

^1H relaxation study in $(\text{NH}_4)_2\text{SbF}_5$

B BANDYOPADHYAY, A GHOSHRAY, R MUKHOPADHYAY*
and R M KADAM†

Saha Institute of Nuclear Physics, 92, Acharya Prafulla Chandra Road, Calcutta 700 009,
India

*Nuclear Physics Division, †Radio Chemistry Division, Bhabha Atomic Research Centre,
Bombay 400 085, India

MS received 7 July 1989

Abstract. ^1H spin-lattice relaxation rate (T_1^{-1}) has been measured using inversion recovery technique in polycrystalline $(\text{NH}_4)_2\text{SbF}_5$ system in the temperature range 140–400 K. From the plot of $\log(M_0 - M)$ against τ , we have estimated two different T_1 corresponding to two inequivalent ammonium ions in the unit cell. Temperature-dependence of T_1 in each case exhibits features of double minima indicating the influence of different correlation times corresponding to different types of motion. Activation energies at different temperature regions have been estimated. Some features of dynamics of motion of the different groups of ions across the phase transitions have been discussed.

Keywords. Nuclear magnetic resonance; relaxation; molecular motion; $(\text{NH}_4)_2\text{SbF}_5$.

PACS Nos 33-25; 61-50

1. Introduction

Compounds of the composition $M_2\text{SbF}_5$ ($M = \text{Na}, \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$) are known to exist in several phases (Avkhutskii *et al* 1983 and Urbonavicius *et al* 1982). For example, ammonium pentafluoro antimonate, $(\text{NH}_4)_2\text{SbF}_5$ shows four phase transformations at 292, 257, 168 and 142 K (Avkhutskii *et al* 1983) during heating cycle. The transition at 257 K has been identified as a superionic phase transition and is associated with large hysteresis (transition occurs at 238 K during cooling cycle). The conductivity jumps by a factor of 10^6 – 10^7 on heating to 257 K. The X-ray studies (Makarova *et al* 1984) of $(\text{NH}_4)_2\text{SbF}_5$ suggest that there exist two inequivalent (NH_4) ions in the unit cell (figure 1). The first crystallographic type $(\text{NH}_4)_I$ is positioned at a relatively short distance (2.75 Å) from fluorine (F_2) atom involving the hydrogen bond and the other type, $(\text{NH}_4)_{II}$ is located at more than 3 Å from the fluorine atom. From NMR and NQR (Avkhutskii *et al* 1983 and Nakamura 1986) studies it has been revealed that the successive phase transformations are connected with the different types of rotation and/or reorientation motion of various groups of ions present in the crystal. In particular, the phase transition at 168 K is believed to be connected with the complexities of reorientational motion of $(\text{NH}_4)_I$ groups in the crystal. Transitions at 292 and 257 K are believed to be connected with the disorder of fluorine atoms. Specifically, the rotation of $[\text{SbF}_5]^{2-}$ around C_4 -axis causes a phase transition at 257 K while the transition at 290 K is caused by the free rotation of $[\text{SbF}_5]^{2-}$ groups (resulting in substantial narrowing of ^{19}F NMR lines (Avkhutskii

