phases was to reduce the polarizability of the rare earth cations significantly, whereas in the absence of this effect, relative polarizability of Sc^{3+} and Al^{3+} is great, and strongly bonded complex compounds with little compositional variability may be formed.[18] On the basis of this inference, phase diagrams of the binary systems of NaF with the group III fluorides, GaF_3, InF_3, and possibly TlF_3, should resemble that for NaF–ScF_3 rather than those of NaF with the heavier lanthanide trifluorides.

Acknowledgments.—The authors are pleased to acknowledge the assistance of G. M. Hebert and H. A. Friedman in the experimental work, T. N. McVay and H. Insley for measurements of optical properties, and J. H. Burns, G. D. Brunton, and D. R. Sears for assistance with the X-ray measurements.

[18] The relationship between polarizabilities in complex fluorides was discussed in ref 4.

CONTRIBUTION FROM THE REACTOR CHEMISTRY DIVISION,
OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE

Equilibrium Dimorphism of the Lanthanide Trifluorides[1a]

BY R. E. THOMA AND G. D. BRUNTON

Received June 3, 1966

The lanthanide trifluorides SmF_3 to LuF_3 and YF_3 were found to undergo high-temperature dimorphism, inverting from hexagonal to orthorhombic crystals on cooling. Equilibrium inversion temperatures were determined for this group using a controlled-atmosphere, high-temperature X-ray diffractometer and were found to lie in the temperature range from 555° for SmF_3 to 1075° for ErF_3. Dimorphism was not observed for the compounds LaF_3 to NdF_3. A hexagonal modification of yttrium trifluoride, not heretofore described, was found to be the stable phase above 1052° and below the melting point. Although the hexagonal and orthorhombic forms of the lanthanide trifluorides SmF_3 to HoF_3 correspond to those described earlier by Zalkin and Templeton,[1b] hexagonal crystals of YF_3 and the lanthanide trifluorides ErF_3 to LuF_3, observed at high temperatures, were not isomorphous with tysonite, as was previously believed.

Introduction

The occurrence of dimorphism among the lanthanide trifluorides was first recognized by Zalkin and Templeton.[1b] They observed that at room temperature the trifluorides LaF_3 to NdF_3 occurred only in a hexagonal form, that SmF_3, EuF_3, HoF_3, and TmF_3 could be obtained either as the hexagonal ($P\bar{3}c1$) or orthorhombic form (Pnma), and that only an orthorhombic form of GdF_3, TbF_3, DyF_3, ErF_3, YbF_3, and LuF_3 could be produced. Melting points of the lanthanide trifluorides were determined later by Spedding and Daane,[2] who noted that SmF_3, GdF_3, ErF_3, YbF_3, and LuF_3 produced thermal effects at temperatures below the melting points. They inferred that these effects were the result of solid-stage crystalline inversions. Evidence of dimorphism was noted by both groups of investigators for SmF_3, by one or the other for EuF_3 to LuF_3, and by neither for LaF_3 to NdF_3, TbF_3, or DyF_3.

In recent investigations of the alkali fluoride–lanthanide trifluoride systems[3] we found that, as NaF–GdF_3 and NaF–TbF_3 mixtures crystallize from the molten state, the trifluoride components invert from the hexagonal (high-temperature) to the orthorhombic (low-temperature) form at 918 and 950°, respectively. Although these values are somewhat lower than those reported by Spedding and Daane for the transition temperatures, they are in sufficiently close agreement to suggest that the thermal effects they observed in the solid state resulted from the hexagonal–orthorhombic transition. We were unable to preserve hexagonal modifications of DyF_3, ErF_3, YbF_3, and LuF_3 on rapid cooling of NaF–LnF_3 mixtures. The results obtained in recent investigations of these and the LiF–LnF_3 systems at this laboratory strongly suggested that all of the lanthanide trifluorides may exhibit equilibrium dimorphic transitions at high temperatures. To test this possibility, we investigated the high-temperature behavior of each of the lanthanide trifluorides (excluding PmF_3) and YF_3 in a controlled-atmosphere X-ray diffractometer.

Experimental Section

The lanthanide trifluorides used in the present study were prepared and purified in this laboratory by conversion of the commercial oxides with ammonium bifluorides. Yttrium fluoride was obtained by the same procedures, described earlier,[4,5] which assure that the oxide contamination does not exceed approximately 300 ppm. The lanthanide oxides used for preparing the trifluorides were obtained from several commercial vendors; cationic purity nominally exceeded 99.9%. The results of

---

[1] (a) Research supported by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.; (b) A. Zalkin and D. H. Templeton, *J. Am. Chem. Soc.*, **75**, 2453 (1953).

