

While parts *A* and *B* consist mainly of rigid fused-ring systems, different conformers of comparable energy are possible by rotation about the linking bond C(4)–C(25). The conformation about this bond observed in the crystal structure is shown in the Newman diagram in Table 6. This is most likely determined by the intramolecular hydrogen bond O(1)···H–O(5), the interactions Br(1)···O(5), 3.17 Å, and Br(2)···O(4), 3.15 Å, both of which may be hydrogen bonds, and the close approach Br(2)···C(26), 3.39 Å. These Br–O distances and the intramolecular hydrogen bonds are shown in Fig. 3 which is a diagram of the molecular packing in the unit cell. There are no other bromine distances shorter than 3.55 Å, but each bromide ion is within 4.75 Å of 29 C, N and O atoms from three different molecular cations. The intermolecular distances less than 4 Å are listed in Table 7.

It is notable that the bromide ions occupy positions which indicate participation in hydrogen bonding in preference to positions which would imply pure ionic interactions with the formally positively-charged quaternary N(2) and N(3) atoms; the shortest Br–N distance is 3.55 Å. The short Br(2)–C(26) distance may be indicative of some localization of positive charge on the carbon atom adjacent to the quaternary nitrogen atom rather than at the nitrogen atom itself.

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Structures of Ferrimagnetic Fluorides of ABF_3 Type.

I. $RbNiF_3$

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The crystal structure of $RbNiF_3$ has been determined from a least-squares refinement of three-dimensional X-ray data. Intensity data were acquired with the CCXD, a computer controlled X-ray diffractometer, operating in a time shared environment on an IBM 1800 Controller System. The space group is $P6_3/mmc$. The lattice constants of the unit cell, which contains six formula units of $RbNiF_3$, are $a = 5.840 \pm 0.002$ and $c = 14.308 \pm 0.004$ Å. All of the ions in this structure occupy special positions. The nickel ions occupy two non-equivalent sites, each the center of a fluorine octahedron. Two-thirds of the NiF_6 octahedra occur in face-sharing pairs to form Ni_2F_9 polyhedra. The remaining NiF_6 octahedra are linked to the Ni_2F_9 polyhedra by sharing of corners. The average Ni–F distance is 2.028 ± 0.008 Å.

Introduction

A great deal of attention has been directed to studies of the interesting magnetic and optical properties of ABF_3 -type ferrimagnetic fluorides with the hexagonal

$BaTiO_3$ structure. $RbNiF_3$, an unusually transparent material, has been one of the most extensively studied compounds of this group, at these Laboratories and elsewhere. Rudorff, Kandler & Babel (1962) first synthesized the compound, reported it as a probable ferri-

magnet, and published powder data indicating a structure similar to that of the hexagonal form of BaTiO₃ (Burbank & Evans, 1948). A more recent paper presented data supporting the ferrimagnetic model and reported on its magneto-optical properties (Shafer, McGuire, Argyle & Fan, 1967). Low temperature single-crystal work done at these Laboratories (Stemple & Wnuk, 1968) confirmed the space group (*P*₆₃/*mmc*) and indicated no structural change down to 30°K. In addition to the work done on the pure compound, McGuire & Shafer (1968) have replaced nickel in the hexagonal structure with other magnetic and nonmagnetic ions, to gain further insight of the magnetic structure.

A precise knowledge of the ionic positions would be useful in making a more accurate interpretation of the magnetic and optical properties of RbNiF₃ and analogous substituted compounds. Because this information has not heretofore been available, the present work was undertaken to provide a detailed structure analysis of RbNiF₃.

Experimental

Crystals of RbNiF₃ used in this work were prepared by M. W. Shafer of these Laboratories, following a procedure described elsewhere in detail (Shafer, McGuire, Argyle & Fan, 1967). Briefly, the method involves the direct reaction of RbF and NiF₂, and subsequent growth of single crystals from a melt of the reacted

materials by the Stockbarger technique. The lattice constants, determined from diffractometer data, are: $a = 5.840 \pm 0.002$ and $c = 14.308 \pm 0.004$ Å. Six formula weights in the unit cell give a calculated density of 4.742 g.cm⁻³; and a linear absorption coefficient for Mo *K*α radiation ($\lambda = 0.7107$ Å) of 247.8 cm⁻¹. An attempt was made to grind a spherical sample from the material in order to facilitate an absorption correction, but difficulties were experienced in obtaining a uniform sphere. After several tries, a sample with approximately 10% variation in diameter was obtained. This sample, with an average radius of 0.0165 cm ($\mu R = 4.09$), was used for the intensity measurements.