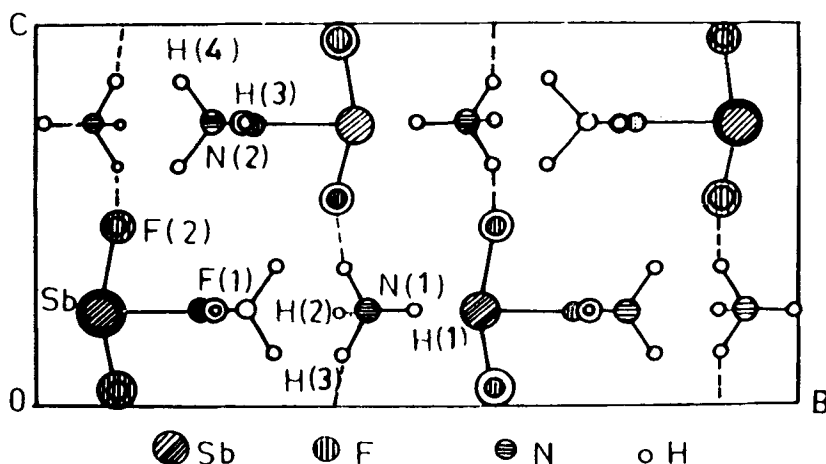


Figure 1. Projection of structure of $(\text{NH}_4)_2\text{SbF}_5$ on coordinate plane BC (Makarova *et al* 1984).

et al 1983) in the 290–350 K interval). Recently, neutron incoherent quasielastic scattering technique has been applied to study the reorientational motion of NH_4^+ ions at 300, 180 and 160 K (Mukhopadhyay *et al* 1987). It has been suggested that the two NH_4^+ ions have similar reorientational times. Thus, so far dynamics of the system is not very clear. In the present paper, we have reported a detailed study of proton (^1H) spin-lattice relaxation time (T_1) in polycrystalline $(\text{NH}_4)_2\text{SbF}_5$ system in the temperature range 140 K to 400 K. The results reveal some features of the dynamics of reorientation of NH_4 ion across the phase transitions. Experimental details are given in §2 and results and discussion in §3. A brief report was presented elsewhere in a symposium (Bandyopadhyay *et al* 1988).

2. Experimental

Ammonium pentafluoro antimonate, $(\text{NH}_4)_2\text{SbF}_5$, is prepared by mixing SbF_3 and NH_4F in the molar ratio of 1:3 in 40% hydrofluoric acid, HF. Crystals are obtained by slow evaporation from the solution kept in a teflon beaker. The required SbF_3 is obtained by dissolving Sb_2O_3 in HF in a platinum crucible and then heated to dryness. The powdered samples were checked for the room temperature phase by X-ray diffraction.

The instrument used for measurements of ^1H spin-lattice relaxation rate was a Bruker MSL 100 spectrometer. A varian V-7400 electromagnet system equipped with a field-dial regulator was used. The ^1H NMR spectra were obtained by the Fourier transformation of free-induction decay (FID) signal observed after a 90° pulse. The ^1H spin-lattice relaxation time (T_1) was measured in the temperature range 140–400 K at 34 MHz using inversion recovery ($180^\circ - \tau - 90^\circ$) technique. At low temperatures, where the resonance line-widths (FWHM) are comparatively larger than those observed at room temperature, solid-echo sequence was used as the monitoring pulse. In this case the complete pulse sequence was $180^\circ - \tau - 90^\circ - \tau_1 - 90^\circ_{(90^\circ)} - \tau_2\text{-echo}$. The spectra were obtained from the Fourier transformation of the FID signal obtained after the monitoring pulse. The peak amplitude of each spectrum was measured as

a function of time τ , and from the change of magnetization, the spin-lattice relaxation time was determined.

The temperature of the sample was controlled to within $\pm 1^\circ$ by heating the flow of pre-cooled nitrogen gas using BVT-1000 temperature controller which also monitors the temperature at the sample using a copper-constantan thermocouple placed close to the sample.

3. Results and discussion

Figure 2 shows three typical ^1H NMR spectra (obtained from Fourier transform of the FID after a $\sim 90^\circ$ pulse) at a resonance frequency of 34.0 MHz at three different temperatures. The line shapes and the line widths (FWHM) are dependent on temperature. A substantial narrowing of FWHM of ^1H spectrum is observed in the temperature range of 350–400 K. This feature is also observed in ^1H NMR spectra obtained by CW method. However, it has not been possible to distinguish two inequivalent (NH_4^+) ions (as observed from X-ray (Makarova *et al* 1984) studies) from the ^1H spectra obtained by both the techniques. Temperature dependence of ^1H NMR linewidth in $(\text{NH}_4)_2\text{SbF}_5$ monocrystal was earlier studied by Avkhutskii *et al* (1983) and was attributed to reorientational motion of NH_4 groups. This sort of motion has profound influence on the spin-lattice relaxation rate (T_1^{-1}). According to well-known BPP theory, T_1^{-1} governed by the fluctuation of the nuclear-dipolar interaction due to the motion of NH_4 ions and/or other groups is given by

