sodium perchlorate solutions. This difference in $\mathring{a}$ values is in good agreement with that found by Näsänen[16] in his study of the dissociation of $CuSO_4$ He found that in potassium sulfate $\mathring{a}$ is 15.4% higher than in sodium perchlorate solutions; this is to be compared with 14.7% for the corresponding difference in the dissociation of $CeSO_4^+$.

It should be pointed out that at zero as well as unit ionic strength $LaSO_4^+$ is more stable than $CeSO_4^+$. Thus, for the dissociation of $LaSO_4^+$ at zero ionic strength, Davies[17] reported 2.2×10^{-4} on the basis of solubility measurements and Jenkins and Monk[18] reported 2.4×10^{-4} on the basis of conductivity measurements. At zero ionic strength the dissociation constant for $LaSO_4^+$ is 44% smaller than the dissociation constant for $CeSO_4^+$. At unit ionic strength Mattern[12] reported 25 for the association quotient or 0.040 for the dissociation quotient of $LaSO_4^+$. This result was obtained by an indirect spectrophotometric method. At this ionic strength the dissociation quotient for $LaSO_4^+$ is 32% smaller than the dissociation quotient of $CeSO_4^+$. As might be expected, the ionic strength dependences of these two equilibria are approximately the same.

Connick and Mayer[2] reported 60 for the association quotient or 0.017 for the dissociation quotient for $CeSO_4^+$ at an ionic strength of 0.5. This value is significantly smaller than 0.0296, which we have found spectrophotometrically; the reason for this discrepancy is not known.

Acknowledgments.—The authors gratefully acknowledge the many helpful discussions with, and the interest of, Dr. J. F. Lemons, under whose general direction this work was done. They also wish to acknowledge helpful discussions with Prof. G. K. Rollefson, of the University of California, and Prof. Henry Taube, of the University of Chicago.

LOS ALAMOS, NEW MEXICO

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[16] R. Näsänen, *Acta Chem. Scand.*, **3**, 959 (1949).

[17] C. W. Davies, *J. Chem. Soc.*, 2421 (1930).

[18] I. L. Jenkins and C. B. Monk, THIS JOURNAL, **72**, 2695 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Crystal Structures of YF_3 and Related Compounds

BY ALLAN ZALKIN AND D. H. TEMPLETON

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The crystal structure of YF_3 has been determined from single crystal X-ray diffraction data. It is orthorhombic, space group Pnma, with $a = 6.353$, $b = 6.850$, $c = 4.393$, $Z = 4$, and $D_x = 5.069$. The atomic parameters are similar to those in cementite, Fe_3C, but the coördination numbers are different. The unit cells have been determined for the compounds SmF_3, EuF_3, GdF_3, TbF_3, DyF_3, HoF_3, ErF_3, TmF_3, YbF_3 and LuF_3 which are isostructural with YF_3. SmF_3, EuF_3, HoF_3 and TmF_3 were also observed with hexagonal structures like that of LaF_3. Three cubic phases are tentatively identified as $NH_4Ho_3F_{10}$, $NH_4Er_3F_{10}$ and $NH_4Tm_3F_{10}$, and a structure is proposed for these and for the cubic "YF_3" of Nowacki. HoOF is cubic with a disordered CaF_2 type structure.

Introduction

In the course of a routine examination of certain rare earth fluorides by the X-ray powder diffraction method, it was found that they had a structure like that of YF_3 prepared in this Laboratory, rather than that of LaF_3. This paper reports the determination of the YF_3 structure from single crystal diffraction data and a study of rare earth fluorides by the powder method. A cubic structure was reported by Nowacki[1] for a sample thought to be YF_3, but we believe it to have been another compound for reasons which are discussed below.

Experimental

Dry Method of Synthesis.—Several milligrams of the appropriate sesquioxide contained in a platinum crucible were placed in a platinum vacuum apparatus. After evacuation, a dry mixture of hydrogen and hydrogen fluoride was passed through the system. The temperature was raised and maintained at 700° for two hours. After cooling, the apparatus was again evacuated and then opened for removal of the fluoride product.

