^1H and ^{19}F NMR Studies on the Motion of Ammonium Ions in Solid Ammonium Tetrafluoroaluminate(III)

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The temperature dependences of the NMR second moment, M_2, and of the spin-lattice relaxation time, T_1, of ^1H and ^{19}F nulcei were observed for NH_4AlF_4. With increasing temperature a decrease of $M_2(^1H)$, attributable to the onset of cationic reorientation, was observed between 77 and 150 K. This was confirmed by measurements of $T_1(^1H)$ observed at two Larmor frequencies. Nonexponential magnetization recovery was detected in the T_1 measurement of both ^1H and ^{19}F, especially below 150 K, indicating strong magnetic coupling between both systems. Therefore, in such cases T_1 was determined from the initial slope of the magnetization recovery curve. The motional parameters of the cation were evaluated from the T_1 data. The log T_1 vs. T^{-1} curves of both nuclei showed a discontinuity around 143 K, indicating a phase transition which has already been suggested by other workers.

Introduction

Ammonium tetrafluoroaluminate(III), NH_4AlF_4, forms at room temperature tetragonal crystals belonging to the space group I4/mcm [1 – 5]. AlF_6 octahedra form layers in which each equatorial fluorine is shared by two octahedra, and each ammonium cation sits between these layers surrounded by slightly deformed cube of fluorines. Accordingly it is expected that the cations have two stable orientations similar to those of the cations in the room temperature phase of NH_4Cl and that the orientation of the cations becomes disordered at high temperatures. Since an unusual phase transition possibly due to this order-disorder transition was found near 150 K, extensive studies have been performed to clarify the nature of the phase transition by means of ESR on the samples doped with paramagnetic ions [3, 4], neutron powder diffraction [5], Raman scattering [6, 7], NMR [8], and infrared absorptions [9]. These studies indicate that the phase transition is closely related to the dynamics of the NH_4^+ ions. In order to obtain more detailed information about this problem, in the present investigation ^1H and ^{19}F NMR has been undertaken over a fairly wide temperature range.

Experimental

NH_4AlF_4 was prepared by adding an aqueous solution of NH_4HF_2 to a hydrofluoric acid solution of aluminium(III) fluoride [1]. The resulting white precipitate was separated, washed with methanol, dried at room temperature and then heated to 200 °C for 10 h to decompose $(NH_4)_3AlF_6$ formed as a by-propduct [10]. The sample was identified by recording its X-ray powder patterns [1, 2], using a Rigaku Denki D-3F diffractometer equipped with a Cu anticathode.

The ^1H and ^{19}F NMR absorption spectra were obtained with a JEOL JNM-MW-40 S spectrometer operated at 40 MHz, whereas the ^1H and ^{19}F spin-lattice relaxation times (T_{1H} and T_{1F}, respectively) were determined by means of a frequency variable pulsed NMR spectrometer described in [11]. Differential thermal analysis (DTA) experiments were carried out with a homemade apparatus described in [12]. Temperatures were measured with a copper constantan thermocouple with an estimated accuracy of ± 3 K for the measurements of NMR absorption spectra and of ± 1 K for the other experiments.

Results

The second moments of ^1H and ^{19}F NMR absorptions, M_{2H} and M_{2F}, respectively, were determined

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at various temperatures between 77 K and room temperature. The results are shown in Figure 1. At 77 K, M_{2H} and M_{2F} were 0.55 and 0.21 mT^2, respectively, with an estimated error of 0.04 mT^2. With increasing temperature M_{2H} decreases markedly while M_{2F} decreases rather gently up to ca. 150 K, above which temperature both moments have almost constant values of 0.055 and 0.15 mT^2, respectively.

