



## Role of $\text{NH}_4$ and $\text{H}_2\text{O}$ in Tutton Salt $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (M=Fe and Zn) Single Crystals Studied by $^1\text{H}$ and $^{14}\text{N}$ NMR at High Temperatures

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**Abstract** At high temperature, the roles of  $\text{NH}_4$  and  $\text{H}_2\text{O}$  in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  single crystals were investigated using a pulse NMR spectrometer. Temperature was shown to have a significant influence, causing changes in the deformation of  $\text{NH}_4$  and  $\text{H}_2\text{O}$ . From the  $^1\text{H}$  NMR and  $^{14}\text{N}$  NMR spectrum, the forms of environment surrounding  $^{14}\text{N}$  in  $\text{NH}_4$  groups is more important than the loss of  $\text{H}_2\text{O}$  groups. NMR studies indicate that  $\text{NH}_4^+$  ions in Tutton salts play an important role in the changes of the crystal structure at high temperatures.

**Keywords** Tutton salts,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , Thermodynamic property, NMR

### Introduction

Development of materials suitable for strong energy absorption by solar collectors has recently gained considerable attention. For domestic heating and hot-water supply, this energy could be stored chemically in reversible reactions, thermally in phase changes, or by increasing the temperature of syringe materials.<sup>1,2</sup> Some inorganic salt hydrates have

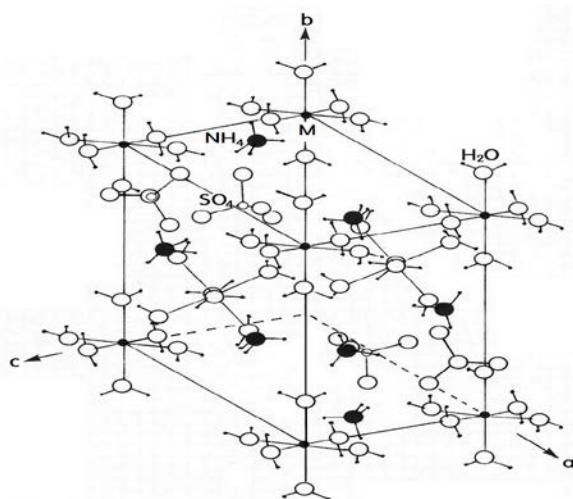
suitable melting temperatures and represent the most promising materials for this purpose. Therefore, further studies of the thermal properties of salt hydrates are needed, especially to obtain precise structural information for metal-water bonded systems. The general formula of Tutton salts is  $\text{M}_2\text{M}^{\text{II}}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , containing two octahedral hexahydrate complexes  $[\text{M}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$  in the crystal unit cell with various divalent ions  $\text{M}^{\text{I}}$  ( $=\text{NH}_4$ , K, Rb, and Cs) and  $\text{M}^{\text{II}}$  ( $=\text{Co}$ , Zn, and Fe).<sup>3-11</sup>

$(\text{NH}_4)_2\text{M}^{\text{II}}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (M<sup>II</sup>=Fe and Zn) single crystals have a monoclinic structure with the space group  $P2_1/a$ . The unit cell contains two  $\text{M}^{2+}$  ions, each surrounded by six water molecules forming an octahedron, as shown in Fig. 1.  $(\text{NH}_4)_2\text{M}^{\text{II}}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  is composed of  $\text{M}^{\text{II}}(\text{H}_2\text{O})_6$  octahedra,  $\text{SO}_4$  square planar forms, and  $\text{NH}_4$  tetrahedra. The crystal structure is stabilized by the three dimensional network of  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds. The water molecules are arranged in a nearly regular octahedron around the  $\text{M}^{\text{II}}$  ( $=\text{Fe}$  and Zn) ions. Each water molecule forms two hydrogen bonds with the sulfate tetrahedron. The ammonium ion is also hydrogen-bonded to the oxygen atoms of the sulfate groups.<sup>12-14</sup>

Tutton salts with interesting properties have been reported by using various methods in recent years;

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however, some questions are yet to be answered, especially those related to ammonium and water protons at high temperatures. Previous studies have examined the thermodynamic properties and phase transition for  $(\text{NH}_4)_2\text{M}^{\text{II}}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Co}, \text{Fe},$  and  $\text{Zn}$ ) by magic-angle spinning (MAS) nuclear magnetic resonance (NMR) and static NMR.<sup>15-17</sup> At high temperatures, the ammonium and water protons in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  crystals are expected to play a dominant role in their thermal properties.



**Figure 1.** Crystal structure of  $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Fe}$  and  $\text{Zn}$ ) with a monoclinic structure at room temperature.