Wet Method of Synthesis.—From 5 to 15 mg. of the appropriate oxide was dissolved in 4 ml. of 6 *M* hydrochloric acid. The solution was neutralized with 6 *M* ammonium hydroxide until the gelatinous hydroxide appeared, and a few drops of hydrochloric acid were added until the solution was again clear. The solution, in a plastic, hydrofluoric acid resistant, test-tube was heated in a boiling water-bath. One to two milliliters of concentrated hydrofluoric acid was added. After one hour of heating, the precipitate was centrifuged, washed with water and dried in air between 100 and 150°. The dried material was heated in an electric furnace in vacuum (10^{-5} to 10^{-6} mm.) to a temperature between 1000 and 1400° for one hour. In all cases the trifluorides were gray in color after heating to the high temperature, while the unheated samples were white. This observation has been made previously by others, but we know of no explanation.

Yttrium Trifluoride.—YF_3 was prepared by the dry method. To obtain single crystals, a few milligrams of the product in a platinum crucible was heated to 1400° in a vacuum (10^{-5} to 10^{-6} mm.). The temperature was lowered about 2°/min. to 1000°, then rapidly to room temperature. When the crucible was cut open, several irregular anhedral single crystal fragments were found adhering to the sides. Spectrographic and spectrophotometric analysis showed the presence of a few per cent. of rare earth impurities, chiefly dysprosium, erbium and ytterbium, in this material which was used for the single crystal work. Another sample of YF_3, prepared by the wet method from yttrium oxide containing less than 0.1% total metallic impurities, was found to have unit cell dimensions equal within experimental error to those found for the impure YF_3. Therefore it is believed that the impurities have a negligible effect on the atomic parameters.

Samarium Trifluoride.—SmF_3 prepared by the dry method one time had the orthorhombic (YF_3 type) structure, one time the hexagonal (LaF_3 type) structure, and in other cases consisted of mixtures of the two. SmF_3 prepared by the wet method after drying was hexagonal; after the high temperature heat treatment it was a mixture of both forms. The samarium used was spectrographically pure of other rare earths.

Europium Trifluoride.—EuF_3 prepared by the dry method was orthorhombic. When made by the wet method, modified in this case by omitting the ammonium hydroxide and

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[1] W. Nowacki, *Z. Krist.*, **100**, 242 (1938).

the high temperature treatment, EuF_3 was hexagonal. The europium oxide used was spectrographically pure.

Gadolinium Trifluoride.—GdF_3 prepared by both wet and dry methods was orthorhombic. The gadolinium oxide used contained 0.1% europium, 0.06% neodymium, but was spectrographically pure of other rare earths.

Terbium Trifluoride.—TbF_3 was prepared from Tb_4O_7 (containing traces of gadolinium, ytterbium and calcium) by the wet method, except that less acid was used for the first step. The dried material was orthorhombic but poorly crystallized; after heat treatment excellent patterns of the orthorhombic form were obtained.

Dysprosium Trifluoride.—DyF_3 prepared by the wet method was orthorhombic with a diffuse pattern after drying and a good pattern after heat treatment. After ten hours heating in air at 500° it was converted completely to Dy_2O_3. Spectrographic analysis of the original oxide showed 0.3% holmium and a trace of terbium.

Holmium Trifluoride.—With holmium, the wet procedure yielded, after drying, a primitive cubic phase believed to be a mixed ammonium holmium fluoride, whose structure is discussed below. After 45 min. at 1100° it was converted to a mixture of hexagonal and orthorhombic HoF_3. Powder patterns of a solid chunk showed primarily the hexagonal form, while after the material was crushed the patterns showed both forms in comparable intensity.

When sodium hydroxide was substituted for ammonium hydroxide in the wet procedure, the pattern of the product after drying was indexed as a mixture of a hexagonal phase believed to be a double sodium holmium fluoride and a cubic phase believed to be HoOF. On heating to 1300°, the sample vaporized completely and was lost. The starting material contained 0.2% of other rare earths.

Erbium Trifluoride.—With erbium, the wet method yielded a product after drying which gave a pattern very similar to that of the cubic ammonium holmium fluoride. After an hour at 1300° in vacuum, the product was converted to orthorhombic ErF_3. The starting material contained 0.1% of other rare earths.