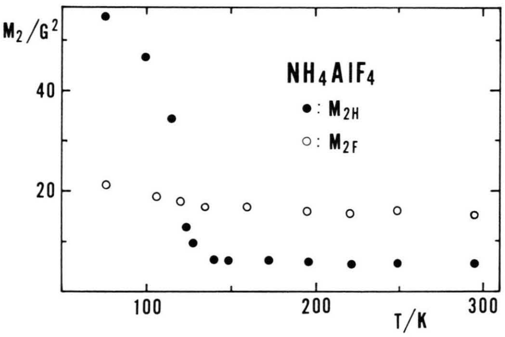

Fig. 1. Temperature dependence of NMR second moments, M_{2H} and M_{2F}, observed for ^1H and ^{19}F nuclei, respectively, in NH_4AlF_4 crystals.

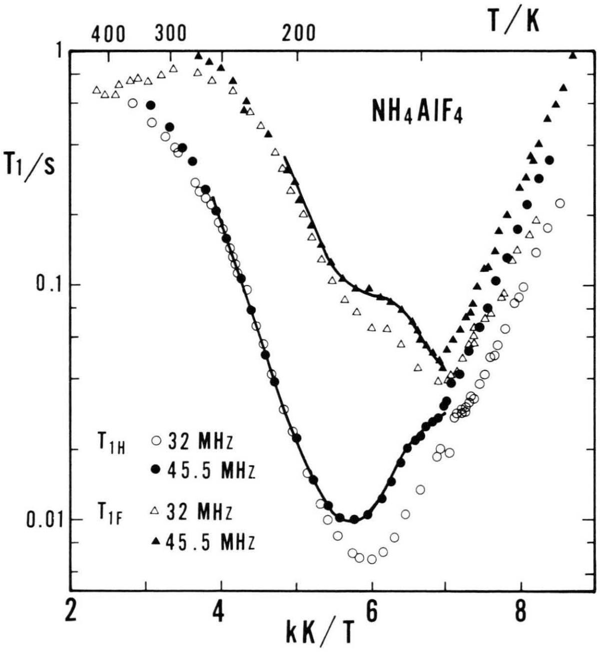

Fig. 2. Temperature dependence of nuclear spin-lattice relaxation times, T_{1H} and T_{1F}, observed for ^1H and ^{19}F nuclei, respectively, in NH_4AlF_4 crystals at the Larmor frequencies of 32 and 45.5 MHz. Solid lines indicate the calculated curves of T_{1H} and T_{1F} in the room-temperature phase.

Figure 2 shows the temperature dependences of T_{1H} and T_{1F} at the Larmor frequencies of 32 and 45.5 MHz. Below ca. 250 K, T_{1H} decreases smoothly with decreasing temperature, and a minimum of 6.8 ms appears at ca. 170 K for the 32 MHz data. When T_{1H} and T_{1F} were determined below 150 K, a marked nonexponential magnetization recovery was observed for both nuclei. This may be due to magnetic dipolar cross coupling between neighboring ^1H and ^{19}F nuclei [13–17]. When nonexponential behavior was observed for the magnetization recovery curves, T_1 was estimated from the initial slope [17].

T_{1F} vs. T^{-1} curves yield a shoulder around 170 K, whereas the T_{1H} vs. T^{-1} curves for both Larmor frequencies yield a minimum. T_{1F} decreases with decreasing temperature down to 143 K and then shows a discontinuity, where $\log T_{1F}$ starts to increase almost linearly with T^{-1}. This can be seen very clearly for the curve at 45.5 MHz and strongly suggests the existence of a phase transition at 143 K. To confirm the presence of the above phase transition suggested, we carried out DTA experiments with various scanning rates, but no heat anomaly could be detected between 100 and 300 K. This is unusual. However, the same DTA results are also reported by Fourquet et al. [2].

Mackowiak and Brown studied the temperarture dependence of the nuclear spin-lattice relaxation time of this compound in both laboratory and rotating frames [8]. Their T_{1H} data are rather coarse and differ somewhat from ours, but they concluded a phase transition at 147 K from a clear discontinuity in the temperature dependence curves of the nuclear relaxation times.

