

## Technical note

 $^1\text{H}$  nuclear magnetic resonance study of the ferroelastic and superionic phase transitions of  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  single crystals

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## ARTICLE INFO

## Article history:

Received 19 April 2008

Received in revised form

27 September 2008

Accepted 31 October 2008

## Keywords:

B. Crystal growth

D. Nuclear magnetic resonance

D. Phase transitions

## ABSTRACT

We investigated the temperature dependences of the line shape, spin–lattice relaxation time,  $T_1$ , and spin–spin relaxation time,  $T_2$ , of the  $^1\text{H}$  nuclei in  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  single crystals. On the basis of the data obtained, we were able to distinguish the “ammonium” and “hydrogen-bond” protons in the crystals. For both the ammonium and hydrogen-bond protons in  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$ , the curves of  $T_1$  and  $T_2$  versus temperature changed significantly near the ferroelastic and superionic phase transitions at  $T_C$  ( $= 232\text{ K}$ ) and  $T_S$  ( $= 405\text{ K}$ ), respectively. In particular, near  $T_S$ , the  $^1\text{H}$  signal due to the hydrogen-bond protons abruptly narrowed and the  $T_2$  value for these protons abruptly increased, indicating that these protons play an important role in this superionic phase transition. The marked increase in the  $T_2$  of the hydrogen-bond protons above  $T_S$  indicates that the breaking of  $\text{O}\cdots\text{H}\cdots\text{O}$  bonds and the formation of new H-bonds with  $\text{HSO}_4^-$  contribute significantly to the high-temperature conductivity of  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  crystals.

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## 1. Introduction

Hydrogen-bonded  $\text{A}_4\text{LiH}_3(\text{XO}_4)_4$  ( $\text{A} = \text{K}, \text{NH}_4, \text{Rb}$  and  $\text{X} = \text{S}, \text{Se}$ ) crystals are well known for their high protonic conductivities, which increase significantly in their high-temperature superionic phases. Crystals of the general formula  $\text{A}_4\text{LiH}_3(\text{XO}_4)_4$  have tetragonal symmetry at room temperature and undergo a structural phase transition to a ferroelastic phase with monoclinic symmetry [1–5].  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  belongs to this family of ferroelastic crystals [6–8], and undergoes a ferroelastic phase transition at 232 K, which was first reported by Pietraszko et al. [9]. Above room temperature, the crystal undergoes an additional phase transition at 405 K [10]. At room temperature,  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  is tetragonal structure (space group  $\text{P4}_1$ ) with lattice constants of  $a = 7.642\text{ \AA}$  and  $c = 29.566\text{ \AA}$  [9]. Below  $T_C = 232\text{ K}$ , the ferroelastic phase is monoclinic with space group  $\text{P2}_1$  [9,11]. Around  $T_f = 162\text{ K}$  a ferroelastic “domain freezing” phenomenon has been observed by Zimmermann and Schranz [12]. An optical study of the ferroelastic–paraelastic phase transition found it to be second order [13,14]. The structure consists of a superposition of sandwiches [9,11,15], with each sandwich composed of  $\text{NH}_4^+$  ions between two layers of  $\text{SO}_4$  groups. The layers are stacked perpendicular to the tetragonal axis. Both the  $\text{SO}_4$  tetrahedra in each layer and the layers forming the sandwiches are connected by  $\text{O}\cdots\text{H}\cdots\text{O}$  hydrogen bonds, as shown in Fig. 1. The Li ions are

intercalated between every two independent layers and are surrounded by tetrahedra of oxygen atoms. Each  $\text{NH}_4^+$  group has an environment of eight oxygens.

Blinic et al. [16] have reported the “superionic” behavior of  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$ . The transition temperature of the associated “protonic” transition was found to be around  $T_S = 415\text{ K}$ . Further, the  $^1\text{H}$  spin–lattice relaxation time,  $T_1$ , and the spin–spin relaxation time,  $T_2$ , for  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  crystals show that proton diffusion begins far below  $T_S$ . The number of diffusing protons increases continuously all the way up to  $T_S$ . Previous  $^1\text{H}$  nuclear magnetic resonance (NMR) investigations have only provided descriptions of the “average” behavior of the protons belonging to the ammonium and hydrogen-bond protons.