In this study, the temperature dependence of the  $^1\text{H}$  NMR and  $^{14}\text{N}$  NMR spectra of  $\text{NH}_4$  and  $\text{H}_2\text{O}$  in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , respectively, was investigated using a pulse NMR spectrometer. As far as we know, the role of  $^{14}\text{N}$  in  $\text{NH}_4$  ions in these two crystals has not yet been investigated, and this is the first report on the  $^{14}\text{N}$  NMR spectrum. Notably, their thermodynamic properties at high temperatures were studied by analyzing these environments.

### Experimental Method

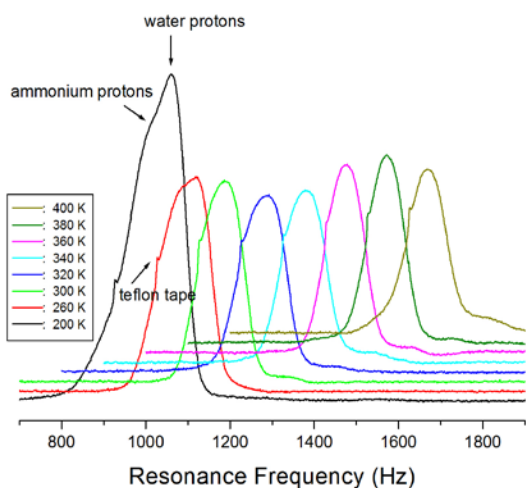
Single crystals of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  were grown by slow evaporation at 293 K from an aqueous solution

containing stoichiometric proportions of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ , and  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$ , respectively. The single crystals of both  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  were hexagonal shapes. Furthermore,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  was a jade-green color, while  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  was colorless and transparent. The  $^1\text{H}$  NMR spectra of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  were measured by using a Varian 200 MHz NMR spectrometer at the Korea Basic Science Institute, Western Seoul Center. The static magnetic field was 4.7 T, and the central radio frequency was set at  $\omega_0/2\pi = 200$  MHz. The  $^1\text{H}$  NMR spectra were measured using a solid-state echo sequence  $\pi/2 - \tau - \pi - \text{acq.}$ , and the  $\pi/2$  pulse time for  $^1\text{H}$  was 2.5  $\mu\text{s}$ .

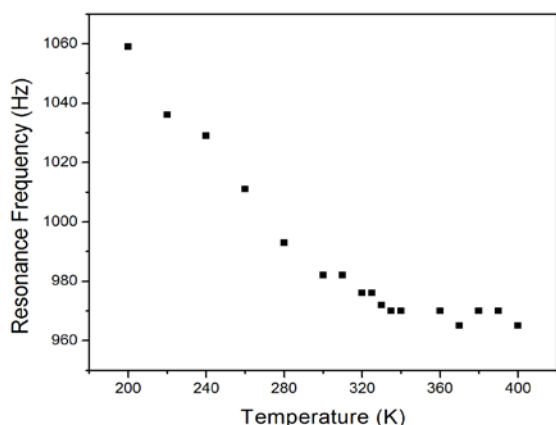
The  $^{14}\text{N}$  NMR spectra of the  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  single crystals, which were obtained by employing a static NMR method, were measured using a Varian UNITY INOVA 600 NMR spectrometer at the Korea Basic Science Institute, Western Seoul Center. The static magnetic field was 14.1 T, and the Larmor frequency was set to  $\omega_0/2\pi = 43.342$  MHz. The magnetic field was applied along the crystallographic c-axis. The spectra were obtained using a solid-state echo sequence  $4 \mu\text{s} - \tau$  (20  $\mu\text{s}$ ) -  $4 \mu\text{s} - \tau$  (20  $\mu\text{s}$ ), and the temperature-dependent NMR measurements were conducted from 180 to 400 K.

### Results and Discussion

The NMR spectrum for the  $^1\text{H}$  nuclei in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  single crystals was measured at several temperatures. Interestingly, the observed  $^1\text{H}$  resonance lines in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  have an asymmetric shape until 320 K and 300 K, respectively. Additionally, the full-width at half-maximum (FWHM) values on the left and right sides are not the same, as shown in Fig. 2 and Fig. 4. The asymmetric line shape is attributed to the two overlapping lines for  $\text{NH}_4$  and  $\text{H}_2\text{O}$ . The protons in  $\text{NH}_4$  and  $\text{H}_2\text{O}$  ions in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  yield two superimposed lines with a ratio of 8:12. The overlapped two signals in



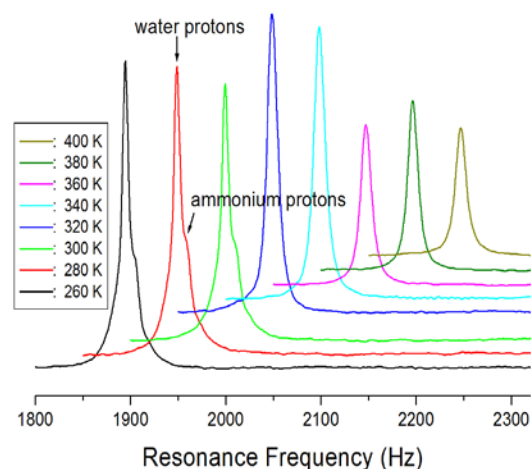
**Figure 2.**  $^1\text{H}$  NMR spectra in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  single crystals as a function of temperature.



