^{1}H NMR Relaxation Study of Molecular Motion in the Paraelectric Phase of (NH$_4$)$_2$Cd$_2$(SO$_4$)$_3$ Single Crystals

Ae Ran Lim[1,*] and Won Ki Jung[2]

^{1}Department of Science Education, Jeonju University, Jeonju, 560-759, Korea
^{2}School of Electrical Engineering Jeonju University Jeonju, 560-759, Korea
Received April 13, 2010

Abstract : The NMR spectrum and spin-lattice relaxation times, T_1, of the ^{1}H nuclei in (NH$_4$)$_2$Cd$_2$(SO$_4$)$_3$ single crystals were obtained. The two minima in T_1 in the paraelectric phase are attributed to the reorientational motions of the NH$_4$$^+$ groups. The ^{1}H T_1 of the (NH$_4$)$_2$Cd$_2$(SO$_4$)$_3$ crystals can be described with Bloembergen-Purcell-Pound (BPP) theory. The experimental value of T_1 can be expressed in terms of an isotropic correlation time τ_H for molecular motions by using the BPP theory, and determine the role of protons in these processes.

Keywords : (NH$_4$)$_2$Cd$_2$(SO$_4$)$_3$, Ferroelectrics, Crystal growth, Nuclear magnetic resonance, Spin-lattice relaxation, Molecular motion

INTRODUCTION

The langbeinite crystals, (M$^+$)$_2$(M^{2+})$_2$(SO$_4$)$_3$, have attracted much attention because some of them exhibit ferroelectric and ferroelastic phase transitions.[1-5] One such crystal, diammonium dicadmium sulfate, (NH$_4$)$_2$Cd$_2$(SO$_4$)$_3$, exhibits a dielectric anomaly at 92 K, and becomes ferroelectric below this temperature.[6-8] The high temperature phase belongs to the space group P2$_1$3 [9] and is prototypic of the ferroelectric phase. The ferroelectric phase belongs to point group 2. The crystal is cubic with lattice constant a=10.35 Å at room temperature and has four molecules in the unit cell.[6] At T$_C$=92 K, there is a first-order

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* To whom correspondence should be addressed. E-mail : aeranlim@hanmail.net

transition in which the symmetry falls to C_2^2 and the unit cell volume doubles in a plane perpendicular to the polarization axis. $(NH_4)_2Cd_2(SO_4)_3$ crystals have previously been studied by using Raman,[10] electron paramagnetic resonance (EPR),[11] and dielectric properties.[7, 12]

Todo and Tatsuzaki [13] have investigated the proton spin-lattice relaxation time of $(NH_4)_2Cd_2(SO_4)_3$ and the activation energies of NH_4^+ motion were reported for the temperature range 77 to 145 K. At T_C, T_1 decreases discontinuously from 7 to 4.5 ms, and this discontinuity is clear evidence of a change in the reorientational motion of NH_4^+ at the ferroelectric phase transition. Although the spin-lattice relaxation time, T_1, of $(NH_4)_2Cd_2(SO_4)_3$ crystals has previously been reported for low temperatures by Todo and Tatsuzaki [13], the spin-lattice relaxation time, T_1, in the paraelectric phase above 170 K has not yet been reported.

In this study, we investigated the molecular motion in the paraelectric phase of $(NH_4)_2Cd_2(SO_4)_3$ crystals above 170 K by measuring the ^1H NMR linewidth and spin-lattice relaxation time, T_1. From these results, the activation energies of the molecular motion of the NH_4^+ ion in the paraelectric phase were obtained. In particular, we aimed to determine the role of protons in these processes by analyzing the ^1H NMR data.

EXPERIMENTAL

Single crystals of $(NH_4)_2Cd_2(SO_4)_3$ with good optical quality were grown by the slow evaporation of an aqueous solution containing a stoichiometric proportion of $(NH_4)_2SO_4$ and $CdSO_4$. The resulting crystals were transparent and colorless with dimensions of approximately $3 \times 3 \times 2$ mm^3.

