

Nuclear Magnetic and Quadrupole Resonance Studies of Phase Transitions in Crystalline $(\text{NH}_4)_2\text{SbF}_5$ and $(\text{ND}_4)_2\text{SbF}_5$

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$(\text{NH}_4)_2\text{SbF}_5$ 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 NH_4^+ 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 SbF_5^{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 ^{121}Sb and ^{123}Sb nuclear quadrupole resonance frequencies show an anomalous temperature dependence; each resonance frequency assumes a minimum at around 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 $\text{N}-\text{H}\cdots\text{F}$ 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.

$(\text{NH}_4)_2\text{SbF}_5$ crystallizes in the orthorhombic space group Cmcm [1, 2]. It consists of two crystallographically non-equivalent ammonium ions and a square-pyramidal antimony (III) pentafluoride anion. We found by differential thermal analysis (DTA) and proton and fluorine spin-lattice relaxation time measurements that this substance undergoes two lambda-type phase transitions at 169 and 292 K [3]. The lower transition was identified as an order-disorder transition with respect to the orientation of the ammonium ions, and the upper one was inferred to be a kind of displacive structural transition associated with some angular displacement of the square-pyramidal SbF_5^{2-} anions. Urbanovitsch et al. measured the complex dielectric constant and the electric conductivity on this material and found a phase transition at 257 K, above which, they reported, the crystal became highly conductive [4]. Later, Avkhutskii et al. measured the wide-line nuclear magnetic resonance, the antimony nuclear quadrupole resonance (NQR), and the heat capacity and reported that at least three phase transitions occur at 169, 257, and 290 K [5].

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 $(\text{NH}_4)_2\text{SbF}_5$ and its deuterated analogue, from which a model will be presented of the phase transitions mechanisms.

Experimental

Crystals of $(\text{NH}_4)_2\text{SbF}_5$ were grown from an aqueous solution containing 6.0 g of NH_4F and 9.5 g of SbF_3 by the evaporation method according to [2]. Analysis: found: $\text{Sb} = 48.1$, $\text{F} = 38.4\%$; calculated: $\text{Sb} = 48.16$, $\text{F} = 37.57\%$. $(\text{ND}_4)_2\text{SbF}_5$ was obtained by repeated replacement of the solvent water by D_2O . 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 T_1 for ^1H and ^{19}F were measured with a home-built pulsed

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spectrometer at 10 MHz by the 90° - τ - 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_{1s} and T_{1l} . 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}Sb and ^{123}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.

$(\text{ND}_4)_2\text{SbF}_5$ 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

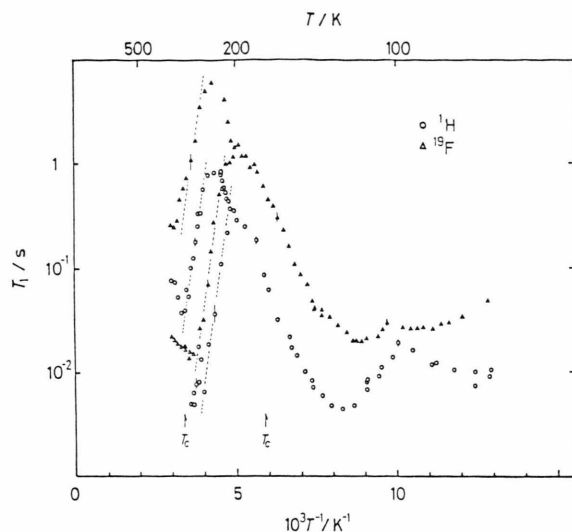


Fig. 1. Temperature dependence of the proton (\circ) and fluorine (Δ) spin-lattice relaxation times in $(\text{NH}_4)_2\text{SbF}_5$ at 10 MHz. The slope of each broken curve above 200 K gives the activation energy for the reorientation of SbF_5^{2-} . The phase transition points are indicated by T_c 's.

