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Note On The Crystal Structure of $RbNiF_3$

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In a previous paper on the structures of hexagonal fluoroperovskites (*1*) we have published our results on the crystal structure of $RbNiF_3$ as derived from *h*0*l* single crystal reflections. Because of the significant differences to the powder work results of Arnott and Longo (*2*) we have now redetermined the $RbNiF_3$ structure using three-dimensional single crystal data.

In fact the use of two-dimensional data leads to a parameter interference which accounts for some of the differences mentioned above. In the structure of $RbNiF_3$[1] the atoms Rb_I and F_I coincide in the [010] projection almost completely and the same is true of the atoms Rb_{II} and F_{II}. Therefore an independent refinement of the positional parameters and the temperature factors of these atoms requires three-dimensional data (rather than *h*0*l* reflections only), although there are only *x* and *z* parameters to refine.

In addition to the 49 *h*0*l* reflections from a preces-

[1] As for notation of atoms we refer to the work of Arnott and Longo (*2*).

TABLE 1

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $RbNiF_3$

h k l	F_0	F_c	*h k l*	F_0	F_c	*h k l*	F_0	F_c
0 0 4	53.49	31.51	5 0 11	48.39	46.05	3 3 2[b]	5.46	8.57
0 0 6	139.79	154.82	5 0 13	34.35	51.56	4 2 2[b]	30.33	36.09
0 0 8	69.33	75.06	6 0 0[a]	174.62	175.97	5 1 2[b]	13.98	15.38
0 0 12	177.63	203.08	1 0 0[b]	2.32	0.80	6 0 2[b]	3.99	2.73
0 0 16	20.63	38.30	1 1 0	251.95	277.44	4 3 2[b]	10.60	14.13
1 0 3[a]	68.47	71.02	2 0 0[b]	3.47	3.66	1 0 3	86.63	71.02
1 0 4[a]	161.14	164.60	2 1 0[b]	2.94	3.25	2 0 3	162.39	146.01
1 0 5[a]	74.09	67.24	3 0 0	228.46	227.38	2 1 3	57.55	47.00
1 0 7	104.81	109.63	2 2 0	299.23	309.42	3 0 3[b]	9.19	7.74
1 0 8	69.09	60.40	3 1 0[b]	3.70	0.04	3 1 3	61.96	54.27
1 0 9	94.43	88.68	4 0 0[b]	5.58	8.16	4 0 3	108.06	95.51
1 0 11	86.59	85.58	3 2 0[b]	4.11	2.36	3 2 3	68.42	57.39
1 0 13	52.17	60.89	4 1 0	174.72	176.13	4 1 3[b]	4.02	3.84
1 0 16	89.62	98.58	5 0 0[b]	5.76	7.50	5 0 3[b]	44.05	36.89
2 0 1[a]	32.19	26.55	3 3 0	161.21	160.38	4 2 3	79.28	75.35
2 0 2[a]	97.67	81.53	4 2 0[b]	3.88	9.82	5 1 3	38.17	40.87
2 0 3[a]	152.00	146.01	5 1 0	3.58	3.28	4 3 3	30.54	35.43
2 0 4	204.34	207.40	6 0 0	164.44	175.97	1 0 4	156.22	164.60
2 0 5	129.50	121.99	4 3 0[b]	2.79	6.64	1 1 4	56.97	50.91
2 0 7	121.93	112.02	5 2 0	132.14	129.82	2 0 4	206.73	207.40
2 0 8	123.95	116.89	1 0 1[b]	18.53	25.35	2 1 4	141.54	135.61
2 0 9	126.64	126.27	2 0 1	49.92	26.55	3 0 4	52.86	44.56
2 0 10	36.23	45.22	2 1 1[b]	2.94	5.34	2 2 4[b]	40.23	32.05

TABLE I—*continued*

h k l	F_0	F_c	*h k l*	F_0	F_c	*h k l*	F_0	F_c
2 0 11	44.93	37.35	3 0 1[b]	18.26	12.04	3 1 4	121.57	117.46
2 0 13	56.25	52.42	3 1 1[b]	7.40	10.39	4 0 4	147.41	137.16
2 0 16	98.66	100.60	4 0 1[b]	22.32	16.64	3 2 4	103.66	100.60
3 0 0[a]	216.81	227.38	3 2 1[b]	16.39	11.61	4 1 4	34.06	34.24
3 0 4	51.81	44.56	4 1 1[b]	8.25	6.22	5 0 4	92.20	90.23
3 0 8	80.17	79.66	5 0 1[b]	5.73	6.68	3 3 4[b]	20.26	29.87
3 0 12	123.01	116.78	4 2 1	20.56	14.22	4 2 4	103.95	103.62
3 0 16	66.71	58.55	5 1 1[b]	3.55	3.34	5 1 4	82.51	84.30
4 0 2[a]	41.06	47.47	6 0 1[b]	4.14	0.60	6 0 4[b]	25.84	28.47
4 0 3[a]	95.97	95.51	4 3 1[b]	11.07	7.18	4 3 4	73.41	74.95
4 0 4	150.20	137.16	5 2 1	9.63	6.74	1 0 5	73.41	67.24
4 0 5	86.01	80.28	1 0 2[b]	2.35	4.69	2 0 5	124.80	121.99
4 0 7	92.02	85.81	1 1 2[b]	3.17	9.62	2 1 5	76.35	66.76
4 0 8	101.83	78.64	2 0 2	103.36	81.53	3 0 5[b]	9.13	10.80
4 0 9	100.70	94.29	2 1 2[b]	5.93	2.93	3 1 5	53.44	49.95
4 0 11	38.87	32.16	3 0 2[b]	4.58	6.25	4 0 5	86.33	80.28
4 0 13	45.87	46.50	2 2 2[b]	5.08	3.94	3 2 5	38.76	38.85
4 0 16	90.46	82.48	3 1 2[b]	14.71	7.99	4 1 5[b]	3.76	5.94
5 0 4	106.04	90.23	4 0 2[b]	44.63	47.47	5 0 5	53.15	46.86
5 0 7	64.33	76.54	3 2 2[b]	8.13	7.71	4 2 5	54.32	59.07
5 0 8	34.52	38.06	4 1 2[b]	4.08	7.20	5 1 5	38.17	38.10
5 0 9	62.05	50.75	5 0 2[b]	11.31	11.47			

