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Bottleneck Behavior of ^{1}H NMR Spin-lattice Relaxation in Ammonium Sulfate

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Abstract: ^{1}H nuclear magnetic resonance (NMR) relaxations have been investigated in ammonium sulfate ($(NH_4)_2SO_4$) powder at temperatures ranging from 102 K to 440 K. There is a bottleneck in the spin-lattice relaxation between the nuclear spin system and the hindered rotation of ammonium ions, which is certified by measuring the relaxation according to the initial condition of the spin system. For temperatures below 318 K the ^{1}H spin-lattice relaxations have double-exponential behaviors with the exponent, n, having a value $2 > n > 1$ initially and $n = 1$ after a long time. Above 318 K not only is the relaxation exponential initially with exponent $n = 1$, but it is a single-exponential over the entire time, resulting in one T_1 value. The two types of NH_4^+ ions have different activation energies for hindered rotation, $E_a^{I} = 0.27 \pm 0.02$ eV and $E_a^{II} = 0.12 \pm 0.01$ eV, in the ferroelectric phase.

INTRODUCTION

Ammonium sulfate (AS) undergoes a first-order paraelectric D_{2h}^{16}-*Pnam* (orthorhombic) to ferroelectric C_{2v}^{9}-*Pna2*$_1$ (orthorhombic) phase transition at T_c = 223 K. There are four formula units in the unit cell and two crystallographically inequivalent ammonium ions, NH_4^+(I) and NH_4^+(II), surrounded by five and six SO_4^{2-} ions, respectively.[1,2] AS has a very large spontaneous strain, a characteristic known as ferroelasticity, and a very small Curie-Weiss constant, C=15.6 K.[3] At room temperature, AS is crystallized to the ferroelastic phase with paraelectric lattice symmetry and normally has three domains separated by the {011} and {031} twin planes.[4] These domains can be switched to each others by external stress; this switching process has an activation energy of 0.11 eV in the paraelectric phase.

The NH_4^+ ions are known to exhibit hindered rotations at temperatures below about

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400 K, thereby explaining the ^1H NMR spin-lattice relaxations.[5,6] O'Reilly and Tsang showed[5] that the two classes of ammonium ions have different activation energies in the temperature range between 77 K and 170 K, $E_a^I = 0.17$ eV and $E_a^{II} = 0.12$ eV, respectively. They also attributed the measured correlation times at temperatures between 170 K and 223 K to temperature dependent activation energies. Above T_c, their measurements indicated a single activation energy $E_a = 0.10$ eV.

In general, the NMR spin-lattice relaxation is a single exponential with exponent $n = 1$. Recently, the relaxations of a stretched exponential with $n < 1$ have been reported in glassy systems, thereby explaining the distribution of correlation times.[7,8] NMR spin-lattice relaxations with exponent $n > 1$ have not been reported, but a number of researchers have reported phonon bottleneck behaviors in EPR (electron paramagnetic resonance)[9,10] and Raman scattering[11,12] experiments. Here we report the ^1H NMR spin-lattice relaxation between 112 K and 440 K for $n > 1$.

EXPERIMENTS

^1H NMR of AS powder samples (Hayashi Pure Chemical Industries Ltd., 99.9 %) were studied at a Larmor frequency 200.13 MHz using a Bruker MSL200 pulse NMR spectrometer at Korea Basic Science Institute. NMR spectra were obtained via fast Fourier transform of the free induction decay signal and the total intensity was obtained by integrating the spectrum numerically. Inversion recovery ($180°(X)$ - t - $90°(X)$) and saturation recovery (($90°(X)$)$_p$ - t - $90°(X)$) pulse sequences[13] were used to measure the spin-lattice relaxation time, T_1. ($90°(X)$)$_p$ indicates that there are p repetitions of the $90°(X)$ pulse, with 30 μs between each pulse. The sample temperature was stabilized within ±0.5 K by controlling the heater current in a dry-air or cold-nitrogen-gas flow, depending on the temperature range selected.