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]

$$\begin{aligned} d\langle F_z \rangle / dt = & -R_F [\langle F_z \rangle - F_0] \\ & -R_{FH} [\langle H_z \rangle - H_0], \end{aligned} \quad (1)$$

$$\begin{aligned} d\langle H_z \rangle / dt = & -R_{HF} [\langle F_z \rangle - F_0] \\ & -R_H [\langle H_z \rangle - H_0], \end{aligned} \quad (2)$$

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]

$$\begin{aligned} R_F = & C_1 \gamma_F^2 \Delta M_{FF} g_F (\omega_F, \tau_F) \\ & + C_2 \gamma_F^2 \Delta M_{FSb} g_F (\omega_F, \tau_F) \\ & + C_3 \gamma_F^2 \Delta M_{FH} g_F (\omega_{HF}, \tau_F) \\ & + C_4 \gamma_F^2 \Delta M'_{FH} g_F (\omega_{HF}, \tau_F), \end{aligned} \quad (3-1)$$

$$R_H = C_1 \gamma_H^2 \Delta M_{HH} g_H(\omega_H, \tau_H) + C_4 \gamma_H^2 \Delta M'_{HF} g_H(\omega_{HF}, \tau_H) + C_3 \gamma_H^2 \Delta M_{HF} g_H(\omega_{HF}, \tau_F), \quad (3-2)$$

$$R_{FH} = C_3 \gamma_H^2 \Delta M_{HF} g(\omega_{HF}, \tau_F) + C_4 \gamma_H^2 \Delta M'_{HF} g(\omega_{HF}, \tau_H), \quad (3-3)$$

$$R_{HF} = C_3 \gamma_F^2 \Delta M_{FH} g(\omega_{HF}, \tau_F) + C_4 \gamma_F^2 \Delta M'_{FH} g(\omega_{HF}, \tau_H), \quad (3-4)$$

where ΔM_{HH} , etc. represent the amounts of the decrease in the second moments, and the power spectra of molecular motion are given by

$$g(\omega_H, \tau_H) = \tau_H / (1 + \omega_H^2 \tau_H^2) + 4 \tau_H / (1 + 4 \omega_H^2 \tau_H^2), \quad (4-1)$$

$$g_i(\omega_{HF}, \tau_j) = \tau_j / [1 + (\omega_H + \omega_F)^2 \tau_j^2] + 3 \tau_j / [1 + \omega_i^2 \tau_j^2] + 6 \tau_j / [1 + (\omega_H + \omega_F)^2 \tau_j^2], \quad (4-2)$$

$$g(\omega_{HF}, \tau_i) = -\tau_i / [1 + (\omega_H - \omega_F)^2 \tau_i^2] + 6 \tau_i / [1 + (\omega_H + \tau_F)^2 \tau_i^2]. \quad (4-3)$$

Below about 200 K it is safely assumed that only the reorientation of the ammonium ions is excited and the pyramidal SbF_5^{2-} remains static. Then we can put $\tau_F = \infty$ in this temperature region. Assuming an Arrhenius activation process,

$$\tau_H = \tau_H^0 \exp(E_a / RT), \quad (5)$$

for the reorientation of the NH_4^+ ions and fitting (3) to the experimental T_1 's for ^1H and ^{19}F 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 , 4.7 ms, 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 NH_4^+ ions with an assumed distance of $r_{H-H} = 0.169 \text{ nm}$ [11]. This discrepancy suggests that the two crystallographically inequivalent 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 NH_4^+ undergoes an axial reorientation about one of its three C_2 axes and thus reduces ΔM_{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 ^1H and ^{19}F , which can be interpreted by a pair of relaxation rates, T_{1s} and T_{1l} . As the correlation