The spin-lattice relaxation time of the ^1H nuclei in $(NH_4)_2Cd_2(SO_4)_3$ single crystals was measured by using a Varian Infinity 200 FT NMR spectrometer at the Korea Basic Science Institute. The static magnetic field was 4.7 T and the central radio frequency was set at $\omega_H/2\pi=200$ MHz. The spin-lattice relaxation time was measured by applying a pulse sequence of $\pi/2-t-\pi/2$. The nuclear magnetization, $S(t)$, of the ^1H nuclei at time t after the

π/2 pulse was determined from the saturation recovery sequence following the pulse.[14] The width of the π/2 pulse was 4 μs. The temperature dependences of the NMR measurements were obtained in the temperature range 180–410 K. The temperature of sample was held constant by controlling the nitrogen gas flow and heater current.

RESULTS AND DISCUSSION

The ^{1}H NMR spectrum for a single crystal of $(NH_4)_2Cd_2(SO_4)_3$ was obtained as a function of temperature, as shown in the inset in Fig. 1. The full-width-at-half-maximum (FWHM) of the ^{1}H NMR signal at a frequency of 200 MHz decreases with increasing temperature in a stepwise manner, as shown in Fig. 1. This stepwise narrowing is attributed to internal motions that have a temperature dependence that observed for the linewidth. When the temperature increases, the line shape changes from the Gaussian-like shape produced by a rigid lattice to a Lorentzian shape. The linewidth is nearly constant between 180 K and 360 K, and has a relatively broad value of approximately 18–20 kHz in this temperature range. Above 360 K, the linewidth is significantly narrower.
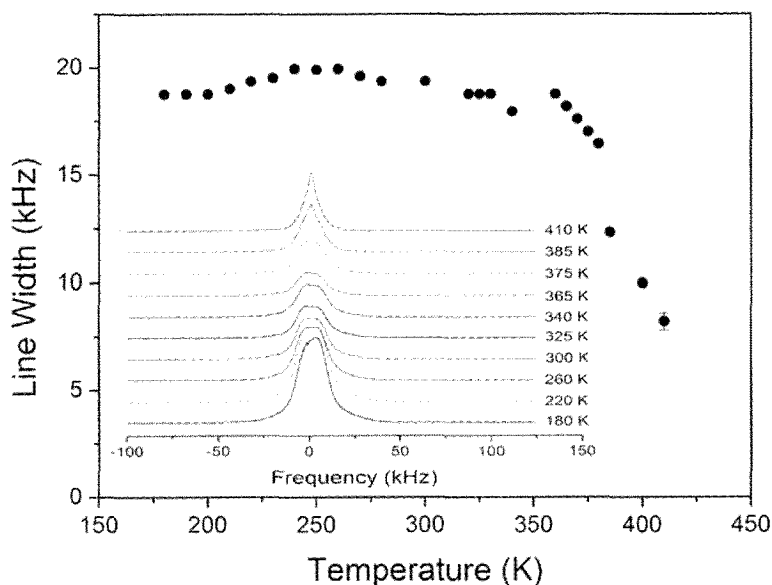

Figure 1. ^{1}H NMR spectrum and linewidth as a function of temperature for $(NH_4)_2Cd_2(SO_4)_3$ crystals.

The spin-lattice relaxation time can be determined by fitting the recovery patterns with the following equation [15]:

$$\frac{S(\infty) - S(t)}{S(\infty)} = \exp(-Wt) \tag{1}$$

where $S(t)$ is the nuclear magnetization at time t.

