibrated for 1 to 7 days if liquid–solid transitions were expected and 2 to 4 weeks if solid-state transitions were expected. In the absence of cooling-curve inflections, verification of the equilibrium phase transitions was obtained by reproducing the transition with specimens which before equilibration contained, in one case, the crystalline phase found above the transition temperature and, in the other case, the crystalline phases found below the transition temperature. Phase identification was accomplished by petrographic and X-ray diffraction analysis. X-Ray determinations of unit-cell dimensions were made with a Norelco diffractometer and Cu Kα radiation.

Results

Few previous reports have recorded properties of the NaF–LnF_3 systems. In general, earlier attention has focused on investigations of the properties of hexagonal NaF·LnF_3 phases.[4,7–11] This report describes in detail the equilibrium relationships in each NaF–LnF_3 system and comprises the first extensive description of the phase diagrams of the lanthanide halide systems. The initial results obtained in the current study of the systems NaF–SmF_3 to NaF–LuF_3 indicated that their equilibrium behavior conformed to that predicted from the NaF–YF_3 model system.[2a] As more complete data were obtained, however, we noted that the NaF–YF_3 model was approximated only by the systems for which the Ln^{3+} and Y^{3+} radii were nearly equal and that the lanthanide group is comprised of a series of related systems, each, in general, gradually more intricate with increasing atomic number of the lanthanide. This behavior is illustrative of the prominent role of cation size in phase behavior of ionic systems and provides interesting examples of the effects caused by small changes in the size of one of the cations.

Phase Diagrams.—Equilibrium phase diagrams of the binary systems of sodium fluoride and the lanthanide fluorides are shown in Figure 1. The compositions and temperatures at which invariant liquid–solid equilibria occur are listed in Table I. The diagrams reported here were constructed from data obtained by the experimental procedures discussed above and on the basis of inferences drawn from observed regularities in phase transition behavior. The NaF-rich sections, for example, were based on the observed regularities in the NaF–NaF·LnF_3 eutectic temperatures together with interpolations and extensions of NaF–LnF_3 liquidus curves reported by Cantor and Ward.[12] The equilibrium diagram of the system NaF–PmF_3 was inferred by interpolation, because investigation was precluded by the high β activity of available Pm isotopes. The intent of the present study was to infer the general characteristics of the lanthanide systems on the basis of the well-established model system NaF–YF_3. Accordingly, fewer data were obtained on phase transition temperatures than have been usual in such work at this laboratory; all phase transition data obtained from thermal gradient quenching experiments are indicated on the phase diagrams (Figure 1).

Two equilibrium compounds of the formulas NaF·LnF_3 and 5NaF·9LnF_3 were observed within each of the 12 NaF–LnF_3 systems from NaF–PrF_3 to NaF–LuF_3. Compounds of the formula NaF·LnF_3 occur throughout all of these systems and at temperatures below approximately 600 to 700° as hexagonal crystalline phases. At temperatures above approximately 700° these hexagonal phases are unstable. On heating, they decompose in a variety of phase reactions, differing sufficiently from each other in character and properties to enable one NaF–LnF_3 system to be distinguished from another. In the systems NaF–LaF_3 and NaF–CeF_3 the

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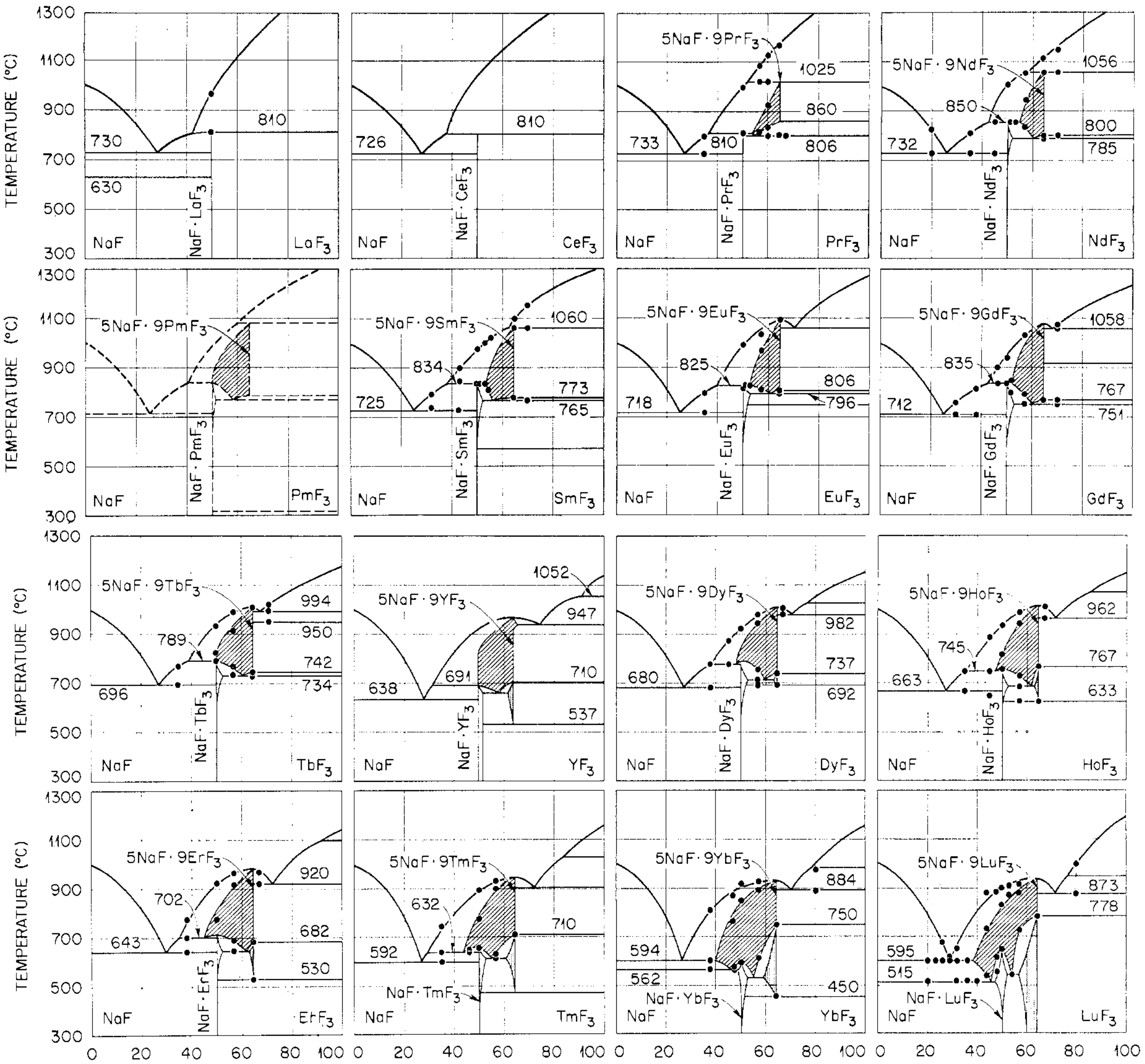