RESULTS and DISCUSSIONS

Fig. 1 shows the temperature dependence of the spin-lattice relaxation for temperatures between 112 K and 407 K. Above 320 K, the relaxations are single exponential; below 320 K, however there are two steps: a Gaussian-like curve initially and later an exponential decay. All the relaxation traces are well fitted by the following function:

$$\frac{M_0 - M_z(t)}{2M_0} = a \times \exp(-(t/T_1')^n) + (1-a) \times \exp(-t/T_1'') \qquad (1)$$

The relaxation times $T_1'$and T_1'' from the Equation (1) are shown in Fig. 2 as well as the spin-lattice relaxation times T_1 at temperatures $T > 320$ K for comparison. Both of the

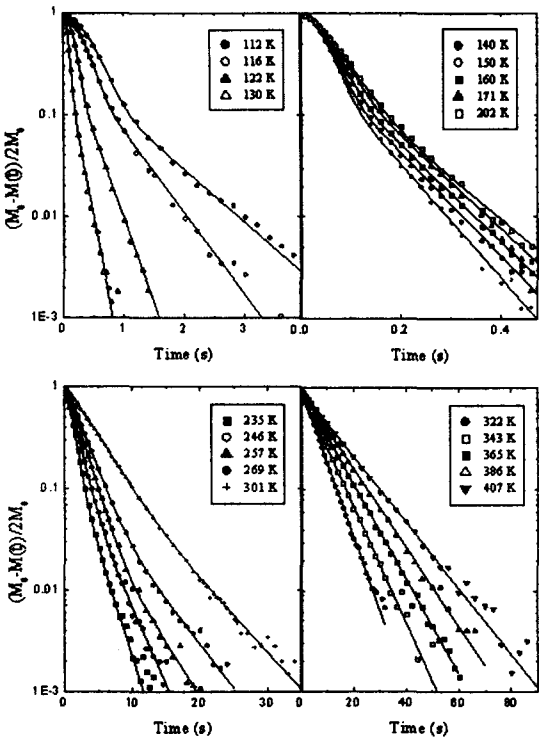


Fig. 1. Temperature dependence of the spin-lattice relaxation. At temperatures $T > 322$ K, the relaxation is a single exponential, but extraordinary behaviors are shown for $T < 301$ K. Initially the relaxations are slow compared to the exponential and after a long time the behavior is exponential, with exponent $n = 1$.

pre-exponential factor, a, and the exponent, n, are given in Fig. 3. There are discontinuous changes in the relaxation times at the ferro-paraelectric phase transition temperature T_c = 223 K, and two minima at 145 K and 190 K. At temperatures between 140 K and 318 K, the exponent n is proportional to $1/T$, and the single exponential occurs at 318 K. The pre-exponential factor a is 0.5 for temperatures around 160 K, and is increased by either increasing or decreasing the temperature. The relaxation effect of the first term of Equation (1) is larger than the second term in the given temperature range. The relaxation becomes a single exponential for $T > 318$ K.

The Zeeman Hamiltonian of the proton nuclear spin $I = 1/2$ in magnetic field $\vec{H} = H_0\hat{z}$ is $H_z = -\vec{\mu} \cdot \vec{H} = \pm \gamma\hbar H_0 I_z = \pm \frac{1}{2} \hbar\omega_0$, where $\hbar$ is Planck's constant divided

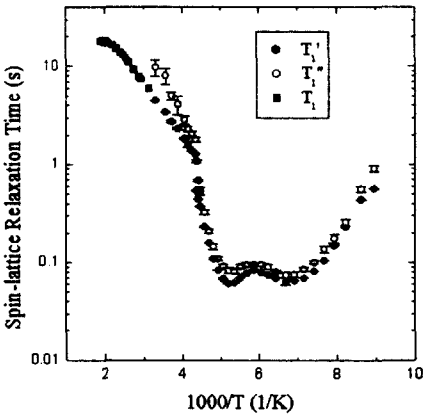


Fig. 2. The spin-lattice relaxation times T_1' and T_1'' from Equation (1) are shown. For comparison, the relaxation times T_1 are shown at temperatures $T > 320$ K.