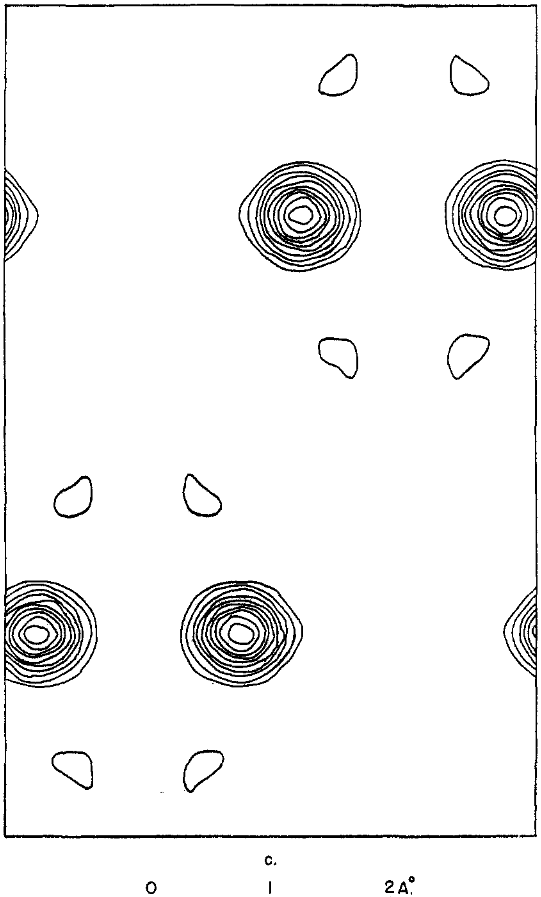

Fig. 1.—The electron density of YF_3 projected on (100). F_{000} is omitted in all projections.

Thulium Trifluoride.—TmF_3 prepared by the dry method was orthorhombic. The dried unheated product of the wet method was cubic like the corresponding holmium and erbium compounds. Heating between 1000 and 1100° for one hour converted the cubic compound into a mixture of comparable amounts of hexagonal and orthorhombic TmF_3. The wet method, with the ammonium hydroxide omitted, yielded the orthorhombic form after drying. The original material contained a trace of ytterbium and no other detectable impurities.

Ytterbium Trifluoride.—YbF_3 prepared by the dry method was orthorhombic, with no evidence of a hexagonal form. The oxide was spectroscopically pure of other rare earths.

Lutetium Trifluoride.—With lutetium, the wet method gave a product, after drying, which appeared to be a mixture of at least two compounds, which were neither hexagonal nor orthorhombic trifluorides. The complicated patterns have not been interpreted further. After an hour at 1000 to 1100°, orthorhombic LuF_3 resulted. The original oxide contained about 2% of other rare earths, mainly thulium and ytterbium.

X-Ray Methods.—Rotation and Weissenberg photographs with CuKα radiation were taken for rotation about the a, b and c axes of several single crystals of YF_3. Intensities were estimated by visual comparison with a series of spots made with graded exposure time. No corrections were made for absorption, and this error is believed to be responsible for most of the discrepancy between observed and calculated intensities. The "F observed" values listed in the microfilm[2] were derived in the usual way from averages from several different photographs of several crystals. The different photographs were normalized by means of common reflections. The different observations showed substantial discrepancies in some cases, due to the absorption error. Subsequent to the determination of the structure, it was found that certain changes in normalization factors led to an "F improved" set[2] which were in better agreement with the calculated values.

Powder patterns were taken with CrKα (λ = 2.2909 Å.) and CuKα (λ = 1.5418 Å.) radiation in cameras of radius 4.5 cm. Data for each substance, other than the cubic phases, are listed on the microfilm.[2]

Crystal Structure of YF_3

Unit Cell and Space Group.—The Weissenberg photographs showed YF_3 to be orthorhombic and permitted indexing of the powder patterns with the unit cell: a = 6.353, b = 6.850, c = 4.393 Å., each ±0.003 Å. With $Z = 4$, $D_x = 5.069$ g. cm.$^{-3}$, compared with $D_m = 5.2$ from Nowacki.[1]

Zachariasen[3] independently indexed the YF_3 powder pattern without the aid of single crystal data and obtained a = 4.37, b = 6.42 and c = 6.89 Å.

The only systematic absences observed were: $hk0$ present only if $h = 2n$, $0kl$ present only if $k + l = 2n$, which permit only space groups Pn-a and Pnma. The positions of the four yttrium atoms are the same in either space group. Since a satisfactory structure for the fluorine atoms was achieved with the higher symmetry, Pnma (D_{2h}^{16}) was assumed to be correct and Pn-a was not considered further.

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(2) For a table of observed and calculated F values, and tables of $\sin^2\theta$ and observed powder intensities order Document 3853 from American Documentation Institute, c/o Library of Congress, Washington 25, D. C., remitting $2.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $3.75 for photostats readable without optical aid.

(3) W. H. Zachariasen, U. S. Atomic Energy Commission, Argonne National Laboratory Report ANL-4400 (January, 1950).

