Paraelectric-Ferroelectric Phase Transition of $(NH_4)_2SO_4$ Single Crystals by ^{14}N NMR

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Abstract The ^{14}N NMR spectra for $(NH_4)_2SO_4$ crystals were obtained near the phase transition temperature T_C=223 K, and were found to precisely reflect the symmetry change in the crystal at this first-order phase transition. Changes in the resonance frequencies near T_C were attributed to the structural phase transition. In the ferroelectric and paraelectric phases, two inequivalent NH_4 groups were distinguished in the ^{14}N NMR spectra. The two types, $NH_4(1)$ and $NH_4(2)$, have slightly different local environments. Consequently, we conclude that the phase transition is caused by the change in the environment of the ^{14}N nuclei in the NH_4 groups, rather than by the SO_4 groups.

**Keywords** Single crystal, Nuclear magnetic resonance, Ferroelectrics

Introduction

The transitions of superionic conductors at high temperatures were observed in many hydrogen-bonded crystals, which exhibit ferroelectricity and ferroelasticity at low temperatures.[1-3] $(NH_4)_2SO_4$ is a well-known hydrogen-bonded crystal, in which all of the protons are from NH_4^+ groups. $(NH_4)_2SO_4$ undergoes a first-order ferroelectric phase transition at T_C=223 K. Ammonium sulfate is an improper ferroelectric below T_C and undergoes a transition to the paraelectric phase above T_C. It is also known to be ferroelastic in both the paraelectric and ferroelectric phases.[4-11]

At room temperature, the crystal possesses orthorhombic symmetry (space group *Pnam*-D_{2h}^{16}), with lattice constants a=7.782Å, b=10.636Å, and c=5.993 Å.[12] They undergo a phase transition without changing the number of formula units Z=4 in the unit cell at T_C.[13] Below T_C, the reflection plane *ab* and the center of inversion disappear, accompanying the change in the space group to *Pna2₁*-C_{2v};[9] however, the crystal structure still possesses orthorhombic symmetry. The unit cell parameters for $(NH_4)_2SO_4$ in the ferroelectric phase are a=7.783Å, b=10.61 Å and c=5.967 Å.[12] The structure of the $(NH_4)_2SO_4$ single crystal at 180 K is shown in Fig. 1. Both the ferroelectric and paraelectric phases have two crystallographically inequivalent types of ammonium ions, namely, $NH_4(1)$ and $NH_4(2)$, which are surrounded by different numbers of neighboring SO_4^{2-} anions; five or six, respectively.[14] The tetrahedral molecules of NH_4^+ and SO_4^- are distorted from a regular tetrahedral shape.

The phenomenological theory of phase transition in

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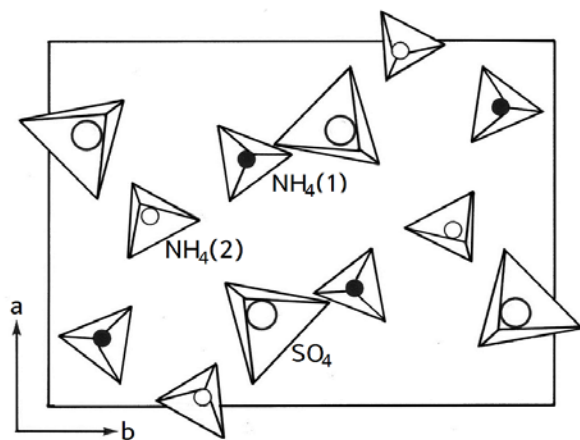
Figure 1. Projection of the $(NH_4)_2SO_4$ single crystal structure onto the ab-plane at 180 K.