[a] Reflections once more measured on the [001] rotation photograph.

[b] Structure factors derived from estimated intensities, not used in refinement,

$$R = \frac{\Sigma||F_0| - |F_c||}{\Sigma|F_0|} = 0.077 \text{ (89 reflections } hkl\text{)}$$

TABLE II

POSITIONAL PARAMETERS, THEIR STANDARD DEVIATIONS AND TEMPERATURE FACTORS OF $RbNiF_3$

	x	σ_x	z	σ_z	B[Å^2]
$Rb_I(2b)$	0	—	0.25	—	0.51
$Rb_{II}(4f)$	0.33333	—	0.09535 [0.09544][a] (0.0954)[b]	0.0005 [0.0007]	0.22
$Ni_I(2a)$	0	—	0	—	1.02
$Ni_{II}(4f)$	0.33333	—	0.8443 [0.8450] (0.8462)	0.0007 [0.0008]	0.57
$F_I(6h)$	0.515_5 $[0.502_3]$ (0.517)	0.0037 [0.0082]	0.25	—	1.17
$F_{II}(12k)$	0.835_1 $[0.831_3]$ (0.830)	0.0027 [0.0089]	0.0742 [0.0740] (0.081)	0.0013 [0.0017]	0.77

[a] Values in brackets [ ] refer to our previous paper (*1*).

[b] Values in parentheses ( ) are those of Arnott and Longo (*2*). See Table I of (*2*).

TABLE III

SOME INTERATOMIC DISTANCES (Å) IN $RbNiF_3$

Rb_I–6 F_I	2.93 (2.93)[a]	F_I–2 F_I	2.65	(2.62)[a]
Rb_I–6 F_{II}	3.02 (2.97)	F_I–2 F_I	3.19	(3.22)
Rb_{II}–6 F_{II}	2.94 (2.93)	F_I–4 F_{II}	2.99	(2.89)
Rb_{II}–3 F_{II}	2.97 (3.02)	F_{II}–2 F_{II}	2.95	(2.86)
Rb_{II}–3 F_I	2.88 (2.89)	F_{II}–2 F_{II}	2.70	(2.89)
Ni_I–6 F_{II}	1.98 (2.07)	F_{II}–2 F_{II}	2.89	(2.98)
Ni_{II}–1 Ni_{II}	2.70 (2.75)	F_{II}–2 F_I	2.99	(2.89)
Ni_{II}–3 F_I	2.04 (2.05)	Rb_I–1 Ni_I	3.58 = $c/4$	
Ni_{II}–3 F_{II}	2.06 (1.95)	Rb_{II}–1 Ni_{II}	3.59	(3.57)

[a] Results of Arnott and Longo in parentheses. See Table III of Ref. (*2*).

sion photograph of our previous refinement 40 reflections *hkl* ($l = 0$–5) were measured on a [001] rotation photograph taken from the same crystal with CuK_α radiation. The structure factors of 45 further reflections, too weak to be measured, were derived from estimated intensities but not considered in the course of refinement. The data are collected in Table I, which also gives the calculated structure factors after five cycles of least-squares refinement. The resulting parameters are listed in Table II, and Table III summarizes some interatomic distances calculated from them.

As may be seen from Table II a significant change of more than the standard deviation given in our previous paper (*1*) occurs only in the *x* parameter of F_I. This change to the new value of $x_{F_I} = 0.515$ removes the main discrepancy to the results of Arnott and Longo (*2*) and indeed leads to a contraction of the fluorine triangle between the two Ni_{II} atoms with F–F distances of 2.65 Å, very close to the radii sum of 2.66 Å. The Ni_{II}–Ni_{II} separation is also shortened to 2.70 Å; both results are in better agreement with the related structures of $CsCoF_3$, $CsNiF_3$ (*1*), and $CsMnF_3$ (*3*).

Another discrepancy to the work of Arnott and Longo is still maintained. As a consequence of their higher z-value of F_{II} they find Ni_I–F_{II} and Ni_{II}–F_{II} distances in the reverse order than we did and still do now. Our new values are Ni_I–F_{II} = 1.98 Å in the single octahedron instead of 2.07 Å (*2*), and Ni_{II}–F_{II} = 2.06 Å in the double group instead of 1.95 Å (*2*). Only the other distances Ni_{II}–F_I in this face sharing octahedra are in good agreement now, 2.04 and 2.05 Å, respectively. The only reason which may be in favour of our new results is the approximate equidistance M–F in the Ni_2F_9 group, also known from the Mn_2F_9 group in $CsMnF_3$ (*3*). But a still more reasonable set of distances would result, if we assume a z-parameter of F_{II} of about 0.077, lying midway between the Arnott-Longo value and ours.

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