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Structure of $(NH_4)_3GaF_6$ Investigated by Multinuclear Magic-Angle Spinning NMR Spectroscopy in Comparison with Rietveld Refinement

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The structure of ammonium gallium cryolite $(NH_4)_3GaF_6$ was investigated by ^{19}F and $^{69,71}Ga$ magic-angle spinning (MAS) NMR in comparison with X-ray powder diffraction followed by Rietveld refinement. In agreement with previous thermodynamic measurements, NMR experiments on $(NH_4)_3GaF_6$ support the model of rigid GaF_6 octahedra. At high spinning speeds (30 kHz), the scalar coupling between the six equivalent ^{19}F nuclei and $^{69,71}Ga$ can be directly observed in the powder spectra. The coupling constants are $J_{^{19}F^{69}Ga} = 197$ Hz and $J_{^{19}F^{71}Ga} = 264$ Hz. To explain the ^{71}Ga spectra recorded at 3 kHz a small distribution of quadrupolar frequencies has to be included. The spread of the spinning sidebands hints to a largest ν_Q value of 28 kHz for ^{71}Ga. This can be explained by the occurrence of highly symmetric GaF_6 octahedra, which are tilted against the surrounding atoms. In addition, the incomplete motional excitation does not average out the quadrupolar effects. NMR findings are in discrepancy to those of Rietveld refinement. As result it appears that X-ray diffraction is not sensitive enough to deliver proper results.

1. Introduction

The mineral *elpasolite* K_2NaAlF_6 is the basic mineral of a large class of compounds of the common formula $M^I_2M^{I'}M^{III}F_6$ (M^I, $M^{I'}$ = Li, Na, K, Rb, Cs, Tl, Ag, NH_4, M^{III} = Al, Ga, In, Sc, Ti, V, Cr, Fe, Y, Ln). *Cryolites* $M^I_3M^{III}F_6$, derived from the mineral Na_3AlF_6, can be regarded as a special class of elpasolites where $M^I = M^{I'}$. In general, these compounds have cubic high-temperature phases and less symmetric structures at lower temperatures.[1] A picture of the structure of the commonly accepted high-temperature phase is given in Figure 1. Because of rather large transition entropy changes, the phase transitions have been explained in terms of order–disorder transitions of the $M^{III}F_6$ octahedra, and suitable models have been proposed.[2–4] Disorder of ammonium ions replacing $M^{I'}$ further contributes to the entropy effects. This has been shown by selectively substituting either M^I or $M^{I'}$ by NH_4 in the phase Cs_2KGaF_6.[5]

The crystal structure of $(NH_4)_3GaF_6$ has been described by Schwarzmann.[6] At room temperature, this phase is cubic with a lattice parameter of $a = 9.041$ Å. Two space groups were proposed, either $Pa\bar{3}$ (ordered) or $Fm\bar{3}m$ (disordered). Later investigations confirmed this lattice parameter.[4,7] Calorimetric measurements indicated a large entropy change for the phase transition of $(NH_4)_3GaF_6$ at 246 K,[4,7,8] and hence, the space group $Fm\bar{3}m$ was confirmed. These findings have been supported by the temperature-dependent behavior of the second moments of the ^1H and ^{19}F NMR signals as determined by broad line measurements.[9] For $(NH_4)_3GaF_6$ and the isotypic $(NH_4)_3FeF_6$ the phase transition entropy between the ordered low-temperature phase to the disordered high-temperature phase is very close to the value $R \ln 16$.[2,7] This can be crystallographically explained by two possible orientations of one-third of the NH_4 tetrahedra and eight

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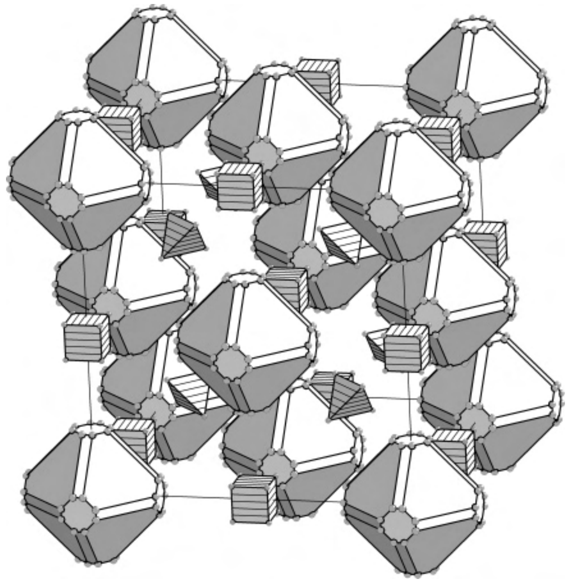

Figure 1. Structure of a disordered ammonium elpasolite $(NH_4)_3MF_6$. Large plain polyhedra: center is M, corners are F with sof $^1/_8$. Small hatched polyhedra: NH_4, H atoms of the tetrahedra are static, H atoms of the cubes are disordered with sof $^1/_2$.