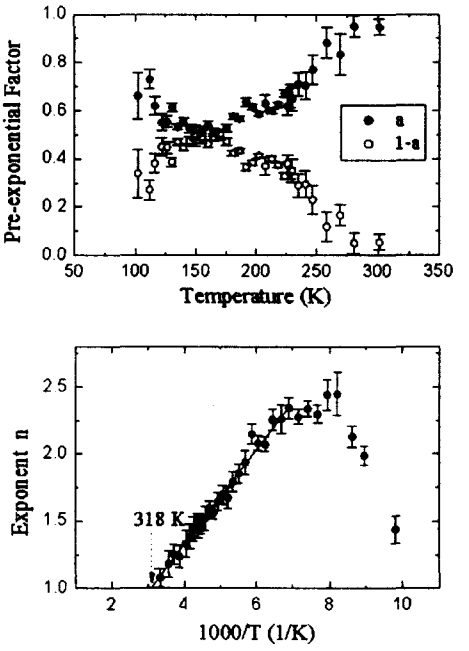


Fig. 3. Temperature dependences of the pre-exponential factor, a, and exponent, n, are shown when the inversion recovery method is used. At temperatures between 140 K and 318 K, the exponent n is proportional to $1/T$, and the initial behavior becomes an exponential at 318 K. The pre-exponential factor, a, is 0.5 at temperatures around 160 K, and it is increased by changing temperature.

by 2π, and ω_0 is the angular Larmor frequency. The numbers of nuclei in spin-up and spin-down levels in thermal equilibrium are N_+ and N_-, respectively; they obey the Boltzmann distribution,

$$N_+ / N_- = \exp(\hbar\omega_0 / k_B T) , \qquad (2)$$

where T is absolute temperature. The population difference between the two levels in thermal equilibrium is $p = N_+ - N_- \equiv p_0$, in which the total number of nuclei is $N = N_+ + N_-$.

The spin-lattice relaxation time is generally measured using the inversion recovery sequence. When the 180° pulse is applied to the spin system, the population of the system is reversed, *i.e.* $p = -p_0$; then the system has its maximum energy. When the 90° pulse is applied $N_+ = N_-$, i.e. $p = 0$. In order to consider the relaxation behavior with regards to the amount of the energy transferred to the spin system, we measured the relaxation behavior by lowering the flip angle of the first pulse from 180° to 90°. Fig. 4 shows the flip angle dependence of the spin-lattice relaxation, the relaxation time T_1', and the exponent n from the initial behavior at 191 K. T_1'' after a long time does not vary as the flip angle varies; however, the exponent n reaches 1 and T_1' is decreased by lowering the flip angle.

These results show that ^{1}H nuclear spin-lattice relaxation changes as the population varies from thermal equilibrium, and that the relaxation initially is slower as the population difference is larger. When the first pulse of the inversion recovery sequence is an 180° pulse, the total energy of the spin system that can be transferred to the lattice is maximal, creating a bottleneck in the energy transfer.

It is known that ^{1}H spin-lattice relaxation in ammonium sulfate is due to the hindered rotation of the ammonium ions. Fig. 5(a) shows the general relaxation diagram corresponding to the simplified mechanism. One of the underlying assumptions of this mechanism is that the nuclear spins relax by passing on their excess energy to the lattice modes, and the spin lattice relaxation time, T_1, is defined as the characteristic time constant τ_{sp-la} associated with this process. The lattice is assumed to comprise a large heat capacity reservoir capable of absorbing any amount of spin energy without an appreciable increase in temperature. However the overall picture of the relaxation is not simple, and the relaxation

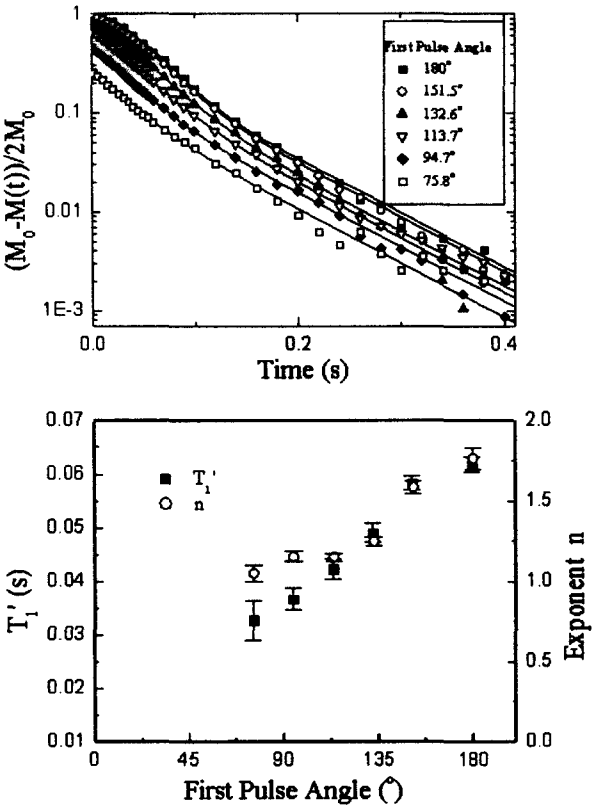
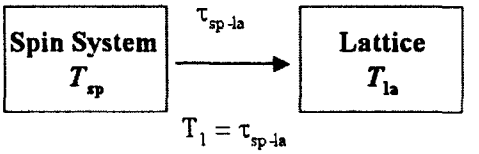