Figure 1.—Equilibrium diagrams of the NaF–LnF₃ systems. Diagonally hatched areas indicate cubic solid solution phases; dotted areas indicate orthorhombic phases. System NaF–CeF₃ from C. J. Barton, J. D. Redman, and R. A. Strehlow, *J. Inorg. Nucl. Chem.*, **20,** 45 (1961).

hexagonal phase melts incongruently to LnF_3 and liquid; in NaF–PrF_3 to NaF–GdF_3 it melts incongruently to a cubic fluorite-like phase and liquid, and in NaF–TbF_3 to NaF–LuF_3 it becomes disordered and inverts into the cubic phase. When formed, the cubic phase is of variable composition, qualitatively similar in its phase behavior to the corresponding phase in the NaF–YF_3 system. Results of the NaF–YF_3 investigation as well as those in the current study suggested originally that a stoichiometric cubic phase, $NaF \cdot LnF_3$, is an equilibrium solid in the binary systems. As compositional limits of the cubic phases in the NaF–LnF_3 systems were established, it became clear that equimolar stoichiometry of this phase is fortuitous. Composition limits of the cubic phases were determined from refractive index, lattice constant, and phase transition data. As in the NaF–YF_3 system, the upper LnF_3 composition limit corresponds to the compound composition $5NaF \cdot 9LnF_3$. The lower composition extends progressively from a limit of 55.5 mole % LnF_3 to one at 39 mole % LnF_3 for the systems NaF–SmF_3 to NaF–LuF_3, respectively.

Cubic NaF–LnF_3 phases have been observed previously by Zalkin and Templeton[3] and Roy and Roy.[10] In their determination of the structures of the rare earth trifluorides, Zalkin and Templeton observed that a cubic phase was precipitated from aqueous solutions of NaF and HoF_3 by HF. They inferred incorrectly that this phase was HoOF. Roy and Roy recognized the existence of some cubic NaF–LnF_3 phases and noted as well that they were of variable composition.

The cubic solid solution phases are unstable below temperatures varying from 800 to 530°. On cooling, they transform to a variety of products depending on the composition of the decomposing phases. At equimolar NaF–LnF_3 compositions, partial ordering occurs and the hexagonal $NaF \cdot LnF_3$ phase forms. At the $5NaF \cdot 9LnF_3$ phase boundary the cubic phase decomposes in the systems NaF–PrF_3 to NaF–TbF_3 on cooling to hexagonal $NaF \cdot LnF_3$ and LnF_3. In the systems