Preliminary orientation of the sample was accomplished by a series of oscillation photographs. The crystal was then set up for intensity measurements on the CCXD, a computer controlled X-ray diffractometer (Cole, Okaya & Chambers, 1963) operating in a time shared environment on an IBM 1800 Controller System (Bednowitz, Ryniker & Cole, 1968). Integrated intensities were obtained by a continuous $\theta-2\theta$ scanning method*, using Mo *K*α radiation and a scintillation counter with pulse height discrimination. Stability of the equipment was monitored by periodic reference to two standard reflections throughout the period of

* Scan lengths were computed by the control program, using the formula $\alpha + \alpha K \tan \theta$ where α and K are empirically determined constants for a given crystal and θ has the usual meaning.

Table 1. Observed and calculated structure amplitudes ($\times 10$) and standard deviations ($\times 10$) for RbNiF₃

Unobserved reflections are marked with asterisks to improve readability of the Table.

L	FO	FC	S	L	FO	FC	S	L	FO	FC	S	L	FO	FC	S	L	FO	FC	S
0	0	0	0	17	0	0	0	17	0	0	0	17	0	0	0	17	0	0	0
4	389	125	25	18	0	0	0	18	0	0	0	18	0	0	0	18	0	0	0
6	398	125	25	19	0	0	0	19	0	0	0	19	0	0	0	19	0	0	0
10	800	879	38	20	0	0	0	20	0	0	0	20	0	0	0	20	0	0	0
12	1900	0	0	21	0	0	0	21	0	0	0	21	0	0	0	21	0	0	0
14	341	350	21	22	0	0	0	22	0	0	0	22	0	0	0	22	0	0	0
16	86	86	18	23	0	0	0	23	0	0	0	23	0	0	0	23	0	0	0
18	840	827	18	24	0	0	0	24	0	0	0	24	0	0	0	24	0	0	0
0	0	0	0	25	0	0	0	25	0	0	0	25	0	0	0	25	0	0	0
2	2	4	0	26	0	0	0	26	0	0	0	26	0	0	0	26	0	0	0
4	389	125	25	27	0	0	0	27	0	0	0	27	0	0	0	27	0	0	0
6	398	125	25	28	0	0	0	28	0	0	0	28	0	0	0	28	0	0	0
10	800	879	38	29	0	0	0	29	0	0	0	29	0	0	0	29	0	0	0
12	1900	0	0	30	0	0	0	30	0	0	0	30	0	0	0	30	0	0	0
14	341	350	21	31	0	0	0	31	0	0	0	31	0	0	0	31	0	0	0
16	86	86	18	32	0	0	0	32	0	0	0	32	0	0	0	32	0	0	0
18	840	827	18	33	0	0	0	33	0	0	0	33	0	0	0	33	0	0	0
20	0	0	0	34	0	0	0	34	0	0	0	34	0	0	0	34	0	0	0
22	0	0	0	35	0	0	0	35	0	0	0	35	0	0	0	35	0	0	0
24	0	0	0	36	0	0	0	36	0	0	0	36	0	0	0	36	0	0	0
26	0	0	0	37	0	0	0	37	0	0	0	37	0	0	0	37	0	0	0
28	0	0	0	38	0	0	0	38	0	0	0	38	0	0	0	38	0	0	0
30	0	0	0	39	0	0	0	39	0	0	0	39	0	0	0	39	0	0	0
32	0	0	0	40	0	0	0	40	0	0	0	40	0	0	0	40	0	0	0
34	0	0	0	41	0	0	0	41	0	0	0	41	0	0	0	41	0	0	0
36	0	0	0	42	0	0	0	42	0	0	0	42	0	0	0	42	0	0	0
38	0	0	0	43	0	0	0	43	0	0	0	43	0	0	0	43	0	0	0
40	0	0	0	44	0	0	0	44	0	0	0	44	0	0	0	44	0	0	0
42	0	0	0	45	0	0	0	45	0	0	0	45	0	0	0	45	0	0	0
