



^1H Nuclear Magnetic Resonance Study of Ferroelectric $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$

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Abstract : ^1H nuclear magnetic resonance (NMR) experiments have been performed at 30 - 300 K and 7 T to investigate dynamics of hydrogen bond network in the single crystal $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$. The two proton sites, ammonium proton and hydrogen-bond proton, are identified from the ^1H NMR MAS spectrum at 340 K. As temperature decreases, the ^1H NMR spectrum shifts to the higher frequency side with a larger linewidth. The spectrum at 65 K shows a distinctive change in line shape toward the ferroelectric transition at 63 K. The measured values of T_1 for ammonium and hydrogen-bond protons are similar in the whole range of temperature. T_1 of ^1H NMR shows a gradual decrease down to 120 K and starts to steeply increase below 100 K. Then T_1 shows abrupt decrease below 70 K with a sharp minimum at 63 K, where the ferroelectric transition occurs. This temperature dependence of spectrum and T_1 clearly prove that the large change in the dynamics of hydrogen bond network is associated with the ferroelectric phase transition at 63 K.

Keywords : $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, Ferroelectric phase transition, Shift, Spin-lattice relaxation time T_1

INTRODUCTION

$\text{M}_3\text{H}(\text{SO}_4)_2$ ($\text{M}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$) crystals exhibit a dynamic network of hydrogen bonds in a high temperature superionic phase and are of great scientific interest because of their phase transitions and proton transport mechanisms.¹ Because of their high proton conductivity at low and intermediate temperatures, these compounds might have practical

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applications in devices such as hydrogen sensors.² Proton conduction occurs in several types of materials, including many hydrogen-bonded systems. $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ belong to the well-known family of superionic proton conductors with the general formula $\text{M}_3\text{H}(\text{SO}_4)_2$.^{3,4} Most crystals in the $\text{M}_3\text{H}(\text{SO}_4)_2$ family undergo a superionic phase transition from a monoclinic room temperature phase to a trigonal high temperature phase. The crystals of the $\text{M}_3\text{H}(\text{SO}_4)_2$ family undergo a superionic phase transition in their high temperature phases. However, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ crystals exhibit phase transitions not only at high temperatures but also below room temperature. This crystal is of special interest because of the diversity in phase transitions. It is known that $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ undergoes five phase transitions at 413, 265, 139, 133 and 63 K, and has six phases,^{5,6} denoted I, II, III, IV, V and VI in order of decreasing temperature. Phase I is a superionic conductor, phase II is ferroelastic,⁷ phases III and V are antiferroelectric, phase IV is incommensurate and phase VI is ferroelectric. It has recently been reported that the $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ crystals undergo additional phase transition at 463 K.⁸ The proton transfer dynamics in the hydrogen bond for the crystals of the $\text{M}_3\text{H}(\text{SO}_4)_2$ family have previously been reported using inelastic neutron scattering, infrared and Raman spectra.¹ In addition, the role of different H-bonds in phases II, III, IV and V of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ has been studied by X-ray diffraction and ¹H solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR).⁹ Recently, Lim et al.¹⁰ reported the spin-lattice relaxation time, T_1 , and the spin-spin relaxation time, T_2 , for the ¹H and ²H nuclei in phases I, II, and III for $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ and $(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$ crystals. This result appeared that the NH_4^+ and $\text{H}(\text{SO}_4)^{2-}$ ions do not play an important role in the III-II phase transition, but do play important roles in the II-I phase transition. And, the appearance of liquid-like proton T_2 above $T=413$ K indicated that a transition to a superionic phase takes place at this temperature. Although the T_1 and T_2 near phases I, II, and III of this crystal have previously been reported, no investigation with NMR in the phases IV, V, and VI has yet been conducted.

CRYSTAL STRUCTURE

The $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ crystal is monoclinic at room temperature.^{4, 11, 12} The crystal structure is shown in Fig. 1. There are 12 ammonium ions and 8 sulfate ions in the unit cell, in which each pair of neighbouring sulfate ions is linked by one hydrogen bond of type $\text{O}-\text{H}\cdots\text{O}$, i.e. there are four hydrogen bonds of this type. The sulfate ion forms a slightly distorted tetrahedron. The NH_4^+ tetrahedra are nearly regular, and linked to SO_4^{2-} ions by hydrogen bonds.¹³ The crystal structure of phase I is trigonal with space group $\text{R}\bar{3}\text{m}$ or $\text{R}\bar{3}\text{C}$.¹⁴ The structure of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ is known to be monoclinic (space group $\text{C}2/\text{c}$ or $\text{A}2$) in phase II, monoclinic (space group $\text{P}2/\text{n}$ or Pn) in phase III and monoclinic (space group $\text{C}2$) in phase V.¹⁵⁻¹⁷