TABLE I

LIQUID–SOLID INVARIANT EQUILIBRIA IN THE NaF–LnF$_3$ SYSTEMS

Ln	Composition (mole % LnF$_3$)	Temperature (°C)	Type of Equilibrium at Invariant Temperature	Equilibrium Reaction
La	29	730[a]	Eutectic	L $\rightleftharpoons$ NaF + hex. $NaF\cdot LaF_3$
	43	810[a]	Peritectic	L + LaF_3 $\rightleftharpoons$ L + hex. $NaF\cdot LaF_3$
Ce[b]	28	726	Eutectic	L $\rightleftharpoons$ NaF + hex. $NaF\cdot CeF_3$
	38	810	Peritectic	L + CeF_3 $\rightleftharpoons$ L + hex. $NaF\cdot CeF_3$
Pr	27	733	Eutectic	L $\rightleftharpoons$ NaF + hex. $NaF\cdot PrF_3$
	37	810	Peritectic	L + cubic ss $\rightleftharpoons$ L + hex. $NaF\cdot PrF_3$
	52	1025	Peritectic	L + PrF_3 $\rightleftharpoons$ L + cubic ss
Nd	26	732	Eutectic	L $\rightleftharpoons$ NaF + hex. $NaF\cdot NdF_3$
	42	850	Peritectic	L + cubic ss $\rightleftharpoons$ L + hex. $NaF\cdot NdF_3$
	58	1056	Peritectic	L + NdF_3 $\rightleftharpoons$ L + cubic ss
Sm	25	725	Eutectic	L $\rightleftharpoons$ NaF + hex. $NaF\cdot SmF_3$
	38	834	Peritectic	L + cubic ss $\rightleftharpoons$ L + hex. $NaF\cdot SmF_3$
	62	1060	Peritectic	L + SmF_3 $\rightleftharpoons$ L + cubic ss
Eu	25	718	Eutectic	L $\rightleftharpoons$ NaF + hex. $NaF\cdot EuF_3$
	39	825	Peritectic	L + cubic ss $\rightleftharpoons$ L + hex. $NaF\cdot EuF_3$
	64.3	1091	Congruent m.p.	L $\rightleftharpoons$ $5NaF\cdot 9EuF_3$
	70	1060	Eutectic	L $\rightleftharpoons$ $5NaF\cdot 9EuF_3$ + EuF_3
Gd	25	712	Eutectic	L $\rightleftharpoons$ hex. $NaF\cdot GdF_3$
	43	835	Peritectic	L + cubic ss $\rightleftharpoons$ L + hex. $NaF\cdot GdF_3$
	64.3	1080	Congruent m.p.	L $\rightleftharpoons$ $5NaF\cdot 9GdF_3$
	68	1058	Eutectic	L $\rightleftharpoons$ $5NaF\cdot 9GdF_3$ + GdF_3
Tb	27	696	Eutectic	L $\rightleftharpoons$ NaF + hex. $NaF\cdot TbF_3$
	39	789	Peritectic	L + cubic ss $\rightleftharpoons$ L + hex. $NaF\cdot TbF_3$
	64.3	1031	Congruent m.p.	L $\rightleftharpoons$ $5NaF\cdot 9TbF_3$
	68	994	Eutectic	L $\rightleftharpoons$ $5NaF\cdot 9TbF_3$ + TbF_3
Dy	27	680	Eutectic	L $\rightleftharpoons$ NaF + hex. $NaF\cdot DyF_3$
	38	780	Peritectic	L + cubic ss $\rightleftharpoons$ L + hex. $NaF\cdot DyF_3$
	64.3	1020	Congruent m.p.	L $\rightleftharpoons$ $5NaF\cdot 9DyF_3$
	70	982	Eutectic	L $\rightleftharpoons$ $5NaF\cdot 9DyF_3$ + DyF_3
Ho	27	663	Eutectic	L $\rightleftharpoons$ NaF + hex. $NaF\cdot HoF_3$
	35	745	Peritectic	L + cubic ss $\rightleftharpoons$ L + hex. $NaF\cdot HoF_3$
	64.3	1010	Congruent m.p.	L $\rightleftharpoons$ $5NaF\cdot 9HoF_3$
	71	962	Eutectic	L $\rightleftharpoons$ $5NaF\cdot 9HoF_3$ + HoF_3
Er	27	643	Eutectic	L $\rightleftharpoons$ NaF + hex. $NaF\cdot ErF_3$
	35	702	Peritectic	L + cubic ss $\rightleftharpoons$ L + hex. $NaF\cdot ErF_3$
	64.3	975	Congruent m.p.	L $\rightleftharpoons$ $5NaF\cdot 9ErF_3$
	72	920	Eutectic	L $\rightleftharpoons$ $5NaF\cdot 9ErF_3$ + ErF_3
Tm	27	592	Eutectic	L $\rightleftharpoons$ NaF + hex. $NaF\cdot TmF_3$
	29	632	Peritectic	L + cubic ss $\rightleftharpoons$ L + hex. $NaF\cdot TmF_3$
	64.3	940	Congruent m.p.	L $\rightleftharpoons$ $5NaF\cdot 9TmF_3$
	~70	~905	Eutectic	L $\rightleftharpoons$ $5NaF\cdot 9TmF_3$
Yb	26	594	Eutectic	L $\rightleftharpoons$ NaF + cubic ss
	64.3	928	Congruent m.p.	L $\rightleftharpoons$ $5NaF\cdot 9YbF_3$
	~70	893	Eutectic	L $\rightleftharpoons$ $5NaF\cdot 9YbF_3$ + YbF_3
Lu	29	595	Eutectic	L $\rightleftharpoons$ NaF + cubic ss
	64.3	930	Congruent m.p.	L $\rightleftharpoons$ $5NaF\cdot 9LuF_3$
	72	873	Eutectic	L $\rightleftharpoons$ $5NaF\cdot 9LuF_3$ + LuF_3

[a] Eutectic and peritectic temperatures were reported by E. Mathes and S. Holz, *Z. Chem.*, **2,** 22 (1962), to be ~630 and 770°, respectively. [b] C. J. Barton, J. D. Redman, and R. A. Strehlow, *J. Inorg. Nucl. Chem.*, **20,** 45 (1961).

TABLE II

OPTICAL AND X-RAY POWDER DIFFRACTION DATA FOR NaF–LnF$_3$ CRYSTALLINE PHASES

A. Hexagonal $NaF\cdot LnF_3$

Ln	a_0(A)	$\sigma(a_0)$	c_0(A)	$\sigma(c_0)$	N_ϵ	N_ω
La	6.157	0.006	3.822	0.008	1.486	1.500
Ce	6.131	0.006	3.776	0.004	1.493	1.514
Pr	6.123	0.004	3.743	0.002	1.494	1.516
Nd	6.100	0.002	3.711	0.002	1.493	1.515
Pm	(6.056)	-	(3.670)	-	(1.492)	(1.515)
Sm	6.051	0.010	3.640	0.007	1.492	1.516
Eu	6.044	0.603	3.613	0.003	1.492	1.516
Gd	6.020	0.003	3.601	0.008	1.483	1.507
Tb	6.008	0.004	3.580	0.002	1.486	1.506
Dy	5.985	0.004	3.554	0.003	1.486	1.510
Ho	5.991	0.001	3.528	0.002	1.486	1.510
Er	5.959	0.002	3.514	0.002	1.482	1.504
Tm	5.953	0.002	3.494	0.002	1.476	1.496
Yb	5.929	0.002	3.471	0.002	1.482	1.504
Lu	5.912	0.003	3.458	0.003	1.484	1.506
(Y)	5.967	0.002	3.523	0.002	1.464	1.486