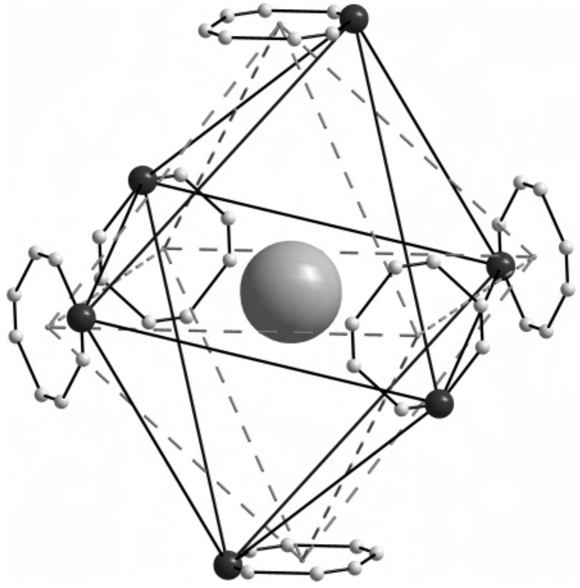

Figure 2. One possible GaF_6 coordination polyhedron (solid line) of the gallium atoms (large gray sphere) by fluorine atoms (black spheres, 192*l* position) according to the model from ref 2. This polyhedron is a trigonally distorted octahedron. F−Ga−F angles are given in Table 1. Dashed polyhedron: hypothetical ideal octahedron connecting the 24*e* positions. Small spheres: unoccupied 192*l* fluorine positions.

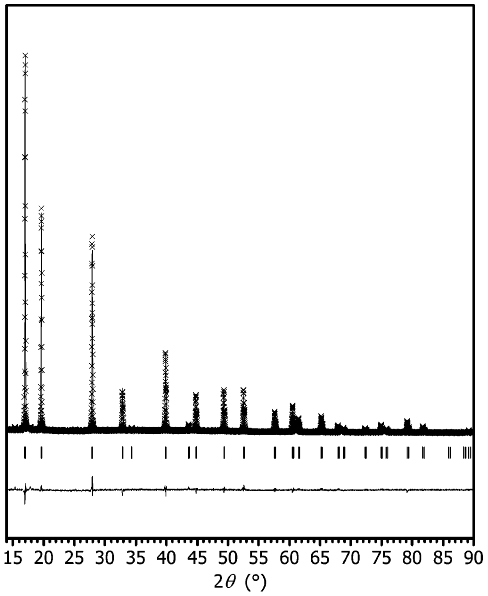

Figure 3. Powder diffraction pattern of $(NH_4)_3GaF_6$ and structure solution with fluorine in the 192*l* position: observed (×), calculated (line). Bragg positions and difference intensity are given below.

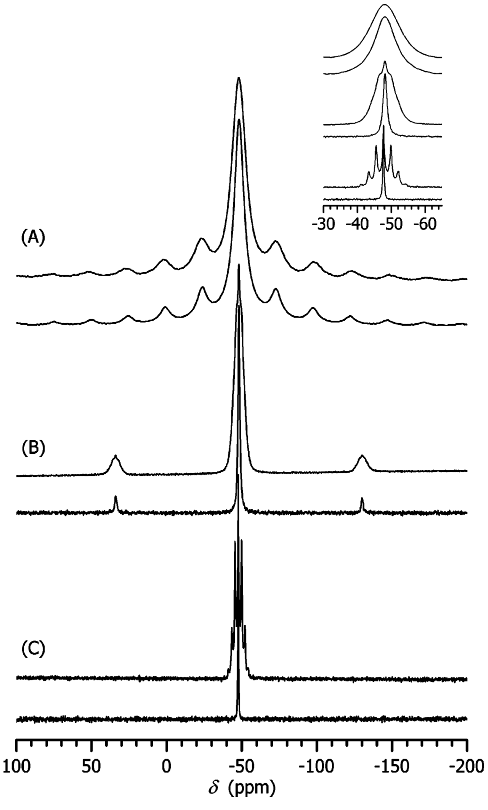

Figure 4. Comparison of ^{71}Ga MAS NMR spectra of $(NH_4)_3GaF_6$ taken at different rotation frequencies: (A) 3, (B) 10, and (C) 30 kHz. Upper lines: no decoupling. Lower lines: ^{19}F decoupled. Inset: corresponding central transitions.

possible orientations of the MF_6 octahedra. Because of the model proposed for these compounds, fluorine is assumed to occupy the 192*l* position in the lattice with a site occupancy frequency (sof) of $^1/_8$ (Figure 1).

During our work with $(NH_4)_3GaF_6$ we came across the point that the proposed model of rigid rotating exact octahedra as derived from calorimetric measurement is not consistent with the structure solutions given for $(NH_4)_3GaF_6$,[6] $(NH_4)_3FeF_6$, and $(NH_4)_3AlF_6$[10] in the space group $Fm\bar{3}m$ with fluorine in 192*l* position. In these structure solutions, none of the F−Me−F angles (Me = Ga, Fe) is 90°. The deviation from O_h symmetry of each octahedron is significant (see Table 1 and Figure 2); the octahedra are strongly distorted.

Therefore, it is the intention of the present study to solve these discrepancies applying two methods: (i) a reinvestigation of $(NH_4)_3GaF_6$ by X-ray powder diffraction followed

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Table 1. Fluorine Coordinates at 192*l* and F−Me−F Angles for the Distorted Octahedra (Figure 2) Given by the Model in Ref 2 and the Structure Solutions of Different Ammonium Elpasolites[a]

compd	x(F)	y(F)	z(F)	$yz/(y+z)$	angle F−Me−F (deg)	ref
$(NH_4)_3AlF_6$	0.0202	0.0406	0.1942	0.03358	85.47/94.53	10
$(NH_4)_3FeF_6$	0.0233	0.0418	0.2030	0.03466	86.33/93.67	10
$(NH_4)_3GaF_6$	0.013	0.052	0.203	0.04140	80.55/99.45	6
$(NH_4)_3GaF_6$	0.01606	0.05456	0.20416	0.04305	81.05/98.95	this work

[a] When $yz/(y+z)$ equals x, then F−Me−F is 90°. See also Figure 2 and the text for further explanation.