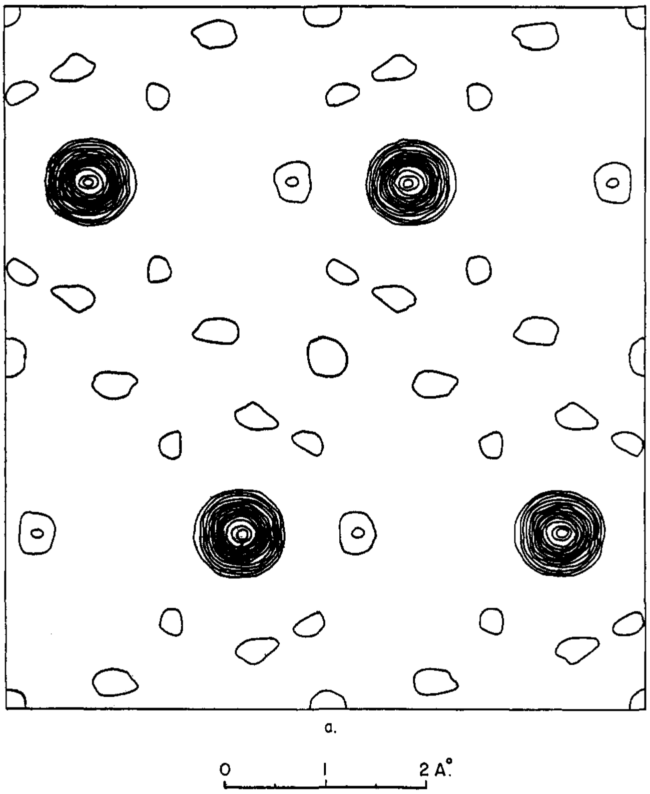

Fig. 2.—The electron density of YF_3 projected on (001).

Yttrium Positions.—Space group Pnma provides three fourfold sets of special positions[4] for the four yttrium atoms. Both 4(a) and 4(b), which are identical except for choice of origin, require special extinctions which (since yttrium provides most of the scattering power in this crystal) would appear as systematic intensity variations according to the rules: (hkl) strong only if $h + l = 2n$ and $k = 2n$. Such variations were not observed, thus leaving positions 4(c): $\pm$ (x, $^1/_4$, z; $^1/_2 + x$, $^1/_4$, $^1/_2 - z$) as the only remaining alternative. Space group Pn-a has only a fourfold general set of positions which is identical with 4(c) above if one makes a suitable choice of origin.

Among the $0k4$ reflections permissible by the space group (004, 024, 044, and 064) only 004 was observed, but even it was very weak. The structure factor for set 4(c) reduces, for these reflections, to

$$A = 4 \cos 8\pi z$$

which is zero only for $z = {}^1/_{16}, {}^3/_{16}, {}^5/_{16}$, etc. These values give only two different atomic arrangements, which can be represented by $z = {}^1/_{16}$ and ${}^3/_{16}$. The squares of the structure factors ($0kl$), computed for set 4(c) for allowed reflections, are independent of k and are in the order $F^2(0m1) < F^2(0n2) < F^2(0p3)$ for $z = {}^1/_{16}$ and $F^2(0m1) > F^2(0n2) > F^2(0p3)$ for $z = {}^3/_{16}$, where m, n and p are any integers consistent with the rule $k + l = 2n$. Inspection of the $0kl$ Weissenberg photograph showed the intensities to be much more consistent with the order for $z = {}^1/_{16}$ than $z = {}^3/_{16}$.

The yttrium atoms form an approximately regular triangular array in the planes $y = \pm {}^1/_4$ and the parameter x only determines how these layers are stacked together. If any yttrium atom in one layer is at the center of triangles in adjacent layers, so that Y–Y distances are maximum, then x must be approximately ${}^3/_8$. A trial structure considering yttrium only, with $x = {}^3/_8$, $z = {}^1/_{16}$, gave signs for F few of which were changed by successive Fourier refinements using 100, 010 and 001 projections and a section at (x $^1/_4$ z). The final Fourier functions are shown in Figs. 1–4. The yttrium parameters, from Fig. 4, are $x = 0.366$, $z = 0.059$. A Fourier section with coefficients calculated from these values was maximum at $x = 0.365$, $z = 0.060$; therefore "back-shift" corrections of $+0.001$ and -0.001 were applied to get the final values listed below.