B. Cubic NaF-LnF$_3$ Phases at Composition Limits

	NaF-Rich Composition Limit				$5NaF\cdot 9LnF_3$ Composition Limit		
Ln	Composition (mole % LnF$_3$)	R.I.	a_0(A)	X-Ray Density (g/cc)	R.I.	a_0(A)	X-Ray Density (g/cc)
Pr	55.5	1.512	5.710		1.526	5.720	5.766
Nd	55.0	1.506	5.670	4.431	1.524	5.685	5.962
Pm	(54.5)	(1.500)	(5.630)	(4.620)	(1.522)	(5.655)	(6.131)
Sm	53.5	1.495	5.605	4.702	1.520	5.627	6.315
Eu	52.5	1.486	5.575	4.809	1.519	5.616	6.392
Gd	51.5	1.470	5.550	4.978	1.502	5.594	6.620
Tb	50.0	1.472	5.535	5.051	1.504	5.565	6.772
Dy	48.5	1.462	5.505	5.205	1.504	5.547	6.939
Ho	47.0	1.458	5.490	5.296	1.504	5.525	7.093
Er	45.0	1.440	5.475	5.387	1.493	5.514	7.203
Tm	43.5	1.427	5.460	5.466	1.494	5.493	7.336
Yb	41.5	1.415	5.440	5.611	1.488	5.480	7.510
Lu	39.0	1.402	5.425	5.698	1.482	5.463	7.580

C. Orthorhombic $5NaF\cdot 9LnF_3$

	Refractive Index			Lattice Constants (A)		
Ln	N_α	N_γ	N_{mean}	a_0	b_0	c_0
Dy	-	-	1.514	5.547	39.23	7.845
Ho	-	-	1.510	5.525	39.07	7.814
Er	1.504	1.509	1.506	5.514	38.99	7.798
Tm	-	-	1.501	5.493	38.84	7.768
Yb	1.482	1.494	1.495	5.480	38.75	7.750
Lu	1.480	1.496	1.487	5.463	38.63	7.725

D. Hexagonal and Orthorhombic LnF$_3$

		Refractive Index		Lattice Constants (A)				
Ln	Symmetry	N_ϵ or N_α	N_ω or N_γ	a_0	b_0	c_0	Density (g/cc)	Reference
La	Hexagonal	1.597	1.603	7.186	-	7.352	5.936	a
Ce	Hexagonal	1.607	1.613	7.112	-	7.279	6.157	b
Pr	Hexagonal	1.614	1.618	7.075	-	7.238	6.14	c
Nd	Hexagonal	1.621	1.628	7.030	-	7.200	6.506	a
Sm	Orthorhombic	1.577	1.608	6.669	7.059	4.405	6.643	a
Eu	Orthorhombic	1.572	1.600	6.622	7.019	4.396	6.793	d
Gd	Orthorhombic	1.570	1.600	6.571	6.985	4.393	7.056	e
Tb	Orthorhombic	1.570	1.600	6.513	6.949	4.384	7.236	e
Dy	Orthorhombic	1.570	1.600	6.460	6.906	4.376	7.465	e
Ho	Orthorhombic	1.566	1.598	6.404	6.875	4.379	7.644	e
Er	Orthorhombic	1.566	1.598	6.354	6.848	4.380	7.814	e
Tm	Orthorhombic	1.564	1.598	6.283	6.811	4.408	7.971	e
Yb	Orthorhombic	1.558	1.568	6.216	6.786	4.434	8.168	e
Lu	Orthorhombic	1.554	1.558	6.181	6.731	4.446	8.44	-

[a] E. Staritzky and L. B. Asprey, *Anal. Chem.*, **29,** 857 (1957). [b] ASTM X-Ray Diffraction Card No. 8–45. [c] ASTM X-Ray Diffraction Card No. 6-0325. [d] A. Zalkin and D. H. Templeton, *J. Am. Chem. Soc.*, **75,** 2453 (1953). [e] ASTM X-Ray Diffraction Card No. 12-788.

NaF–DyF$_3$ to NaF–LuF$_3$ the cubic phase again becomes partially ordered on cooling and transforms into an orthorhombic form of the compound which, except for $5NaF\cdot 9LuF_3$, is also unstable at lower temperatures with respect to $NaF\cdot LnF_3$ and LnF$_3$.

The dimensions of the crystal unit cells of the compounds observed in the NaF–LnF$_3$ systems vary monotonically with increasing atomic number of the lanthanides. Refractive indices, however, reach their maximum values for the phases in the NaF–PrF$_3$ system. Standard values for the crystallographic properties of NaF–LnF$_3$ phases, as measured in the current study, are given in Table II. These data reveal the effect of the lanthanide contraction on the crystal properties of the fluorides. Of interest is the marked effect of polarizability of lanthanide ions on refractive indices of complex compounds. As the radius of the tripositive ion decreases, refractive indices of isostructural phases also decrease, although densities of these phases increase. Levin[13] noted corresponding behavior in the rare earth oxides. Comparisons of refractive indices and densities of the lanthanide fluoride complex compounds and trifluorides are shown in Table II.

Optical data were obtained for the room-temperature forms of the lanthanide trifluorides, for which LaF$_3$ to SmF$_3$ are hexagonal and GdF$_3$ to LuF$_3$ are orthorhombic. Current results of an investigation of LnF$_3$ dimorphism[14] confirmed Zalkin and Templeton's conclusion that the hexagonal form of the heavier lanthanides is the high-temperature modification. The NaF–LnF$_3$ phase diagrams reported here are drawn so as to indicate the hexagonal–orthorhombic inversion.

A salient feature of the NaF–LnF$_3$ systems is the unusual behavioral sequence produced by the compositional variability of the fluorite-like phases. This behavior shows the remarkable effect of cation size and polarizability in lanthanide systems. As shown in Figure 1, the cubic phase is not formed at all in the systems NaF–LaF$_3$ and NaF–CeF$_3$, is formed by NaF and PrF$_3$, and is extended to an increasingly broad composition range throughout the rest of the system sequence. That equilibrium occurrence of the compositionally variable cubic phase is a size-related phenomenon and is not restricted to the lanthanide- or NaF-based systems was verified by tests with binary mix-

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(13) E. M. Levin, "Refractivities of the Rare Earth Oxides," Proceedings of the Third Rare Earth Conference, Clearwater, Fla., April 21–24, 1963.