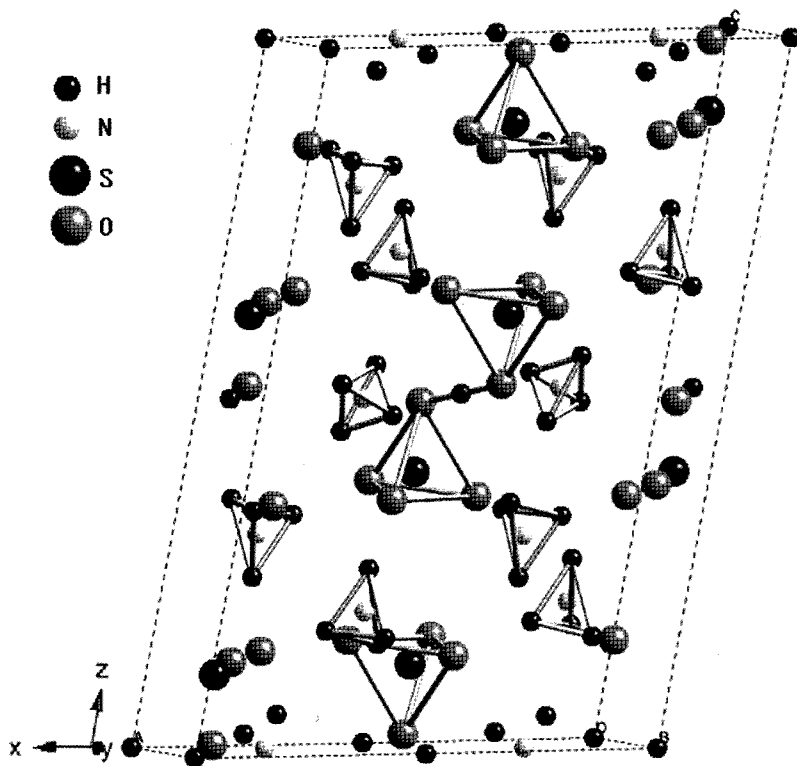


Fig. 1 The crystal structure of a $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ single crystal projected along the b axis.

EXPERIMENTAL

The single crystal of $(\text{NH}_3)_4\text{H}(\text{SO}_4)_2$ of $6 \times 4 \times 2 \text{ mm}^3$ size was grown by slow evaporation method from an $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 solutions. Then the sample was stored in a dry-keeper to prohibit moisture penetration into the sample due to the deliquescence property of $(\text{NH}_3)_4\text{H}(\text{SO}_4)_2$. Before carrying out NMR experiments, the sample was kept for several hours in a weak vacuum circumstance to remove adsorbed moisture from the sample.

The ^1H NMR experiments for the $(\text{NH}_3)_4\text{H}(\text{SO}_4)_2$ single crystal were performed with a home-built spectrometer and a home-made probe in a 7 Tesla superconducting magnet (Oxford, UK) in the temperature range of 35 - 300 K in a cryostat (SpectrostatCF, Oxford, UK). The temperature was controlled by temperature controller model 340 (Lakeshore, Ohio, USA) mounted on the cryostat. The c-axis of the crystal was kept parallel to the external magnetic field for all measurements. The spin-lattice relaxation time T_1 was measured by using $\pi/2-\tau-\pi/2$ -acquire pulse sequence¹⁸ varying τ delay at the offset frequency of 298.479 MHz. The typical $\pi/2$ pulse length was 5μ .

RESULTS AND DISCUSSION

The ^1H NMR spectra measured before and after removing adsorbed moisture by evacuating out at 300 K are shown in Fig. 2. The sharp peak at the center of the spectrum observed before evacuating disappears after evacuating, namely, removing moisture. Unlike the previous report,¹⁰ this clearly proves that the sharp peak comes from the water molecules adsorbed on the sample.

The ^1H NMR spectrum at 300 K in Fig. 2 shows a single broad peak with a large linewidth of ~ 30 kHz. Since $(\text{NH}_3)_4\text{H}(\text{SO}_4)_2$ has two proton sites, ammonium proton and hydrogen-bond proton sites, in the structure as shown in Fig. 3, the broad resonance must be a composite peak of the two proton sites. In order to identify the respective contribution of two proton sites to the total spectrum, we have carried out ^1H NMR MAS experiments at 340 K at the spinning speed of 14 kHz, as shown in Fig. 4. The main peak

at 5.5 ppm comes from the ammonium protons whereas the small peak at 13.4 ppm originates from the hydrogen-bond protons connecting the two SO_4^- tetrahedra. The intensity ratio of two peaks is 12.8, which is very close to the expected value of 12. Therefore, it is confirmed that the hydrogen-bond proton contributes to the high frequency side of the broad ^1H NMR spectrum in Fig. 2. From this identification, T_1 can be obtained separately for two proton sites by measuring the respective time evolution of the echo signal for the different parts of the whole spectrum. Then the results show that T_1 values of ^1H NMR are similar for the ammonium protons and the hydrogen-bond protons at all temperatures.