Fluorine Positions.—The only arrangement which could be found with reasonable interatomic distances has fluorine atoms in sets 4(c) and 8(d). The fluorine parameters are determined to within about 0.03 by the small peaks in Figs. 1, 3 and 4. Figure 2 has peaks in locations which agree with these, but so many others also, due to diffraction effects, that it cannot be given much weight. The best values for the parameters are considered to be those derived from geometrical considerations, based on the positions for yttrium determined above.

The final structure for space group Pnma (D_{2h}^{16}) is

4Y in (c): $\pm(x, {}^1/_4, z;\ {}^1/_2 + x, {}^1/_4, {}^1/_2 - z)$ with $x = 0.367$, $z = 0.058$

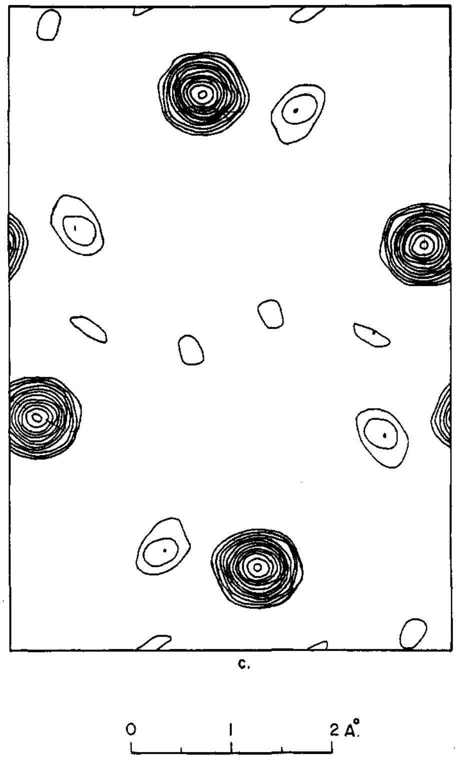

Fig. 3.—The electron density of YF_3 projected on (010). In this projection the 8-fold F atoms coincide by pairs.

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[4] "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Vol. I, Edwards Brothers, Ann Arbor, Mich., 1944, pp. 138–139.

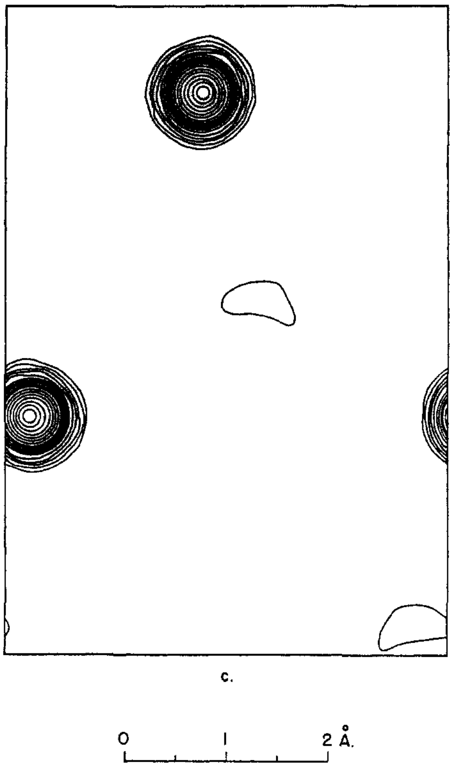

Fig. 4.—The electron density section at $y = 1/4$. F_{0k0} terms are omitted.

$4F_I$ in (c) with $x = 0.528$, $z = 0.601$

$8F_{II}$ in (d): $\pm(x, y, z;\ x, {}^1/_2-y, z;\ {}^1/_2 + x, y, {}^1/_2-z;\ {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 - z)$ with $x = 0.165$, $y = 0.060$, $z = 0.363$

The arrangement of atoms is indicated in Fig 5.

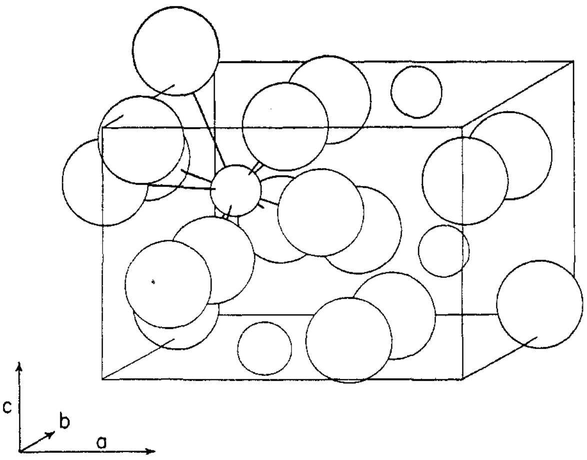

Fig. 5.—Structure of YF_3.