(14) G. D. Brunton and R. E. Thoma, unpublished data.

tures of NaF–BiF_3 and KF–LaF_3, whose $Na^+:M^{3+}$ cation radius ratios, 1.05 and 1.25, are comparable to those of the NaF–LnF_3 pairs. In both systems hexagonal and cubic analogs of the NaF–LnF_3 phases were observed.

Previously, it was noted that a solid phase occasionally was nucleated metastably[2a] when NaF–YF_3 melts containing 35 to 40 mole % YF_3 were rapidly cooled. The phase was found to be metastable with respect to the equilibrium solids NaF and NaF·YF_3. In the present investigation a corresponding phase was found to form metastably in the NaF–ErF_3 to NaF–LuF_3 systems. Its formula is tentatively regarded as 5NaF·3LnF_3. Crystals of the YF_3 member have been indexed as orthorhombic,[15] with lattice constants a_0 = 6.24, b_0 = 3.88, and c_0 = 5.82 A, and have a mean refractive index of 1.422.

In attempts to produce the hexagonal form of NaF·LuF_3, we found that this phase was difficult to nucleate because of the slow transformation rate of the cubic solid solution phase. As the cubic phase transformed partially to the hexagonal NaF·LuF_3, we found that at least one metastable solid phase was formed during the process. Because the metastable material was poorly crystallized and of low symmetry, it was not possible to ascertain whether one or more discrete phases were formed.

Apart from the formation of the nonequilibrium solids described above, metastable nucleation in the NaF–LnF_3 systems was not noted. The solid-state transformations require long periods for equilibrium to be attained, but, in general, proceed without generating metastable phases.

Several trends are developed in the NaF–LnF_3 systems as $Na^+:Ln^{3+}$ size disparity increases and as tripositive ion polarizability decreases. As predicted,[16] there is a marked tendency for the total number of intermediate crystal phases produced by the interactions of a given NaF–LnF_3 component pair to increase throughout the series. A trend also develops toward broadening the composition limits and extension of the temperature range through which the cubic and orthorhombic phases are stable. The trends toward increasing number, compositional variability, and stability of the NaF–LnF_3 crystal phases appear to be distinct, not only with respect to the crystal chemistry of the complex compounds but also in their modes of crystallization from molten mixtures. The cubic solid solution phase, for example, has no equilibrium stability below approximately 500° with respect to the hexagonal NaF·LnF_3 and LnF_3 phases but is increasingly easier to retain metastably in cooled melts of appropriate compositions in the system group NaF–DyF_3 to NaF–LuF_3. This tendency is so marked that in the NaF–LuF_3 system the cubic phase can be crystallized from the melt even under slow-cooling conditions. These trends are believed to be indicative of an increase in the lattice energies of the crystalline phases resulting from the lanthanide contraction and of a corresponding decrease in polarizability. The decrease in polarizability is probably the most influential factor in enabling compositional variability of the phases to be extended with increasing atomic number of the lanthanide. The more polarized ions of the lighter lanthanides should tend to form crystalline phases of fixed stoichiometry, while the less polarized ions, by being more electronically symmetrical and of smaller size than Na^+, should exhibit less selectivity for given whole-number stoichiometric ratios. The vertical phase boundary at the 5NaF·9LnF_3 composition represents LnF_3 saturation of the fluorite-like phase. Presumably, the equimolar composition represents a packing limit for Na^+ in hexagonal NaF·LnF_3 as well. Considered as resulting directly from size and polarizability factors, the trends in the NaF–LnF_3 systems, as discussed above, appear to be surprising chiefly in the gross influence these factors play in affecting phase behavior and crystal chemistry.

Size factors alone dictate that fluorite-like phases should also be found in the actinide systems NaF–UF_3 and NaF–PuF_3, where, in fact, no such phases have been observed. The absence of cubic phases in the actinide systems may be attributed to polarizability of the actinide ions. As evidenced by trends in the molar refractivities of the lanthanide and actinide fluoride compounds, reduction in polarizability of the actinides corresponding to that in the lanthanides is not manifest. Molar refraction of NaF–LnF_3 crystalline phases decreases approximately 20% across the lanthanide series with increasing Z. Data are not available for comparison with analogous actinide phases. However, the calculated values of molar refraction for the three actinide compounds 2RbF·ThF_4, 2RbF·UF_4, and 2RbF·AmF_4 are 26.50, 32.27, and 28.98 cc, respectively. We infer from the trend in these values that reduction in polarizability of the trivalent actinide ions does indeed occur with increasing atomic number but that the decrease begins with the series rather than initially as in the rare earth group. Assuming that polarizability of the heavy-metal ions influences formation of the cubic phase in a significant way, it is anticipated that such phases will occur with the heavier actinides. Comparisons of the available information on the trifluoride systems of the lanthanides and actinides indicate that, although the systems are not exact analogs, they are sufficiently similar to permit qualitative estimates concerning the characteristics of the sodium fluoride–actinide trifluoride systems. The fact, for example, that all of the sodium fluoride–heavy metal trifluoride systems in the $Na^+:M^{3+}$ cation size ratio 0.93 to 1.21, including all of the NaF–LnF_3 systems, NaF–BiF_3, NaF–UF_3, and NaF–PuF_3, form the hexagonal NaF–MF_3 phase indicates that this phase is to be expected throughout the sodium fluoride–actinide trifluoride series.

Crystal Structures.—Three types of equilibrium crystalline phases are produced from the reactions of NaF with the lanthanide trifluorides, a hexagonal NaF·LnF_3 phase, a compositionally variable high-tempera-

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(15) J. H. Burns, unpublished data.

