Nuclear Magnetic and Quadrupole Resonance Studies of Phase Transitions in Crystalline (NH₄)₂SbF₅ and (ND₄)₂SbF₅

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(NH₄)₂SbF₅ undergoes two successive phase transitions at 169 and 292 K, both of which are of typical lambda-type and without thermal hysteresis. Proton and fluorine spin-lattice relaxation time measurements showed that the isotropic reorientation of the NH₄⁺ ions is highly excited below the lower transition point with an activation energy of 15.5 kJ mol⁻¹ and that the uniaxial reorientation of the square pyramidal SbF₅⁻² anion is excited above about 200 K with an activation energy of 42.0 kJ mol⁻¹. There is strong cross relaxation between the proton and the fluorine over the whole temperature range of the measurements. The ¹²¹Sb and ¹²³Sb nuclear quadrupole resonance frequencies show an anomalous temperature dependence; each resonance frequency assumes a minimum at about 100 K and increases on heating, reaches a maximum at the lower transition point, decreases drastically in the middle temperature phase and then fades out just below the upper transition point. The anomalous increase in the resonance frequencies stems from the reorganization of the N—H...F type hydrogen bonds with the progress of the lower phase transition. The lower and the upper transition temperatures shift to 173.0 and 290.1 K, respectively, on deuteration of the ammonium ion.

We now attempted to track down the source of the discrepancy between our previous results and those reported in [4] and [5] by changing the conditions of the sample preparation. We also made more detailed measurements of the NQR frequencies for the antimony isotopes as well as of the spin-lattice relaxation times for proton and fluorine in order to clarify the nature of the phase transitions in this substance. This paper describes our experimental results on (NH₄)₂SbF₅ and its deuterated analogue, from which a model will be presented of the phase transitions mechanisms.

Experimental

Crystals of (NH₄)₂SbF₅ were grown from an aqueous solution containing 6.0 g of NH₄F and 9.5 g of SbF₅ by the evaporation method according to [2]. Analysis: found: Sb = 48.1, F = 38.4%; calculated: Sb = 48.16, F = 37.57%. (ND₄)₂SbF₅ was obtained by repeated replacement of the solvent water by D₂O. Calculated deuteration fraction: 98.8%. Both specimens were ground into fine powder and dried under vacuum for 48 hours. For the measurements of the relaxation times each specimen was sealed into a glass ampoule with about 2 kPa of helium as the heat exchange gas. The spin-lattice relaxation times T₁ for ¹H and ¹⁹F were measured with a home-built pulsed...
spectrometer at 10 MHz by the 90°-π-90° pulse sequence method. The recovery of the magnetization for both nuclei was very non-exponential above about 200 K, being described with two exponential time constants, $T_{1*}$ and $T_{11}$. The experimental errors in the $T_{1*}$ of $^1H$ and $^{19}F$ were estimated to be 5 and 12% below 200 K, increasing to 10 and 16% above 200 K, respectively.

The NQR frequencies for $^{121}\text{Sb}$ and $^{123}\text{Sb}$ for the NH$_4^-$ and ND$_4^-$ salts were measured with a super-regenerative spectrometer. The maximum errors in the frequency measurements were ±5 kHz and ±10 kHz for the NH$_4^-$ and ND$_4^-$ salts, respectively.

The temperature measurements for NMR and NQR and the differential thermal analysis were carried out with Chromel-P-constantan thermocouples calibrated against a platinum thermometer within an experimental error of ±0.1 K and ±0.3 K above and below 100 K, respectively.

### Results and Discussion

#### Phase transitions:

The differential thermal analysis for the NH$_4^-$ salt showed two λ-type phase transitions with the maxima at 169.7 and at 292.6 K. The specimen dried under vacuum did not give any other thermal anomaly. However, when the drying was incomplete, there appeared another relatively large peak around 248 K and a small anomaly centering at 165 K, which is superposed on the lower transition. These facts suggest strongly that the anomalies detected in the previous measurements of the heat capacity and the electric conductivity in [4] and [5] were caused by trace of occluded water in the sample.