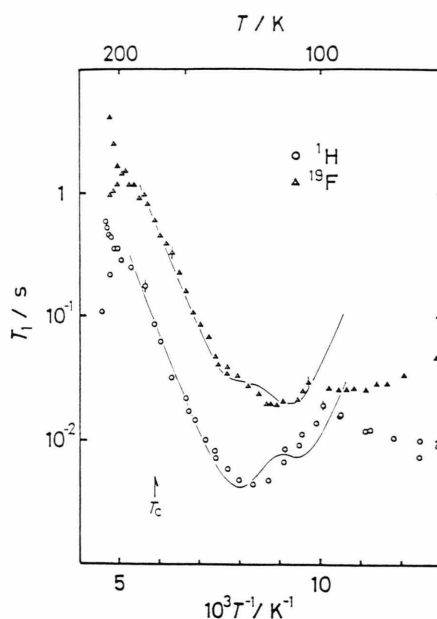


Fig. 2. Experimental and calculated spin-lattice relaxation times for the proton (\circ) and the fluorine (Δ) in $(\text{NH}_4)_2\text{SbF}_5$ at 10 MHz at low temperatures. Calculated T_1 's are shown by solid curves.

time τ_H for the reorientation of 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 SbF_5^{2-} anions. As the 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 $T_{1l}(\text{H}) = T_{1l}(\text{F})$. 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 ^1H and ^{19}F . 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 SbF_5^{2-} .

In the case of $(\text{ND}_4)_2\text{SbF}_5$ the relaxation of ^{19}F 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 ^{19}F and the antimony isotopes amounts to 37 percent of the total relaxation rate.

NQR of the Antimony Isotopes

The NQR frequencies of ^{121}Sb and ^{123}Sb in $(\text{NH}_4)_2\text{SbF}_5$ were measured at 77 K by Kravchenko

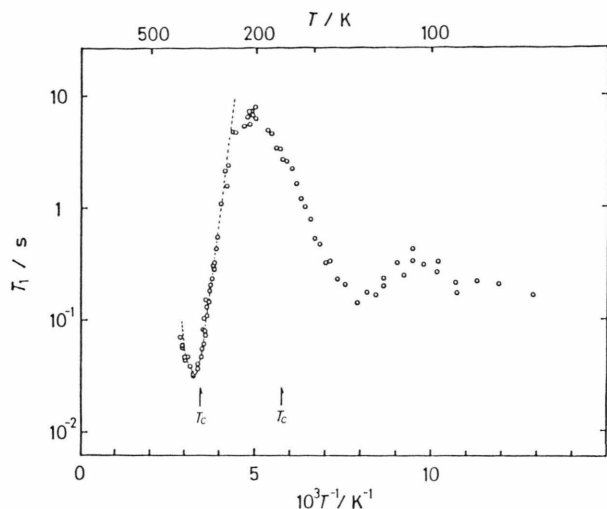


Fig. 3. Temperature dependence of the fluorine spin-lattice relaxation time in $(\text{ND}_4)_2\text{SbF}_5$ at 10 MHz.

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 $\nu(\pm 1/2 \rightarrow \pm 3/2)$ for ^{121}Sb and ^{123}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}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}Sb in the NH_4 and ND_4 salts: The corresponding transition in ^{123}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 η calculated from the ν_1 's of ^{121}Sb and ^{123}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