The recovery traces of the magnetizations were obtained from the NMR signals of the ^1H nuclei in the $(NH_4)_2Cd_2(SO_4)_3$ single crystals at several temperatures. In the measurements of the T_1 values, the saturation recovery pulse sequence was utilized over the whole temperature range. The recovery traces for ^1H can be represented by a single exponential form at all temperatures investigated.[16] Thus, the spin-lattice relaxation time T_1 can be determined directly from the slope of a plot of $\log\{[S(\infty) - S(t)] / S(\infty)\}$ versus time t. Figure 2 shows the recovery traces of ^1H NMR fitted with a single exponential function at 200 K, 300 K, and 410 K; note that the recovery traces at each temperature are different and that the slopes of the traces decrease with increasing temperature. These results are due to the variation in the dynamics of the ammonium proton. We measured the temperature variation of the relaxation time for the ^1H NMR. The spin-lattice relaxation time, T_1, for ^1H NMR is shown as a function of temperature in Fig. 3. There are two minimum values in the plot of T_1 vs. 1000/T in the vicinity of 220 K and 340 K. The form of the proton T_1 vs. inverse temperature curve leads us to believe that the relaxation process is caused by NH_4^+ motion. Reorientation motions are responsible for the minima in T_1 at 220 K and 340 K, and these motions are the dominant contributor to T_1 over the ranges 180 K < T < 280 K and 280 K < T < 410 K respectively of the paraelectric phase.

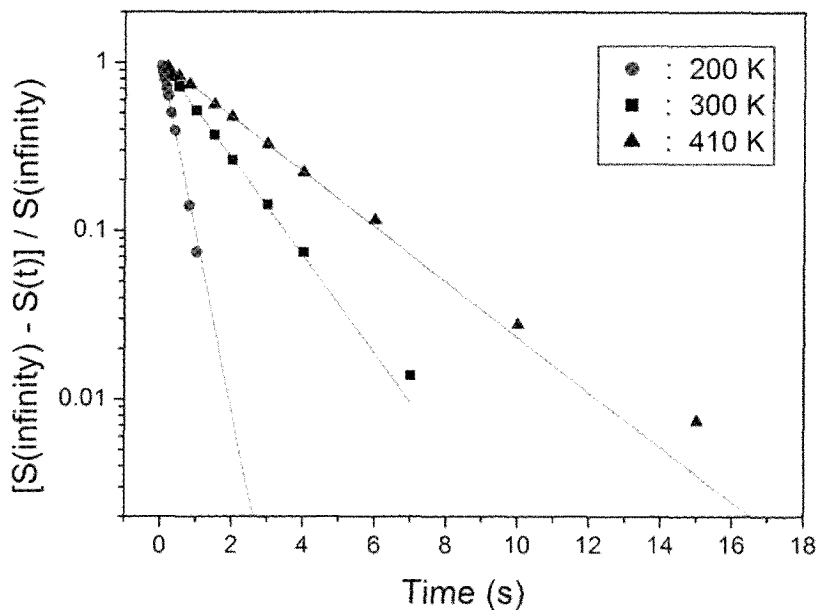**Figure 2.** ^{1}H NMR spin-lattice relaxation recovery traces for $(NH_4)_2Cd_2(SO_4)_3$ crystals obtained at 200 K, 300 K, and 410 K.

In studies of molecular motion that use measurements of the relaxation time, it is important to determine whether the relaxation time is located on the slow or fast side of the minimum as a function of temperature. The T_1 values can then be related to corresponding values of the rotational correlation time, τ_H. The rotational correlation time is the length of time that a molecule remains in a given state before the molecule reorients, and is thus a direct measure of the rate of motion. The experimental value of T_1 can be expressed in terms of an isotropic correlation time, τ_H, for molecular motion by using the Bloembergen-Purcell-Pound (BPP) function.[17] From the ^{1}H NMR T_1 data shown in Fig. 3, we can derive the correlation time τ_H for the reorientation of NH_4 ions in $(NH_4)_2Cd_2(SO_4)_3$.