Table 2. Magnetic Properties of Fluorine and Gallium Nuclei

	^{19}F	^{69}Ga	^{71}Ga
I	$^1/_2$	$^3/_2$	$^3/_2$
Q (10^{-28} m^2)	0	0.168	0.106
Larmor freq (MHz)	376.5	96.0	122.0
natural abundance	100%	60.1%	39.9%

by a refinement of the structure and (ii) ^{19}F and ^{69,71}Ga magic-angle spinning (MAS) NMR with rotation speeds ranging from 3 to 30 kHz. Whereas a spinning speed of 30 kHz could allow drawbacks regarding a possible scalar coupling between ^{19}F and the gallium nuclei, at 3 kHz spinning speed, the ^{69,71}Ga MAS NMR spectra should allow conclusions concerning the quadrupolar interaction, especially after decoupling of ^{19}F. Information about symmetry and motional effects of GaF_6 octahedra is gained performing MAS NMR experiments at higher temperature (363 K).

2. Experimental Section

Synthesis of $(NH_4)_3GaF_6$. A solution of 3.94 g of $Ga(NO_3)_3 \cdot 9H_2O$ in 20 mL of water was added to a solution of 5.20 g of NH_4F (F/Ga ratio >14) in 10 mL of water under vigorous stirring within 30 min. After further stirring overnight, a white precipitate of $(NH_4)_3GaF_6$ occurred, which was filtered off, washed with water and ethanol, and dried at 120 °C. Neither FTIR nor ^{1}H MAS NMR shows evidence of OH groups in the solid being substituted for fluorine.

XRD and Structure Determination by Rietveld Refinement. The X-ray diffraction pattern was recorded on a Seifert XRD3003TT diffractometer (Cu Kα; 40 kV, 44 mA; receiving slit, 0.1 mm; step width, 0.01°(2θ); counting time, 10 s). The substance was mortared and passed through a 38 μm sieve to avoid eventual preferential orientation. For structural determination a profile fitting procedure and a subsequent Rietveld refinement were performed using the program FULLPROF.[11]

MAS NMR. ^{19}F, ^{69}Ga, and ^{71}Ga MAS NMR spectra were recorded on a Bruker AVANCE 400 spectrometer using both 4 and 2.5 mm MAS probes (Bruker Biospin) and applying spinning speeds up to 30 kHz. The magnetic properties of the nuclei are summarized in Table 2.

If not stated otherwise, ^{69}Ga and ^{71}Ga MAS NMR spectra were recorded with 512 accumulations, an excitation pulse lengths of $p1 = 1\ \mu$s, a recycle delay of 2 s, and a sweep width of 100 kHz (800 ppm). The ^{71}Ga spectrum at 3 kHz with ^{19}F decoupling was recorded with 160 000 accumulations. The radio frequency magnetic field strength for ^{71}Ga was taken as 39.7 kHz in frequency units ($t_{\pi/2} = 6.3\ \mu$s). The spectra are referenced with respect to the chemical shift of ^{69}Ga and ^{71}Ga in 1.1 M aqueous $Ga(NO_3)_3$ solution. ^{19}F MAS studies were performed with a $\pi/2$ pulse length of 2.0 μs and a recycle delay of 20 s. Existent background signals of ^{19}F could be completely suppressed with the application of a phase-cycled depth pulse sequence according to Cory and Ritchey.[12] Values of the isotropic chemical shifts of ^{19}F are given with respect to $CFCl_3$. Chemical shifts for all spectra are accurate to ±0.5 ppm.

^{69,71}Ga−{^{19}F} CW decoupling was performed at spinning speeds of 30 kHz as well as at 3 and 10 kHz, respectively. ^{19}F−{^{69,71}Ga} CW decoupling was performed at 30 kHz spinning speed.

Fitting of the spectra was performed with the program DMFIT, version 2006.[13]

3. X-ray Diffraction

Results. The powder diffractogram of $(NH_4)_3GaF_6$ is shown in Figure 3. The diffractogram could be indexed as face-centered cubic with a lattice constant of around 9.04 Å. Reflection conditions for *hkl* are $h + k$, $h + l$, $k + l = 2n$. After a successful profile fitting procedure in the space group $Fm\bar{3}m$ (a = 9.0449 Å), a subsequent Rietveld refinement was carried out. Fluorine was set to position 192*l* (sof $^1/_8$). Positions of the H(1) and H(2) atoms were chosen in such a way that the N−H bond length is 0.88 Å. H(1) is disordered (sof $^1/_2$). Positions and isotropic displacement factors of the H atoms have been set to constant and were not optimized. A picture of the structure is given in Figure 1, the results and refined parameters are given in Tables 3 and 4. The fluorine coordinates of our solution are very close to the proposition given by Schwarzmann.[6]

Additionally, structure solutions with other positions of the fluorine atom were checked; the *R*-values are given in parentheses: (v1) position 24*e*, sof 1 ($R_p = 4.50$, $R_{\omega p} = 6.41$), (v2) position 96*k*, sof $^1/_4$ ($R_p = 3.52$, $R_{\omega p} = 4.61$), (v3) position 24*e*, sof $^1/_3$ and position 96*j*, sof $^1/_6$ ($R_p = 3.46$, $R_{\omega p} = 4.49$). Rietveld solution of the structure in the space group $Pa\bar{3}$ as proposed in ref 6 was impossible and did not converge.

Coordination of the Gallium Atoms: A Controversial Model. On the basis of the isotypic compound $(NH_4)_3FeF_6$, a model for the description of the coordination geometry of these disordered phases was proposed in the literature.[2]

(i) The octahedra are rigid and have eight different orientations.

(ii) The F−Me−F angles are 90° (Me = Fe, Ga, Al).

It has been stated that this is the case, when fluorine occupies the 192*l* position. However, it is not stated explicitly, but fluorine does not have three degrees of freedom.