44	0	0	0	46	0	0	0	46	0	0	0	46	0	0	0	46	0	0	0
46	0	0	0	47	0	0	0	47	0	0	0	47	0	0	0	47	0	0	0
48	0	0	0	48	0	0	0	48	0	0	0	48	0	0	0	48	0	0	0
50	0	0	0	49	0	0	0	49	0	0	0	49	0	0	0	49	0	0	0
52	0	0	0	50	0	0	0	50	0	0	0	50	0	0	0	50	0	0	0
54	0	0	0	51	0	0	0	51	0	0	0	51	0	0	0	51	0	0	0
56	0	0	0	52	0	0	0	52	0	0	0	52	0	0	0	52	0	0	0
58	0	0	0	53	0	0	0	53	0	0	0	53	0	0	0	53	0	0	0
60	0	0	0	54	0	0	0	54	0	0	0	54	0	0	0	54	0	0	0
62	0	0	0	55	0	0	0	55	0	0	0	55	0	0	0	55	0	0	0
64	0	0	0	56	0	0	0	56	0	0	0	56	0	0	0	56	0	0	0
66	0	0	0	57	0	0	0	57	0	0	0	57	0	0	0	57	0	0	0
68	0	0	0	58	0	0	0	58	0	0	0	58	0	0	0	58	0	0	0
70	0	0	0	59	0	0	0	59	0	0	0	59	0	0	0	59	0	0	0
72	0	0	0	60	0	0	0	60	0	0	0	60	0	0	0	60	0	0	0
74	0	0	0	61	0	0	0	61	0	0	0	61	0	0	0	61	0	0	0
76	0	0	0	62	0	0	0	62	0	0	0	62	0	0	0	62	0	0	0
78	0	0	0	63	0	0	0	63	0	0	0	63	0	0	0	63	0	0	0
80	0	0	0	64	0	0	0	64	0	0	0	64	0	0	0	64	0	0	0
82	0	0	0	65	0	0	0	65	0	0	0	65	0	0	0	65	0	0	0
84	0	0	0	66	0	0	0	66	0	0	0	66	0	0	0	66	0	0	0
86	0	0	0	67	0	0	0	67	0	0	0	67	0	0	0	67	0	0	0
88	0	0	0	68	0	0	0	68	0	0	0	68	0	0	0	68	0	0	0
90	0	0	0	69	0	0	0	69	0	0	0	69	0	0	0	69	0	0	0
92	0	0	0	70	0	0	0	70	0	0	0	70	0	0	0	70	0	0	0
94	0	0	0	71	0	0	0	71	0	0	0	71	0	0	0	71	0	0	0
96	0	0	0	72	0	0	0	72	0	0	0	72	0	0	0	72	0	0	0
98	0	0	0	73	0	0	0	73	0	0	0	73	0	0	0	73	0	0	0
100	0	0	0	74	0	0	0	74	0	0	0	74	0	0	0	74	0	0	0
102	0	0	0	75	0	0	0	75	0	0	0	75	0	0	0	75	0	0	0
104	0	0	0	76	0	0	0	76	0	0	0	76	0	0	0	76	0	0	0
106	0	0	0	77	0	0	0	77	0	0	0	77	0	0	0	77	0	0	0
108	0	0	0	78	0	0	0	78	0	0	0	78	0	0	0	78	0	0	0
110	0	0	0	79	0	0	0	79	0	0	0	79	0	0	0	79	0	0	0
112	0	0	0	80	0	0	0	80	0	0	0	80	0	0	0	80	0	0	0
114	0	0	0	81	0	0	0	81	0	0	0	81	0	0	0	81	0	0	0
116	0	0	0	82	0	0	0	82	0	0	0	82	0	0	0	82	0	0	0
118	0	0	0	83	0	0	0	83	0	0	0	83	0	0	0	83	0	0	0
120	0	0	0	84	0	0	0	84	0	0	0	84	0	0	0	84	0	0	0
122	0	0	0	85	0	0	0	85	0	0	0	85	0	0	0	85	0	0	0
124	0	0	0	86	0	0	0	86	0	0	0	86	0	0	0	86	0	0	0
126	0	0	0	87	0	0	0	87	0	0	0	87	0	0	0	87	0	0	0
128	0	0	0	88	0	0	0	88	0	0	0	88	0	0	0	88	0	0	0
130	0	0	0	89	0	0	0	89	0	0	0	89	0	0	0	89	0	0	0
132	0	0	0	90	0	0	0	90	0	0	0	90	0	0	0	90	0	0	0
134	0	0	0	91	0	0	0	91	0	0	0	91	0	0	0	91	0	0	0
136	0	0	0	92	0	0	0	92	0	0	0	92	0	0	0	92	0	0	0
138	0	0	0	93	0	0	0	93	0	0	0	93	0	0	0	93	0	0	0
140	0	0	0	94	0	0	0	94	0	0	0	94	0	0	0	94	0	0	0
142	0	0	0	95	0	0	0	95	0	0	0	95	0	0	0	95	0	0	0
144	0	0	0	96	0	0	0	96	0	0	0	96	0	0	0	96	0	0	0
146	0	0	0	97	0	0	0	97	0	0	0	97	0	0	0	97	0	0	0
148	0	0	0	98	0	0	0	98	0	0	0	98	0	0	0	98	0	0	0
150	0	0	0	99	0	0	0	99	0	0	0	99	0	0	0	99	0	0	0
152	0	0	0	100	0	0													

