

**NdTe.**—This phase has been reported as isostructural with NaCl.<sup>2,3</sup> Powder diffraction patterns taken with Cu K $\alpha$  radiation do not show diffraction lines for odd Miller indices. Such lines are due to the difference of the scattering power of the two atoms and with this radiation the difference is further decreased because of the dispersion corrections. The ratio of intensities of (200) to (111) is approximately 10<sup>3</sup> and it is therefore not surprising that (111) is not observed in a powder pattern. A very long exposure of a single crystal of NdTe using Mo K $\alpha$  radiation and a precession camera showed that the (111) reflection was present and confirms the ordered, NaCl-type, arrangement of the atoms.

### Discussion

The intermediate phases common to this system and the lanthanum-tellurium system<sup>7</sup> are isostructural and also duplicate the melting behavior, except that the lanthanum analogs melt at somewhat lower temperatures. The presence of the Nd<sub>2</sub>Te<sub>5</sub> phase is unique

for this system. The X-ray diffraction patterns for NdTe<sub>3</sub> and Nd<sub>2</sub>Te<sub>5</sub> are very similar and the materials also have the same space group, so that the layer structures are very much alike. The compound NdTe<sub>3</sub> contains two Nd layers and six Te layers in the unit cell which on the average are 3.2 Å. apart. Nd<sub>2</sub>Te<sub>5</sub> results from a substitution of some Te layers by Nd in the NdTe<sub>3</sub> structure so that the ordered structure contains four Nd and ten Te layers in the unit cell which on the average are 3.14 Å. apart. The shrinkage of the layer separation is due to the introduction of a smaller rare earth atom for the metalloid.

The phase transition exhibited by Nd<sub>2</sub>Te<sub>3</sub>-Nd<sub>3</sub>Te<sub>4</sub> solid solution compositions is not observed in the corresponding lanthanum compounds. The low-temperature structure appears to be isostructural with Sb<sub>2</sub>S<sub>3</sub><sup>4</sup> and Sb<sub>2</sub>Se<sub>3</sub>.<sup>11</sup> The occurrence of this transition may be a function of the radius ratio.<sup>4</sup>

(11) N. W. Tideswell, F. H. Kruse, and J. D. McCullough, *Acta Cryst.*, **10**, 99 (1957).

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## Crystal Structure of Hexagonal Sodium Neodymium Fluoride and Related Compounds<sup>1</sup>

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A single-crystal X-ray analysis has established the structure of hexagonal NaNdF<sub>4</sub>. The unit cell has  $a = 6.100$ ,  $c = 3.711$  Å.; the space group is P $\bar{6}$ . Fluoride ions lie in triangular arrays at  $z = 0, 1/2$ . Cation sites are of three types: a onefold site occupied by Nd<sup>3+</sup>, a onefold site occupied randomly by  $1/2\text{Na}^+$ ,  $1/2\text{Nd}^{3+}$ , and a twofold site occupied randomly by Na<sup>+</sup> and vacancies. The fluoride coordination about the first two sites is ninefold, a trigonal prism with each vertical face bearing a pyramid, and about the third site is irregular octahedral. It is proposed that this structure becomes the same as that of several other compounds having Nd<sup>3+</sup> replaced by other rare earth ions or Y<sup>3+</sup> and of the mineral gagarinite when the cations of the first two sites are completely intermixed. Bond distances and thermal displacements are given for NaNdF<sub>4</sub>.

### Introduction

Sodium neodymium fluoride is a member of a series of 1:1 compounds existing in the binary systems NaF-MF<sub>3</sub>, in which M is a rare earth or yttrium atom. The phase diagrams for these systems were reported by Thoma<sup>2</sup> and further details are forthcoming. Of interest to the present work is that all of the NaMF<sub>4</sub> compounds have a hexagonal crystalline form, while those for M = Y and Nd to Lu have a high-temperature form with the cubic, fluorite structure. Hund<sup>3</sup> deduced the structure of high-temperature NaYF<sub>4</sub> and concluded that Na<sup>+</sup> and Y<sup>3+</sup> ions are distributed randomly over the cation sites. Recently the low-temperature NaYF<sub>4</sub> was observed to be hexagonal by

Burns<sup>4</sup> and by Roy and Roy,<sup>5</sup> who assigned to it the  $\beta_2$ -Na<sub>2</sub>ThF<sub>6</sub> structure proposed by Zachariasen<sup>6</sup> for NaLaF<sub>4</sub> and NaCeF<sub>4</sub>, and by Sobolev *et al.*,<sup>7</sup> who called it isomorphous with the mineral gagarinite,<sup>8</sup> NaCaMF<sub>6</sub>.

A complete single-crystal structure analysis has been carried out to establish the details of the hexagonal form of NaNdF<sub>4</sub>, to resolve the points of conflict, and to aid in explaining the phase behavior of NaF-MF<sub>3</sub> systems.

### Experimental

A 1:1 mixture of NaF and NdF<sub>3</sub> was melted and allowed to cool slowly; large, violet crystals of NaNdF<sub>4</sub> were obtained. X-Ray

(1) Research sponsored by U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

(2) R. E. Thoma, Transactions of the Fourth Rare Earth Research Conference, Phoenix, Ariz., 1964, in press.

(3) F. Hund, *Z. anorg. allgem. Chem.*, **261**, 106 (1950).

(4) J. H. Burns, U.S.A.E.C. Report ORNL-3262, 1962, p. 15.

(5) D. M. Roy and R. Roy, *J. Electrochem. Soc.*, **111**, 421 (1964).