[2] F.H. Spedding and A. H. Daane, Ed., "The Rare Earths," John Wiley and Sons, Inc., New York, N. Y., 1961, p 78.

[3] R. E. Thoma, H. Insley, and G. M. Hebert, *Inorg. Chem.*, **5**, 1222 (1966).

[4] J. Walker and E. Olson, "Preparation of Yttrium Fluoride Using Ammonium Bifluoride," USAEC, IS-2, 1959.

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

Table I

Crystal Data for the Rare Earth Trifluorides

	Hexagonal modification							Orthorhombic modification[a]			
						Transition temp, °C					
Formula	Opt char	N_ω	N_ϵ	a_0	c_0	Mp	$H \rightleftharpoons O$	Opt char	$2V$	N_α	N_γ
LaF_3	U−	1.603[b]	1.597[b]	7.186[b]	7.352[b]	1493[c]					
CeF_3	U−	1.613	1.607	7.112[d]	7.279[d]	1430[c]					
PrF_3	U+	1.614	1.618	7.075[d]	7.238[d]	1395[c]					
NdF_3	U−	1.628[b]	1.621[b]	7.030[b]	7.200[b]	1374[c]					
SmF_3				7.07 ± 0.01	7.24 ± 0.01	1306[c]	555	B−	72°	1.577	1.608
EuF_3				7.04 ± 0.01	7.26 ± 0.01	1276[c]	700	B+	85°	1.572	1.600
GdF_3				7.06 ± 0.01	7.20 ± 0.01	1231[c]	900	B−	85°	1.570	1.600
TbF_3				7.03 ± 0.01	7.10 ± 0.01	1172[c]	950	B−	80°	1.570	1.600
DyF_3				7.01 ± 0.01	7.05 ± 0.01	1154[c]	1030	B−	85°	1.570	1.600
HoF_3				7.01 ± 0.01	7.08 ± 0.01	1143[c]	1070	B−	~90°	1.566	1.598
ErF_3				6.97 ± 0.01	8.27 ± 0.01	1140[c]	1075	B−	80°	1.566	1.598
TmF_3				7.03 ± 0.01	8.35 ± 0.01	1158[c]	1030	B−	~90°	1.564	1.598
YbF_3				6.99 ± 0.01	8.32 ± 0.01	1157[c]	985	B+	85° [b]	1.558[b]	1.594[b]
LuF_3				6.96 ± 0.01	8.30 ± 0.01	1182[c]	945	B+	85°	1.554	1.588
YF_3				7.13 ± 0.01	8.45 ± 0.01	1144	1052	B−	85° [b]	1.536[b]	1.569[b]

[a] X-Ray diffraction data given in: ref 1b; H. E. Swanson, *et al.*, National Bureau of Standards Monograph No. 25, U. S. Government Printing Office, Washington, D. C., 1964; National Bureau of Standards Circular No. 539, U. S. Government Printing Office, Washington, D. C., Vol. 5, 1955; Vol. 7, 1957; and Vol. 8, 1959. [b] E. Staritzky and L. B. Asprey, *Anal. Chem.*, **29**, 855 (1957). [c] Reference 2. [d] See references to Swanson, *et al.*, in footnote *a*.

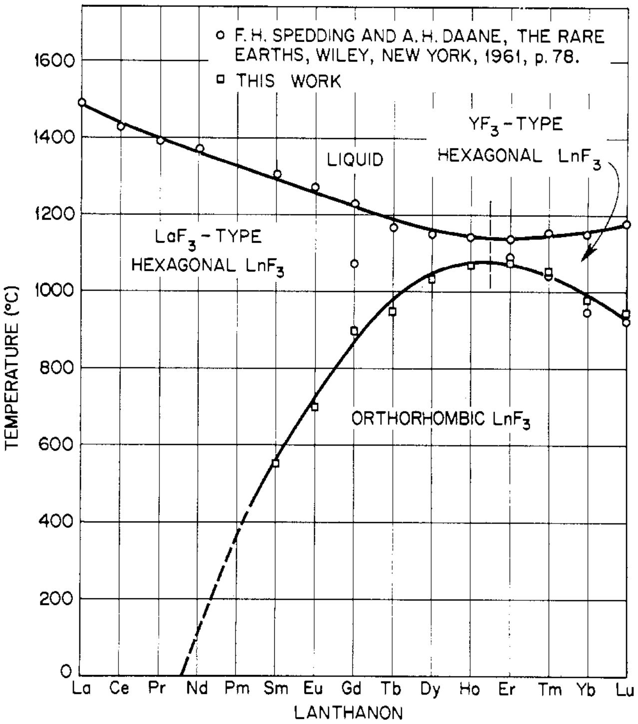

Figure 1.—Dimorphism among the rare earth trifluorides.