(ND$_4^-$)$_2\text{SbF}_5$ also gave two λ-type thermal anomalies in its DTA curve with the transition temperatures, 173.0 and 290.1 K. The shape of the lower transition and a small but significant isotope effect on the temperature of the transition together with the fact that there are two possible orientations for each NH$_4^+$ ion at room temperature [6, 7] imply that this transition is an order-disorder transition with respect to the orientation of the NH$_4^+$ ions. The nature of the upper transition is not obvious.

#### Nuclear magnetic relaxation:

Figure 1 shows the spin-lattice relaxation times, $T_1$, for $^1H$ and $^{19}F$ in the NH$_4^-$ salt. Below about 200 K the relaxation of both nuclear species can be described each with a single $T_1$. The $T_1$ for $^1H$ assumes a minimum value of 4.5 ms at 120.4 K whereas $T_1$ for $^{19}F$ gives a minimum value of 19 ms at about 112 K. One may expect another minimum for the $T_1$ of $^1H$ below 80 K but the drastic line-broadening that takes place makes the accurate determination of the $T_1$ difficult below 80 K. The nuclear relaxation below 200 K is governed probably, from the minimal value of the $T_1$, by the isotropic reorientation or rotation of one of the two inequivalent NH$_4^+$ ions in the presence of a relatively weak cross-relaxation between the protons and the fluorines.

The relaxation of $^1H$ and $^{19}F$ due to the dipolar interaction between them is described by the coupled equations [8–10]

$$\frac{d\langle F_z \rangle}{dt} = -R_F \langle F_z \rangle + F_0$$

$$\frac{d\langle H_z \rangle}{dt} = -R_{HF} \langle H_z \rangle + H_0 + R_{HF} \langle F_z \rangle - F_0$$

where $H_0$ and $F_0$ are the magnetization of proton and fluorine, respectively, at thermal equilibrium.

The four elements in the relaxation matrix are given in the weak collision case by [8]

$$R_F = C_1 \gamma_F^2 \Delta M_{FF} g_F(\omega_F, \tau_F) + C_2 \gamma_F^2 \Delta M_{FS} g_F(\omega_F, \tau_F) + C_3 \gamma_F^2 \Delta M_{FH} g_F(\omega_H, \tau_F) + C_4 \gamma_F^2 \Delta M_{HF} g_F(\omega_H, \tau_F),$$

Fig. 1. Temperature dependence of the proton (○) and fluorine (△) spin-lattice relaxation times in (NH$_4$)$_2$SbF$_5$ at 10 MHz. The slope of each broken curve above 200 K gives the activation energy for the reorientation of SbF$_5^2$-. The phase transition points are indicated by $T_c$.\"
\[ R_H = C_1 \gamma_H^2 \Delta M_{HH} g_H(\omega_H, \tau_H) + C_2 \gamma_H^2 \Delta M_{HF} g_H(\omega_{HF}, \tau_H) + C_3 \gamma_H^2 \Delta M_{HF} g_H(\omega_{HF}, \tau_F) , \]  
\[ R_{FH} = C_4 \gamma_F^2 \Delta M_{HH} g(\omega_{HF}, \tau_F) + C_5 \gamma_F^2 \Delta M_{HF} g(\omega_{HF}, \tau_H) , \]  
\[ R_{HF} = C_6 \gamma_F^2 \Delta M_{HH} g(\omega_{HF}, \tau_F) + C_7 \gamma_F^2 \Delta M_{HF} g(\omega_{HF}, \tau_H) , \]

where \( \Delta M_{HH} \), etc. represent the amounts of the decrease in the second moments, and the power spectra of molecular motion are given by