(6) W. H. Zachariasen, *Acta Cryst.*, **1**, 265 (1948).

(7) B. P. Sobolev, D. A. Mineev, and V. P. Pashutin, *Dokl. Akad. Nauk SSSR*, **160**, 791 (1963).

(8) A. V. Stepanov and E. A. Severov, *ibid.*, **141**, 954 (1961).

precession, Weissenberg, and rotation photographs were used to establish the diffraction symmetry,  $6/mP6$ -, and unit-cell dimensions. Refined parameters for the unit cell were obtained by least-squares fitting<sup>9</sup> of a Cu  $K\alpha$  X-ray powder diffractometer pattern. They are  $a = 6.100 \pm 0.003$ ,  $c = 3.711 \pm 0.003$  Å. There are  $3/2$  formula weights per unit cell.<sup>9</sup>

For the collection of intensity data a crystal was ground to approximately spherical shape. This sphere was mounted on a G.E. single-crystal orienter equipped with a scintillation-counter detector, and all independent reflections ( $hkl$ ), out to  $2\theta = 116.2^\circ$ , were measured with Mo  $K\alpha$  radiation by the  $2\theta$ -scan technique. About 35 reflections of ( $hkl$ ) type were measured also to check the absolute configuration (see later).

Crystal specimens of most of the  $\text{NaMF}_4$  series were obtained from the phase studies<sup>2</sup> and were photographed by precession and rotation techniques. The unit-cell dimensions<sup>10</sup> decreased with increasing atomic number through the lanthanide series.

A feature of the X-ray photographs present to varying degrees for all the compounds was diffuse streaks perpendicular to  $c^*$  and interleaving the rows of sharp spots at half the reciprocal spacing. These were most pronounced in pictures of the  $hhl$  zone. An explanation of this phenomenon is offered later.

The intensity data were corrected for the Lorentz-polarization factor and for absorption by a sphere<sup>11</sup> with  $\mu R = 1.31$  and were reduced to a set of observed squared structure factors,  $F_o^2$ .

### Structure Determination

Possible space groups  $P6$  and  $P6/m$  were ruled out by simple geometrical considerations. One important factor was the length of the  $c$  axis, 3.71 Å., which disallowed the presence of ions repeated along  $c$  within one unit cell. With  $P\bar{6}$  established as the space group, it was possible to interpret sections of the three-dimensional Patterson map at  $z = 0$  and  $1/2$  to the extent that a heavy atom would occupy the origin and a site at  $2/3, 1/3, 1/2$ . Whether this atom was  $\text{Nd}^{3+}$  or a statistically mixed species  $\text{Na}^+, \text{Nd}^{3+}$  was not ascertained until refinement. The positioning of  $\text{F}^-$  ions in threefold arrays around the sites at 0, 0, 0 and  $1/3, 2/3, 1/2$  was rather closely determined by requirements of interatomic distances.

The resultant trial structure was tested first by calculation of structure factors with various distributions of  $\text{Nd}^{3+}$  and  $\text{Na}^+$  ions, from which it was readily ascertained that one  $\text{Nd}^{3+}$  lies at 0, 0, 0 and an average ion, ( $1/2\text{Na}^+, 1/2\text{Nd}^{3+}$ ), is at  $2/3, 1/3, 1/2$ . The other  $\text{Na}^+$  ion was assumed to be at  $1/3, 2/3, 1/2$  and a discrepancy factor (based on  $F^2$ ) of about 10% indicated this structure to be essentially correct.

The parameters of the trial structure were adjusted by the method of least squares employing a CDC 1604 computer and the Fortran program of Busing, Martin, and Levy.<sup>12</sup> The variable parameters included those atomic coordinates not fixed by symmetry, individual anisotropic temperature factors for each atom, and two scale factors. Because neodymium has a moderate sized imaginary component of anomalous dispersion<sup>13</sup> for Mo  $K\alpha$  X-rays, its contribution was included

in the structure-factor calculations. The structure factor is given by

$$F_o = \sum_n (f_o + \Delta f' + i\Delta f'')_n (\cos \varphi_n + i \sin \varphi_n)$$

where  $f_o$ ,  $\Delta f'$ , and  $\Delta f''$  are, respectively, the normal part and the real and imaginary anomalous parts of the scattering factor;  $\varphi = 2\pi(hx_n + ky_n + lz_n)$ , and the sum is taken over all  $n$  atoms of the unit cell. In the computation the real and imaginary components are grouped together to give  $F_o = A' + iB'$ , where

$$A' = \sum_n (f_o + \Delta f') \cos \varphi_n - \sum_n \Delta f'' \sin \varphi_n$$

and

$$B' = \sum_n (f_o + \Delta f') \sin \varphi_n + \sum_n \Delta f'' \cos \varphi_n$$

Atomic scattering factors for  $\text{Nd}^{3+}$ ,  $\text{Na}^+$ , and  $\text{F}^-$  were all taken from the International Tables,<sup>14</sup> and the values  $\Delta f' = -0.3$  and  $\Delta f'' = 3.6$  electrons were used for the anomalous dispersion of neodymium. An average of the scattering factors of  $\text{Na}^+$  and  $\text{Nd}^{3+}$  (including anomalous dispersion) was used for the statistically distributed atoms.

