JOURNAL OF SOLID STATE CHEMISTRY 2, 416–420 (1969)

The Crystal Structure of Hexagonal $RbNiF_3$(6H)*

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Received May 6, 1970

At atmospheric pressure, $RbNiF_3$ has the hexagonal $BaTiO_3$ structure. The variation of its lattice parameters is studied from −175 to 600°C and shows no anomaly. The coefficient of thermal expansion α_a increases from 14×10^{-6} to $27 \times 10^{-6}\,°C^{-1}$ and α_c increases from 11×10^{-6} to $28 \times 10^{-6}\,°C^{-1}$. Our refinement of position parameters using powder pattern intensities leads to results that are in essential agreement with those of Babel. However, disagreement in the fluorine positions lead to significantly different interatomic distances and angles. These differences are discussed in terms of similar known structures, published nmr data and electrostatic repulsion and screening of ions.

$RbNiF_3$ exists in two modifications. At ambient pressure (*1*), it has the hexagonal $BaTiO_3$ (6H) structure (*2*) while at high pressure (~ 25 kbar) its structure transforms to the cubic perovskite type (*3, 4*) with $a = 4.07$ Å. This pressure transformation is similar to those found for many compounds with a general formula ABX_3 having hexagonal or cubic close-packed AX_3 layers (*3–6*).

The hexagonal form of $RbNiF_3$ is of considerable interest because of its ferrimagnetic (*7, 8*) and optical properties (*9, 10*). Since accurate bond distances and angles are necessary for any quantitative interpretation of physical properties, we undertook the refinement of the atomic position parameters of $RbNiF_3$ (6H).

The structure has only five variable parameters. Since the powder pattern is not complex, we chose to use intensity data collected on powdered samples. After we had obtained a satisfactory refinement of our data, we became aware of a recent paper by Babel (*11*), who refined the parameters of this structure using intensity data from a single crystal. Our results are in essential agreement with those of Babel, but we find significant discrepancies in the positions of the fluorines. The resulting differences in bond distances (Ni–F, F–F, Rb–F) and Ni–F–Ni angles are discussed in light of published nmr data (*12*) and the structures of $BaTiO_3$ (*2*), $CsMnF_3$ (*13*), $CsCoF_3$ (*11*), and $CsNiF_3$ (*11*).

Experimental

All material used in this study was taken from a large single crystal of $RbNiF_3$ prepared by the Bridgman method using a graphite crucible sealed in a nickel bomb. Lattice parameters of hexagonal $RbNiF_3$ were obtained over the temperature range −175 to 600°C. At room temperature, peak positions were taken from a slow-scan (¼°/min) diffractometer pattern using a Norelco goniometer and monochromated (LiF crystal) CuKα radiation. These were corrected by use of an external standard. For lattice parameters below room temperature, the same equipment was used except that the sample was deposited on a copper plate with acetone. The copper plate is cooled in a stream of N_2 which has been passed through a large copper coil immersed in liquid N_2. The temperature is controlled by varying the gas flow rate and monitored by a copper-constantan thermocouple attached to the copper plate. A G.E. diffractometer with a Tem-Pres furnace attachment was used to determine the lattice constants of $RbNiF_3$ above room temperature. The sample was held in a nickel holder and protected by a continuous flow of dry nitrogen. Lattice parameters were obtained for all temperatures by refinement of 2θ values using the simplex method with a computer program written in our laboratory.

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* This work was sponsored by the Department of the Air Force.

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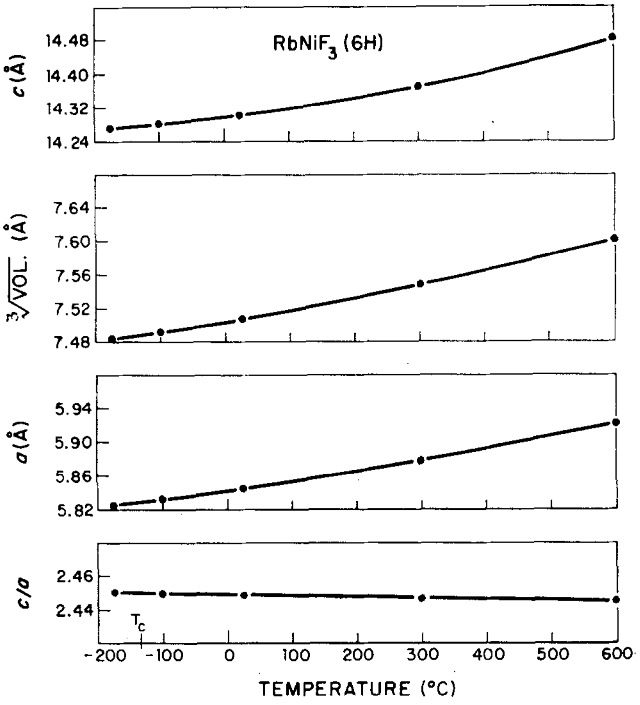

FIG. 1. Crystallographic parameters of RbNiF$_3$(6H) as a function of temperature.