The quantity $r = \Sigma\ ||F_c| - |F_a||/\Sigma|F_o|$ is 0.23 for the original F observed values (about 190 independent non-zero values) and 0.16 for the improved set. The calculated values are based on the parameters before the "back-shift" correction was applied.

As an aid to identification of YF_3 and isostructural substances, the first 15 lines observed in the powder pattern are listed in Table I.

TABLE I

POWDER DATA FOR YF_3

d	hkl	Intensity, CrKα Obsd.	Calcd.
3.707	011	m	23
3.610	101	s−	64
3.427	020	s−	62
3.194	111	vs	100
2.882	210	s−	53
2.486	121	m+	14
2.409	211	w	8
2.328	220	vw	3
2.196	002	m−	11
2.058	221	m−	24
1.987	112	s	39
1.931	131	s	46
1.907	301	m+	35
1.854	230	m−	36
1.849	022	m−	17

Discussion of the Structure

Interatomic distances calculated from the above parameters are listed in Table II. Each yttrium has eight fluorine neighbors at about 2.3 Å. and another at 2.60 Å. The arrangement of these nine neighbors, shown in Fig. 6, is approximately like the arrangement found in $Y(OH)_3$.[5] In the latter substance, six oxygens are at the corners of a regular trigonal prism with an yttrium in the center. Three more oxygens are adjacent to the lateral faces of this prism. In YF_3, the triangular bases of the coördination polyhedron are not parallel and there are substantial deviations from threefold symmetry. Perhaps the coördination should be described as eightfold, because of the greater dsitance to the ninth neighbor.

TABLE II

INTERATOMIC DISTANCES[a] IN YF_3

	Y	F_I	F_{II}
Y		2.25 (1) 2.26 (1) 2.60 (1)	2.27 (2) 2.30 (2) 2.32 (2)
F_I	2.25 (1) 2.26 (1) 2.60 (1)		2.57 (2) 2.71 (2) 2.83 (2) 2.85 (2) 2.89 (2)
F_{II}	2.27 (1) 2.30 (1) 2.32 (1)	2.57 (1) 2.71 (1) 2.83 (1) 2.85 (1) 2.89 (1)	2.55 (2) 2.58 (4) 2.60 (1)

[a] Distances are in Å. The numbers in parentheses are the number of each kind of neighbor for the atom listed in the left-hand column.

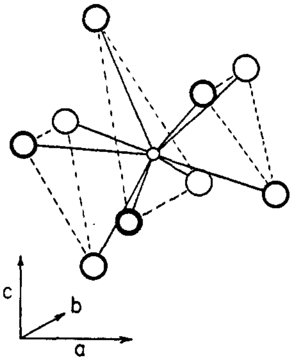

Fig. 6.—Coördination of Y^{+3} in YF_3.

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[5] K. Schubert and A. Seitz, *Z. anorg. Chem.*, **254**, 116 (1947).

The fluorine atoms occupy most of the space of the crystal and approach close packing in their coördination with each other, having 10 or 12 fluorine neighbors each.

Compounds Isostructural with YF_3

Rare Earth Trifluorides.—The trifluorides of all the rare earths elements from samarium to lutetium exist with the YF_3 type structure. Their lattice dimensions, derived from powder photographs taken with CrKα radiation,[2] are listed in Table III. The trend of molecular volume, plotted in Fig. 7, is characteristic of the well known lanthanide contraction, with a hint of a cusp in the curve at gadolinium.

TABLE III

ORTHORHOMBIC (YF_3 TYPE) TRIFLUORIDES

Compound	Cell dimensions in Å.			Unit cell volume, Å.³	Calculated density, g./cc.
	a	b	c		
YF_3	6.353	6.850	4.393	191.2	5.069
SmF_3	6.669	7.059	4.405	207.4	6.643
EuF_3	6.622	7.019	4.396	204.3	6.793
GdF_3	6.570	6.984	4.393	201.6	7.047
TbF_3	6.513	6.949	4.384	198.4	7.236
DyF_3	6.460	6.906	4.376	195.2	7.465
HoF_3	6.404	6.875	4.379	192.8	7.644
ErF_3	6.354	6.846	4.380	190.5	7.814
TmF_3	6.283	6.811	4.408	188.6	7.971
YbF_3	6.216	6.786	4.434	187.0	8.168
LuF_3	6.151	6.758	4.467	185.7	8.332
BiF_3[a]	6.56	7.03	4.86	224	7.88

[a] Zachariasen, reference 3.