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Table 3. Atomic Coordinates of the Rietveld Refinement

formula	$(NH_4)_3GaF_6$					
space group	$Fm\bar{3}m$ (225)					
Z	4					
		x	*y*	*z*	sof	B_{iso}(F) (Å^2)
Ga	4[a]	0	0	0	1	1.392(47)
N1	4*b*	0.5	0.5	0.5	1	3.293(19)
H1[a]	32*f*	*0.5564*	*0.5564*	*0.5564*	*0.5*	*5.0*
N2	8*c*	0.25	0.25	0.25	1	2.986(13)
H2[a]	32*f*	*0.3064*	*0.3064*	*0.3064*	*1*	*5.0*
F	192*l*	0.01606(22)	0.05456(70)	0.20416(27)	0.125	2.527(13)

[a] Hydrogen atoms were set to constant and not refined.

Table 4. Parameters of the Rietveld Refinement

no. of reflns	62
no. of ref params	20
no. of background params	3
η (pseudo-Voigt)	0.4287(80)
half-width params	0.0128(28)
(*U*, *W*, *V*)	0.099(19)
	0.00511(28)
asymmetry params	0.273(42)
	0.01394(93)
	−0.668(83)
cos θ shift param	−0.0093(11)
R_p[a]	3.46
$R_{\omega p}$[a]	4.54
χ^2[a]	0.564

[a] Rietveld factors, not corrected for background.

The model of rigid exact octahedra is based on the following assumptions:[2] The coordinates of the six corners of one coordination polyhedron are (u v w), (w u v), (v w u), along with the inversed values. To achieve orthogonality of these position vectors and, hence, an exact octahedral geometry, the equation

$$vw + wu + uv = 0 \tag{1}$$

must be valid. It is claimed in the model in ref 2 that this will be the case for

$$|u| \geq |v| \geq |w| \qquad \text{and} \qquad u > v > 0 > w \tag{2}$$

In our opinion this is not sufficient. Equation 1 is not automatically valid with the assumptions of the inequations (eq 2). The variables u, v, and w are not independent from each other. When two of the variables are known, the third one is given by eq 3:

$$w = -\frac{uv}{u + v} \tag{3}$$

This is essentially another version of eq 1. Spoken in crystallographic terms, u, v, and w must be chosen among the coordinates of the fluorine atom $\pm x$, $\pm y$, and $\pm z$ (Table 3). In our case this would be $u = z$, $v = y$, and $w = -x$. When eq 3 is not fulfilled, then none of the F−Me−F angles can be 90°, meaning that the scalar product of two of the position vectors of fluorine is never zero. As one can easily calculate, eq 3 is not valid:

$$-0.04305 = -\frac{yz}{y + z} \neq -x = -0.01606 \tag{4}$$

Moreover, the condition from eq 3 is not even fulfilled for any other of the structure solutions of distorted ammonium elpasolites in the space group $Fm\bar{3}m$ (Table 1). The octahedra would be trigonally distorted. The F−Me−F angles (Me = Al, Ga, Fe) would be greater and less than 90°. A picture of one of these octahedra is given in Figure 2; values are given in Table 1. If eq 3 is not fulfilled, it is impossible to choose any two F atoms around Ga in such a way that the angle between them is 90°.

These discrepancies show that the crystallographic data are not consistent with the model of rigid, exactly symmetric octahedra, possessing eight possible different orientations. This means that either the crystallographic data is not correct enough or the model is wrong.

4. Magic-Angle Spinning NMR

Results. ^{71}Ga MAS NMR spectra recorded at spinning speeds 3, 10, and 30 kHz and performed with and without decoupling are given in Figure 4. The ^{69}Ga MAS NMR spectra look very similar and are not shown in this Article. For further evaluation, spectra of ^{71}Ga were used because of the higher receptivity and as a consequence narrower line width and better signal-to-noise ratio of this nucleus.

Fitting was carried out for the ^{71}Ga spectrum taken at 30 kHz with and without ^{19}F decoupling (see Figure 5), the parameters are given together with result of the fit for ^{69}Ga in Table 5. The ^{71}Ga spectrum taken at 30 kHz could be simulated using isotropic lines, including a scalar *J*-coupling to six equivalent spin $^1/_2$ nuclei (Table 5 and Figure 5B). Here, the scalar coupling constant is $J_{^{19}\text{F}^{71}\text{Ga}} = 263.9$ Hz. A comparable result was obtained for the fit of the ^{69}Ga spectrum (see Table 5). Here, the scalar coupling constant to the six equivalent fluorine nuclei was determined as $J_{^{19}\text{F}^{69}\text{Ga}} = 197$ Hz.

Three ^{19}F MAS NMR spectra of $(NH_4)_3GaF_6$ taken at a spinning speed of 30 kHz are given in Figure 6: (A) without decoupling, (B) with ^{69}Ga decoupling, and (C) with ^{71}Ga decoupling. All these spectra could be fit using two isotropic Lorentzian lines with simultaneous consideration of a scalar *J*-coupling to the two Ga isotopes ^{69}Ga and ^{71}Ga (both $I = {}^3/_2$). Parameters for the fits are given in Table 6.