As protons are expected to play a dominant role in the physical properties and phase transition mechanisms of hydrogen-bonded crystals, probing their proton motions with  $^1\text{H}$  NMR is expected to be a powerful means of studying their microscopic nature. The relationship between the dynamic transfer of hydrogen atoms and structural phase transitions has been a subject of keen interest. In this connection, the ammonium and hydrogen-bond protons of  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  single crystals are particularly worthy of study. The ammonium protons can be distinguished from the hydrogen-bond protons by using solid-state NMR methods. In the present study, we characterized the dynamics of the ammonium and hydrogen-bond protons in  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  single crystals through measurements of the spin–lattice relaxation time,  $T_1$ , and the spin–spin relaxation time,  $T_2$ . In particular, we examined the temperature dependences of  $T_1$  and  $T_2$  for the  $^1\text{H}$  nuclei in  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  single crystals in order to gain insight into the

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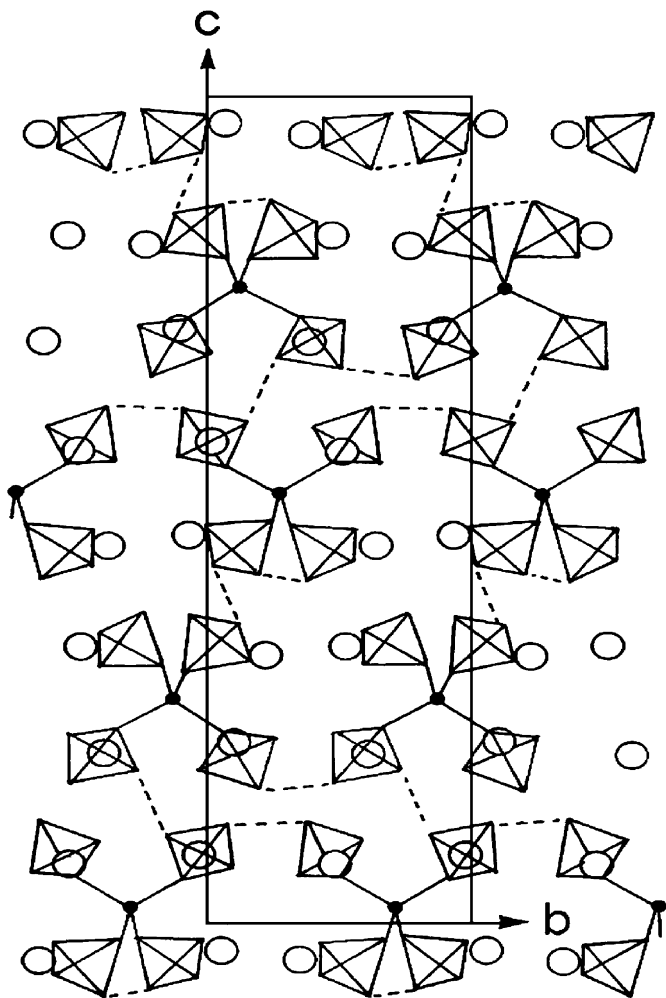


Fig. 1. The structure of the  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  crystal projected along the  $bc$ -plane. Sulfate groups are represented by tetrahedra,  $\text{NH}_4$  groups by large circles and Li by small dark circles. The Li–O linkages are denoted by continuous lines and the hydrogen bonds by dashed lines.

role of the ammonium and hydrogen-bond protons in the phase transitions of these crystals. The results of the present study are significantly different to those of previous studies, especially with regard to the influences of the ammonium and hydrogen-bond protons.

## 2. Experimental method

Crystals of  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  were grown at room temperature from a non-stoichiometric acid aqueous solution of  $\text{Li}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{H}_2\text{SO}_4$  by slow evaporation of water. The crystals are colorless and transparent with polygonal plates parallel to the  $(100)$  cleavage plane. The crystals exhibit twin structures below  $T_c = 232$  K, and were found to be slightly hygroscopic. Because of the hygroscopic nature of the material, the crystals were encapsulated in sealed quartz tubes.