Discussion

(a) In NH_4AlF_4 crystals there are four kinds of magnetic nuclei, namely, ^1H, ^{14}N, ^{19}F, and ^{27}Al, all of which must contribute to some extent to the second moments M_{2H} and M_{2F}. However contribution from ^{14}N nuclei to M_{2H} and M_{2F} may be neglected because of the small gyromagnetic ratio of ^{14}N nulcei. Accordingly, M_{2H} and M_{2F} can be written as

$$M_{2H} = M_2(H-H) + M_2(H-F) + M_2(H-Al), \quad (1)$$

and

$$M_{2\mathrm{F}} = M_2(\mathrm{F-F}) + M_2(\mathrm{F-H}) + M_2(\mathrm{F-Al}) \,. \tag{2}$$

Here, $M_2(\mathrm{H-H})$, $M_2(\mathrm{H-F})$, and $M_2(\mathrm{H-Al})$ denote the contributions arising from the nuclear magnetic interactions between a resonant ^{1}H nucleus and the other ^{1}H, ^{19}F, and ^{27}Al nuclei, respectively; similarly $M_2(\mathrm{F-F})$, $M_2(\mathrm{F-H})$, and $M_2(\mathrm{F-Al})$ denote the contribution to the ^{19}F NMR second moments resulting from the nuclear magnetic interactions between a resonant ^{19}F nucleus and the other ^{19}F, ^{1}H, and ^{27}Al nuclei, respectively.

For a polycrystalline sample, the rigid lattice second moment of like spins $[M_2(I-I)]$ having a spin quantum number I is given for the i-th nucleus by [18]

$$M_2(I_i - I) = \left(\frac{3}{5}\right) \gamma_I^2 \hbar^2 I(I+1) \sum_j r_{ij}^{-6} \,, \tag{3}$$

whereas for unlike spins the second moment is

$$M_2(I_i - S) = \left(\frac{4}{15}\right) \gamma_S^2 \hbar^2 S(S+1) \sum_k r_{ik}^{-6} \,. \tag{4}$$

Here, γ_I and γ_S are gyromagnetic ratios of the nuclei with spin quantum numbers I and S, respectively. The distances between the spin pairs ij (ik) are denoted by r_{ij} (r_{ik}).

In the present calculation of M_2, NH_4^+ was assumed to be tetrahedral with the H−H distance 1.70 Å and the N−H distance 1.041 Å [19, 20]. Other internuclear distances necessary for the calculation of $M_{2\mathrm{H}}$ and $M_{2\mathrm{F}}$ were determined from the structural data of this crystal [1−4]. The values of $M_{2\mathrm{H}}$ and $M_{2\mathrm{F}}$ calculated by means of (3) and (4) are given in Table 1. At 77 K they agree well with the measurements, indicating that NH_4^+ can be assumed to be rigid at 77 K. However, this may be somewhat questionable because we failed to observe the definite plateau value of $M_{2\mathrm{H}}$ above 77 K.

For another motional model in which the cation undergoes isotropic reorientation rapidly enough, M_2 was calculated by assuming the positions the four protons of a cation to coincide with that of the corresponding nitrogen atom. The $M_{2\mathrm{H}}$ and $M_{2\mathrm{F}}$ values calculated with this model are also given in Table 1. These values agree very well with the corresponding plateau values determined above ca. 150 K. Accordingly it is concluded that the cation undergoes isotropic reorientation in NH_4AlF_4 crystals above ca. 150 K.