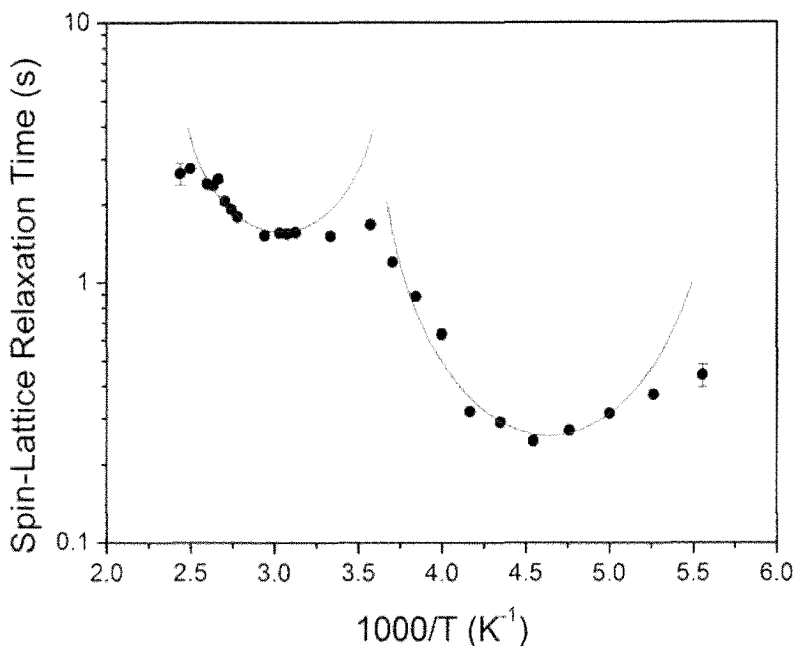**Figure 3.** Temperature dependence of the ^1H NMR spin-lattice relaxation time, T_1, for $(NH_4)_2Cd_2(SO_4)_3$ crystals.

The proton spin-lattice relaxation is mainly controlled by the H–SO_4 interdipolar interaction modulated by HSO_4 reorientation, which yields the following equation for T_1 [18-20].

$$\frac{1}{T_1} = \left(\frac{\mu_o}{4\pi}\right)^2 \left(\frac{\gamma^4 \hbar^2}{r^6}\right) \left[\frac{\tau_H}{1+(\omega_H \tau_H)^2} + \frac{4\tau_H}{1+(2\omega_H \tau_H)^2}\right] \tag{2}$$

where γ is the gyromagnetic ratio for the ^1H nucleus, $\hbar = h/2\pi$ where h is the Planck's constant, r is the proton-proton distance, and ω_H is the proton Larmor frequency. The minimum in T_1 occurs when $\omega_H \tau_H = 0.616$. Since the T_1 curve contains two minima, it is possible to determine the value of the $(\mu_o/4\pi)^2 (\gamma^4 \hbar^2/r^6)$ in the BPP [17] formula. Each of the correlation times can be calculated as a function of temperature from that constant by using the proton Larmor frequency $\omega_H/2\pi = 200$ MHz and the values of T_1 obtained from our experimental results.

Since the correlation time τ_H of ^{1}H NMR for a thermally activated reorientation follows the usual Arrhenius expression [15, 20]:

$$\tau_H = \tau_0 \exp\left(\frac{-E_a}{k_B T}\right)$$

(3)

where the parameters E_a and τ_0 are the activation energy and the pre-exponential factor respectively, the E_a values were determined from the slopes of the straight line portions of the semilog plots of the correlation time vs. 1000/T.