emission spectrographic analyses obtained in this laboratory[6] do not, in general, corroborate the manufacturers's claims as to purity but indicate rather that contamination by other rare earths is occasionally as much as 0.3%. The accuracy of transition temperature measurements is, of course, sensitive to cationic as well as to anionic impurity of the reagents. Considerable imprecision is intrinsic also in the thermometric methods employed in routine use of high-temperature diffractometers.

Determinations of dimorphic transition temperatures were made using an MRC high-vacuum X-ray diffractometer attachment mounted on a Norelco goniometer. Pressures were monitored by use of a Veeco ionization gauge and were maintained at $4–6 \times 10^{-6}$ torr (instrument readings) throughout each experiment. The camera was modified to include a cold finger which was filled with liquid nitrogen before high-temperature experiments were conducted. The presence of the cold trap within the camera was beneficial not only in minimizing the moisture but also in reducing the period required to achieve good vacuum within the camera. Temperatures were measured by means of a platinum—platinum–rhodium thermocouple welded to the underside of the platinum hot stage of the instrument. Thermocouple voltages were read to ±0.01 mv; the reference temperature was the triple point of water. Specimens used in these experiments were approximately 0.3 g in weight.

Transition temperatures of the rare earth trifluorides were calibrated by use of the well-established inversion of YF_3 which occurs at 1052°. The mean value of eight measurements of the YF_3 phase transition temperature using our apparatus was 1029 ± 6°, the deviations representing 95% confidence limits. Measured transition temperatures for the lanthanide trifluorides were corrected by +23° on the basis of these calibrations.

Lattice constants of the high-temperature modifications were measured at temperatures of 10–15° above the hexagonal $\rightleftharpoons$ orthorhombic phase transition.

The quantitative effects of cationic impurities were not clearly assignable in this study. In attempts to ascertain whether the influence of small amounts of metal ion impurities on transition temperatures could be detected, we also examined the dimorphic transition using single crystals of GdF_3 and DyF_3[7] which were of higher purity than the polycrystalline materials. In examining the crystal symmetry changes with single crystals, it became evident that the diffraction patterns were more clearly resolved initially but deteriorated to such an extent on continued cycling that comparisons of transition temperatures, based on purity alone, could not be made.

Results

The composition–temperature relationships of the dimorphic forms of the lanthanide trifluorides are shown in Figure 1. Crystallographic data and transition temperatures (±6°, at 95% confidence limits) are listed in Table I. Dimorphism was not observed in the group of lanthanide trifluorides LaF_3 to NdF_3. The trend of increasing temperatures for the hexagonal $\rightleftharpoons$ orthorhombic transition found in the group SmF_3 to HoF_3 led us to believe that NdF_3 might invert to the orthorhombic form at low temperatures. How-

---

[6] Analyses were provided through the courtesy of the ORNL Analytical Chemistry Division.

[7] Single crystals of GdF_3 and DyF_3 were furnished for this study through the courtesy of H. Muir, representing Varian Associates, Palo Alto, Calif.

ever, attempts to induce the transformation by equilibration of NdF_3 at liquid nitrogen temperature for 0.5-hr periods were unsuccessful. The trend indicates, nevertheless, that NdF_3 as well as the lighter lanthanide trifluorides may undergo equilibrium dimorphism at low temperatures. The hexagonal and orthorhombic forms of SmF_3 to HoF_3 were found to be identical with those described by Zalkin and Templeton.[1b] Refractive indices of the room-temperature forms are shown in Figure 2. We found that the diffraction patterns of crystalline YF_3 and of the trifluorides ErF_3 to LuF_3, recorded at temperatures above the solid-state transition values indicated in Figure 1 and Table I, were of hexagonal phases which cannot be described by the space group of tysonite, $P\bar{3}c1$.[8] The X-ray powder diffraction for the high-temperature modification of YbF_3 is contrasted in Figure 3 with the powder pattern for the tysonite form of NdF_3. Assignment of hexagonal symmetry to the high-temperature forms of YF_3 and the lanthanide trifluorides ErF_3 to LuF_3 is tentative because crystals of these phases are so unstable below their inversion temperatures that only the limited diffraction data which can be obtained within the restricted goniometric range of the high-temperature diffractometer may be used.