In both cases the fit of the ^{69,71}Ga MAS spectra yields smaller scalar coupling constants than are obtained by the fit of the ^{19}F MAS NMR spectra (for comparison see Tables 5 and 6). This issue is attributed to the smaller line widths of gallium compared to those of fluorine, which are

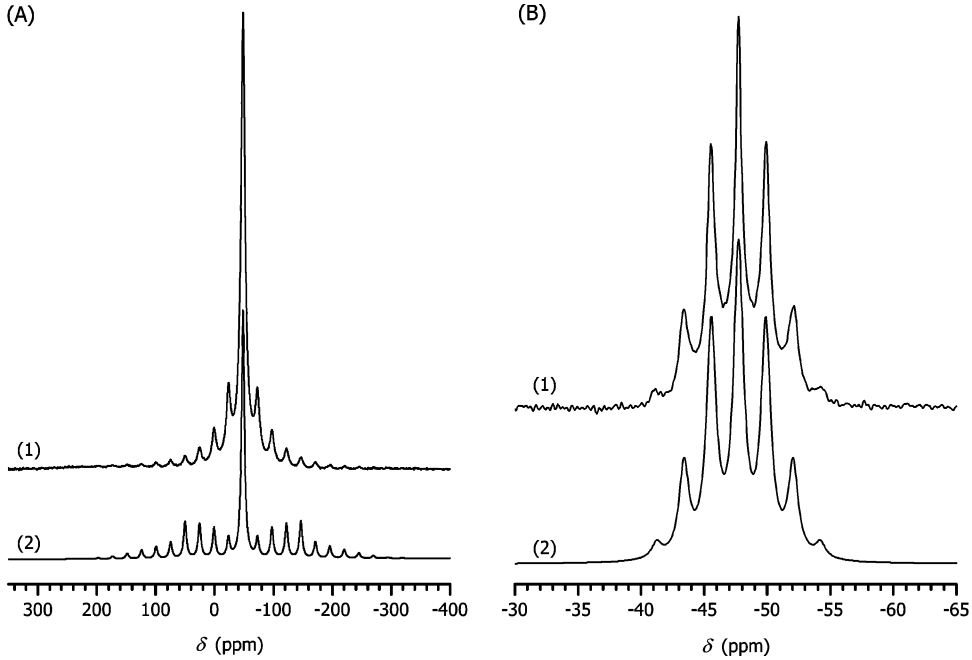

Figure 5. Experimental and simulated ^{71}Ga MAS NMR spectra of $(NH_4)_3GaF_6$: (A) rotation frequency 3 kHz, ^{19}F decoupled; (1) measured spectrum; (2) simulation with a maximum value of $\nu_Q = 28$ kHz, covering the complete spread of the spinning sidebands; (B) rotation frequency 30 kHz, no decoupling; (1) measured spectrum; (2) simulated spectrum; parameters of the simulation are given in Table 5.

Table 5. Parameters of the Simulation of the Ga MAS NMR Spectra of $(NH_4)_3GaF_6$[a]

measured nucleus[b]	δ_i (ppm)[c]	fwhm (Hz)[d]	parameters[e,f]
^{69}Ga{^{19}F} (30 kHz)[g]	−47.7	54.4	single line
^{71}Ga{^{19}F} (30 kHz)	−47.7	51.0	single line
^{71}Ga (30 kHz)	−47.7	114.4	$J = 263.9$ Hz ($6I = {}^{1}/_{2}$ (^{19}F))
^{69}Ga (25 kHz)[g]	−48.1	143.5	$J = 197.0$ Hz ($6I = {}^{1}/_{2}$ (^{19}F))
^{71}Ga (3 kHz, 293 K)	−48.2	1052.0	$\nu_{Qmax} = 28$ kHz
^{71}Ga (3 kHz, 363 K)	−48.2	918.0	$\nu_{Qmax} = 20$ kHz

[a] If not stated otherwise, all lines have Lorentzian shape. If no temperature is given, the spectrum was taken at room temperature. [b] The decoupled nucleus is given in braces. [c] δ_i: value of the isotropic chemical shift. [d] fwhm: full width at half-height of the signal. [e] J: scalar coupling constant. [f] ν_Q: quadrupolar frequency; here the maximum values are given estimated from the spread of the spinning sidebands. [g] These spectra are not shown.

broadened by homonuclear dipolar coupling and lead finally to a worse resolution of the spectra. It means, the scalar coupling constants (Table 6) show a deviation up to 7% from the values derived from the ^{69,71}Ga spectra.

The intensity of the spinning sidebands of the ^{71}Ga spectrum obtained at 3 kHz could not be fit satisfactorily with one single parameter set of ν_Q and η_Q (see Figure 5A). Instead, an unambiguous fit is only possible with a small distribution of quadrupolar frequencies. Because of the high symmetry of the system, the parameter ν_Q has the largest influence on the spectrum, being an indicator of the total deviation from cubic symmetry, whereas η_Q is a dimensionless asymmetry parameter, which contributes only to a minor degree. For that reason, the parameters η_Q have been fixed to be zero. The spread of the spinning sideband (see Figure 5A) supports a maximum value for ν_Q of 28 kHz, accurate within error bars of ±10%.

Scalar Coupling between the Spins of the Gallium and Fluorine Nuclei. At high rotation frequencies, up to 30 kHz, the scalar coupling between the spins of ^{19}F and ^{69,71}Ga can be resolved in the powder spectra of $(NH_4)_3GaF_6$. This effect is very seldom in solid-state NMR. In the case of $(NH_4)_3GaF_6$, the possibility of the observation of the scalar coupling derives from the comparatively narrow line width, large coupling constants between the nuclei, and small nuclear quadrupolar interaction.

The central lines of the ^{19}F spectra, shown in Figure 6, represent the spectra typically expected for isolated ions GaF_6^{3-} in liquid NMR: an isotropic signal, which is split into several components. Gallium consists of the two isotopes ^{69}Ga and ^{71}Ga (Table 2). Hence, the observed ^{19}F spectrum is a superposition of the spectra of $^{69}GaF_6^{3-}$ and $^{71}GaF_6^{3-}$. The signal of each component is split into four lines of equal intensity because of the coupling to spin $^{3}/_{2}$ nuclei (Figure 6A). It is even possible to decouple one of the Ga nuclei. Then a spectrum is observed, which is a superposition of a single line, deriving from the decoupled species, and four equal lines due to the coupling of ^{19}F with ^{71}Ga (Figure 6B) and ^{19}F with ^{69}Ga (Figure 6C), respectively. In all three cases, the ratio of the integral intensities of both components matches the natural isotope abundance (Table 2).