In the least-squares method each observation should be weighted equal to the reciprocal of its variance,  $\sigma^2$ . The following empirical equation was used to approximate the variance in this case.

$$\sigma^2(F_o^2) = [T + B + 0.0009(T - B)^2 + 0.01E^2]/[A(Lp)^2]$$

In this,  $1/A(Lp)^2$  is a factor used in converting counts to structure factors ( $Lp =$  Lorentz polarization,  $A =$  absorption factor),  $T =$  total and  $B =$  background counts, and  $E =$  extinction correction in counts. An expression of this form with counter-measured data was employed and discussed previously by Busing and Levy<sup>15</sup> and by others.

The quantity  $\sum w |F_o^2 - F_c^2|^2$  was minimized, and the summation was taken over all 708 observed reflections. After a few preliminary cycles of refinement, two problems arose: the strong reflections were all calculating too large, suggesting extinction effects, and the  $\beta_{33}$  thermal parameter of the  $\text{Na}^+$  ion at  $1/3, 2/3, 1/2$  became very large. The latter was resolved by splitting the  $\text{Na}^+$  ion into two half-atoms at  $1/3, 2/3, \pm z$  and allowing  $z$  to vary. The  $z$  parameter refined quickly to a final value, the temperature factors became normal, and the discrepancy factor dropped sharply.

Since the crystals are rather hard and the strong reflections were all observed too small compared to the calculated values, extinction seemed likely to be present. A correction was made in the manner derived by Zachariasen<sup>16</sup> for a spherical crystal. First the suspect reflections were omitted from the refinement; then the parameters obtained were used to calculate

(9) The Fortran Program, ORGLS, by W. R. Busing and H. A. Levy, ORNL TM-271 (1962), was adapted by D. R. Sears for this application.

(10) R. E. Thoma, *et al.*, in preparation.

(11) "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, 1959, p. 302.

(12) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, 1962.

(13) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

(14) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, 1962.

(15) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(16) W. H. Zachariasen, *Acta Cryst.*, **16**, 1139 (1963).

TABLE I  
ATOMIC PARAMETERS FOR NaNdF<sub>4</sub> FROM LEAST-SQUARES REFINEMENT

Atom	Site	$x \pm (\sigma)$	$y \pm (\sigma)$	$z \pm (\sigma)$	$\beta_{11} \pm (\sigma)$	$\beta_{22} \pm (\sigma)$	$\beta_{33} \pm (\sigma)$	$\beta_{12} \pm (\sigma)$
Nd	1(a)	0	0	0	0.00433 (3)	<i>a</i>	0.00411 (7)	<i>a</i>
1/2Na, 1/2Nd	1(f)	2/3	1/3	1/2	0.00390 (5)	<i>a</i>	0.0120 (2)	<i>a</i>
1/2Na	2(h)	1/3	2/3	0.656 (3)	0.0135 (8)	<i>a</i>	0.050 (5)	<i>a</i>
F(1)	3(j)	0.6337 (7)	0.0429 (7)	0	0.0073 (6)	0.0109 (7)	0.059 (3)	0.0059 (5)
F(2)	3(k)	0.7339 (5)	0.7549 (5)	1/2	0.0092 (5)	0.0063 (5)	0.0123 (8)	0.0023 (4)

<sup>a</sup> These parameters are fixed by the symmetry relations:  $\beta_{22} = \beta_{11}$ ,  $\beta_{12} = 1/2\beta_{11}$ . In addition, the relation  $\beta_{13} = \beta_{23} = 0$  for all atoms; see H. A. Levy, *Acta Cryst.*, 9, 879 (1956).

TABLE II  
OBSERVED<sup>a</sup> AND CALCULATED STRUCTURE FACTORS FOR NaNdF<sub>4</sub>