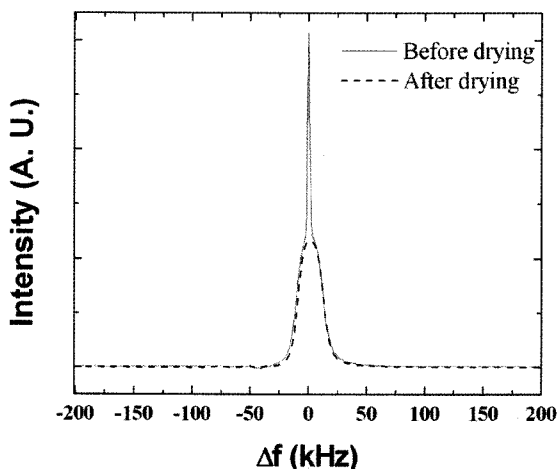


Fig. 2 The ^1H NMR spectra of $(\text{NH}_3)_4\text{H}(\text{SO}_4)_2$ obtained before and after removing the absorbed moisture by pumping out at 300 K. The narrow peak at the center for the as-received sample disappears after pumping out

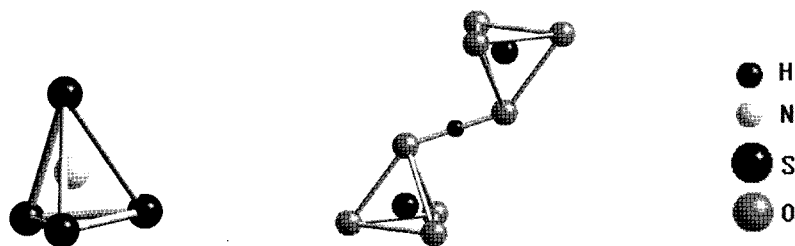


Fig. 3 The two proton sites in $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$. The left figure shows the ammonium proton sites in the NH_4 tetrahedron whereas the right figure shows the hydrogen-bond proton site connecting two SO_4 tetrahedra.

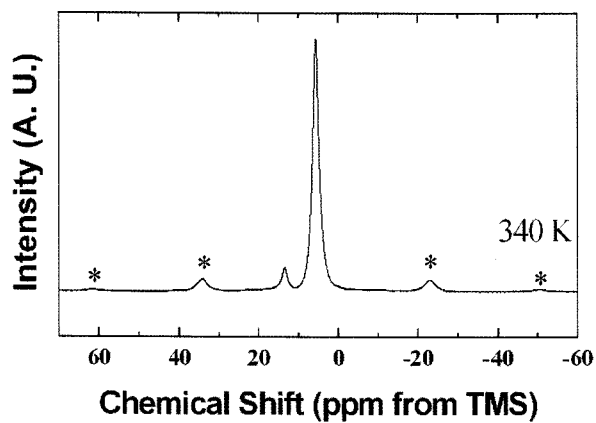


Fig. 4 The ¹H MAS spectrum at 340 K for (NH₃)₄H(SO₄)₂. The asterisks represent side bands of the spinning speed at 14 kHz.