Intensity data at room temperature were collected on a Norelco diffractometer by accumulating counts while scanning ($\frac{1}{4}$°/min) over the peak, or groups of peaks, and subtracting background. The value of background at any particular 2θ value was taken from a curve constructed from background readings in regions containing no peaks.

Below room temperature, intensity data were collected by measuring the area under the peaks of the same diffractometer tracings used for lattice-parameter determinations.

Refinement of variable atomic-position parameters and cell temperature factor was made using a Fortran program which minimized the discrepancy factor

$$R = 100\cdot\sum_i |I_i^{\text{calcd}} - I_i^{\text{obsd}}| / \sum_i I_i^{\text{obsd}}.$$

The atomic scattering factors for Rb^+, Ni^{2+}, and F^- were those of Cromer and Waber (*14*), while the real and imaginary parts of the anomalous dispersion terms were taken from Cromer (*15*). The intensity data were corrected for the polarization due to the curved LiF diffracted-beam monochromator.

Results and Discussion

We found the lattice parameters of RbNiF$_3$ (6H) at room temperature to be $a = 5.843$ Å and $c = 14.309$ Å, which are identical to those previously reported (*1*). The variation of the lattice parameters in the temperature range −175 to 600°C is shown in Fig. 1. No change in symmetry or anomaly in the temperature dependence of the lattice parameters was noted over the entire temperature range, which includes the Curie point. Although this structure can be described in terms of RbF$_3$ close-packed layers with nickel ions filling the fluorine octahedra formed between layers, the coefficients of linear thermal expansion in the a and c directions are very similar. Over the temperature range studied, α_a increases from 14×10^{-6} to 27×10^{-6}°C^{-1} and α_c from 11×10^{-6} to 28×10^{-6}°C^{-1}. This almost constant c/a ratio (2.450–2.446) is consistent with our determination of the three-dimensional character of the bonding in this structure.

RbNiF$_3$(6H) has the hexagonal BaTiO$_3$ structure (2) indicated in Fig. 2. It contains face-shared pairs of NiF$_6$ octahedra connected by single octahedra sharing only corners. The rubidium ions, which fill the six large voids per unit cell of this octahedra network have twelvefold coordination. There are two different positions for each type of atom, as shown in Fig. 2 and Table I.

Refinement on thirty-five intensities gives the cell temperature factor and the five variable position parameters listed in Table I with a reliability factor

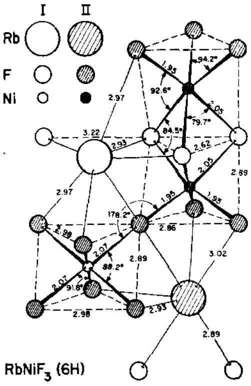

FIG. 2. Essential features of the RbNiF$_3$(6H) structure.

$R = 5.8$. The estimated errors were established by determining the amount of change in the parameters which would cause a significant deterioration in the R factor. Table II presents a comparison of all the observed intensities with those calculated from the results of the refinement. The reliability factor here is $R = 6.9$. It should be noted that seven of the intensities listed were not used in the refinement. The strongest line (100, 104) was eliminated because it had too much influence on the refinement; the other six lines were not used because they contained more than three reflections contributing to a single intensity. A value of 0.05 was assigned in the refinement to those reflections whose intensities were not observed. They are labeled in Table II by an asterisk.

Refinement of intensity data collected at −100 and −175°C resulted in essentially the same structure as at room temperature, but with larger error brackets for the parameters. The very rough surface of the sample resulting from the method used to apply it to the copper block no doubt reduced the quality of the data.

Babel's position parameters (*11*) from a single-crystal structure refinement are included in Table I. They show good agreement with our cation parameters, but significant differences with our fluorine positions. Most affected by this discrepancy are the F_I–F_I distance and Ni_{II}–F_I–Ni_{II} angle. A comparison of interatomic distances and angles resulting from Babel's refinement and ours is given in Table III. The important interatomic distances and bond angles obtained from our refinement are also shown in Fig. 2, which gives all the essential features of this structure.