$$T_1^{-1} = C[\{\tau_c/(1 + \omega^2\tau_c^2)\} + \{4\tau_c/(1 + 4\omega^2\tau_c^2)\}] \quad (1)$$

where τ_c is the correlation time of motion, ω the angular resonance frequency and C a constant independent of ω and τ_c .

While measuring T_1 of proton in polycrystalline $(\text{NH}_4)_2\text{SbF}_5$, the change of magnetisation with τ does not follow a single exponential behaviour in the entire range

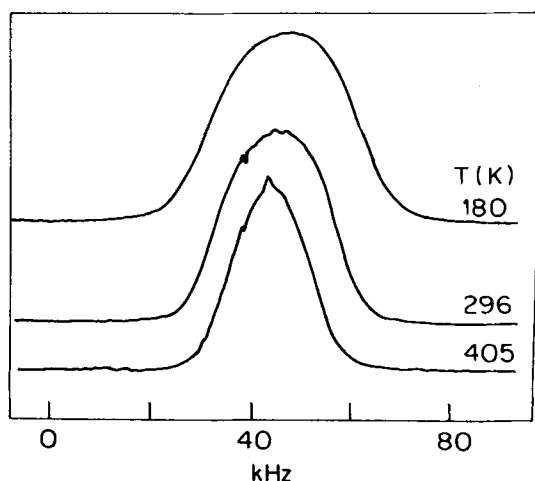


Figure 2. Typical ^1H NMR spectra at a resonance frequency of 34 MHz at three different temperatures.

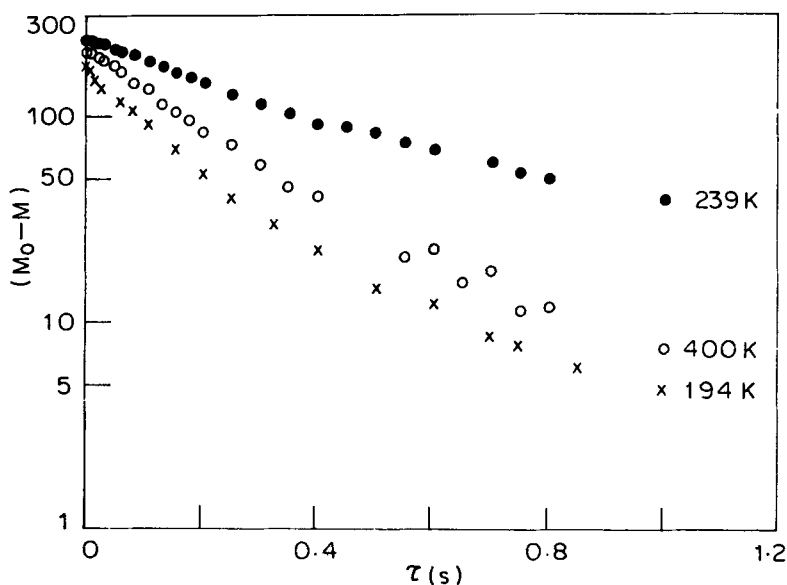


Figure 3. Plot of $\log(M_0 - M)$ vs τ at different temperatures. Signature of two exponents is evident in the entire temperature range.

of temperature studied. This feature is shown in the plot of $\log(M_0 - M)$ against τ at different temperatures (figure 3). This sort of behaviour is commonly observed if the spectrum contains signature of different species of protons having different spin-lattice relaxation rates. The observation in the present case is not surprising as there are two inequivalent NH_4 groups in the unit cell as evidenced from X-ray studies (Makarova *et al* 1984). Assuming two different reorientational rates (corresponding to two different correlation times) for the two NH_4 groups at any temperature, we have fitted the behaviour of $\log(M_0 - M)$ vs τ with two characteristic times T_1^I and T_1^{II} from initial linear portion for shorter τ and the extreme linear portion for longer τ values respectively. Simultaneous estimation of T_1^I and T_1^{II} have been possible in the temperature range of 180–400 K where the two relaxation rates are not widely different. Below 180 K, where T_1^I and T_1^{II} differ at least by an order of magnitude, the estimation of longer T_1 among the two has not been reliable enough and has been omitted in our discussion.