Bismuth Trifluoride.—According to Zachariasen[3] BiF_3 is isostructural with YF_3 with the unit cell dimensions listed in Table II.

Cementite.—The structure reported by Lipson and Petch[6] for Fe_3C, cementite, is formally very closely related to that of YF_3 as shown by the atomic parameters listed in Table IV. However, the axial ratios differ so much that the coördination number of carbon is only six, and the iron atoms are more nearly close packed than are the fluorine atoms in YF_3. Therefore we do not consider Fe_3C and YF_3 to have equivalent structures.

TABLE IV

COMPARISON OF YF_3 AND Fe_3C STRUCTURES

	YF_3, Å.	Fe_3C,[a] ref. 6
a	6.353	5.089
b	6.850	6.742
c	4.393	4.523
x (Y,C)	0.367	0.36
z (Y,C)	.058	.03
x (F,Fe)	.528	.540
z (F,Fe)	.601	.667
x (F,Fe)	.165	.183
y (F,Fe)	.060	.065
z (F,Fe)	.363	.333

[a] Cell constants are changed from kX. The designation of axes and of parameters has been permuted to agree with YF_3.

Other Fluoride Structures

Compounds Isostructural with LaF_3.—The lattice dimensions of the hexagonal fluorides are listed in Table V. The powder patterns can be indexed on a hexagonal cell with $a' = a/\sqrt{3}$, but the data in the table refer to the larger cell of Oftedal.[7] This larger cell is required by faint reflections noted by Oftedal in single crystal photographs of the mineral tysonite, (La, Ce)F_3. That these faint reflections are not due to a superstructure among the metal atoms is shown by the observation[8] of similar reflections in Weissenberg photographs of single crystals of pure synthetic CeF_3.

TABLE V

HEXAGONAL (LaF_3 TYPE) TRIFLUORIDES

Compound	Cell constants, Å.		Unit cell volume, Å.³	X-ray density, g./cc.
	a	c		
SmF_3[a]	6.99	7.16	303.0	6.82
SmF_3	6.956	7.120	298.3	6.925
EuF_3	6.916	7.091	293.7	7.088
HoF_3	6.833	6.984	282.4	7.829
TmF_3	6.763	6.927	274.4	8.220

[a] Oftedal, reference 7.

Other trifluorides which have this structure are those of the rare earth elements preceding samarium[7] and those of actinium, uranium, neptunium, plutonium and americium.[9]

The plot of molecular volume, Fig. 7, shows that the hexagonal structure is from 2 to 4% more dense than the orthorhombic one.

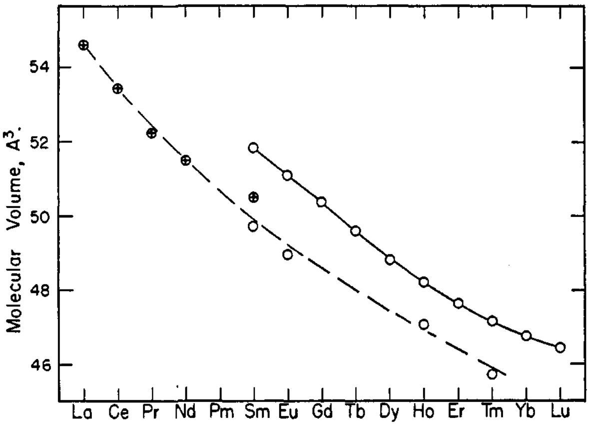

Fig. 7.—Molecular volume of rare earth trifluorides as a function of atomic number of the rare earth element: upper curve, YF_3 type; lower curve, LaF_3 type; ○, this work; ⊕, Oftedal, reference 7.

Relative Stability of the Hexagonal and Orthorhombic Forms.—The hexagonal trifluoride seems to be the only stable form for elements from lanthanum to neodymium. It is likely that it can be produced under the proper conditions for the rest of the rare earth elements and also yttrium, although this has not been achieved in several cases. The best explanation for our data seems to be that for elements samarium to lutetium the hexagonal form is stable only at elevated temperatures,

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(6) H. Lipson and N. J. Petch, *J. Iron and Steel Inst. (London)*, **142**, 95 (1940).

(7) I. Oftedal, *Z. physik. Chem.*, **B5**, 272 (1929); **B13**, 190 (1931).

(8) C. H. Dauben and D. H. Templeton, unpublished work.