H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)
1	0	0	46.73	43.33	4	0	1	34.55*	31.85	11	1	1	11.91	11.64	5	9	2	7.48	7.57
2	0	0	39.33	36.39	5	0	1	43.87*	44.99	2	11	1	3.33	3.21	0	10	2	9.07	9.19
3	0	0	83.40	86.60	6	0	1	12.26	11.31	0	10	2	19.25	19.03	0	11	3	13.52	13.24
4	0	0	35.68*	34.81	7	0	1	27.16	27.12	1	12	1	12.18	11.82	2	10	2	9.27	9.26
5	0	0	30.03*	29.47	8	0	1	22.59	23.09	3	10	2	7.64	7.62	0	0	4	54.38*	52.49
6	0	0	18.64	18.74	9	0	1	6.35	5.67	0	0	2	96.20*	96.35	0	0	4	27.35	27.36
7	0	0	19.23	17.88	10	0	1	18.10	18.54	1	0	2	42.32	41.38	0	1	1	14.40	13.70
8	0	0	23.55	23.99	11	0	1	13.59	14.07	2	0	2	36.26*	36.26	2	0	2	25.20	25.02
9	0	0	9.07	9.25	12	0	1	3.11	2.93	3	0	2	64.08*	62.38	3	0	2	42.65*	41.36
10	0	0	8.98	9.13	13	0	1	10.50	10.57	4	0	2	35.13*	34.26	4	0	2	25.95	24.85
11	0	0	15.25	15.16	1	1	1	39.54*	39.31	5	0	2	29.44*	29.08	0	0	4	21.33	21.42
12	0	0	73.68*	70.82	1	1	1	29.45*	29.46	6	0	2	33.99*	33.43	1	0	3	43.32*	42.93
1	1	0	18.01*	19.23	2	1	1	61.38*	59.31	7	0	2	19.08	18.90	2	0	3	51.60*	49.65
2	1	0	23.65	23.82	3	1	1	48.91*	47.18	8	0	2	13.69	13.86	7	0	4	15.98	15.31
3	1	0	54.43*	53.24	4	1	1	10.13	9.98	9	0	2	22.99	21.79	8	0	4	14.70	14.65
4	1	0	13.17	14.34	5	1	1	37.97*	37.34	10	0	2	9.20	9.36	9	0	4	18.39	18.48
5	1	0	18.33	19.06	6	1	1	36.21*	35.62	11	0	2	8.80	9.20	10	0	4	7.87	8.38
6	1	0	30.75	31.19	7	1	1	8.32	8.78	12	0	2	14.62	14.11	11	0	4	8.39	8.20
7	1	0	14.06	13.76	8	1	1	24.13	24.03	0	1	2	40.83*	42.04	0	1	4	27.16	27.72
8	1	0	12.66	13.43	9	1	1	21.09	21.36	1	1	2	52.36*	51.80	1	1	4	38.76*	38.06
9	1	0	17.76	18.23	10	1	1	5.30	4.77	1	1	2	21.29	21.69	2	1	4	19.15	19.30
10	1	0	9.99	9.63	11	1	1	15.42	15.45	3	1	2	27.39*	27.33	3	1	4	22.50	21.59
11	1	0	7.03	7.00	12	1	1	11.43	11.41	4	1	2	44.38*	43.06	4	1	4	33.31	32.66
12	1	0	42.63*	43.09	0	2	1	76.95*	78.51	5	1	2	15.56	16.23	5	1	4	14.53	14.65
2	2	0	61.38*	60.72	1	2	1	67.89*	68.46	6	1	2	19.41	19.79	6	1	4	15.88	16.21
3	2	0	33.62*	33.58	2	2	1	14.31	14.78	7	1	2	27.44*	27.49	7	1	4	22.72	22.51
4	2	0	14.90	15.25	3	2	1	59.26*	59.39	8	1	2	13.49	13.19	8	1	4	12.00	11.82
5	2	0	43.51*	43.67	4	2	1	38.42*	39.23	9	1	2	12.59	13.28	9	1	4	10.86	11.15
6	2	0	18.84	19.28	5	2	1	11.68	10.79	10	1	2	16.23	16.28	10	1	4	14.39	14.42
7	2	0	10.70	10.13	6	2	1	31.46	31.96	11	1	2	9.63	9.28	11	1	4	24.41	24.29
8	2	0	25.92	26.46	7	2	1	24.16	24.47	0	2	2	35.64*	35.90	12	1	4	26.15	26.51
9	2	0	10.78	11.14	8	2	1	7.86	8.08	1	2	2	39.51*	40.46	1	2	4	35.56*	34.85
10	2	0	8.21	8.12	9	2	1	15.71	15.96	2	2	2	47.28*	46.88	2	2	4	22.62	22.12
11	2	0	14.70	14.20	10	2	1	14.37	14.20	3	2	2	12.62	13.64	3	2	4	17.49	17.47
12	2	0	35.00*	35.13	11	2	1	4.74	5.04	4	2	2	21.56	21.64	4	2	4	15.25	15.00
1	3	0	20.55	19.94	0	3	1	16.03	16.32	5	2	2	37.05*	36.91	5	2	4	15.26	15.00
2	3	0	47.06*	46.73	1	3	1	38.38*	38.23	6	2	2	19.33	18.93	6	2	4	9.82	10.18
3	3	0	23.56	23.29	2	3	1	45.95*	45.77	7	2	2	11.10	11.10	7	2	4	19.07	19.06
4	3	0	20.88	21.02	3	3	1	13.72	13.56	8	2	2	23.34	23.60	8	2	4	9.91	9.63
5	3	0	28.25	28.40	4	3	1	27.69*	27.82	9	2	2	10.42	10.42	9	2	4	7.32	7.48
6	3	0	12.83	12.63	5	3	1	25.70	25.83	10	2	2	8.21	8.26	10	2	4	42.21*	41.29
7	3	0	12.83	13.00	6	3	1	6.88	7.14	11	2	2	13.71	13.12	11	2	4	25.15	24.66
8	3	0	19.31	19.55	7	3	1	21.74	22.00	0	3	2	62.45*	63.75	12	2	4	18.26	18.64
9	3	0	6.87	6.94	8	3	1	15.54	15.83	1	3	2	35.55*	34.64	1	3	4	30.29	29.60
10	3	0	61.28*	60.73	9	3	1	3.63	3.53	2	3	2	22.98	22.88	2	3	4	13.98	14.41
11	3	0	14.05	15.07	10	3	1	13.96	13.75	3	3	2	22.98	22.88	3	3	4	17.26	16.96
12	3	0	22.22	22.92	1	4	1	33.28*	34.32	4	3	2	23.79	23.40	4	3	4	21.16	20.93
1	4	0	41.26*	41.36	1	4	1	10.13	9.46	5	3	2	21.89	21.00	5	3	4	11.13	10.90
2	4	0	13.84	14.37	2	4	1	39.04*	40.04	6	3	2	25.25	25.26	6	3	4	11.00	10.95
3	4	0	15.63	15.63	3	4	1	35.29*	35.21	7	3	2	13.04	12.74	7	3	4	15.77	15.19
4	4	0	22.00	22.61	4	4	1	7.37	7.25	8	3	2	12.71	12.86	8	3	4	24.47	24.67
5	4	0	11.22	11.59	5	4	1	24.65	24.88	9	3	2	17.46	17.98	9	3	4	22.43	22.08
6	4	0	9.65	9.92	6	4	1	26.08	26.30	10	3	2	7.22	7.01	10	3	4	8.22	8.36
7	4	0	12.88	12.55	7	4	1	6.28	5.48	0	4	2	35.01*	34.94	0	4	4	18.79	19.47
8	4	0	23.53	24.15	8	4	1	49.03*	49.40	1	4	2	49.03*	48.77	1	4	4	13.86	14.20
9	4	0	37.95*	37.67	9	4	1	15.05	14.74	2	4	2	16.80	17.30	2	4	4	4.14	4.01
10	4	0	20.10	20.27	10	4	1	3.65	3.36	3	4	2	22.83	23.21	3	4	4	12.24	12.33
11	4	0	12.69	12.99	0	5	1	43.80*	44.05	4	4	2	36.07*	35.57	4	4	4	28.99	29.04
12	4	0	26.17	26.17	1	5	1	15.47	15.12	5	4	2	32.78*	32.64	5	4	4	10.19	9.65
1	5	0	10.52	8.44	0	5	1	13.13	11.77	6	4	2	14.99	15.39	6	4	4	29.28*	28.94
2	5	0	8.09	7.92	3	5	1	33.08*	32.84	7	4	2	20.55	20.56	7	4	4	21.03	21.01
3	5	0	16.50	16.47	4	5	1	25.36	25.41	8	4	2	11.28	11.32	8	4	4	18.67	18.90
4	5	0	6.59	6.59	5	5	1	8.37	7.88	9	4	2	9.36	9.46	9	4	4	25.56	26.01
5	5	0	38.98*	39.42	6	5	1	20.35	19.78	0	5	2	28.47	28.69	0	5	4	15.74	15.60
6	5	0	17.36	17.13	7	5	1	16.21	16.34	1	5	2	17.46	17.98	1	5	4	12.64	12.05
7	5	0	16.77	16.67	8	5	1	4.79	4.22	2	5	2	23.78*	23.66	2	5	4	15.95	15.49
8	5	0	27.26	27.48	9	5	1	12.00	11.33	3	5	2	31.89	32.28	3	5	4	18.31	18.23
9	5	0	14.37	14.02	0	6	1	12.17	12.63	4	5	2	19.75	19.82	4	5	4	9.06	9.45
10	5	0	13.70	13.83	1	6	1	28.98	29.14	5	5	2	13.41	13.50	5	5	4	8.08	7.88
11	5	0	19.96	19.98	2	6	1	27.38	27.83	6	5	2	23.44	23.43	6	5	4	27.18	26.48
12	5	0	9.07	9.01	3	6	1	8.63	9.41	7	5	2	10.67	10.84	7				