The Ni^{2+}_{II} ions, which share a common octahedral-site face, are forced apart by electrostatic repulsive forces, and are separated by 2.75 Å instead of 2.38 Å (1/6 of c). Similarly, the Rb^{+}_{II} ions are displaced along the z axis away from the approaching Ni^{2+}_{II}, but to a lesser extent because of the larger separation and smaller charges involved. The F^{-}_{I} ions forming the common octahedral-site face between the Ni^{2+}_{II} ions should be drawn in tightly to form a smaller triangle that can better screen the Ni^{2+}_{II} ions from one another. Since the Ni_{II}–Rb_{II} separation is smaller than the Rb_I–Ni_I separation the triangle of F^{-}_{II} ions between the Ni_{II}–Rb_{II} pair

TABLE I

CRYSTAL STRUCTURE OF RbNiF$_3$(6H)

Space group:	$P6_3/mmc$ (No. 194)
Unit cell dimensions:	$a = 5.843$ Å; $c = 14.309$ Å
Cell contents:	6RbNiF$_3$
Rb_I in (2*b*)	± (0, 0, 1/4)
Rb_{II} in (4*f*)	± (1/3, 2/3, z; 2/3, 1/3, 1/2 + z)
	$z = 0.0954(2)$; $0.0954(7)^a$
Ni_I in (2*a*)	(0, 0, 0; 0, 0, 1/2)
Ni_{II} in (4*f*)	± (1/3, 2/3, z; 2/3, 1/3, 1/2 + z)
	$z = 0.8462(5)$; $0.8450(8)^a$
F_I in (6*h*)	± (x, $2x$, 1/4; $2x$, x, 3/4; x, $\bar{x}$, 1/4)
	$x = 0.517(1)$; $0.5023(82)^a$
F_{II} in (12*k*)	± (x, $2x$, z; $2x$, x, $\bar{z}$; x, $\bar{x}$, z; x, $2x$, $1/2 - z$; $2x$, x, $1/2 + z$; $\bar{x}$, x, $1/2 + z$)
	$x = 0.830(3)$, $0.8313(89)^a$; $z = 0.081(1)$, $0.0740(17)^a$
Cell temperature factor:	B = 1.9(1)

[a] Our results are listed first with estimated error limits in parentheses; Babel's results (*11*) are listed second for comparison.

TABLE II

OBSERVED AND CALCULATED INTENSITIES FOR $RbNiF_3$(6H)

I_{obsd}	I_{cacld}	*hkl*
*	0.01	002
*	0.02	100
2.7	2.34	101
0.1	0.15	102
0.4	0.99	004
12.2	12.23	103
100.0†	105.51	110 104
0.2	0.08	112
*	0.00	200
6.4	6.29	201 105
14.9	14.82	202 105
23.7	23.09	114 203
*	0.00	106
34.7	34.54	204
11.3†	12.61	210 211 205 107
0.2	0.26	212 116
2.7	2.93	008 213
*	0.00	206
26.4	26.42	300 214 108
*	0.01	302
8.6	8.73	303 215 207
6.1	6.10	304 118 109
*	0.01	216
14.8	17.89	220 208 305
*	0.00	222 0010
4.6	4.55	310 311 217

I_{obsd}	I_{calcd}	*hkl*
0.3	0.36	312 306 1010
5.6	5.87	224 313 209
7.7	6.72	314 218 307
*	0.06	1110
2.3†	2.02	400 401 315 1011
4.2	3.84	402 226 2010
5.1†	4.56	308 403 219 316
*	0.00	316
5.4	4.59	404 0012
3.6†	2.76	320 1012 321 405 317 309 2011
2.2	1.53	228 323
*	0.00	406
12.8†	8.91	410 324 318 1112 411
*	0.05	412 3010
3.3†	2.63	2012 413 325 407 2111 1013
1.7	1.27	414 319

* Not observed but assigned an intensity of 0.05 during refinement.

† Not used in refinement.