data acquisition. A profile of each reflection was obtained with an on-line IBM 1627 Plotter, as an aid in judging the validity of the data. One set of independent reflections was obtained out to a limit of $\sin \theta/\lambda = 0.75 \text{ \AA}^{-1}$; altogether 327 reflections were measured, of which 91 registered zero intensity, as listed in Table 1.

Lorentz-polarization and absorption corrections were applied to the raw data (stored on disk) using a program written for the IBM 1800. The absorption corrections used were based on values given for spherical samples in *International Tables for X-ray Crystallography* (1959). A calculation of the standard deviation for each reflection was also made in the course of the data processing according to the formula

$$\sigma^2 = \sigma_c^2 + (C_1 N)^2 + \left[C_2 N \left(\frac{1}{A^*} - 1 \right) \right]^2,$$

where σ_c is the estimated standard deviation based on counting statistics, C_1 is an estimate of non-systematic errors, C_2 is an estimate of the error due to uncertainty in the absorption correction, A^* , and N is the total peak-less-background count recorded during the scan.

Refinement of the structure

All of the ions in the RbNiF_3 structure lie in special positions, as indicated in Table 2. Since the general arrangement of the structure was known, it was possible

to proceed directly with a least-squares refinement. Initially, a modified version of a full matrix least-squares program of Gantzel, Sparks & Trueblood (1961), which minimizes the quantity $\sum w(|F_o| - |F_c|)^2$, was employed for the calculations on an IBM System/360, Model 91 computer. Starting coordinates and isotropic temperature factors were estimated from the previously reported structures of BaTiO_3 (Burbank & Evans, 1948) and CsMnF_3 (Zalkin, Lee & Templeton, 1962). In general, the least-squares weight was computed as $w = 1/\sigma^2$ from the estimated values of the variance obtained in the processing of the raw data (see *Experimental*); unobserved reflections were given zero weight, but included in the structure factor calculations. Scattering factors and dispersion corrections for Rb^+ , Ni^{2+} , and F^- were taken from *International Tables for X-ray Crystallography* (1962).

The first attempt at refinement, utilizing the complete set of observed reflections, resulted in convergence after only three cycles, with a reliability index, $R = 0.093$, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. However, examination of the data at this point showed substantial discrepancies between observed and calculated structure factors for low angle data, particularly among the stronger reflections, indicating a probable extinction effect. For this reason, a number of low angle data were given zero weight in subsequent computations. The final refinement with this program utilized only 214 of the 236 observed reflections, with zero weight given to the 22

Table 2. *Final coordinates, thermal parameters and standard deviations for RbNiF_3*

Anisotropic thermal parameters are given only for the four metal atoms. The β_{ij} are defined by

$$T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

$\beta_{13} = 0$ and $\beta_{23} = 0$ for all metal atoms.