the strong reflections accurately. A multiplicative correction factor whose maximum value was 1.27 was derived and applied to the  $F_o$  of each extinction-affected reflection; 88 reflections were corrected in this manner.

After these changes were applied, further cycles of refinement were carried out using all 708 observations. The final parameters and their standard deviations are given in Table I. The observed and calculated structure factors are presented in Table II. The discrepancy factor,  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ , is 0.019 for all reflections, while the standard deviation of an observation of unit weight,  $[\sum w(F_o^2 - F_c^2)^2 / (n_o - n_v)]^{1/2}$ , is 1.56. In this expression,  $w$  = weight of the observation,  $n_o$  = number of observations, and  $n_v$  = number of variables.

For noncentrosymmetric crystals containing an anomalous scatterer it is possible to determine the absolute configuration.<sup>17</sup> Friedel's law that  $F(hkl) = F(\bar{h}\bar{k}\bar{l})$  breaks down for this case, and measurements of pairs of reflections of this type can be used for the determination. Since no other physical measurements, such as optical rotation, have been made on NaNdF<sub>4</sub>, the question of absolute configuration is largely academic; however, the anomalous component of scattering for neodymium is not large (3.6 electrons), so the measurements were made to see if the effect could be detected. Some 35 pairs were measured and the intensity ratios agreed with those for  $(hkl)$  and  $(\bar{h}\bar{k}\bar{l})$  calculated from the parameters of Table I in 30 cases, providing strong evidence that this is the true configuration of the crystal used.

### Results and Discussion

**Description of the Structure.**—A perspective drawing of the structure is shown in Figure 1, which includes one unit cell and the fluoride ion neighbors of the corner atoms. Lengths of bonds and significant nonbonded contacts are shown in the drawing; a list-

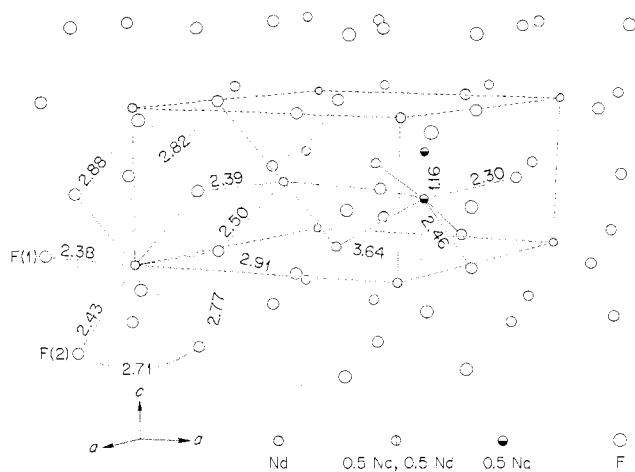


Figure 1.—Perspective drawing of one unit cell and its fluoride ion neighbors. Distances are in Å.

ing including the standard deviations is given in Table III. The standard errors of these distances were evaluated<sup>18</sup> from the least-squares standard errors of the

TABLE III  
INTERATOMIC DISTANCES AND STANDARD DEVIATIONS  
IN NaNdF<sub>4</sub><sup>a</sup>

Bond	$d$ , Å.	$\sigma(d)$ , Å.	Nonbonded contact	
			$d$ , Å.	$\sigma(d)$ , Å.
Nd-F(1)	2.377	0.004	F(2)-F(2)	2.708 0.005
Nd-F(2)	2.426	0.002	F(1)-F(2)	2.768 0.004
(Na,Nd)-F(2)	2.393	0.003	F(1)-F(2)	2.825 0.004
(Na,Nd)-F(1)	2.503	0.003	F(1)-F(2)	2.879 0.004
Na-F(2)	2.298	0.004	F(1)-F(1)	2.910 0.007
Na-F(1)	2.459	0.006	F(1)-F(1)	3.641 0.007

<sup>a</sup> See Figure 1 for identification of the atoms.