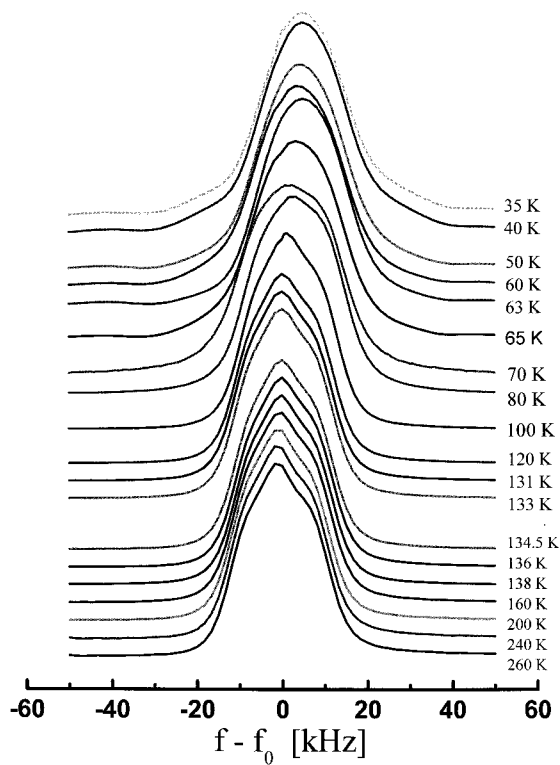


Fig. 5 The temperature evolution of ¹H NMR spectra for (NH₃)₄H(SO₄)₂

The ^1H NMR spectrum of $(\text{NH}_3)_4\text{H}(\text{SO}_4)_2$ is obtained as a function of temperature in Fig. 5. As temperature decreases, the peak shifts to the higher frequency side whereas the linewidth remains almost same. On the other hand, the overall line shape starts to change below 100 K and then shows a distinctive evolution in the temperature range of 70 – 60 K. The spectrum at 65 K is much broader and spread over the whole range of two spectra at 120 and 60 K. Actually, the spectrum at 65 K looks like a composite of 120 K and 60 K spectra. This suggests that new dynamics start to set in toward the ferroelectric transition at 63 K. The temperature range of 70 - 60 K corresponds to the ferroelectric phase transition. This distinctive change in spectrum may originate from proton transfer dynamics, which usually trigger the ferroelectric transition.

The spin-lattice relaxation time T_1 as a function of temperature is shown in Fig. 6. The spin-lattice relaxation recovery of ^1H NMR shows a single exponential decay at all temperatures. This figure exhibits tremendous change (three orders of magnitude) in proton dynamics of hydrogen bond networks associated with the successive phase transitions. The T_1 values monotonically decrease down to 120 K, which is just below

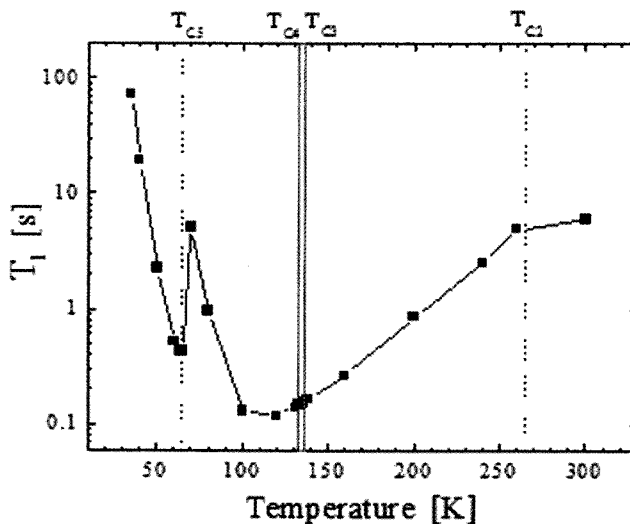


Fig. 6 The temperature dependence of the spin-lattice relaxation time for ^1H NMR of $(\text{NH}_3)_4\text{H}(\text{SO}_4)_2$.

incommensurate phase (phase IV) and increase steeply below 120 K. However, there is a sharp minimum at 63 K, where ferroelectric phase transition occurs. Below 63 K, T_1 increases abruptly. Thus Fig. 6 shows two minima of T_1 occurring at 120 and 63 K. Usually a minimum in the T_1 vs. T plot is usually regarded as a signature of atomic or molecular motions with a characteristic time scale in the order of NMR procession period.¹⁸ For the NMR frequency of 300 MHz, the minima of T_1 observed in Fig. 6 suggest that the proton motions in the time scale of $\sim \mu\text{s}$ or slower are involved in the incommensurate and ferroelectric phase transitions.

CONCLUSION

¹H NMR experiments have been performed in the temperature range of 30 - 300 K at 7 T to investigate dynamics of hydrogen bond network in the $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ single crystal. From ¹H NMR MAS spectrum at 340 K, the two proton sites, ammonium proton and hydrogen-bond proton, are identified. As temperature decreases, the ¹H NMR spectrum shifts to the higher frequency side with a larger linewidth. The overall line shape starts to change below 100 K and then shows a distinctive evolution in the temperature range of 70 – 60 K. This distinctive change in spectrum may originate from proton transfer dynamics, which usually trigger the ferroelectric transition.

The spin-lattice relaxation recovery shows a single exponential decay at all temperatures. The spin-lattice relaxation time T_1 exhibits the tremendous variation in proton dynamics of hydrogen bond networks associated with the successive phase transitions. The T_1 values of ¹H NMR are measured to be similar for the ammonium protons and the hydrogen-bond protons in the whole temperature range. T_1 of ¹H NMR shows a gradual decrease down to 120 K and then starts to steeply increase below 100 K. Below 70 K, T_1 shows abrupt decrease with a sharp minimum at 63 K where the ferroelectric transition occurs. This temperature dependence of spectrum and T_1 clearly proves that the dramatic change in the dynamics of hydrogen bonds is associated with the ferroelectric phase transition at 63 K.

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