	Position	x	y	z	β_{11} or B (\AA^2)	β_{22}	β_{33}	β_{12}
Rb(1)	2(b)	0.0000	0.0000	0.2500	0.00607 (63)	β_{11}	0.00124 (10)	$\beta_{11}/2$
Rb(2)	4(f)	0.3333	0.6667	0.0948 (1)	0.00577 (32)	β_{11}	0.00135 (6)	$\beta_{11}/2$
Ni(1)	2(a)	0.0000	0.0000	0.0000	0.00229 (73)	β_{11}	0.00047 (11)	$\beta_{11}/2$
Ni(2)	4(f)	0.3333	0.6667	0.8453 (1)	0.00304 (39)	β_{11}	0.00056 (6)	$\beta_{11}/2$
F(1)	6(h)	0.5172 (7)	2x	0.2500	0.50 (8)	—	—	—
F(2)	12(k)	0.8328 (7)	2x	0.0798 (3)	0.69 (7)	—	—	—

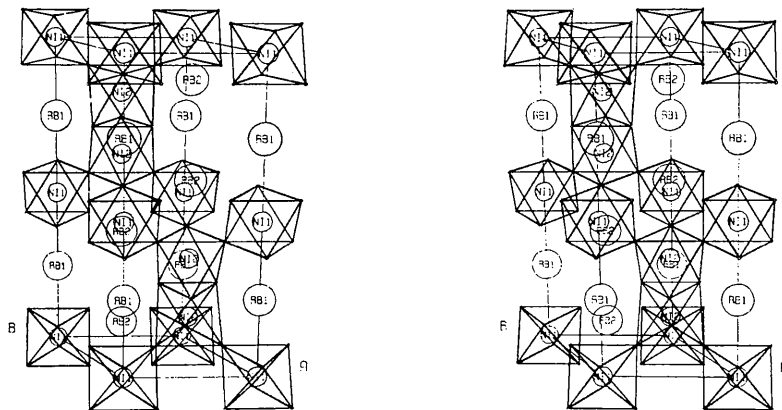


Fig. 1. Stereodiagrams of the RbNiF_3 unit cell.

for which $\sin \theta/\lambda < 0.30 \text{ \AA}^{-1}$. The refinement again converged quickly and resulted in an improvement of the reliability index to $R=0.068$.

At this point, a version of the Busing, Martin & Levy (1962) least-squares program, modified by Coppen & Hamilton (1970) to include a correction for secondary extinction according to the method suggested by Zachariasen (1963, 1967) was made available to us. Seven cycles with this program were used to complete the refinement, including all 236 observed reflections. Anisotropic thermal parameters for the metal* ions were also introduced at this time, in addition to the extinction parameter. Five cycles were sufficient to reduce the parameter shifts to less than one-tenth of their calculated standard deviations. A listing of the observed and calculated structure factors resulting from the last cycle is given in Table 1; for these data, $R=0.042$, $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.041$ and the standard deviation of an observation of unit weight = 1.009.

* A refinement with anisotropic thermal parameters assigned to all ions converged to the values for the other parameters given in Table 2, within the calculated standard deviations. However, errors in several of the β_{ij} for the fluorine ions were so large, that it was decided to return to isotropic temperature factors for these ions.

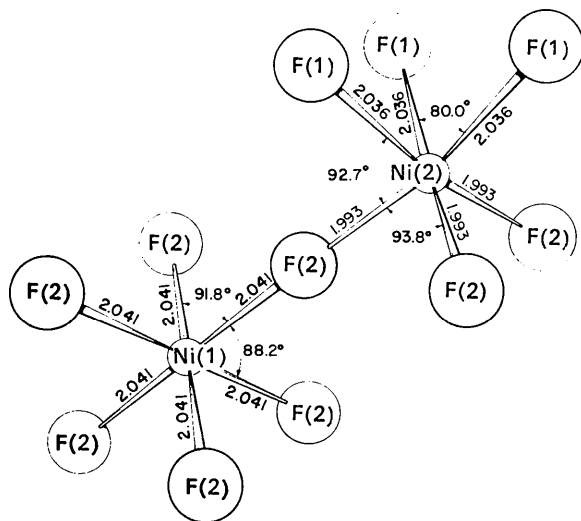


Fig. 2. NiF_6 octahedra in RbNiF_3 .

Table 2 lists the coordinates and thermal parameters along with their standard deviations, from the final refinement. A value of $g = 38 \pm 5 \times 10^{-6}$ was obtained for the extinction parameter. It should be mentioned at this point that the introduction of the extinction correction did not produce appreciable shifts in the positional parameters (*i.e.* not greater than the range of e.s.d. calculated from the refinement without extinction correction); the thermal parameters, conversely, were all reduced significantly.