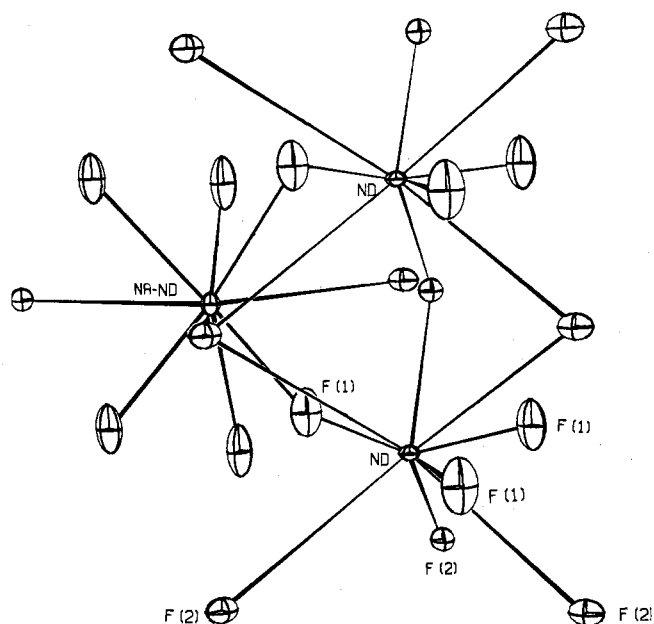
parameters and the standard errors of the unit-cell constants, given above. The fluoride ions lie in mirror planes at  $z = 0, 1/2$  and form triangular arrays. The cation sites are of three kinds: the Nd<sup>3+</sup> at the origin is coordinated by a trigonal prism of fluoride ions with each vertical face bearing a pyramid, making a total of nine neighbors. The site occupied randomly by Na<sup>+</sup> and Nd<sup>3+</sup> at  $2/3, 1/3, 1/2$  is also nine-coordinated in the same manner, but with longer bond distances, resulting, probably, from the smaller average charge on the cation. The third site is within a similar, although smaller, prism but with the cation displaced from the center, along  $\pm c$ , by 0.58 Å. In this position the coordination is (irregular) octahedral, which is generally preferred by Na<sup>+</sup> ions. Because of the symmetry of the prism, the cation has the same energy when it is displaced in either direction (neglecting short-range order), giving rise to disorder.

The refinement of anisotropic temperature factors for NaNdF<sub>4</sub> provides a rather detailed picture of the thermal motion of the atoms. A means of graphic representation of the probability ellipsoids of thermal motion employing a computer and  $x$ - $y$  recorder was devised by Johnson<sup>19</sup>; it was applied to NaNdF<sub>4</sub> to produce Figure 2, which shows a portion of the NaNdF<sub>4</sub> structure in which the effect of its neighbors on the thermal motion of each kind of atom can be seen. The scale of the ellipsoids relative to interatomic separations is such as to represent 65% probability of finding the atom within each ellipsoid. It is seen that the motions of the fluorides are larger than those of the Nd or (Na,Nd) ions and are quite anisotropic. The F(1) ion is much freer to move perpendicular to its bond to Nd than along it and is unrestrained by the 2.51 Å. bond to the (Na,Nd) atom, but the F(2) ion is restricted by shorter bonds of 2.40 and 2.43 Å. to Nd and (Na,Nd) ions. The Na<sup>+</sup> ion (omitted from the drawing for clarity) shows a motion approximately equal in magnitude to that of the F<sup>-</sup> ions, reflecting not only its small mass but the uncertainty of site occupancy.

(18) These computations were made with the Fortran Crystallographic Function and Error program by W. R. Busing, K. O. Martin, and H. A. Levy, U.S.A.E.C. Report ORNL-TM-306 (1964).

(19) C. K. Johnson, American Crystallographic Association Bozeman Meeting Abstracts, Paper A-11, 1964; U.S.A.E.C. Report ORNL-3679 (1964).

(17) J. M. Bijvoet, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **B62**, 313 (1949); A. F. Peerdeman, A. J. van Bommel, and J. M. Bijvoet, *ibid.*, **B54**, 16 (51); J. M. Bijvoet, *Nature*, **173**, 888 (1954).

Figure 2.—Ellipsoids of thermal motion in NaNdF<sub>4</sub>.

The (Na,Nd) ion motion is rather small since the site, although disordered, is fully occupied. An attempt to obtain more detail about the disorder was made by varying the occupancy factors at the disordered sites, but values not significantly different from the ideal numbers of Table I were obtained. There remains the possibility that the temperature factors do not describe the actual thermal motions but compensate for an inadequate description of the disorder.