(16) R. E. Thoma, *Inorg. Chem.*, **1**, 220 (1962).

ture cubic phase, and an orthorhombic $5NaF \cdot 9LnF_3$ phase. In addition, two metastable solids have been observed: an orthorhombic phase, $5NaF \cdot 3LnF_3$, and an $NaF \cdot LnF_3$ phase of low but unknown symmetry. Structural studies of the equilibrium solids show that in all $NaF–LnF_3$ crystal phases the cation lattices are partially or extensively disordered. For systems in which the $Na^+:Ln^{3+}$ cation ratio is unity or slightly less, entropy-related disordering at elevated temperatures is great, and the least ordered crystalline solids, the cubic and orthorhombic phases, do not form. The trend toward their formation as cation size disparity increases is evident in Figure 1.

Hexagonal $NaF–LnF_3$ Compounds.—The crystal structure of $NaF \cdot NdF_3$ was described by Burns[11] as consisting of an ordered array of F^- ions interspersed with cations on three types of sites. Two-thirds of the Nd^{3+} ions occupy one kind of site; one-third of the Na^+ ions are randomly mixed in a second site; and two-thirds of the Na^+ ions are randomly distributed with vacancies on a third kind of site. Examination of single crystals of this phase containing each of the lanthanides (except Yb and Lu) and Y showed them to be essentially isostructural. A change in space group, observed in some cases, was attributed to intermixing of cations between the first two kinds of sites.[11] We have made X-ray powder diffractometric measurements of the entire series of compounds and have obtained refined lattice parameters by least squares. The results are shown in Table II. Some of the compounds were measured previously by Roy and Roy;[10] our values are in agreement with theirs.

Cubic $NaF–LnF_3$ Compounds.—The structure of $NaYF_4$, established by Hund,[17] is typical of the cubic form of $NaF–LnF_3$ cubic phases. It is of the CaF_2 (fluorite) type (Figure 2), with the Ca^{2+} ionic sites randomly occupied by Na^+ and Ln^{3+} ions. The isomorphism of the high-temperature $NaF–LnF_3$ cubic phases with $NaYF_4$, for Ln = Nd to Lu, has been determined by X-ray powder diffraction; values for a_0 at equimolar compositions are given in Figure 3, and a_0 values at the phase composition limits are given in Table II.

For this structure the unit-cube dimension can be calculated from the ionic radii.[18] Fair agreement between observed and calculated lattice constants, Figure 3, is achieved if the radius, $r(\mathrm{Na, Ln})$, of the ion is assumed to have the following values: for $r(\mathrm{Ln}) > r(\mathrm{Na})$, $r(\mathrm{Na, Ln}) = r(\mathrm{Ln})$, and for $r(\mathrm{Ln}) < r(\mathrm{Na})$, $r(\mathrm{Na, Ln}) = {}^1/_2[r(\mathrm{Ln}) + r(\mathrm{Na})]$. The use of these radii is rationalized by noting that, when $r(\mathrm{Ln}) > r(\mathrm{Na})$, the repulsion of the trivalent ions keeps them at equilibrium distances much as if the Na ions were not present, while, for $r(\mathrm{Na}) > r(\mathrm{Ln})$, the larger Na ion is compressed by the Ln–F attractive forces to the extent that an average cation radius is attained. Thus, because of the disorder among the cations, the lanthanide contraction is less pronounced in the present group than would be the case in a comparable isomorphous series of ordered crystals.

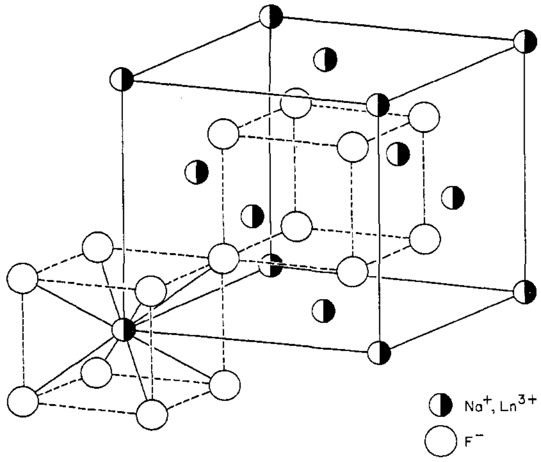

Figure 2.—Structure of cubic $NaLnF_4$. Equal numbers of F^- cubes (dotted lines) contain cations and vacancies.

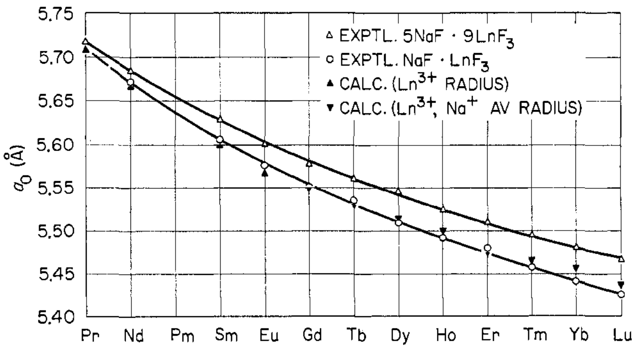

Figure 3.—Unit-cell constants of $NaF \cdot LnF_3$ and $5NaF \cdot 9LnF_3$.

In the fluorite structure each cation, such as the one at the origin of the unit cell, Figure 2, is coordinated by a cube of F^- ions, but, for each cube with a cation at its center, there is another which is empty, such as the one at the center of the unit cell. It was shown by Hund[19] that the solution of YF_3 in cubic $NaYF_4$ occurs by substituting Y^{3+} for Na^+ ions and by filling some of the vacancies with F^- ions to produce electroneutrality. We have found that the limit of substitution is at the composition $5NaF \cdot 9YF_3$ and that this phase region exists in all of the $NaF–LnF_3$ systems which contain a fluorite-like phase. The unit-cell constants for these compounds are given in Table II and Figure 3. Their larger values relative to the corresponding $NaLnF_4$ compounds are due to the lattice stuffing.