Fig. 4. The first-pulse flip angle dependences of the spin-lattice relaxation, the relaxation time T_1', and exponent n are shown. The T_1'' is the same with the flip angle of the first pulse after long times, however the exponent n reaches 1 and T_1' is decreased by decreasing the flip angle.

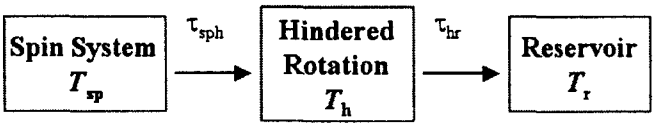
is better characterized by more than two steps, as shown in Fig. 5(b).

When the energy capacity of the hindered rotation is small compared to the nuclear spin energy and the speed with which the energy is transferred from the hindered rotation to the reservoir is slow, *i.e.* $\tau_{hr} > \tau_{sph}$, a bottleneck for the energy transfer between the spin system and the hindered rotation occurs. From the results of Fig. 4, we can conclude that the hindered rotation of the ammonium ions is well isolated from the reservoir at 191 K.

The bottleneck effect should be removed in order to measure the intrinsic spin-lattice relaxation time, T_1, between the nuclear spin system and the hindered rotation of the ammonium ions. Therefore the T_1 from the saturation recovery method can be used in order



(a)



(b)

Fig. 5. The general relaxation diagram corresponding to simplified mechanisms is shown in (a). The spin energy is transferred with the time constant τ_{sp-la} and then the relaxation time is given by $T_1 = \tau_{sp-la}$. The overall picture of the relaxation is actually made in more than two steps: the hindered rotation is interacted with the reservoir as shown in (b).

to measure intrinsic T_1 initially, and this value is denoted by T_1'''. In the saturation recovery sequence we used 20 pulses in order to saturate the nuclear spin population (the interpulse spacing was 50 μs, which is comparable to the spin-spin relaxation time T_2). For temperatures between 102 K and 301 K, we measured the exponent $n \approx 1$ with the saturation recovery sequence. The temperature dependence of T_1''', as compares to the T_1 measured by a single exponential fitting at $T > 320$ K, is shown in Fig. 6(a). The T_1''' is connected to the T_1; this was expected based on the behavior of the pre-exponential factor a and the exponent n given in Fig. 3. There is discontinuous change at $T_c = 223$ K, and two minima occur at 147 K and 190 K. These two minima have been attributed to the two inequivalent NH_4^+ ions, *i.e.* NH_4^+(I) and NH_4^+(II).[5] The minimum T_1 value is about 40 ms, which is comparable to the theoretical value 46 ms calculated by the BPP (Bloembergen-Purcell-Pound) function:[14,15]

$$\frac{1}{T_1} = \frac{9}{10}\frac{\gamma^4\hbar^2}{r^6}\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right), \tag{3}$$

where ω_0, γ, and r are the angular Larmor frequency, gyromagnetic ratio of proton, and interproton distance, respectively. It is known that the T_1 reaches a minimum when

$\omega_0\tau_c = 0.616$, where τ_c is the correlation time. When the molecular motions are thermally activated, the correlation time at a temperature T can be expressed as

$$\tau_c = \tau_0 \times \exp(E_a / k_B T), \quad (4)$$

where τ_0 and E_a are the pre-exponential correlation time extrapolated to infinite temperature and the activation energy for the molecular motions, respectively.