**Relationship to Other Compounds.**—The structure of NaNdF<sub>4</sub> is not the  $\beta_2$ -Na<sub>2</sub>ThF<sub>6</sub>-type which Zachariassen<sup>6</sup> described and assigned to  $\beta_2$ -K<sub>2</sub>UF<sub>6</sub>,  $\beta_2$ -Na<sub>2</sub>UF<sub>6</sub>, NaPuF<sub>4</sub>, NaLaF<sub>4</sub>, and NaCeF<sub>4</sub>. Although none of these compounds has been the subject of a complete crystal-structure determination, our unit-cell and space-group data on the last two compounds suggest strongly that they are isostructural with NaNdF<sub>4</sub>. There are similarities between the two structures, but a significant difference from a crystal chemical viewpoint is that in Zachariassen's structure some of the rare earth ions are in octahedral sites, whereas in NaNdF<sub>4</sub> they are all nine-coordinated. The larger coordination is generally present in other rare earth compounds. The structure of  $\beta_2$ -Na<sub>2</sub>ThF<sub>6</sub> and the compounds of similar stoichiometry still seems likely to be that given by Zachariassen; in those cases the two Na<sup>+</sup> ions are octahedrally coordinated, and the heavy ions are nine-coordinated. Although we X-ray photographed some single crystals of  $\beta_2$ -Na<sub>2</sub>ThF<sub>6</sub>, the large absorption effects have prevented us from ascertaining the Laue symmetry or space group. The diffuse streaks are absent from these photographs, since there is no disorder of cations.

The mineral gagarinite<sup>8</sup> with ideal formula NaCaMF<sub>6</sub>, where M is a rare earth or yttrium ion, has been studied crystallographically,<sup>20</sup> and a structure has been derived

for it which is similar to that of NaNdF<sub>4</sub>. Moreover, the hexagonal NaYF<sub>4</sub> has been said to be isomorphous with it.<sup>7</sup> A comparison of atomic positions in gagarinite and in NaNdF<sub>4</sub> (Table IV) shows that the struc-

TABLE IV  
COMPARISON OF PARAMETERS FOR GAGARINITE<sup>a</sup>  
AND NaNdF<sub>4</sub>

Atom(s)	Gagarinite (NaCaREFe)			NaNdF <sub>4</sub>			Atom(s)
	x	y	z	x	y	z	
R.E., <sup>b</sup> Ca	0	0	0.000	0	0	0	Nd
R.E., Ca	2/3	1/3	0.500	2/3	1/3	1/2	1/2Na, 1/2Nd
F	0.651	0.060	0.000	0.634	0.043	0	F(1)
F	0.726	0.742	0.500	0.734	0.755	1/2	F(2)
Na	1/3	2/3	3/4	1/3	2/3	0.656	1/2Na, vacancy

<sup>a</sup> In order to superimpose the structures for comparison, the origin of the NaNdF<sub>4</sub> structure was placed at 2/3, 1/3, 0.25 in the gagarinite structure; the fluorine atom parameters given for gagarinite are two members of a symmetry-related set. <sup>b</sup> R.E. = rare earth.

tures are almost identical except for the sodium atom in the last row of the table. The authors pointed out that their structure for gagarinite has the symmetry of space group  $P\bar{3}$ , but that all atoms except the sodium conform to the higher symmetry of  $P6_3/m$ , the space group indicated by systematic absences. Implicit in this statement is the fact that reflections of type (00l) were observed only for  $l = 2n$  and that the scattering by the sodium atoms, which alone contribute to (00l) reflections with  $l = 2n + 1$ , was too small to be observed. We believe that sodium atoms at the origin, in an ordered arrangement, would produce measurable intensity for these reflections and suggest instead that the sodium atoms are distributed randomly over twofold sites (displaced from the origin of  $P\bar{3}$ ) as in NaNdF<sub>4</sub>. This would reduce their contribution by one-half by random occupancy and further by phase shift. Moreover, with regard to the other atoms in the gagarinite structure, the authors themselves pointed out the surprising feature that the z coordinates of these atoms all have values of exactly 1/4 and 3/4 although not required to by symmetry. This is easily accounted for by assignment to the space group  $P6_3/m$  (or  $P\bar{6}$ ) where such specialized coordinates are available.

Single crystals of NaMF<sub>4</sub> were photographed and the diffraction symmetries established. For M = La, Ce, Pr, Nd, Eu, Gd, Tb, Ho, and Er the symmetry found was  $6/mP6$ --; for M = Y, Sm, and Tm it was  $6/mP6_3$ --; and for two different crystals of NaDyF<sub>4</sub>, one of each symmetry was found. It is easily shown, by arguments similar to those used in establishing the space group of NaNdF<sub>4</sub>, that the only space groups having the above diffraction symmetries and allowing reasonable structures for the NaMF<sub>4</sub> compounds are  $P\bar{6}$  and  $P6_3/m$ .

The main features of the NaNdF<sub>4</sub> structure can be described in space group  $P\bar{6}$  or  $P6_3/m$ . Details which require the former are: the slightly different x,y parameters in F(1) and F(2) and the position of the 1/2 Na atom. The intensity of 00l reflections ( $l = 2n + 1$ ), used to distinguish between  $P\bar{6}$  and  $P6_3/m$ , depends

(20) A. A. Voronkov, N. G. Shumyatskaya, and Yu. A. Pyatenko, *Zh. Strukt. Khim.*, **3**, 691 (1962).

primarily on the difference in scattering power of atoms in 0, 0, 0 and  $2/3, 1/2, 1/2$ . If the  $\text{Nd}^{3+}$  and  $\text{Na}^+$  ions in these sites are randomly intermixed, their contributions become zero and only those  $\text{Na}^+$  ions in  $\pm 0, 0, z$  contribute; these may be barely detectable as described above. Thus it is probable that the  $\text{NaMF}_4$  crystals showing  $P6_3/m$  symmetry (and also gagarinite) have very nearly, if not precisely, the  $\text{NaNdF}_4$  structure, but with random mixing of the  $\text{M}^{3+}$  and  $\text{Na}^+$  ions in 0, 0, 0 and  $2/3, 1/3, 1/2$ . The fact that their high-temperature forms have complete mixing of cations in the fluorite structure adds credence to this view. Some of the crystals were obtained from slowly cooled melts, while others were made by quenching, and indeed it may be possible to prepare all of these compounds in both forms; *i.e.*, the degree of randomness may be determined by the cooling rate.