$(NH_4)_2SO_4$ was discussed previously by Bajpai et al. [15,16] They reported that the changes in the NH_4^+ ions and the hydrogen bonds in $(NH_4)_2SO_4$ at T_C are minor and gradual, while those in the SO_4^{2-} ion are sudden. On the other hand, the NH_4^+ ions in $(NH_4)_2SO_4$ have been shown to have hindered rotations at temperatures below 400 K by the ^1H spin-lattice relaxation times obtained using nuclear magnetic resonance (NMR).;[17-21] the ^1H in the two kinds of ammonium ions have different activation energies. The deuteron quadrupole parameters, e^2qQ/h and η in $(ND_4)_2SO_4$, were reported for $NH_4(1)$ and $NH_4(2)$, respectively.[22] In addition, the two inequivalent ammonium ion sites were indicated by ^{15}N (=1/2) magic angle spinning (MAS) NMR. Furthermore, the ^{15}N spin-lattice relaxation time for $NH_4(1)$ and $NH_4(2)$ was reported for the ferroelectric and paraelectric phases.[23] Consequently, it can be seen that this transition has been the subject of a large number of investigations; however, the role of the ^{14}N nuclei of NH_4 ions in $(NH_4)_2SO_4$ crystals was not yet investigated. It is a topic of interest to determine if the structural geometry of these ions changes in transitioning from the paraelectric to the ferroelectric phase at 223 K.

In this study, the NMR spectra of the ^{14}N (I=1) nuclei in $(NH_4)_2SO_4$ single crystals were discussed in order to elucidate the structural geometry near the phase transition temperature T_C. The temperature dependence of ^{14}N NMR for $(NH_4)_2SO_4$ crystals was newly obtained. These experiments were carried out with the purpose of investigating the role of two inequivalent forms of NH_4 near T_C. Based on these results, the role of ^{14}N nuclei in the paraelectric and ferroelectric phases was discussed.

Experimental Methods

$(NH_4)_2SO_4$ single crystals were grown by the slow evaporation of saturated aqueous solution at 300 K. Transparent single crystals with a dominant face of (100) were obtained.

The ^{14}N NMR spectra of $(NH_4)_2SO_4$ single crystals were obtained using the Unity INOVA600 FT NMR spectrometer at the Korea Basic Science Institute, Western Seoul Center. The static magnetic field used was 14.1 T. The central radio frequency was set at $\omega_0/2\pi$=43.342 MHz for the ^{14}N nucleus. Here, the resonance frequency was obtained relative to the reference signal of NH_4Cl_4. The ^{14}N NMR experiments were performed using a solid-state echo sequence: 4 μs – τ (12 μs) – 4 μs – τ (12 μs). The NMR spectra were obtained for temperatures ranging between 180–440 K. The temperature of the sample was held constant by controlling the nitrogen gas flow and heater current, giving an accuracy of ±0.5 K.

Results and Discussion

The NMR spectrum of ^{14}N (I=1) was obtained using static NMR at a Larmor frequency of $\omega_0/2\pi$=43.342MHz. The crystal orientation with respect to the magnetic field was along the crystallographic a-axis. Two resonance lines arose from the quadrupole interactions of the ^{14}N nucleus. The temperature dependence of the ^{14}N NMR spectra of $(NH_4)_2SO_4$ single crystals is shown in Fig. 2 and 3. The resonance frequency shifts near the phase transition temperature, indicating a change in the structural geometry surrounding the ^{14}N nuclei. Here, the N(1) and N(2) atoms corresponding to $NH_4(1)$ and $NH_4(2)$ ions, respectively, can be distinguished. Note that in the paraelectric phase, the low-frequency resonance is assigned to $NH_4(1)$ on the basis of ^{15}N and ^2H NMR data;[22-24] in $(ND_4)_2SO_4$, the quadrupole