As represented by the Lorentz–Lorenz equation, molar refraction approximates the volume occupied by the constituent ions in crystalline phases. A measure of the crystal free space can therefore be estimated from the difference between molar volume, as computed from unit-cell dimensions, and the molar refraction. As the atomic number increases, small increases in the free space fraction are noted for the lanthanide trifluorides and for hexagonal $NaF \cdot LnF_3$ phases (Table III). A more pronounced increase in free space fraction is found

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(17) F. Hund, *Z. Anorg. Allgem. Chem.*, **261**, 106 (1950).

(18) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).

(19) F. Hund, *Z. Anorg. Allgem. Chem.*, **263**, 102 (1950).

Table III

Molar Volumes and Free Space for Some LnF_3 Compounds

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
A. Lanthanide Trifluorides														
U.C.V.[a]	54.79	53.14	52.29	51.36	51.85	51.08	50.40	49.60	48.80	48.20	47.63	47.15	46.75	46.43
M.V.[b]	33.00	32.01	31.49	30.93	31.23	30.77	30.36	29.87	29.39	29.03	28.69	28.40	28.16	27.30
M.R.[c]	11.30	11.10	10.90	10.70	10.36	10.20	10.00	9.80	9.62	9.45	9.25	9.06	8.88	8.68
M.F.S.[d]	21.70	20.91	20.59	20.21	20.87	20.57	20.36	20.07	19.77	19.58	19.44	19.34	19.28	18.62
% F.S.[e]	65.76	65.32	65.39	65.34	66.83	66.85	67.06	67.19	67.27	67.44	67.76	68.10	68.47	68.20
B. Tetragonal $LiF \cdot LnF_3$														
U.C.V.	-	-	-	-	-	74.78	74.65	73.33	72.79	71.56	71.24	70.54	69.95	69.41
M.V.	-	-	-	-	-	45.04	44.96	44.17	43.84	43.10	42.91	42.49	42.13	41.81
M.R.	-	-	-	-	-	12.87	12.78	12.64	12.57	12.28	12.24	12.05	11.91	11.79
M.F.S.	-	-	-	-	-	32.07	32.18	31.53	31.27	30.82	30.67	30.44	30.22	30.02
% F.S..	-	-	-	-	-	71.20	71.57	71.38	71.32	71.50	71.47	71.64	71.73	71.80
C. Hexagonal $NaF \cdot LnF_3$														
U.C.V.	83.65	81.94	80.76	79.72	76.73	76.19	75.34	74.60	73.49	73.10	72.04	71.48	70.44	69.77
M.V.	50.38	49.35	48.64	48.02	46.21	45.89	45.38	44.93	44.26	44.03	43.39	43.05	42.43	42.02
M.R.	14.65	14.55	14.45	14.25	13.72	13.55	13.25	13.15	12.98	12.92	12.60	12.45	12.18	12.05
M.F.S.	35.73	34.80	34.19	33.77	32.49	32.34	32.12	31.78	31.28	31.11	30.79	30.60	30.25	29.97
% F.S.	70.92	70.52	70.29	70.33	70.31	69.00	70.78	70.73	70.67	70.65	70.96	71.08	71.29	71.32
D. Cubic $NaF-LnF_3$ (Equimolar) s.s.														
U.C.V.	-	-	-	-	-	-	-	84.78	83.41	82.73	82.06	81.39	80.49	79.83
M.V.	-	-	-	-	-	-	-	51.06	50.24	49.83	49.42	49.02	48.48	48.08
M.R.	-	-	-	-	-	-	-	14.11	13.85	13.51	13.20	12.89	12.71	12.46
M.F.S.	-	-	-	-	-	-	-	36.95	39.39	46.32	36.22	36.11	35.77	35.62
% F.S.	-	-	-	-	-	-	-	72.36	72.43	72.89	73.29	73.66	73.78	74.08
E. Cubic $5NaF \cdot 9LnF_3$														
U.C.V.	-	-	-	-	-	-	-	86.17	85.34	84.33	83.82	82.87	82.28	81.52
M.V.	-	-	-	-	-	-	-	51.90	51.40	50.79	50.49	49.91	49.56	49.10
M.R.	-	-	-	-	-	-	-	18.77	18.60	18.24	17.98	17.59	17.50	17.35
M.F.S.	-	-	-	-	-	-	-	33.13	32.63	32.59	32.51	32.32	32.06	31.75
% F.S.	-	-	-	-	-	-	-	63.83	63.48	64.17	64.39	64.76	64.69	64.66

[a] Unit-cell volume ($\times 10^{-24}$ cm.^{3}). [b] Molar volume (cm^3). [c] Molar refraction (cm^3). [d] Molar free space (cm^3). [e] % free space.

for the fluorite-like $NaF-LnF_3$ phases, with an even greater increase in the free space fraction for the equimolar cubic phases than for the cubic $5NaF \cdot 9LnF_3$ phases as Z increases. Substitutional solution of Ln^{3+} into the fluorite unit cell gives rise to cation vacancies but is partly compensated for by the filling of interstitial positions with fluoride ions as described by Roy and Roy.[10] The fact that the space fraction occupied by the ions in the cubic structure at the $5NaF \cdot 9LnF_3$ saturation limit is greater than at the equimolar composition lends additional evidence to the validity of the interstitial fluorine model for solution mechanism. We conclude that the combined effect of the reduction in polarizability of the lanthanide ions and the increase in free space within the crystal lattice is to reduce the specificity of Na^+ and Ln^{3+} ions with regard to the cation sites they occupy in fluorite-like, orthorhombic, and hexagonal crystals. The consequence of this effect is thereby to increase the compositional variability of the crystal phases observed in the $NaF-LnF_3$ systems with increasing atomic number of the lanthanide.