**Diffuse X-Ray Reflections.**—The diffuse streaks observed in X-ray photographs of  $\text{NaNdF}_4$  are of the type reported for the mineral wollastonite,  $\text{CaSiO}_3$ . A discussion of the origin of this phenomenon is given by Wooster.<sup>21</sup> An analogous explanation for  $\text{NaNdF}_4$

(21) W. A. Wooster, "Diffuse X-Ray Reflections from Crystals," Clarendon Press, Oxford, 1962, pp. 118–121.

is as follows. Consider the site at  $2/3, 1/3, 1/2$ , which is occupied by both  $\text{Na}^+$  and  $\text{Nd}^{3+}$  ions. It is 3.71 Å. from the equivalent site in the next unit cell along *c*, but is 6.10 Å. from equivalent sites in the (001) plane. Thus, for example, when an  $\text{Na}^+$  ion occupies the site, it is highly probable that  $\text{Nd}^{3+}$  ions will be at  $\pm c$ , but at adjacent sites in the (001) plane either kind of ion may be found with equal probability. This results in an ordered string of cations along *c* but permits parallel strings to be shift in the *c* direction by 3.71 Å. Willis<sup>22</sup> has studied the diffraction patterns obtained from this kind of disorder as a function of the probability that a shift occurs in going from one string to the next. By comparison with his examples the  $\text{NaNdF}_4$  photographs indicate that this probability is about 0.5; *i.e.*, the shifts are completely random.

**Acknowledgments.**—The author wishes to thank R. E. Thoma for advice and encouragement in carrying out this study and G. M. Hebert for preparing the crystals. Computer programs were supplied by C. K. Johnson and R. D. Ellison.

(22) B. T. M. Willis, *Proc. Roy. Soc. (London)*, **A248**, 183 (1958).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
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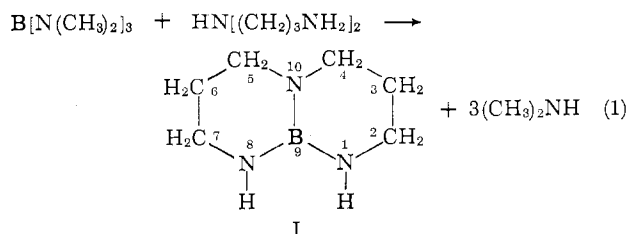
## Boron-Nitrogen Compounds. XVII.<sup>1,2</sup> Reactions of 1,8,10,9-Triazaboradecalin

By PETER FRITZ, KURT NIEDENZU, AND JOHN W. DAWSON

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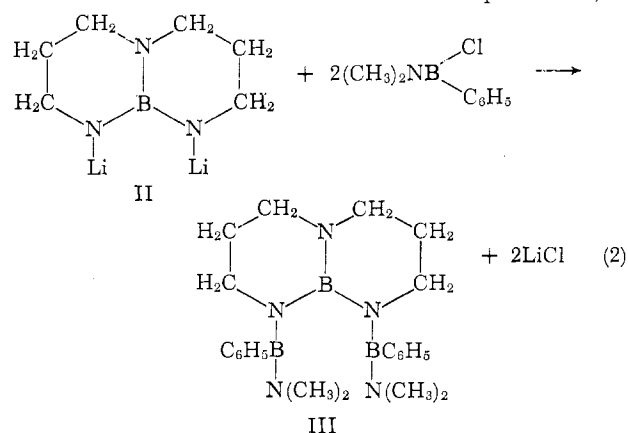
Several reactions of 1,8,10,9-triazaboradecalin which indicate a new route to the synthesis of unsymmetrically substituted borazines as well as for several new boron-nitrogen-carbon heterocycles have been studied. This research has also led to the discovery of a novel type of boron-nitrogen heterocycle, containing four nitrogen and three boron atoms as annular members, *i.e.*, the 1,3,5,6-tetraaza-2,4,7-triborine system.

Recently, the preparation of 1,8,10,9-triazaboradecalin (I) by a very simple method as illustrated in eq. 1 was reported.<sup>1</sup> We now wish to present a more detailed study of the chemical reactions of I.



The NH groups in I can be metallated by allowing that compound to react with lithium alkyl; the resultant dilithium salt, II, is extremely sensitive toward moisture. It, in turn, was allowed to react *in situ*

with dimethylaminophenylchloroborane, to provide compound III, 1,8-bis(dimethylaminophenylboryl)-1,8,10,9-triazaboradecalin as shown in eq. 2. III, in



like manner, reacts with aniline to yield the unsymmetrically substituted borazine, IV, hexahydro-1,2,3-

(1) Part XVI: K. Niedenzu, P. Fritz, and J. W. Dawson, *Inorg. Chem.*, **3**, 1077 (1964).

(2) Supported by the U. S. Army Research Office—Durham.