The effect of the coupling between the chemically different nuclei on the shape of the ^{71}Ga spectra can be seen in Figure 4. Large line widths prevent at 3 kHz spinning speed the observation of the scalar coupling. At 10 kHz, the scalar coupling is still not resolved, but ^{19}F decoupling causes a significant line narrowing. At 30 kHz, the scalar coupling is well resolved in the ^{71}Ga MAS NMR spectrum and a liquid-

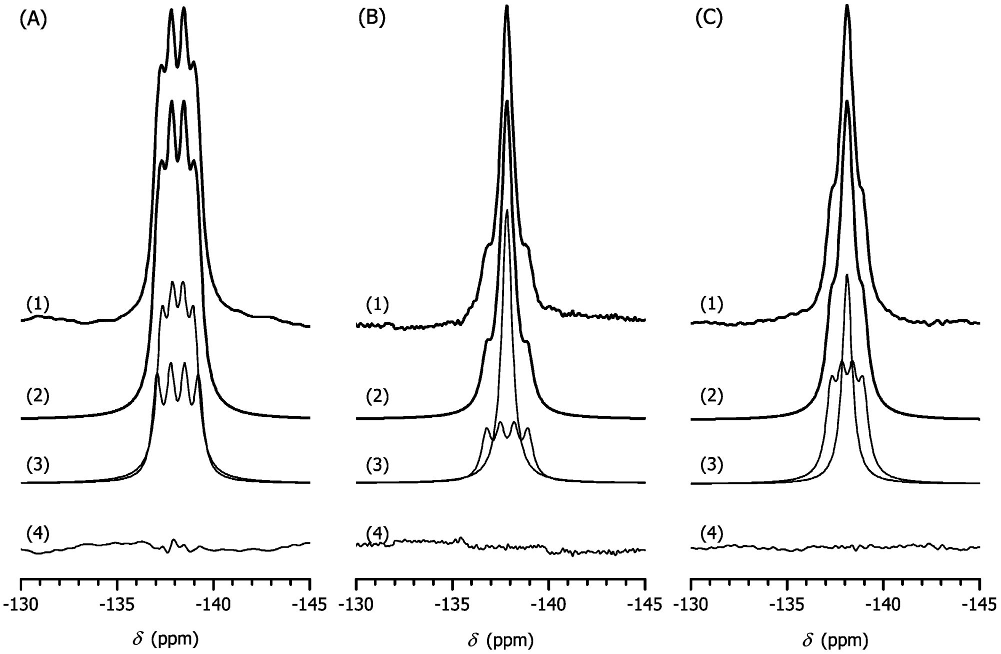

Figure 6. Experimental and simulated ^{19}F MAS NMR spectra of $(NH_4)_3GaF_6$ without (A) and with (B and C) Ga decoupling (rotation frequency 30 kHz): (A) ^{19}F spectra, (B) ^{19}F{^{69}Ga} spectra, and (C) ^{19}F{^{71}Ga} spectra; (1) measured spectra, (2) simulated spectra, (3) deconvolution of the simulated spectrum into individual lines, and (4) difference between measured and simulated spectra. Parameters of the simulation are given in Table 5.

Table 6. Parameters of the Simulation of the ^{19}F MAS NMR Spectra of $(NH_4)_3GaF_6$ (Rotation Frequency 30 kHz)[a]

measured nucleus[b]	line no.	δ_i (ppm)[c]	fwhm (Hz)[d]	J (Hz)[e],[f]	intensity (%)
^{19}F	1	−138.1	215.1	271.8	39.6
(Figure 6A)	2	−138.1	233.7	209.7	60.4
^{19}F{^{69}Ga}	1	−137.8	234.7	271.8	39.2
(Figure 6B)	2	−137.8	239.6	*s*	60.8
^{19}F{^{71}Ga}	1	−138.1	228.6	*s*	38.9
(Figure 6C)	2	−138.1	241.6	209.7	61.1

[a] All lines have Lorentzian shape. [b] The decoupled nucleus is given in braces. [c] δ_i: value of the isotropic chemical shift. [d] fwhm: full width at half-height of the signal. [e] J: scalar coupling constant. [f] The scalar coupling constants given here are larger than the values given in Table 5 as discussed in 4. The deviation goes up to +7% for the ^{19}F−^{69}Ga coupling because of the worse resolution of the spectra.

like spectrum is obtained (Figure 5B). The coupling pattern expected for an isolated $^{71}GaF_6^{3-}$ species is seven lines with intensity ratios of 1:6:15:20:15:6:1. ^{19}F decoupling at this rotation speed results in a single narrow resonance line. The ratio of the coupling constants between ^{19}F and the gallium nuclei, $197.9/263.9 = 0.746$ is close to the ratio of the magnetogyric ratios $\gamma(^{69}\mathrm{Ga})/\gamma(^{71}\mathrm{Ga}) = 0.787$.