The NMR signals of the  $^1\text{H}$  nuclei in the  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  single crystals were measured using the Varian 200 FT NMR spectrometer at the Korea Basic Science Institute. The static magnetic field and the central radio frequency for the  $^1\text{H}$  nucleus were 4.7 T and  $\omega_0/2\pi = 200.13$  MHz, respectively. The  $^1\text{H}$   $T_1$  measurement was performed using a  $\pi$ - $t$ - $\pi/2$  pulse sequence, and  $T_2$  was measured with the solid echo sequence. The nuclear magnetizations  $S(t)$  of the  $^1\text{H}$  nuclei at time  $t$  after the  $\pi$  pulse

were determined from the inversion recovery sequence following the pulse. The width of the  $\pi$  pulse was  $3.33\ \mu\text{s}$ . The NMR measurements were obtained in the temperature range 160–430 K. The sample temperatures were maintained at a constant value by controlling the nitrogen gas flow and the heater current, giving an accuracy of  $\pm 0.5$  K.

To determine the phase transition temperatures of  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$ , differential scanning calorimetry (DSC) was carried out on the crystals using a Dupont 2010 DSC instrument. The measurement was performed at a heating rate of 10 K/min. Two phase transitions were detected for  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$ , at about 232 and 405 K.

## 3. Experimental results and analysis

The NMR spectrum for the  $^1\text{H}$  nuclei in a  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  crystal was determined as a function of temperature. There are two kinds of protons in  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$ , the “ammonium” protons and the “hydrogen-bond” protons. In our NMR results, the proton signals due to the ammonium and hydrogen-bond protons overlap, as shown in Fig. 2. Here, the orientation of the crystal with respect to the applied magnetic field was along the arbitrary direction. The 16 ammonium protons and the 3 hydrogen-bond protons should yield two superimposed lines with intensities in a theoretical ratio of 16:3. The observed ratio of the intensities of the ammonium and hydrogen-bond proton spectra is in agreement with the theoretical ratio. The broad and narrow signals in spectrum to the ammonium and hydrogen-bond protons are assigned by the number of the 16 protons in the  $\text{NH}_4$  groups and 3 protons in the hydrogen-bond proton, respectively. The line width of the signal due to the ammonium protons is very broad at low temperatures, whereas the line width of the signal

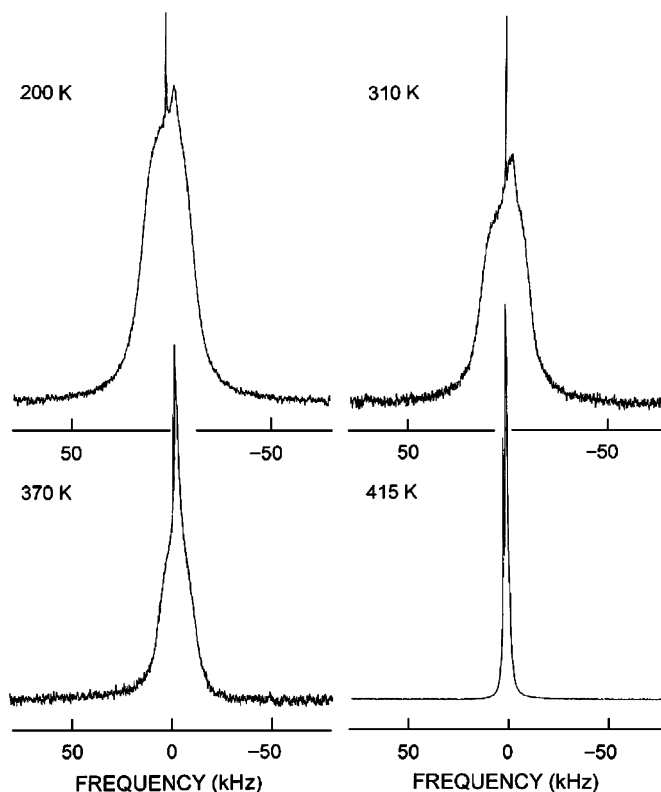


Fig. 2. The “ammonium” and “hydrogen-bond” proton NMR spectra for a  $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$  crystal as a function of temperature (broad line: ammonium protons, narrow line: hydrogen-bond protons).

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