(9) W. H. Zachariasen, *Acta Cryst.*, **2**, 388 (1949).

although it may be precipitated from solution under certain conditions because of greater ease of crystal nucleation and growth.

Primitive Cubic Phases.—Nowacki[1] was able to prepare the primitive cubic "yttrium trifluoride" only once, by precipitation in the presence of sodium ion. The lattice constant was 5.675 Å. In three cases (holmium, erbium and thulium) we obtained primitive cubic phases when precipitations were done in the presence of ammonium ion. In each of the latter cases, heating produced the trifluoride. The lattice dimensions of the holmium, erbium and thulium compounds were 5.81, 5.78 and 5.74 Å., respectively, each ±0.01 Å. The intensities we observed are in excellent agreement with those reported by Nowacki. Thus it seems highly probable that these four compounds are of similar structure.

That these compounds are another trifluoride structure is unreasonable since holmium and erbium have almost the same crystal radii as yttrium, while thulium is even smaller. The molecular volume in the cubic phase, if a trifluoride, is 61 Å.^{3} for the yttrium compound and 63 to 65 Å.^{3} for the others, compared with about 48 Å.^{3} for the orthorhombic and 47 Å.^{3} for the hexagonal trifluoride structures. If the compounds are a double sodium yttrium fluoride and double ammonium rare earth fluorides, respectively, then the molecular volumes can be explained. If one uses the recipe of Zachariasen[10] which assigns effective atomic volumes of 18 Å.^{3}, 7 Å.^{3}, and zero to fluorine, sodium and yttrium, respectively, then the resulting formula per unit cell for Nowacki's compound is $Na_{0.8}Y_3F_{9.8}$, or NaY_3F_{10}. A structure which is in excellent agreement with the observed intensities is

NaY_3F_{10}: Space group Pm3n (O^1_h)
Na in (a): 000
3 Y in (c): 0 $^1/_2$ $^1/_2$; $^1/_2$ 0 $^1/_2$; $^1/_2$ $^1/_2$ 0
10 F randomly distributed in
  1 (b): $^1/_2$ $^1/_2$ $^1/_2$
  3 (d): $^1/_2$ 0 0; 0 $^1/_2$ 0; 0 0 $^1/_2$
  8 (g): $\pm(xxx;\ \bar{x}xx;\ x\bar{x}x;\ xx\bar{x})$ with $x = {}^1/_4$.

This structure is closely related to that proposed by Nowacki. Very likely there are other structures similar to these which fit the intensities, since the yttrium atoms in 3(c) contribute the major part of the scattering power. The above structure requires that the yttrium crystals had sufficient defects, voids or impurities to lower the density about 10% to give agreement with the experimental density of Nowacki.

If this structure is correct, then the other compounds are $NH_4Ho_3F_{10}$, $NH_4Er_3F_{10}$ and $NH_4Tm_3F_{10}$.

Hund[11] failed to produce a primitive cubic phase in his study of the solid solutions of β-$NaYF_4$ and YF_3.

Hexagonal Holmium Phase.—The product of the precipitation of holmium in the presence of sodium gave a pattern with smooth lines which are attributed to HoOF, discussed below, and with spotty lines which were indexed according to a hexagonal lattice, a = 8.862 Å., c = 5.041 Å. We presume that the latter phase is a mixed sodium holmium fluoride, but have no proof of its identity. The diffraction data are listed in the microfilm.[2]

Structure of HoOF.—The smooth lines, in the pattern just mentioned above, were indexed as face-centered cubic with a = 5.523 ± 0.003 Å. The intensities suggested a fluorite type structure. Either $NaHoF_4$ or HoOF might have such a structure, with cations or anions, respectively, distributed randomly. The observed cell constant is about what is expected for HoOF, while $NaHoF_4$ should be similar to $NaYF_4$, which has a = 5.459 Å.[12] The intensities calculated for HoOF are in better agreement with the observed intensities than are those calculated for $NaHoF_4$.

Zachariasen[13] has found YOF and LaOF to exist as two different ordered superstructures based on the fluorite type, one form being rhombohedral and the other tetragonal. A search in the pattern of HoOF for superstructure lines failed, but the presence of the hexagonal phase interferes with some of the possible lines. However, the width of the 420 reflection shows the deviation from a cubic cell is slight. If the cell is rhombohedral, then α must deviate from the ideal value 33.56° by less than 0.03°. If tetragonal, c/a deviates from $\sqrt{2}$ by less than 0.001. Thus this sample of HoOF is similar to AcOF, for which Zachariasen[13] could detect no deviation from cubic symmetry.

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