Quadrupolar Interaction. MAS NMR spectroscopy of quadrupolar nuclei like ^{71}Ga is sensitive to changes in the symmetry of the environment of the nucleus.[14] The envelope of the intensities of the spinning sidebands strongly depends on the quadrupolar frequency ν_Q, which itself depends on the local symmetry: For O_h symmetry it is $\nu_Q = 0$; for lower symmetry it is $\nu_Q > 0$.[15] Since line widths of the ^{71}Ga MAS NMR spectra of $(NH_4)_3GaF_6$ taken at 30 kHz are unusually small for solids (see Table 5) along with very small quadrupolar interactions, it was impossible to obtain a spectrum with an adequate number of spinning sidebands. Spinning speeds as low as 3 kHz and ^{19}F broad-band decoupling had to be applied. (see Figure 4A).

Although the crystal phase of $(NH_4)_3GaF_6$ is cubic, it became obvious that a reproduction of the spectrum is only possible with more than one species with nonzero quadrupolar frequencies. A maximum value of $\nu_Q = 28$ kHz can be estimated. This indicates that on the NMR time scale the symmetry of the Ga site cannot be exactly O_h. On the other hand, these values are very small compared to the large quadrupole moment of ^{71}Ga (Table 2) and compared, e.g., to ν_Q for crystalline GaF_3, which has a value of 500 kHz.[16] For the most oxidic materials the quadrupolar frequency ν_Q is even higher and ranged in the order of magnitude of a few megahertz.[17−19] This explains, why such low rotation frequencies as 3 kHz have to be used to observe the spinning sidebands. Because of such low values for ν_Q, the asymmetry parameter η_Q does not have significant influence on the shape of the powder spectrum.

It can be concluded that the deviation of the GaF_6 octahedra from exact cubic symmetry is very low, but not negligible. These findings encouraged us to perform MAS NMR measurements of $(NH_4)_3GaF_6$ at higher temperature (here 363 K). A further increase of temperature (above 363

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(19) Note that in many publications the value C_q is given instead of ν_Q. Their relation is $\nu_Q = 3C_q/[2I(2I-1)] = 0.5C_q$ (for $I = {}^3/_2$).

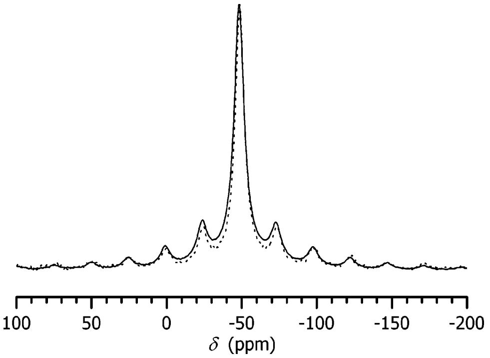

Figure 7. Comparison of $^{71}Ga-\{^{19}F\}$ decoupled MAS NMR spectra of $(NH_4)_3GaF_6$ taken at 293 K (solid line) and 363 K (dotted line) (rotation frequency 3 kHz).

K) was impossible because of beginning decomposition processes in the sample above 373 K. Heating up to 363 K leads in the $^{71}G-\{^{19}F\}$ decoupled spectrum (3 kHz) to a line narrowing (see Figure 7). In addition the spread of the spinning sidebands is reduced, and a maximum ν_Q value of 20 kHz can now be estimated. The ^{19}F MAS NMR spectrum taken at 363 K and 10 kHz shows broadening effects and has, together with the respective ^{71}Ga spectrum, a pronounced tendency to a better resolution of the $^{19}F-^{69,71}Ga$ coupling (not shown here).

5. Discussion

Model of Rigid Octahedra. The discrepancies mentioned in the section 3 show that the crystallographic data is not consistent with the model of rigid, exact symmetric and disordered octahedra. This means that either the crystallographic data is not correct enough or the model is wrong. In addition, it is known that XRD does not allow one to distinguish between dynamic elongations or changes from an ideal position and static elongations, which may be statistically distributed.[20]

Our own refinement (Table 3) gave very similar values as those given by Schwarzmann as one possible solution.[6] However, supported by MAS NMR results it is clear now that the crystallographic data are too much subjected to errors. The two following points underline these facts:

(i) The resolution of the scalar $^{71}Ga-^{19}F$ coupling in $(NH_4)_3GaF_6$ with a coupling pattern of seven lines and intensity ratios of 1:6:15:20:15:6:1 as expected for isolated $^{71}GaF_6^{3-}$ species can only be obtained if the six fluorine ligands are equivalent. The latter is only possible for high symmetric (nearly exact) GaF_6^{3-} octahedra.

(ii) The very small quadrupolar interactions ($\nu_Q < 28$ kHz in the cubic phase) in the ^{71}Ga MAS NMR spectra indicate that the first coordination sphere, i.e., the fluorine coordination, allows only extremely small deviations from exact octahedral symmetry. Here a comparison with the structure of α-GaF_3 is useful:[21] GaF_3 consists of linked, trigonally distorted octahedra. The F−Ga−F angles are 89.67° and 90.33°, which is already close to exact octahedral symmetry. The quadrupolar frequency of Ga ($\nu_Q = 500$ kHz)[16] is about 2 magnitudes higher than those assumed as a mean value of the ν_Q distribution of the Ga species in $(NH_4)_3GaF_6$ at about 10 kHz. Thus, accepting the model of rigid exact octahedra, the F−Ga−F angles in $(NH_4)_3GaF_6$ should be even closer to 90° than those in α-GaF_3. The deviation can be estimated at least 1 magnitude lower than in α-GaF_3; an realistic upper bound would be 0.05°. This is in strong contrast to Table 1.

(iii) The position of fluorine possesses only two degrees of freedom (see eq 2), although it is located on a 192*l* position. But Rietveld refinement of the 192*l* position always assumes three degrees of freedom, meaning that *x*, *y*, and *z* are totally independent from each other. Equation 3 shows that this is not true and that only two degrees of freedom exist. The F−Ga−F angle is very sensitive to the position of *x*, but the *R*-value of the refinement is not very sensitive to small changes of *x*. This results in large errors in the F−Ga−F angle. Consequently, refinement with just two degrees of freedom should be done, but unfortunately, Rietveld solution with the constraint from eq 3 was not possible with the available software.