Orthorhombic $5NaF \cdot 9LnF_3$ Compounds.—As temperature is lowered, the cubic phases $5NaF \cdot 9LnF_3$ to $5NaF \cdot LuF_3$ undergo a solid-state transition and invert from cubic to orthorhombic symmetry. The low-temperature modification exhibits an X-ray diffraction powder pattern which is consistent with a cubic unit cell of approximately the same dimension as that of the high-temperature form, but the space lattice has changed from face-centered to primitive. In this form the cations have segregated into definite crystallographic sites, thus lowering the symmetry. Incomplete results of a current investigation of single crystals of orthorhombic $5NaF \cdot 9LnF_3$[20] show that the diffraction symmetry of $5NaF \cdot 9LuF_3$ is Cmmm. The space groups consistent with this diffraction symmetry are Cmmm, C222, and Cmm2 or the other axial variations of Cmm2. The orthorhombic cell has dimensions obtained in measurements of the single crystals: $a = 7.74$, $b = 38.5$, and $c = 5.52$ A. Ideally, the relationships among the unit-cell dimensions are such that $a = \sqrt{2}c$ and $b = 5\sqrt{2}c$. Since c has the value of the fluorite-cell parameter, it is not unreasonable to expect that the fluorite structure remains and the eight anions surround the cation sites as in that structure. The orthorhombic symmetry and the long dimensions of the unit-cell parameters are then caused by an ordering of the cations.

Phase Change and Structure.—Some of the features of the $NaF-LnF_3$ phase diagrams can be explained from a crystal-chemical viewpoint. At the higher temperatures the fluorite-like phase occurs (for Ln = Nd to Lu) with randomized distribution of cations on certain sites. The eight-coordinated holes can accommodate F^- ions to a certain extent, so that substitutional (cation) and interstitial (anion) solid solution occurs to a limit of $5NaF \cdot 9LnF_3$. As the temperature is lowered, differently charged and sized cations tend to find different environments and, hence, to segregate. At least three recognizable influences are considered as contributory to the solid-state phase behavior involving the cubic, hexagonal, and orthorhombic phases. As

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(20) H. Steinfink, University of Texas, and G. D. Brunton, Oak Ridge National Laboratory, unpublished results, 1964.

temperature is lowered, the kinetic energy is lowered and there is greater tendency for ordering of the cations resulting in the separation of crystalline phases with definite stoichiometry. Cooling NaF–LnF$_3$ mixtures reflects this tendency by exhibiting the exsolution behavior which occurs as is indicated by the lower temperature phase boundary of the cubic phase. A somewhat opposite tendency is introduced as the reduction in polarizability of the lanthanide (with increasing atomic number of Ln) tends to allow increasing compositional variability in the low-temperature hexagonal and orthorhombic crystalline phases.

Stoichiometry of $5Na \cdot 9LnF_3$.—The formula of this phase has been established by entirely empirical microscopic and X-ray diffraction analytical methods which are considered to be accurate within ±0.5 mole %. Investigation of the structure of the orthorhombic form of the compound has not yet advanced to the point that the exact stoichiometry is certain. Accordingly, confirmation of the formula of this compound necessitates completion of the structural investigation currently in progress.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Contrasting Behavior of Boron Trifluoride and Phosphorus Pentafluoride toward Sulfolane[1]

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Sulfolane forms a 1:1 complex with boron trifluoride. The complex has $\delta^{19}F = +144.1$ ppm (δ relative to CCl_3F) and $\delta^{11}B = +19.2$ ppm (δ relative to trimethyl borate). In contrast to this, sulfolane forms no stable solid complex with phosphorus pentafluoride, though the ^{19}F resonance shows evidence of interaction and of P–F bond breaking.

Introduction

Sulfolane has been found to be a good aprotic solvent, dissolving molecular and ionic substances[3] without being attacked by even such strongly reactive species as the nitronium ion.[4] In this laboratory it has been used for nmr studies of pyridine–Lewis acid adducts[5] because its very low proton basicity ($pK_{BH^+} = -12.88$)[6] suggested that it might be a very weak Lewis base, unable to displace a strong base, such as pyridine, from its adducts with Lewis acids.

However, despite some reported failure[7] to prepare adducts of Lewis acids with sulfones, Lindqvist and Einarsson[8a] have prepared solid adducts of dimethyl and diphenyl sulfones with antimony tri- and pentachloride, the structure of $Me_2SO_2 \cdot SbCl_5$ having been determined,[8b] and Langford and Langford[9] succeeded in preparing weak hygroscopic complexes of sulfolane itself with anhydrous cobalt(II) salts. More recently Laughlin[10] has found that 1 mole of methyl *n*-dodecyl sulfone dissolved in benzene would take up 1 mole of boron trifluoride, though he could isolate no solid complex, and Drago, *et al.*,[11] found spectroscopic evidence for charge-transfer interaction with iodine. Lastly, in a footnote, Alder and Whiting[12] observed that sulfolane and boron trifluoride react to give a solid product.

These findings suggested that although sulfones are such weak Brønsted bases that they are not protonated in 100% H_2SO_4, they may be good Lewis bases. Accordingly, it was decided to investigate the action of boron trifluoride and phosphorus pentafluoride on sulfolane.

Experimental Section

Sulfolane (kindly supplied by the Shell Chemical Co., Shell Center, London S.E.1, U. K.) was purified in 500-ml batches by first treating with 25 ml of "100 volume" hydrogen peroxide and 25 ml of 96% H_2SO_4, which together oxidize any sulfoxide present. The remaining hydrogen peroxide and water were distilled off under vacuum and then the main body of solvent was collected by vacuum distillation, bp 90–100° (4–7 mm), dry nitrogen being passed through the vacuum leak. This sulfolane, now water-

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[1] Tetrahydrothiophene 1,1-dioxide; tetramethylene sulfone.

[2] ICI Research Fellow. This work was supported by the University of Sheffield. Thanks are expressed to the Shell Chemical Co. for a gift of sulfolane.

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