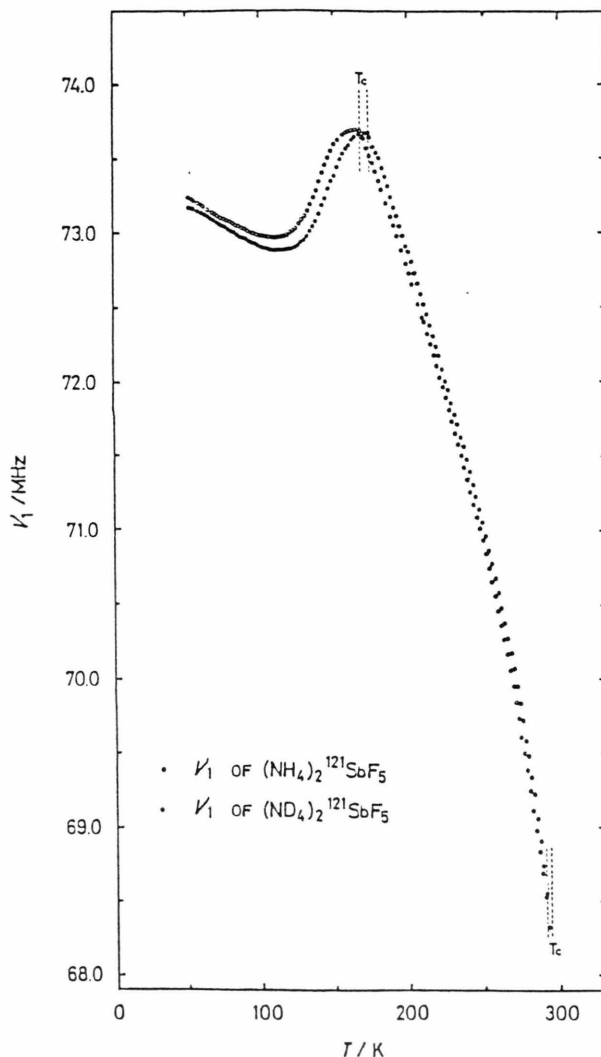


Fig. 4. Temperature dependence of the pure quadrupole transition frequencies between the levels $\pm 1/2$ and $\pm 3/2$ of ^{121}Sb in $(\text{NH}_4)_2\text{SbF}_5$ and $(\text{ND}_4)_2\text{SbF}_5$.

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

$$\nu(T) = \nu_0(T) + (\nu_r \tau_r + \nu_t \tau_t) / (\tau_r + \tau_t), \quad (6)$$

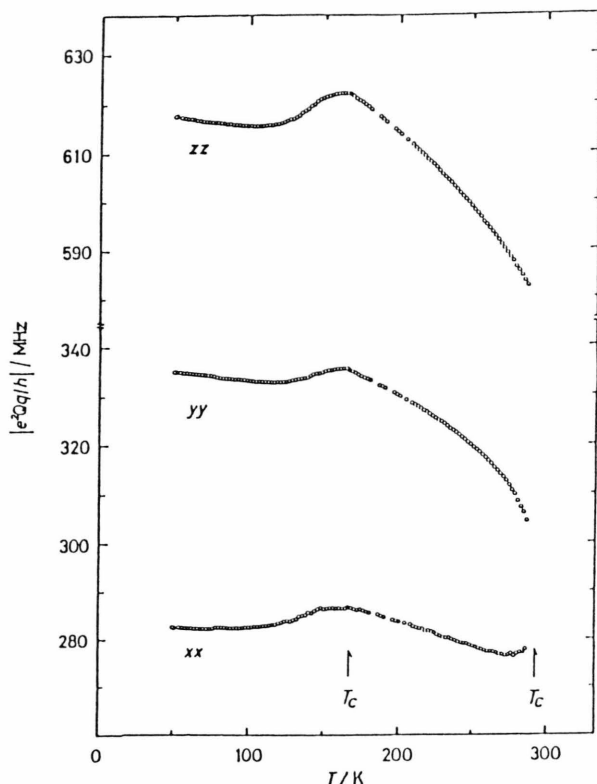


Fig. 5. Temperature dependence of the principal tensor components of the pure quadrupole coupling constant, $e^2 Q q_{xx}/h$, $e^2 Q q_{yy}/h$, $e^2 Q q_{zz}/h$ for ^{121}Sb in $(\text{NH}_4)_2\text{SbF}_5$.

where ν_r and τ_r are the resonance frequency and the residence time when the NH_4^+ is in the stable, hydrogen-bonded orientation, and, ν_t and τ_t relate to the case when NH_4^+ is in the rotational period, respectively. $\nu_0(T)$ is the frequency which would otherwise be observed as a result of the usual vibration effect. Equation (6) holds when $2\pi\nu(T)\tau_r$, $2\pi\nu(T)\tau_t \ll 1$.