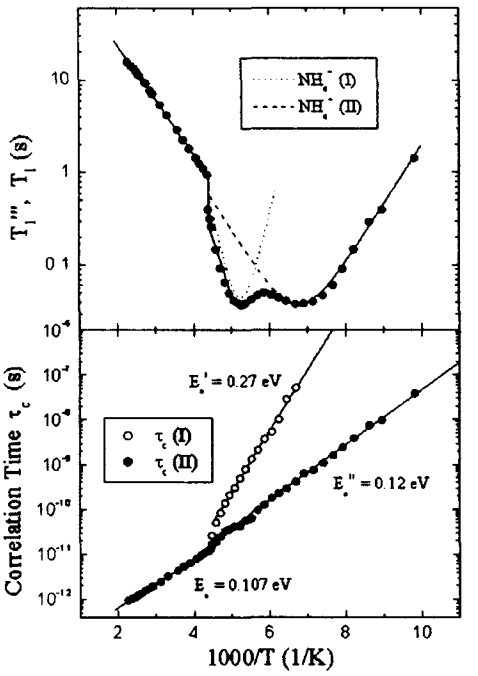


Fig. 6. The temperature dependence of T_1''' compared to the T_1 measured by a single exponential fitted at $T > 320$ K is shown in (a). There is a discontinuous change at $T_c = 223$ K and two minima at 147 K and 190 K. The dotted and dashed curves at $T < T_c$ are theoretical fits to the data using the BPP functions corresponding to the two groups of ions, NH_4^+(I) and NH_4^+(II), respectively. Correlation times τ_c^I and τ_c^{II} of the ammonium ions in ammonium sulfate, computed from the T_1 data, are shown in (b). In the paraelectric phase the two ions have the same correlation time. The straight lines are the best exponential fits to the data.

According to the neutron diffraction study,[1] the mean interproton distances of NH_4^+ ions at 298 K and 180 K are 1.74 Å and 1.72 Å, respectively. Considering only the nearest neighbor distance, the change in crystal structure through the transition can change T_1 by about 7 %. The much larger change in T_1 at T_c is due to the change in correlation time of the interproton dipolar interactions, mainly determined by the molecular reorientations. The dotted and dashed curves in Fig. 6(a) at $T < T_c$ are fits to the data with the BPP functions corresponding to the two inequivalent NH_4^+ ions, NH_4^+(I) and NH_4^+(II), respectively. The NH_4^+(II), which are surrounded by six SO_4^{2-} ions, thereby creating a more symmetric structure, are more susceptible to hindered rotations and the minimum T_1 is located at a lower temperature, *i.e.* 147 K. The NH_4^+(I) ions provide the relaxation curve with a minimum at 190 K.

Fig. 6(b) shows the temperature dependence of the correlation times τ_c^I and τ_c^{II} for the two groups of protons in the ferroelectric phase and τ_c in the paraelectric phase calculated from the relaxation curves. There is a discontinuous change in the correlation time at T_c from $\tau_c^I \approx 5.1 \times 10^{-11}$ s and $\tau_c^{II} \approx 1.9 \times 10^{-11}$ s to $\tau_c \approx 1.3 \times 10^{-12}$ s. The straight lines in Fig. 6(b) are the best fits of the data according to Equation (4). In the ferroelectric phase the two groups of ammonium ions have temperature independent activation energies, $E_a^I = 0.27 \pm 0.02$ eV and $E_a^{II} = 0.12 \pm 0.01$ eV, respectively. The correlation times τ_c^I of NH_4^+(I) ions are longer than those of NH_4^+(II) ions, but the difference between the two correlation times becomes smaller as the temperature approaches T_c. At temperatures above T_c, the activation energy $E_a = 0.107 \pm 0.005$ eV is slightly smaller than E_a^{II} in the ferroelectric phase.

CONCLUSIONS

There is a bottleneck effect in the ^{1}H NMR spin-lattice relaxation of ammonium sulfate in the temperature range 102 K ~ 318 K. We measured the intrinsic T_1 value between the nuclear spin system and the hindered rotation of ammonium ions by saturation recovery sequence. In the ferroelectric phase the activation energies of the two NH_4^+ ion groups are different: $E_a^I = 0.27 \pm 0.02$ eV and $E_a^{II} = 0.12 \pm 0.01$ eV. At and above T_c, the correlation times of the two groups become identical. The activation energy in the paraelectric phase is $E_a = 0.107 \pm 0.005$ eV.

We suggest that the bottleneck behavior in the NMR spin-lattice relaxation should be studied theoretically.

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