In conclusion, it can be stated that the results from Table 1 should be taken critically, because the structural model used for the structure solution and refinement of the coordinates is highly subject to errors due to too many degrees of freedom.

Interaction of the Ga Quadrupolar Moment with the Local Environment. As stated in the previous subsection, the first coordination sphere of Ga is either of exact octahedral symmetry or at least very close to it. However, since the octahedra are tilted relative to the surrounding matrix, the overall symmetry is not exact octahedral but lower. Field gradients induced by such tilting have been explicitly calculated for K_2NaFeF_6.[20] In other words, this means that the second and third coordination spheres contribute to the small, but nonvanishing, measured quadrupolar frequencies.

In these further coordination spheres also occur disordered structures, namely, eight $NH_4(1)$ (two orientations, second sphere) and six other GaF_6 (eight orientations, third sphere). Provided that the orientations of these ions in further coordination spheres are independent from each other, a certain number of different field gradients are possible and have to be considered. As a consequence, an exact reproduction of the ^{71}Ga MAS NMR spectrum is only possible with more than one set of quadrupolar constants, i.e., a small distribution of quadrupolar parameters is necessary.

Beside the arguments given above within the frame of static rigid octahedra and an overall symmetry lower than octahedral, MAS NMR experiments gave strong indications for motional effects in the sample. As already announced by Sasaki et al.,[9] the temperature-dependent behavior of the second moments of the ^1H and ^{19}F signals (broad line measurements) indicates that both NH_4^+ ions and GaF_6^{3-} octahedra undergo rapid reorientation rotations. Issues of motional effects obtained in the present MAS NMR study at room temperature are (i) Lorentzian line shapes together with narrow lines, this is usually typical for liquids, and (ii)

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(21) Roos, M.; Meyer, G. *Z. Kristallogr.* **2001**, *216*, 18.

the resolution of the scalar *J*-coupling between Ga and F nuclei indicating the existence of six equivalent fluorine neighbors of gallium.

It should be stated at this point here that the use of more than one set of quadrupolar parameters is not based on the occurrence of crystallographically different Ga sites in the cubic phase. The quadrupolar frequencies are statistically distributed around a mean value. The motional averaging could be improved at 363 K with the observation of a smaller overall quadrupolar frequency (see Figure 7) and a reducing of the maximum ν_Q value to about 20 kHz.

However, a spectrum without any quadrupolar interaction could not be obtained. Here, the beginning decomposition of the matrix prevents further experiments at higher temperatures above 363 K. Finally, it can be stated that because of a local symmetry lower than octahedral combined with not completely averaged motional effects of the cations and anions the unambiguous existence of a distribution of quadrupolar parameters (although small) can be explained for the cubic phase of $(NH_4)_3GaF_6$.

6. Conclusions

The structures of disordered ammonium cryolites $(NH_4)_3$-MeF_6 crystallizing in the space group $Fm\bar{3}m$ have often been discussed in the literature. A geometrical structure model, explaining the thermodynamics of phase transitions due to the rotational disorder of rigid MeF_6 with octahedral symmetry was developed earlier.[2]

Our MAS NMR experiments on $(NH_4)_3GaF_6$ performed here for the first time unambiguously support the model of rigid octahedra: The scalar coupling constants between the fluorine and gallium nuclei could be directly determined from both the ^{69,71}Ga and the ^{19}F 30 kHz MAS NMR spectra. This observation is usually very rare for powders and applying MAS NMR. Because of narrower line widths and the better resolution the values determined from the Ga spectra as $J(^{19}F^{69}Ga) = 197$ Hz and $J(^{19}F^{71}Ga) = 264$ Hz are more reliable. A coupling pattern of seven lines and intensity ratios of 1:6:15:20:15:6:1 as expected for isolated $^{71}GaF_6^{3-}$ species together with Lorentzian line shapes can only be obtained if the six fluorine ligands are equivalent. The latter is only possible for high symmetric (nearly exact) GaF_6^{3-} octahedra underlying motional effects.

The quadrupolar frequency of the ^{71}Ga nucleus cannot be determined exactly; the simulation of the spectra is only possible with a distribution of quadrupolar frequencies. These quadrupolar frequencies are very small but not vanishing. A maximum ν_Q value can be given as 28 kHz as determined from the spread of the spinning sidebands. This can be explained by the occurrence of highly symmetric GaF_6 octahedra, which are tilted against the surrounding atoms. In addition, the incomplete motional excitation does not average out the quadrupolar effects. The motional averaging of quadrupolar effects can be improved by thermal excitation. Thus, the existence of more than one set of quadrupolar parameters is not based on the occurrence of crystallographically different Ga sites but is a consequence of the statistical distribution of *local* quadrupolar parameters.

These MAS NMR findings are in discrepancy to the results of the crystallographic refinement, where especially the refinement of the fluorine 192*l* position is much subjected to errors. Refinement is usually carried out using three independent coordinates. But the structure model shows the existence of only two independent coordinates, whereas the third one is fixed (see eq 3).

The structure model of rigid exact octahedra, as it could be verified by ^{71}Ga MAS NMR, requires *mandatory* the condition $x = yz/(y + z)$ for the refinement of the coordinates of the fluorine atom. For this kind of question it appears that X-ray diffraction is not sensitive enough to deliver proper results.

Supporting Information Available: CIF file of the structure of $(NH_4)_3GaF_6$ in $Fm3m$; output files of FULLPROF for all four structure solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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