Figure 4 shows the temperature dependence of relaxation times T_1^I and T_1^{II} of ^1H in $(\text{NH}_4)_2\text{SbF}_5$ observed in the temperatures range 140–400 K. Apparently, it is not easy to conclusively associate any of these two relaxation times with any one of the two inequivalent NH_4^+ ions. However, we assign T_1^I and T_1^{II} with $(\text{NH}_4)_I$ and $(\text{NH}_4)_{II}$ groups respectively from consideration of structural aspects and different structural transformation exhibited by $(\text{NH}_4)_2\text{SbF}_5$ during temperature cycling. It has been discussed earlier that $(\text{NH}_4)_I$ groups are located closer to F-atoms and are hydrogen bonded. On the other hand, $(\text{NH}_4)_{II}$ groups are located far away from F-atoms and are thought to rotate freely in the whole temperature range studied. Regarding the successive phase transitions, it is known that the transitions at 142 and 168 K respectively are connected with the reorientational motion of the $(\text{NH}_4)_I$ groups, whereas the disorder of fluorine atoms causes transitions at 257 and 292 K respectively.

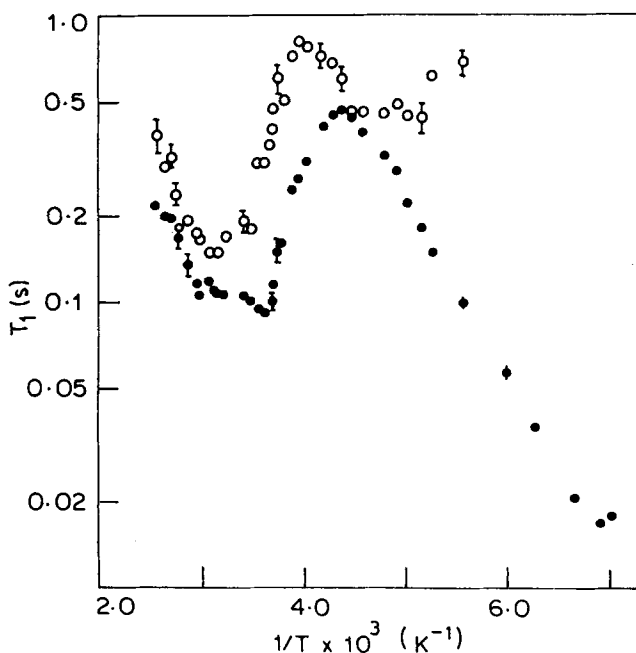


Figure 4. Temperature dependence of the proton relaxation time T_1 in $(\text{NH}_4)_2\text{SbF}_5$ at 34 MHz. Two different T_1 's (T_1^I and T_1^{II} , shown as unfilled and filled circles respectively) are distinctly observed in the entire temperature range.