(b) By considering the above M_2 results, the temperature dependence of $T_{1\mathrm{H}}$ and $T_{1\mathrm{F}}$ observed above ca. 150 K was interpreted in terms of isotropic reorientation of the cations surrounded by rigid fluoride ions. If one neglects the effects from couplings with the ^{27}Al spins, the relaxation matrix becomes 2 × 2 [13−17] and in the exponential approximation considered in this work the observed spin-lattice relaxation rates $T_{1\mathrm{H}}^{-1}$ and $T_{1\mathrm{F}}^{-1}$ can be expressed by

$$T_{1\mathrm{H}}^{-1} = R_{\mathrm{HH}} \,, \tag{5a}$$

$$T_{1\mathrm{F}}^{-1} = R_{\mathrm{FF}} \,, \tag{5b}$$

where for rapidly reorienting cations in NH_4AlF_4 crystals one has [14−17, 21]

$$\begin{aligned} R_{\mathrm{HH}} &= T_1(\mathrm{H-H})^{-1} + T_1(\mathrm{H-F})^{-1} \\ &= \left(\tfrac{2}{3}\right) \gamma_{\mathrm{H}}^2 \,\Delta M_2(\mathrm{H-H})\, f(\omega_{\mathrm{H}}, \tau_{\mathrm{H}}) \\ &\quad + \left(\tfrac{1}{2}\right) \gamma_{\mathrm{H}}^2 \,\Delta M_2(\mathrm{H-F})\, g(\omega_{\mathrm{H}}, \omega_{\mathrm{F}}, \tau_{\mathrm{H}}) \,, \end{aligned} \tag{6}$$

and

$$\begin{aligned} R_{\mathrm{FF}} &= T_1(\mathrm{F-H})^{-1} \\ &= \left(\tfrac{1}{2}\right) \gamma_{\mathrm{F}}^2 \,\Delta M_2(\mathrm{F-H})\, g(\omega_{\mathrm{F}}, \omega_{\mathrm{H}}, \tau_{\mathrm{H}}) \,. \end{aligned} \tag{7}$$

Table 1. NMR second moments, $M_{2\mathrm{H}}$ and $M_{2\mathrm{F}}$, calculated for ^{1}H and ^{19}F nuclei, respectively, on the two motional states of the cation in NH_4AlF_4. $M_2(\mathrm{H-H})_{\mathrm{intra}}$ and $M_2(\mathrm{H-H})_{\mathrm{inter}}$ indicate M_2 values arising from magnetic interactions between intra- and inter-cationic protons, respectively. All data are in units of G^2 ($G^2 = 10^{-8}\,T^2$).

Motional state	$M_2(\mathrm{H-H})_{\mathrm{intra}}$	$M_2(\mathrm{H-H})_{\mathrm{inter}}$	$M_2(\mathrm{H-F})$	$M_2(\mathrm{H-Al})$	$M_{2\mathrm{H}}$	$M_2(\mathrm{F-F})$	$M_2(\mathrm{F-H})$	$M_2(\mathrm{F-Al})$	$M_{2\mathrm{F}}$
Rigid	44.5	7.3	4.5	0.4	56.7	9.0	5.1	5.5	19.6
Overall reorientation	0	3.3	2.7	0.3	6.3	9.0	3.1	5.5	17.6

The spectral density functions of $f(\omega_H, \tau_H)$ and $g(\omega_L, \omega_J, \tau_H)$ are given by

$$f(\omega_H, \tau_H) = \frac{\tau_H}{1+\omega_H^2 \tau_H^2} + \frac{4\tau_H}{1+4\omega_H^2 \tau_H^2} \tag{8}$$

and

$$g(\omega_L, \omega_J, \tau_H) = \frac{\tau_H}{1+(\omega_L-\omega_J)^2 \tau_H^2} + \frac{3\tau_H}{1+\omega_L^2 \tau_H^2} + \frac{6\tau_H}{1+(\omega_L+\omega_J)^2 \tau_H^2}. \tag{9}$$

Here, ω_L and ω_J (L, J = H, F or F, H) are the angular resonance frequencies of L and J nuclei, respectively, and τ_H is the correlation time of the cationic motion. $\Delta M_2(\mathrm{L-J})$ denotes the reduction of $M_2(\mathrm{L-J})$ through the onset of the motion of magnetic nuclei and is determined by partially averaging the L–J magnetic dipolar interactions by the cationic motion.