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 τ_r in its original right site and for some other finite time τ_w in its disordered, wrong site. Therefore the apparent transient time τ_t may be taken as this second residence time. In this case we must modify the (6) so as to read

$$\nu(T) = \nu_0(T) + (\nu_r \tau_r + \nu_w \tau_w + \nu_t \tau_t)/(\tau_r + \tau_w + \tau_t), \quad (7)$$

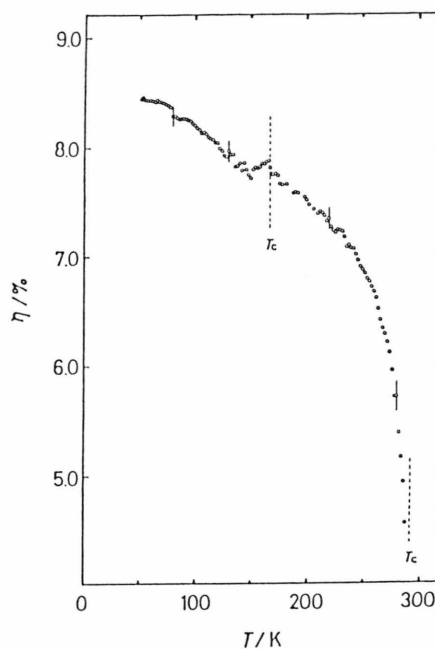


Fig. 6. Temperature dependence of the asymmetry parameter η of the electric field gradient tensor for ^{121}Sb in $(\text{NH}_4)_2\text{SbF}_5$.

where ν_w is the contribution from NH_4^+ in the disordered orientation to the NQR frequency. As the order of magnitude of τ_t is 10^{-12} s, it may be ignored compared with τ_r and τ_w , and the above equation simplifies to

$$\nu(T) = \nu_0(T) + (\nu_r \tau_r + \nu_w \tau_w)/(\tau_r + \tau_w). \quad (8)$$

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

$$s = (\tau_r - \tau_w)/(\tau_r + \tau_w), \quad (9)$$

and the relation

$$\tau_w/\tau_r = \exp(-\Delta/RT) \quad (10)$$

holds, where Δ 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

$$\nu(T) = A + BT + (\nu_w - \nu_r) \cdot \exp(-\Delta/RT)/\{1 + \exp(-\Delta/RT)\}, \quad (11)$$

where the term $A + BT$ 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

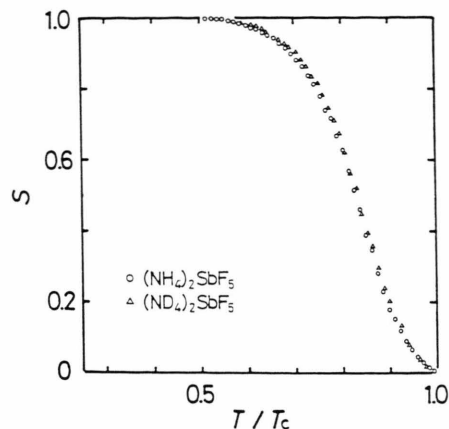


Fig. 7. The order parameter s for the phase transition in $(\text{NH}_4)_2\text{SbF}_5$ and $(\text{ND}_4)_2\text{SbF}_5$.

parameters from the anomalous part in the resonance frequency and calculate the order parameter s . The results for $(\text{NH}_4)_2\text{SbF}_5$ and $(\text{ND}_4)_2\text{SbF}_5$ 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 $\nu(T)$ 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^{2-} 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 ^1H and ^{19}F in $(\text{NH}_4)_2\text{SbF}_5$ and $(\text{ND}_4)_2\text{SbF}_5$ led to the activation parameters for the rotational motion of NH_4^+ and the axial reorientation of the square pyramidal SbF_5^{2-} . The cross-relaxation effect between ^1H 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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