\[ g(\omega, \tau_H) = \frac{\tau_H}{1 + \omega_H^2 \tau_H^2} + \frac{4 \tau_H}{1 + 4 \omega_H^2 \tau_H^2} , \]  
\[ g(\omega_{HF}, \tau_H) = \frac{\tau_H}{1 + \omega_H^2 + \omega_{HF}^2 \tau_H^2} + \frac{3 \tau_H}{1 + \omega_H^2 \tau_H^2} + \frac{6 \tau_H}{1 + (\omega_H + \omega_{HF})^2 \tau_H^2} , \]

\[ g(\omega_{HF}, \tau_F) = -\frac{\tau_H}{1 + (\omega_H - \omega_F)^2 \tau_F^2} + \frac{6 \tau_F}{1 + (\omega_H + \omega_F)^2 \tau_F^2} . \]

Below about 200 K it is safely assumed that only the reorientation of the ammonium ions is excited and the pyramidal \( \text{SbF}_5^2^- \) remains static. Then we can put \( \tau_F = \infty \) in this temperature region. Assuming an Arrhenius activation process,

\[ \tau_H = \tau_H^0 \exp(\frac{E_a}{RT}) , \]

for the reorientation of the \( \text{NH}_4^+ \) ions and fitting (3) to the experimental \( T_1 \)'s for \( ^1\text{H} \) and \( ^1\text{H} \) below 200 K, we obtain \( E_a = 15.5 \text{kJ mol}^{-1} \) and \( \tau_H^0 = 3.27 \times 10^{-14} \text{s} \). The calculated \( T_1 \)'s are shown in Figure 2. The experimental minimum value of the \( T_1 \) is 4.7 ms, which is more than twice as long as 2 ms as predicted by the simple BPP theory [8] for the isotropic reorientation of the two kinds of \( \text{NH}_4^+ \) ions with an assumed distance of \( r_{\text{H-H}} = 0.169 \text{nm} \) [11]. This discrepancy suggests that the two crystallographically inequivalent \( \text{NH}_4^+ \) ions rotate at different rates, and that one kind of the ions gives the \( T_{1,\text{min}} \) at 120 K and the other below 80 K. Another possibility is that \( \text{NH}_4^+ \) undergoes an axial reorientation about one of its three \( C_2 \) axes and thus reduces \( \Delta M_{HH} \); this is consistent with the recent X-ray diffraction study [6].

Above 200 K, the recovery of the magnetization becomes non-exponential due to strong cross-relaxation between \( ^1\text{H} \) and \( ^1\text{H} \), which can be interpreted by a pair of relaxation rates, \( T_{1s} \) and \( T_{11} \). As the correlation time \( \tau_H \) for the reorientation of \( \text{NH}_4^+ \) is too short to contribute to the relaxation at this temperature, these relaxation rates are probably governed by some sort of reorientation of the \( \text{SbF}_5^2^- \) anions. As the \( \text{NH}_4^+ \) undergoes very rapid reorientation, we can put \( \tau_H \sim 0 \) and then (3) predicts that \( T_{1s}(\text{H}) = T_{1s}(\text{F}) \) and \( T_{11}(\text{H}) = T_{11}(\text{F}) \). As is seen in Fig. 1, however, the experimental \( T_1 \)'s do not satisfy these relations; there may be some other relaxation mechanism which leads to different \( T_1 \)'s for \( ^1\text{H} \) and \( ^1\text{H} \). The \( T_1 \)'s between 200 K and the upper transition point lead to an average activation energy of 42.0 kJ mol\(^{-1}\), which may be attributed to the axial reorientation of the \( \text{SbF}_5^2^- \).