**Figure 3.** Resonance frequency of the  $^1\text{H}$  NMR spectra for  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  single crystals as a function of temperature.

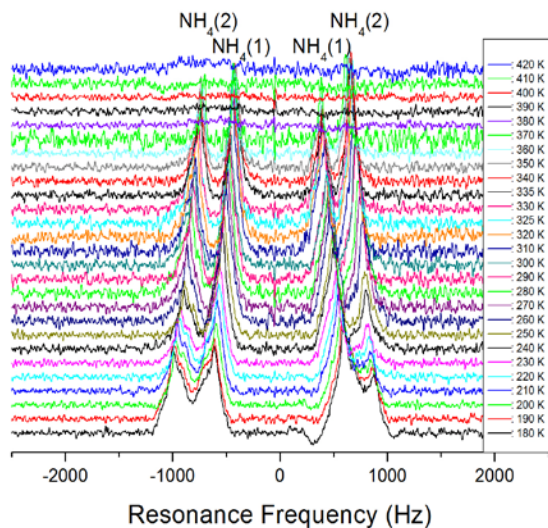
the spectrum for ammonium and water protons, as shown in Fig. 2 and Fig. 4, are obtained by using 8 protons in  $\text{NH}_4$  and 12 protons in  $\text{H}_2\text{O}$ , respectively. The resonance frequency in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  is shown as a function of temperature in Fig. 3. It first shifts abruptly with temperature, and then become nearly constant above 330 K. This change in resonance frequency means that the structural geometry surrounding the protons has changed. It is not easy to separate the signals obtained by  $\text{NH}_4$  and  $\text{H}_2\text{O}$  protons. The signal caused by  $\text{NH}_4$  protons

might include a signal formed by  $\text{H}_2\text{O}$  protons with a broad linewidth. Furthermore, the proton signals do not disappear until 400 K. The line widths due to the  $\text{NH}_4$  and hydrogen bond protons are different in each system. For  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , the line widths are very broad, on the order of 100 Hz, whereas for  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , they are much narrower, on the order of 10 Hz. The line widths of  $^1\text{H}$  nuclei in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  with paramagnetic ions are much broader than those of  $^1\text{H}$  nuclei in  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  without paramagnetic ions. Usually, the line width of crystals with paramagnetic ions is broader than those without paramagnetic ions. The line width is broadened by the magnetic dipole field produced by the paramagnetic ions at the site of  $^1\text{H}$  nucleus.<sup>18</sup> The dipole field of the paramagnetic ions is much stronger (several thousand times greater) than that due to the magnetic moments of the nucleus.

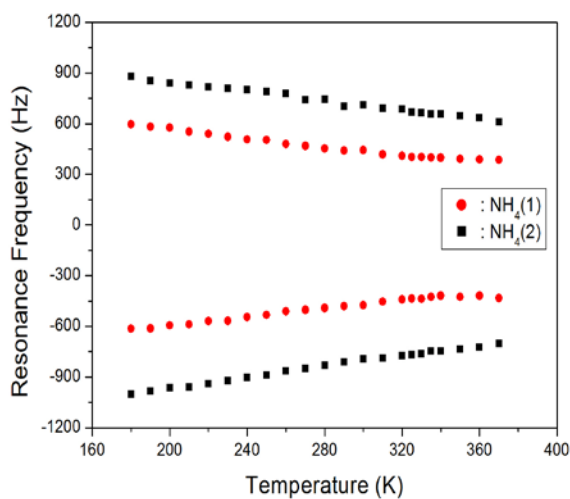


**Figure 4.**  $^1\text{H}$  NMR spectra in  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  single crystals as a function of temperature.