TABLE III

SOME INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN $RbNiF_3$(6H)

Rb_I–$6F_I$	2.93(2.92)[a]	F_I–$2F_I$	2.62 (2.88)
$6F_{II}$	2.97(3.04)	$2F_I$	3.22(2.96)
		$4F_{II}$	2.89(3.02)
Rb_{II}–$6F_{II}$	2.93(2.94)		
$3F_{II}$	3.02(2.94)	F_{II}–$2F_{II}$	2.86(2.89)
$3F_I$	2.89(2.80)	$2F_{II}$	2.89(2.72)
		$2F_{II}$	2.98(2.96)
Ni_I–$6F_{II}$	2.07(2.01)	$2F_I$	2.89(3.02)
Ni_{II}–$1Ni_{II}$	2.75(2.72)		
$3F_I$	2.05(2.15)		
$3F_{II}$	1.95(2.03)		

F_{II}–Ni_I–F_{II}	88.2(85.2); 91.8(94.78)
F_I–Ni_{II}–F_I	79.7(84.2)
$F_{II}N{:}_{II}F_{II}$	94.2(90.6)
F_I–Ni_{II}–F_{II}	92.6(92.5)
Ni_{II}–F_I–Ni_{II}	84.5(78.5)
Ni_I–F_{II}–Ni_{II}	178.2(177.0)

[a] The values in parentheses are those reported by Babel (*11*).

would also contract somewhat causing the F_{II}-triangle between the Ni_I–Rb_I pair to expand. Thus we would expect the F_I triangles between the Ni_{II}–Ni_{II} pairs to have the shortest edges, the F_{II} triangles between the Ni_{II}–Rb_{II} pairs to have the next shortest edges, the F_{II} triangles between Ni_I–Rb_I pairs to have longer edges, and the F_I triangles between the Rb_{II}–Rb_{II} pairs to have the longest edges.

As the Ni^{2+}_{II} ions move apart, the Ni_{II}–F_{II} distances would be significantly shortened relative to the other Ni–F distances. The Ni_{II}–F_I distance would tend to be lengthened by the Ni displacement but shortened by the contraction of the F_I triangle. The Ni_I–F_{II} distance would tend to be lengthened by the expansion of the F_{II} triangle but be compensated by a compression of the F_{II} octahedra along the z axis so as to keep the bond distance nearly normal. Thus we would expect the Ni_{II}–F_{II} distance to be the shortest and the other Ni–F distances to be about equal and close to normal.

Our F–F and Ni–F distances are in agreement with the above description and are shown in Fig. 2 and in Table III, which also includes Babel's results for comparison. It should be noted that there is a significant difference between the F_I–F_I distances we find (2.62 and 3.22 Å) and those found by Babel (2.88 and 2.96 Å). In isostructural compounds, the shorter of these distances always shows a marked contraction and is 2.69 Å in $CsMnF_3$ (*13*) and 2.49 Å in hexagonal $BaTiO_3$ (*2*). In other close packed ABF_3 compounds a similar contraction is found for the fluorine triangle that forms the common octahedral-site face [2.64 Å in $CsCoF_3$ (*11*) and 2.68 Å in $CsNiF_3$ (*11*)]. This reduction in anion–anion distance to screen pairs of cations is even more general and extends to the corundum-type structures. For example, in Cr_2O_3 (*16*) the O_I–O_I distance is reduced from an average distance of 2.80 Å to 2.62 Å.

It should also be noted that the average Ni–F distance found by Babel (2.049) is higher than our average distance (2.035 Å) or the sum of the ionic radii (2.02 Å) (*17*). The very long Ni_{II}–F_I distance (2.15 Å) found by Babel results because his small F_I triangle is not contracted although his Ni_{II}–Ni_{II} distance is lengthened. This leads also to a smaller Ni_{II}–F_I–Ni_{II} angle in Babel's refinement (78.5°) than in ours (84.5°). This angle approaches 90° in the isostructural compounds $CsMnF_3$ (88.0°) and $BaTiO_3$ (85.8°). In the structurally related $CsCoF_3$ (*11*) the corresponding angle is 84.5°. Furthermore, Smolenskii et al. (*12*) have shown by nmr studies that this Ni_{II}–F_I–Ni_{II} angle in $RbNiF_3$ (6H) is $90° \pm 4°$. Their data also show the Ni_I–F_{II}–Ni_{II} angle to be $180° \pm 10°$, which agrees both with our value (178°) and that of Babel (177°).

One can only speculate as to why there is a difference between our results and those of Babel. We do feel however that our atomic positions are more probable since they are in agreement with similar structures, nmr data and our understanding of electrostatic repulsion and screening.

Acknowledgments

We are grateful to J. R. O'Connor for providing us with a large single crystal of $RbNiF_3$. Also we are happy to acknowledge valuable discussions with J. B. Goodenough and the technical assistance of D. A. Batson.

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