In the case of \( \text{(ND}_4)_2\text{SbF}_5 \) the relaxation of \( ^1\text{H} \) is described by a single relaxation rate between 77 and 345 K. The result of the \( T_1 \) measurements is shown in Figure 3. The analysis of \( T_1 \) in terms of the four-site jump model [12] results in \( E_a = 47.6 \text{kJ mol}^{-1} \) and \( \tau_F^0 = 6.63 \times 10^{-17} \text{s} \). It was found that the contribution from the dipolar interaction between \( ^1\text{H} \) and the antimony isotopes amounts to 37 percent of the total relaxation rate.

**NQR of the Antimony Isotopes**

The NQR frequencies of \( ^{121}\text{Sb} \) and \( ^{123}\text{Sb} \) in \( \text{(NH}_4)_2\text{SbF}_5 \) were measured at 77 K by Kravchenko
et al. [13]. The results of our present measurements at 77 K agree with theirs within the experimental errors; our measurements at other temperatures give the result that \( v(\pm 1/2 \to \pm 3/2) \) for \(^{121}\text{Sb}\) and \(^{123}\text{Sb}\) in the NH\(_4\) salt are, respectively, 73.229 and 45.239 MHz at 53.1 K and 68.689 and 41.92 MHz at 288.0 K. The transition between the \( \pm 1/2 \) and \( \pm 3/2 \) levels of \(^{121}\text{Sb}\) in the ND\(_4\) salt gives a single resonance line at 73.1677, 73.033, 72.972, and 68.74 MHz at 52.1, 77.9, 196.0, and 288.0 K, respectively.

Figure 4 shows the temperature dependence of the NQR transition frequencies between the \( \pm 1/2 \) and \( \pm 3/2 \) levels of \(^{121}\text{Sb}\) in the NH\(_4\) and ND\(_4\) salts: The corresponding transition in \(^{123}\text{Sb}\) in the NH\(_4\) salt gives a similar temperature dependence. The principal components of the electric field gradient (EFG) tensor and the asymmetry parameter \( \eta \) calculated from the \( v_i \)'s of \(^{121}\text{Sb}\) and \(^{123}\text{Sb}\) are given in Figs. 5 and 6. The resonance frequency and the quadrupole coupling tensor components below 100 K can be interpreted in terms of a slightly anisotropic vibrational effect (Bayer effect) [14]. Above about 100 K, however, these parameters increase with temperature, reach a maximum at the lower transition point, and then decrease rapidly. The resonance signals disappeared just below the higher transition point.

The temperature dependence of the resonance frequencies as well as the tensor components of the quadrupole coupling constant below the lower transition point cannot be interpreted in terms of the usual Bayer effect on the EFG which predicts monotonous decrease of these NQR parameters [14]. For unusual positive temperature coefficients in a narrow temperature region, which have been observed in some ammonium salts, we presented a theory by which this is interpreted as the averaging effect on the EFG caused by instantaneous breaking of the hydrogen bond between the NH\(_4^+\) and the anion on which the resonant nucleus sits; the breaking occurs during the transient period of the rotation of the NH\(_4^+\) ion [15–17]. When such an effect works, the NQR frequency at a temperature \( T \) is given by

\[
v(T) = v_0(T) + (v_1 \tau_r + v_1 \tau_i)/(\tau_r + \tau_i),
\]  

(6)
where $v_r$ and $\tau_r$ are the resonance frequency and the residence time when the NH$_4^+$ is in the stable, hydrogen-bonded orientation, and, $v_t$ and $\tau_t$ relate to the case when NH$_4^+$ is in the rotational period, respectively. $v_0(T)$ is the frequency which would otherwise be observed as a result of the usual vibration effect. Equation (6) holds when $2\pi v(T)\tau_r, 2\pi v(T)\tau_t \ll 1$.