The influence of ^{27}Al magnetic and also quadrupolar nuclei on the observed relaxation rates in the present system can be neglected because the estimated $\Delta M_2(\mathrm{F-Al})$ is practically zero and $\Delta M_2(\mathrm{H-Al})$ may be much smaller than $\Delta M_2(\mathrm{H-H})$ and $\Delta M_2(\mathrm{H-F})$ because the H–Al distances are longer than those of the other ones in the crystal.

Equations (5a) and (5b) may be good approximations for the observed relaxation time when they are determined from the initial linear portion of magnetic recovery curves even if they are heavily nonexponential [17]. In the present investigation, we employed this method for the determination of both $T_{1\mathrm{H}}$ and $T_{1\mathrm{F}}$. Assuming an Arrhenius relationship, τ_H can be expressed with an activation energy E_a of the cationic motion by

$$\tau_H = \tau_{H0} \exp(E_a/RT), \tag{10}$$

where τ_{H0} denotes the correlation time in the limit of infinite temperature.

Table 2. Motional parameters of the cation. Activation energy E_a, correlation time τ_{H0}, and observed and calculated second moment reduction $\Delta M_2(\mathrm{L-J})$ in NH_4AlF_4 crystals as determined from ^{1}H T_1 ($T_{1\mathrm{H}}$) and ^{19}F T_1 ($T_{1\mathrm{F}}$) data observed below and above the phase transition temperature.

Motional mode	E_a/kJ mol^{-1}	τ_{H0}/s	$\Delta M_2(\mathrm{L-J})/\mathrm{G}^2$	
			obs.	calc.
Low-temperature				
Overall reorient.	15	–	–	–
Room-temperature				
Overall orient.	18	7.8×10^{-15}	38 (H–H) 2.4 (H–F)	48.5 (H–H) 1.8 (H–F)

For the room temperature phase of NH_4AlF_4, the motional parameters of the cation were evaluated from the least-squares fitting to the $T_{1\mathrm{H}}$ and $T_{1\mathrm{F}}$ points determined at 45.5 MHz by means of (5) and (10). The motional parameters obtained in this way are listed in Table 2. The values of ΔM_2 evaluated from the above T_1 data agree fairly well with the calculated ones. This supports the foregoing conclusion about the motion of the cation derived from the temperature dependence study of the ^{1}H and ^{19}F second moments.

From a neutron powder diffraction study, Bulou et al. [5] showed that the ammonium cations of NH_4AlF_4 crystals are in an ordered state at 5 K. The compound has a layer structure. All the cations on a (0 0 1) layer have the same orientation but the cations located on the two neighboring layers have a different kind of orientation. This means that the cations have a ferro-type orientation within a layer whereas they have an antiferro-type orientation between neighboring layers. For the overall reorientation of the cation in this low-temperature phase we estimated E_a as 15 kJ mol^{-1} from the gradients of the log $T_{1\mathrm{H}}$ and log $T_{1\mathrm{F}}$ vs. T^{-1} curves below the phase transition. This value is slightly smaller than that obtained for the room temperature phase (see Table 2). This is probably because the crystal becomes loosely packed in the ordered state.

Couzi et al. [6, 7] recorded Raman spectra at various temperatures for a single crystal of NH_4AlF_4 and concluded that the phase transition taking place near 150 K is a purely order-disorder transition about the cationic orientations. If this mechanism is truely governing in this phase transition, a rather large heat anomaly of transition ($RT \ln 2$) should be observed. However, DTA experiments carried out previously by other researchers [2] and also presently by us yielded no heat anomaly, suggesting that the transition proceeds or occurs fairly gradually in the crystal. This has also been suggested from the study of ESR experiments for the crystal doped with paramagnetic ions [4].

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