The  $^{14}\text{N}$  NMR spectra for  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  single crystals were obtained using static NMR. Since the  $^{14}\text{N}$  nuclei has a spin  $I=1$ , the presence of a quadrupole perturbation, in addition to the Zeeman coupling, results in the appearance of two NMR lines with a splitting for each physically equivalent site within the unit cell. The in-situ  $^{14}\text{N}$  NMR spectra and the resonance frequency in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

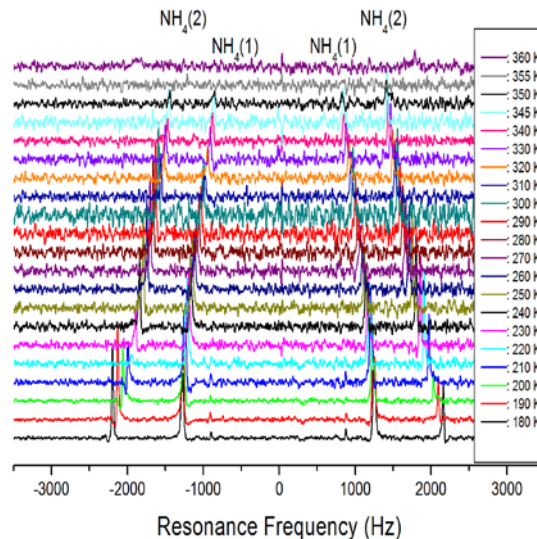


**Figure 5.** In-situ  $^{14}\text{N}$  NMR spectra in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  single crystals as a function of temperature.

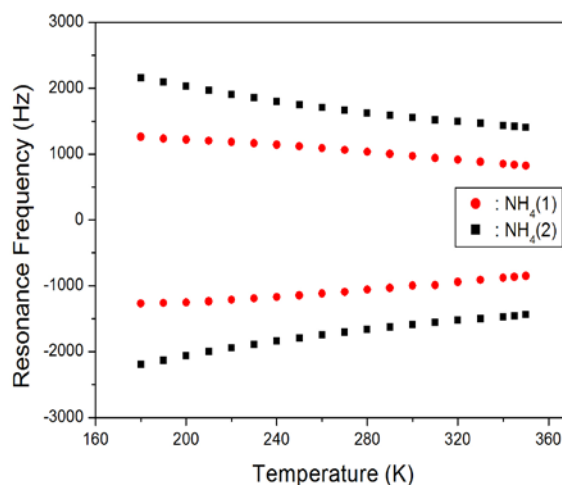


**Figure 6.** Resonance frequency of the  $^{14}\text{N}$  NMR spectra for  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  single crystals as a function of temperature.

single crystals are plotted, respectively, in Fig. 5 ~ Fig. 8, as a function of temperature. The  $^{14}\text{N}$  NMR spectra shown in Fig. 5 ~ Fig. 8 are attributed to the  $\text{NH}_4(1)$  and  $\text{NH}_4(2)$  sites of the two physically inequivalent sites, respectively. Here, the N(1) and N(2) sites in the  $\text{NH}_4(1)$  and  $\text{NH}_4(2)$  ions can be distinguished. Furthermore, the degree of deformation of the  $\text{NH}_4(2)$  ions is larger than that of



**Figure 7.** In-situ  $^{14}\text{N}$  NMR spectra in  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  single crystals as a function of temperature.



**Figure 8.** Resonance frequency of the  $^{14}\text{N}$  NMR spectra for  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  single crystals as a function of temperature.

the  $\text{NH}_4(1)$  ions. This splitting of the  $^{14}\text{N}$  resonance lines slightly decreases with increasing temperature. Note that temperature-dependent changes in the  $^{14}\text{N}$  resonance frequency are generally attributed to changes in the structural geometry, indicating a change in the quadrupole coupling constant of the  $^{14}\text{N}$  nuclei. Here, the electric field gradient (EFG)

tensors at the N sites vary, reflecting the changes in the configuration of the atoms neighboring the  $^{14}\text{N}$  nuclei. In addition, the  $^{14}\text{N}$  signal near 370 K and 350 K for  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , respectively, during heating indicates that the crystal geometry in the vicinity of  $^{14}\text{N}$  in  $\text{NH}_4$  of the two crystals changes. The disappearance of  $^{14}\text{N}$  NMR spectra near 370 K and 350 K may be related to the breaking of the ammonium ions.

## Conclusion

Paramagnetism of the host ions was found to have asignificant effect on the  $^1\text{H}$  line width. The

deformation of  $\text{NH}_4$  and  $\text{H}_2\text{O}$  depends on the temperature of  $\text{NH}_4$  and  $\text{H}_2\text{O}$ . As expected from the crystal structure, there are two physically inequivalent nitrogen sites, N(1) and N(2). The change in the temperature dependence of the signal at high temperatures is related to the loss of  $\text{NH}_4$ . These mechanisms are related to the breakage of weak ammonium ions. From the  $^1\text{H}$  NMR and  $^{14}\text{N}$  NMR spectra results, the type of environment surrounding  $^{14}\text{N}$  in  $\text{NH}_4$  groups than due to the loss of  $\text{H}_2\text{O}$  groups might be disrupted. NMR studies indicate that  $\text{NH}_4^+$  ions in Tutton salts play a crucial role in changing the crystal structure at high temperatures.

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