The analysis of the data in Fig. 4 using (6) leads to $\tau_t = 10^{-9}$ s. Since the normal lifetime for the transient rotational state of NH$_4^+$ should lie around $10^{-12}$ s [16], this value cannot be taken as the rotational lifetime of the NH$_4^+$ ions in the present material. When an order-disorder transition with respect to the orientation of the NH$_4^+$ ions is in progress, each ion must spend some finite time $\tau_r$ in its original right site and for some other finite time $\tau_w$ in its disordered, wrong site. Therefore the apparent transient time $\tau_t$ may be taken as this second residence time. In this case we must modify the (6) so as to read

$$v(T) = v_0(T)$$

$$+ (v_r \tau_r + v_w \tau_w + v_t \tau_t)/(\tau_r + \tau_w + \tau_t),$$

where $v_w$ is the contribution from NH$_4^+$ in the disordered orientation to the NQR frequency. As the order of magnitude of $\tau_t$ is $10^{-12}$ s, it may be ignored compared with $\tau_r$ and $\tau_w$, and the above equation simplifies to

$$v(T) = v_0(T) + (v_r \tau_r + v_w \tau_w)/(\tau_r + \tau_w).$$

The order parameter $s$ for the transition in this case is given by

$$s = (\tau_r - \tau_w)/\tau_w,$$

and the relation

$$\tau_w/\tau_r = \exp(-\Delta/R T)$$

holds, where $\Delta$ is the energy difference between the right and the wrong orientations of each NH$_4^+$ ion. For $T \geq T_c, \Delta = 0$, and so $\tau_r/\tau_w = 1$ is satisfied.

To analyze the experimental NQR data we modify (8) using (10) to

$$v(T) = A + B T + (v_w - v_r)$$

$$\cdot \exp(-\Delta/R T)/(1 + \exp(-\Delta/R T)),$$

where the term $A + B T$ represents the normal Bayer effect and is determined from the experimental NQR frequency below about 80 K; $A = 73.4694$ MHz, $B = -5.7146$ MHz/K. We then deduce the remaining
parameters from the anomalous part in the resonance frequency and calculate the order parameter $s$. The results for (NH$_4$)$_2$SbF$_5$ and (ND$_4$)$_2$SbF$_5$ are plotted against the reduced temperature $T/T_c$ in Figure 7. Apart from the slightly unrealistic shape of the parameter curve in the close vicinity of the transition temperature, we can see that the order parameter for the order-disorder phase transition in this ammonium salt can be deduced from the anomalous NQR data using a simple theoretical treatment. This type of treatment may be applicable to other systems in which the phase transition is associated with the dynamics of hydrogen bonds.

Presently it is hard to explain the very sharp decrease in the resonance frequency and the asymmetry parameter in the middle temperature phase, and the mechanism of the upper phase transition in these substances. The behavior of $v(T)$ and also the result of the recent X-ray study that the electron distribution around the central antimony atom is highly deformed due probably to the hydrogen-bonding between F and H [7] suggest strongly that the geometrical structure as well as the electronic structure of SbF$_5^-$ anion vary gradually with temperature, reflecting the change in the interaction with the rotating ammonium ions. Therefore the upper phase transition may be regarded as a displacive one with respect to the structural change of the tetragonal pyramidal anions. More detailed experimental works, e.g., X-ray or neutron diffraction, neutron scattering etc., will help to get insight into the microscopic mechanism of the upper phase transition.

**Conclusion**

The spin-lattice relaxation time measurements on $^1$H and $^{19}$F in (NH$_4$)$_2$SbF$_5$ and (ND$_4$)$_2$SbF$_5$ led to the activation parameters for the rotational motion of NH$_4^+$ and the axial reorientation of the square pyramidal SbF$_5^-$.

The cross-relaxation effect between $^1$H and $^{19}$F was shown to be dominant in the high temperature region. A simple theoretical treatment was presented for the anomalous temperature dependence of the $^{121}$Sb NQR frequencies in the lowest temperature phase, from which the order parameter of the order-disorder phase transition at 169 K was evaluated. The NQR data in the middle temperature phase suggest that the hydrogen bond dynamics between H and F concerns the molecular mechanism of the upper phase transition at 292 K.

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