Description of the structure and discussion

The interionic distances calculated from the final coordinates are given in Table 3. Fig. 1 shows stereo diagrams of one unit cell of RbNiF_3 prepared with the ORTEP computer program (Johnson, 1965). There are two nonequivalent sets of rubidium ions and two nonequivalent sets of nickel ions shown within the unit cell. The fluorine ions are represented by the corners of octahedra about the nickel ions. The fluorine ions at height $z = \frac{1}{4}, \frac{3}{4}$ are of type F(1); all remaining fluorine ions are of type F(2).

Each Rb(1) and Rb(2) ion has twelve fluorine ion neighbors at distances which are summarized in Table 3. The Ni(1) and Ni(2) ions each have six fluorine neighbors in an octahedral arrangement. As shown in Fig. 1, two-thirds of the NiF_6 octahedra in the structure occur in face-sharing pairs to form Ni_2F_9 polyhedra [4(*f*) sites]. The remaining NiF_6 octahedra [2(*a*) sites] do not share faces, but are linked to the Ni_2F_9 polyhedra by sharing of corners.

The local symmetry and bond distances within the NiF_6 octahedra are the most significant structural features from the standpoint of magnetic and optical studies; hence these are reproduced in greater detail in Fig. 2. For Ni(1) [2(*a*) site], with point symmetry $\bar{3}m$, all Ni-F distances are identical, and the octahedron is very nearly regular. However, for Ni(2) [4(*f*) site] with point symmetry $3m$, the Ni(2)-F(1) and Ni(2)-F(2) distances are dissimilar, and the octahedron is more distorted because of the repulsive forces between the Ni(2) ions in adjacent face-sharing octahedra. It is interesting to note that the average Ni-F bond distance of $2.028 \pm 0.008 \text{ \AA}$ is in nearly exact agreement with the value (2.03 Å) calculated from the empirical set of effective ionic radii in oxides and fluorides recently

Table 3. *Interionic distances in RbNiF₃*

Estimated standard deviations in parentheses are in units of the last place.

Ni(1)-2Rb(1)	3.577 (2) Å	Rb(1)-6F(2)	2.965 (8) Å
Ni(1)-6Rb(2)	3.635 (2)	Rb(2)-3F(1)	2.896 (7)
Ni(1)-6F(2)	2.041 (8)	Rb(2)-6F(2)	2.928 (8)
Ni(2)-3Rb(1)	3.637 (2)	Rb(2)-3F(2)	3.011 (8)
Ni(2)-Rb(2)	3.570 (2)	F(1)-4F(2)	2.92 (1)
Ni(2)-3Rb(2)	3.479 (2)	F(2)-2F(2)	2.84 (2)
Ni(2)-Ni(2)	2.728 (3)	F(2)-2F(2)	2.91 (2)
Ni(2)-3F(1)	2.036 (7)	F(2)-2F(2)	2.93 (3)
Ni(2)-3F(2)	1.993 (8)		
Rb(1)-6F(1)	2.925 (7)		

published by Shannon & Prewitt (1969), assuming coordination numbers of six for nickel, twelve for rubidium, and six for fluorine. The average Rb-F bond distance of 2.943 ± 0.008 Å, however, is considerably shorter than the value of 3.06 Å calculated from the empirical radii. This discrepancy is significant, but not surprising, in light of the discussion given by Shannon & Prewitt in their paper. These authors point out the difficulty in applying the empirical radii to highly symmetric structures and give examples which indicate that the discrepancies are particularly large for cations with a coordination number of twelve. One specific example is the Cs-F bond distance in $CsMnF_3$, a similar structure, where a nearly identical discrepancy is found between observed and calculated values.

The observed differences in the degree of distortion in the two types of octahedra help to provide an understanding of site preferences observed when various other ions are substituted for nickel in the $RbNiF_3$ lattice. The work of McGuire & Shafer (1968) showed that ions larger than nickel prefer the 2(a) sites while ions of the same size as nickel probably substitute randomly on both the 2(a) or 4(f) sites. It was suggested that the larger ions prefer the 2(a) sites because they produce the minimum distortion within the octahedra which share only corners. Ions comparable in size, however, can occupy either octahedral site without producing further distortion. The results of this structure analysis would appear to confirm this line of reasoning.

Note added in proof:—Since the completion of this work Babel (1969) has also reported a structure determination on this compound, based on a set of $h0l$ precession data. Although his data do not permit the degree of accuracy reported here, his description of the structure agrees substantially with ours except for the x coordinate of the F(1) atom.

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