coupling constant and the asymmetry parameter for $^2H(1)$ and $^2H(2)$ are $e^2qQ/h=4.17$ kHz and $\eta=1.0 \sim 0.95$ for $NH_4(1)$, while for $NH_4(2)$, $e^2qQ/h=2$ kHz and $\eta=1.0\sim0.8$.[19] The four spectral pairs of signals as shown in Fig. 2 and 3 are consistent with the unit cell having Z=4. The ^{14}N NMR spectra from the eight signals are attributed to the N(1) and N(2) sites of the $NH_4(1)$ and $NH_4(2)$ ions, respectively. The lines represented by the same color indicate the same pairs for ^{14}N. From this, it can be seen that the degree of deformation of the $NH_4(1)$ ion is larger than that of the $NH_4(2)$ ion, as shown by the ^2H NMR experiment. In addition, the average bond lengths for N(1)–H are 1.075 Å in the paraelectric phase, whereas those for N(2)–H are 1.062 Å.[12]
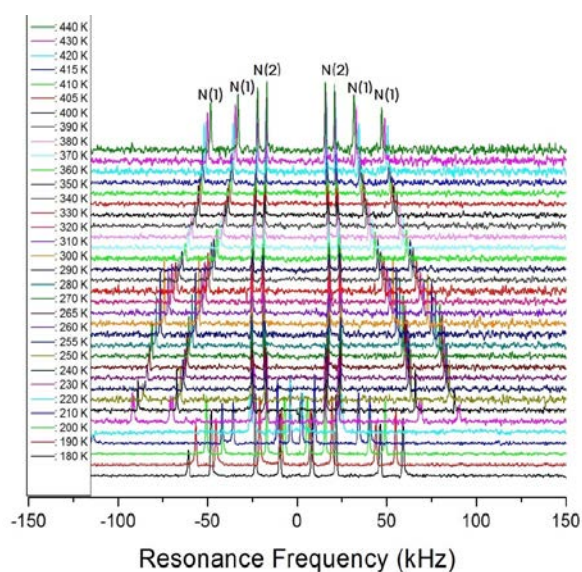
Figure 2. In-situ ^{14}N NMR spectrum of $(NH_4)_2SO_4$ single crystals in the paraelectric and ferroelectric phases.

A marked discontinuity in the ^{14}N NMR spectrum was found in the vicinity of the ferroelectric phase transition, which is reported to be of the first-order. The splitting of the ^{14}N NMR resonance frequency in NH_4^+ is larger in the paraelectric than in the ferroelectric phase, and we can say that the transition to the ferroelectric phase involves a change in the quadrupole parameter.
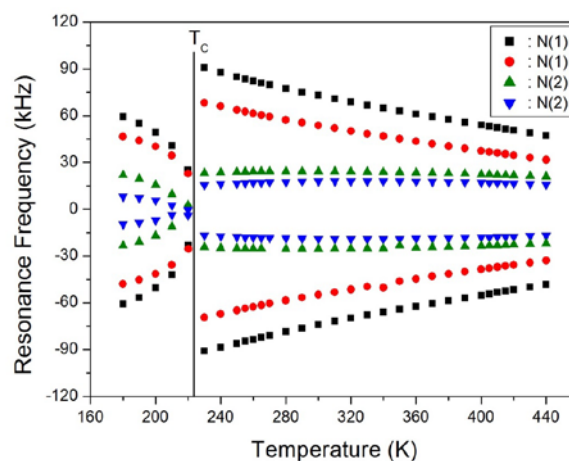
Figure 3. The ^{14}N resonance frequency of $(NH_4)_2SO_4$ single crystals as a function of temperature.

Note that these temperature- dependent changes in the ^{14}N resonance frequencies are generally attributed to changes in the structural geometry near $T_C=223$ K. Here, the electric field gradient (EFG) tensors at the N sites are varied, reflecting the changing atomic configurations around the ^{14}N nuclei.

Conclusion

Information about the structural geometry of $(NH_4)_2SO_4$ single crystals near the phase transition temperature $T_C=223$ K was obtained through ^{14}N NMR spectra recorded at various temperatures. The ^{14}N NMR spectrum exhibits the NMR lines for four spectral pairs, which is consistent with the four groups of inequivalent ^{14}N nuclei. The abrupt change seen in the resonance frequency near T_C is generally attributed to a structural phase transition. The NH_4 atoms in the structure are coordinated by the sulfate atoms, as shown in Fig. 1. Therefore, the atomic displacements in the environments of the ^{14}N nuclei with temperature are correlated with the sulfate ions. The variations in the ^{14}N NMR spectra as a function of temperature provide a good approximate description of the degree of distortion of the H–N tetrahedral groups in NH_4. The average N-H bond length for one type of ammonium ion, $NH_4(1)$, decreases from 1.075 to 1.052 Å, while for the other,

NH_4(2), r_{NH} decreases from 1.062 to 1.048 Å.[12] In both phases, the two distinctive ammonium ions have slightly different local environments. The present study indicates that the ^{14}N nuclei in $(NH_4)_2SO_4$ play important roles near the phase transition temperature T_C. Consequently, the main factor causing the phase transition is the change in the surroundings of the ^{14}N nuclei in the NH_4 groups, rather than the SO_4 groups.

Acknowledgment

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