Figures 4(a) and (b) show the correlation times for the proton nuclei as a function of inverse temperature for the ranges 180 K < T < 280 K and 280 K < T < 410 K respectively. The activation energies in the paraelectric phase for these ranges were determined to be 3.75 ± 0.87 kcal/mol and 2.71 ± 0.42 kcal/mol respectively. The activation energies reported by Todo and Tatsuzaki [13] are 2.7 kcal/mol and 0.9 kcal/mol for the ranges 92 K < T < 140 K and T < 92 K respectively.
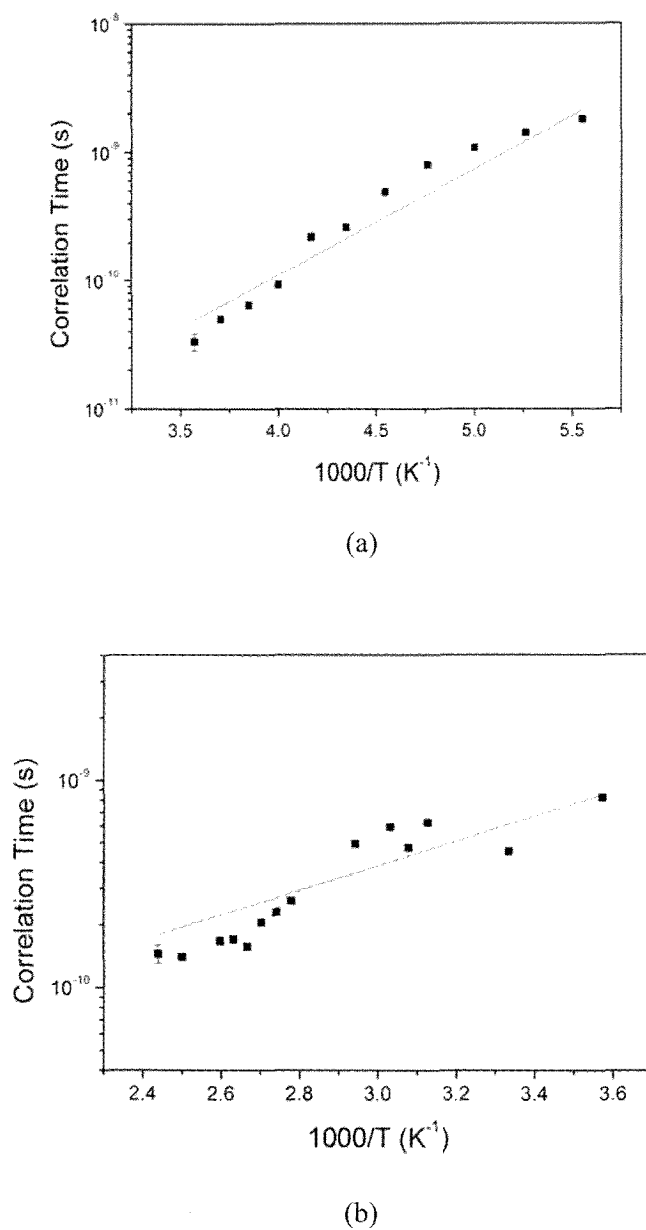
(a)

(b)

Figure 4. Correlation times as a function of inverse temperature for ^1H in $(NH_4)_2Cd_2(SO_4)_3$ crystals: (a) in the low temperature range (180 K < T < 280 K) and (b) in the high temperature range (280 K < T < 410 K).

CONCLUSION

$(NH_4)_2Cd_2(SO_4)_3$ single crystals were grown via the slow evaporation method. The NMR spectra and spin-lattice relaxation time, T_1, of the ^{1}H NMR in $(NH_4)_2Cd_2(SO_4)_3$ single crystals were determined by using NMR spectrometry. From these results, the rotational correlation times were calculated and the activation energies were obtained. The T_1 for the ^{1}H in the $(NH_4)_2Cd_2(SO_4)_3$ crystals was found to be well described by the BPP theory. For the spin-lattice relaxation times, the experimental value of T_1 can be expressed in terms of an isotropic correlation time τ_H for molecular motion by using the BPP theory. The minima in T_1 at low and high temperatures were attributed to the reorientational motions of the NH_4^+ groups. The activation energies for NH_4^+ molecular motion were found to be 3.75 and 2.71 kcal/mol for the two minima in the paraelectric phase.

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