Therefore, it may be argued that the fluctuation of nuclear dipolar interaction arises due to different types of motions and would in all probability strongly influence the relaxation rate of $(\text{NH}_4)_I$ groups. Nevertheless, the effect of disorder of fluorine atoms on the relaxation rate of $(\text{NH}_4)_{II}$ groups cannot be neglected. Thus, we can think of the existence of at least two different correlation times (τ_c) for each ammonium ions. This can easily be visualized in $(\text{NH}_4)_{II}$ groups. Since this ammonium group rotates freely even at the lowest temperature studied, the correlation time for its motion must be shorter than that of the motion of the hydrogen bonded ammonium group. Thus the monotonic increase of T_1^{II} in the temperature region 140–220 K is characteristic of motional behaviour of $(\text{NH}_4)_{II}$ groups in the $\omega_0\tau_c \ll 1$ region of eq. (1). Experimental limitations prohibit us from searching for a possible minima at a lower temperature. As the temperature is raised above 220 K, the value of T_1^{II} , instead of increasing further, exhibits a maximum at around 230 K and then decreases. The behaviour of T_1^{II} in the 230–400 K region, including a broad minimum centered around 294 K, clearly indicates the occurrence of another type of motion over and above the already mobile $(\text{NH}_4)_{II}$ ions. Thus the reorientational motion of $[\text{SbF}_5]^-$ group associated with the superionic transition at 257 K, further facilitates the relaxation of $(\text{NH}_4)_{II}$ ions through the fluctuation of nuclear dipolar interaction caused by the motion of F ions and this consequently results in the decrease of T_1^{II} .

The results of T_1^{II} studies for the ammonium group, $(\text{NH}_4)_{II}$ can be summarized as follows. To the right and to the left of the maximum near 230 K the observed relaxation times are determined by two different correlation times associated with free ammonium and $[\text{SbF}_5]^-$ reorientational motion respectively. To the right of the maximum, the

Table 1. Activation energies at different temperatures.

NH ₄ ⁺ ion type	Activation energies (kcal/mol) in the temperature range		
	140–220.K	250–300 K	300–400 K
I	—	5.5 ± 0.5	4.3 ± 0.5
II	2.9 ± 0.2	5.5 ± 0.5	3.6 ± 0.5

correlation time for the rotation of (NH₄)_{II} groups is such that the minimum of T_1 at $\omega_0\tau_c = 0.62$ should appear below 140 K. Whereas at the left side of maximum the variation of correlation time due to mobile F^- ions is such that the condition of minimum is satisfied at around 294 K. This feature of double minima has been observed in (NH₄)₂SO₄ (O'Reilly and Tung Tsang 1967).

The temperature dependence of T_1^I which corresponds to (NH₄)_I groups can also be explained in a framework similar to the one we have used T_1^{II} behaviour. To the right of the maximum at 248 K, the reorientational motion of the hydrogen bonded ammonia, (NH₄)_I is such that the condition of minimum in τ_c is observed near 200 K. Left side of the maximum is again due to the motion of [SbF₅]⁻ groups. Therefore, we can say that at the left of the minimum, T_1 for reorientational motion of (NH₄)_I is very long and thus T_1 due to the motion of fluorine atoms seems to be predominant.

At temperature in the motional region, the correlation time τ_c fits the Arrhenius relation $\tau_c = \tau_0 \exp(E_a/RT)$ and T_1 can be written as $T_1 = C_1 \exp(\pm E_a/RT)$ where C_1 is a constant, E_a is the activation energy, R is the universal gas constant. Thus a linear plot of $\ln T_1$ as a function of $1/T$ provides an estimate of the activation energy for the rotation of NH₄ groups. Table 1 shows the activation energy of the two ammonium groups at different temperature ranges. In principle, the activation energies in the two regions ($\omega_0\tau_c \ll 1$ and $\omega_0\tau_c \gg 1$) about the minimum should be identical. However, in this case, the transition at 292 K may alter the barrier height and thus the activation energy in the 300–400 K region has been found to be different from that in the 250–300 K region.

In conclusion, ¹H spin-lattice relaxation studies in (NH₄)₂SbF₅ revealed two distinct NH₄ ions with different reorientational rates. Though the variation of T_1 with temperature in each case does not contain any distinct signature of phase transition, the results reveal some informations regarding the successive phase transitions. We have mentioned earlier that the peculiarities of the reorientational motion of the different groups of ions viz. NH₄ and SbF₅ are believed to be connected with the transitions. Effect of the different reorientational rates of the different groups exhibit profound influence on T_1 via the modulation of the motion of particular ammonium ions.

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