Crystal structure of two modifications of ammonium trifluoro nickelate(II), NH_4NiF_3

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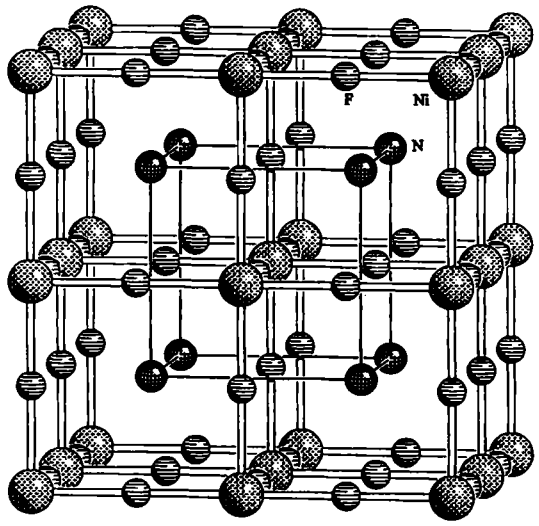
1. Crystal structure of the cubic low temperature modification of ammonium nickel trifluoride, NH_4NiF_3-I



Source of material: NH_4NiF_3-I in the cubic (low temperature) modification was obtained from nickel powder and NH_4HF_2 (molar ratio 1:1.5) at 573 K (four weeks) in a sealed Monel metal container. The yellow powder contains many square yellow plates (see ref. 1).

NH_4NiF_3-I crystallizes like $KNiF_3$ (see ref. 2) in the cubic $CaTiO_3$ type of structure. The $[NiF_6]$ octahedra share common corners with Ni^{2+}–F distances of 204.38(14) pm to form a three-dimensional network. The Ni^{2+}–Ni^{2+} distances are 408.8(3) pm. H positions of NH_4^+ are not determined.

F_3H_4NNi, cubic, $Pm3m$ (No. 221), a =4.088(3) Å, V =68.3 Å^3, Z =1, $R(F)$ =0.026, $R_w(F^2)$ =0.045.

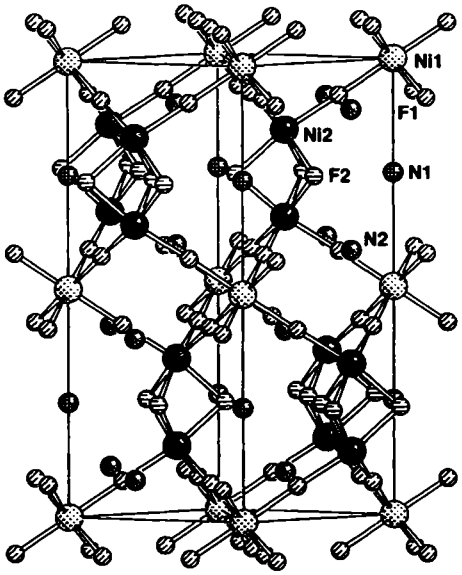
Table 1. Parameters used for the X-ray data collection

Crystal:	yellow, square plate, size 0.05 x 0.20 x 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	67.10 cm^{-1}
Diffractometer:	STOE IPDS
Scan mode:	20 plates, $\Delta\varphi = 5°$
$T_{measurement}$:	293 K
$2\theta_{max}$:	55.84°
N(hkl)$_{unique}$:	32
Criterion for I_o:	$I_o > 2\,\sigma(I_o)$
N($param$)$_{refined}$:	5
Program:	SHELXL-93

Table 2. Final atomic coordinates and displacement parameters (in Å^2)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	1*b*	1/2	1/2	1/2	0.0123(7)	U_{11}	U_{11}	0	0	0
F	3*c*	1/2	1/2	0	0.018(2)	U_{11}	0.013(3)	0	0	0
N	1*a*	0	0	0	0.017(3)	U_{11}	U_{11}	0	0	0

2. Crystal structure of the hexagonal high temperature modification of ammonium nickel trifluoride, NH_4NiF_3-II



Source of material: NH_4NiF_3-II in the hexagonal (high temperature) modification was obtained from nickel powder and NH_4HF_2 (molar ratio 1:2) at 673 K (four weeks) in a sealed Monel metal container in the presence of a tungsten sheet on which the green crystals grew (see ref. 3).

NH_4NiF_3-II crystallizes like $RbNiF_3$ (see ref. 4) in the hexagonal $BaTiO_3$ type of structure. Two $[NiF_6]$ octahedra share a common face forming a double octahedron $[Ni_2F_9]$ with Ni^{2+}–$F(2)^-$ distances of 201.1(2) pm (6x) and Ni^{2+}–$F(1)^-$ distances of 203.8(2) pm (6x). These double octahedra share common corners with $[NiF_6]$ octahedra to form a three-dimensional network. The Ni^{2+}–$F(1)^-$ distances are 202.6(1) pm (6x) in these ideal octahedra. The Ni^{2+}–Ni^{2+} distance in the confacial bioctahedron is 275.0(1) pm.The H postions are not determined.

F_3H_4NNi, hexagonal, $P6_3/mmc$ (No. 194), a =5.8456(3) Å, c =14.3563(3) Å, V =424.9 Å^3, Z =6, $R(F)$ =0.024, $R_w(F^2)$ =0.083.

Table 3. Parameters used for the X-ray data collection

Crystal:	green, rectangular plate, size 0.05 x 0.20 x 0.10 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	66.48 cm^{-1}
Diffractometer:	Siemens-Stoe
Scan mode:	profile fitted ω /2θ
$T_{measurement}$:	293 K
$2\theta_{max}$:	80.1°
$N(hkl)_{unique}$:	554
Criterion for I_o:	$I_o > 2\,\sigma(I_o)$
$N(param)_{refined}$:	21
Program:	SHELXL-93

Table 4. Final atomic coordinates and displacement parameters (in Å^2)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	2*a*	0	0	0	0.0127(2)	U_{11}	0.0132(3)	$U_{11}/2$	0	0
Ni(2)	4*f*	1/3	2/3	0.84581(3)	0.0135(1)	U_{11}	0.0129(2)	$U_{11}/2$	0	0
F(1)	6*h*	0.5181(2)	2*x*	1/4	0.0210(7)	0.0154(8)	0.0163(7)	$U_{22}/2$	0	0
F(2)	12*k*	0.8342(2)	2*x*	0.07898(9)	0.0216(5)	0.0170(6)	0.0195(6)	$U_{22}/2$	0.0028(2)	$2U_{13}$
N(1)	2*b*	0	0	1/4	0.018(1)	U_{11}	0.019(2)	$U_{11}/2$	0	0
N(2)	4*f*	1/3	2/3	0.0953(3)	0.0188(8)	U_{11}	0.019(1)	$U_{11}/2$	0	0

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