Within each group of the lanthanide trihalides, the lowest melting member of each group is found with increasing z in the order: $I^-(Pr^{3+})$, $Br^-(Sm^{3+})$, $Cl^-(Dy^{3+})$, $F^-(Er^{3+})$. Dimorphism of only the fluorides has been examined. Here, perhaps fortuitously, it is found that the trihalide member which exhibits the minimum melting point is also the member which exhibits the highest inversion temperature. In the trifluoride series this discontinuity also denotes a change in the crystal structure of the high-temperature form. This phenomenon possibly is evidence that a minimum in the lattice energy of the hexagonal crystals is induced by the lanthanide contraction to the point that the prevailing structure is distorted and transforms to a more stable symmetry with further increase in the atomic number.

We have attempted unsuccessfully to obtain single crystals of the hexagonal phases formed by YF_3 and the heavier lanthanide trifluorides. Although these phases nucleate readily from melts of their own composition or from mixtures, they invert to their orthorhombic low-temperature modifications extremely rapidly. The transformation is so energetic that we have not found it possible to retain the high-temperature phases by rapidly quenching either the pure fluorides or molten alkali fluoride–lanthanide trifluoride mixtures saturated with the trifluoride. An effort is being made[9] to obtain more precise and extensive information concerning the hexagonal YF_3 type of lanthanide trifluorides with a high-temperature microfocusing diffractometer.

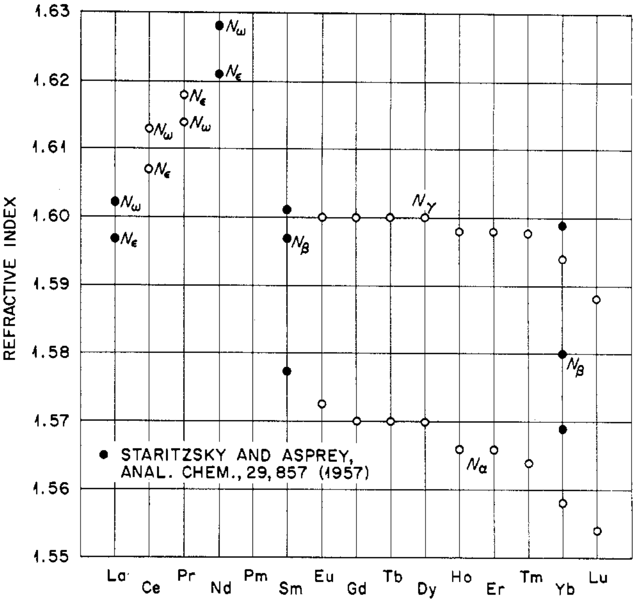

Figure 2.—Refractive indices of the rare earth trifluorides.

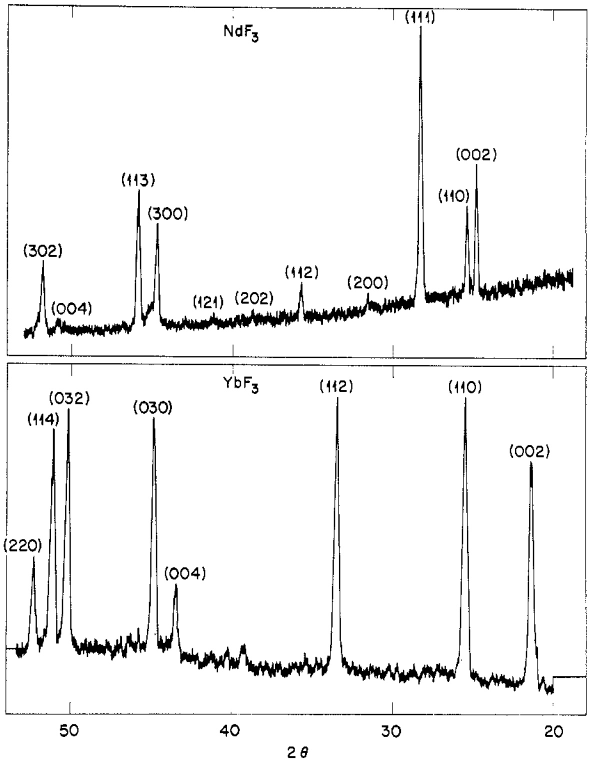

Figure 3.—Comparison of the Cu Kα X-ray powder diffraction patterns of hexagonal YbF_3 and the tysonite form of NdF_3.

---

(8) V. M. Mansmann, *Z. Krist.*, **122**, 375 (1965).

(9) T. Hahn, Institut fur Kristallographie, Technische Hochschule, Aachen, Germany.