



^1H and ^{13}C MAS NMR analysis for the role of chemically inequivalent a- $\text{N}(\text{CH}_3)_4$ and b- $\text{N}(\text{CH}_3)_4$ ions in $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$



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H I G H L I G H T S

- The spin–lattice relaxation times T_1 and $T_{1\rho}$ in $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$.
- The static NMR and MAS NMR for ^1H and ^{13}C in $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$.
- Two inequivalent ions a- $\text{N}(\text{CH}_3)_4$ and b- $\text{N}(\text{CH}_3)_4$ by ^{13}C CP/MAS NMR.
- The behaviors of two chemically inequivalent $\text{N}(\text{CH}_3)_4$ groups.

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The spin–lattice relaxation times in the laboratory frame, T_1 , and in the rotating frame, $T_{1\rho}$, for ^1H and ^{13}C in $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ were measured by static NMR and magic angle spinning (MAS) NMR as functions of temperature. The intensities of the ^1H and ^{13}C signals changed near phase transition temperatures T_{C1} and T_{C3} , which indicated that $\text{N}(\text{CH}_3)_4$ plays an important role in these phase transitions. It was thus apparent that the T_1 and $T_{1\rho}$ for ^1H are governed by the same molecular motions. Two inequivalent ions, a- $\text{N}(\text{CH}_3)_4$ and b- $\text{N}(\text{CH}_3)_4$, were identified by ^{13}C cross-polarization (CP)/MAS NMR. From these results, the behaviors of these two chemically inequivalent $\text{N}(\text{CH}_3)_4$ groups in the paraelastic and ferroelastic phases are discussed.

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1. Introduction

The $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ crystal belongs to a large family of well-investigated tetramethylammonium tetrahalogenmetal compounds $[\text{N}(\text{CH}_3)_4]_2\text{MX}_4$ (where M is a bivalent metal and X is a halogen) [1–3]. Crystals of this type have attracted considerable interest because of their multiple phase transitions. In particular, the appearance of successive lattice transformations from a prototype structure to an incommensurate structure to a commensurate structure is a relatively new phenomenon in the investigation of phase transitions. $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ crystals with high optical quality have been reported to undergo three such phase transitions at 263 K, 291 K, and 301 K [4].

$[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ exhibits four phases, I, II, III, and IV, with transition temperatures of $T_{C1} = 301$ K (I–II), $T_{C2} = 291$ K (II–III), and $T_{C3} = 263$ K (III–IV). The highest temperature phase, phase I, has an orthorhombic structure (D_{2h}^{16} space group with $Z = 4$), and its

orthorhombic lattice constants are $a = 9.039$ Å, $b = 15.515$ Å, and $c = 12.268$ Å, which are slightly different from those for the hexagonal form [5,6]. In this phase, a unit cell contains four formula units consisting of two inequivalent kinds of tetramethylammonium ions, hereafter abbreviated a- $\text{N}(\text{CH}_3)_4$ and b- $\text{N}(\text{CH}_3)_4$, and one kind of CuCl_4^{2-} ion [7,8]. A projection of the normal phase I structure viewed from the a -direction is shown in Fig. 1. In phase I, the two stable configurations of CuCl_4 ions or a- $\text{N}(\text{CH}_3)_4$ can be related to each other by a rotation about an axis passing through the center of mass that lies nearly along the c -direction, while for the b- $\text{N}(\text{CH}_3)_4$ configuration, the axis lies nearly along the b -direction. At the other extreme, the space group of the lowest temperature phase, phase IV, is $P112_1/n$ (C_{2h}^5 space group with $Z = 4$), and the unique axis is parallel to the c -axis of phase I. The structure of phase III is monoclinic $P12_1/c1$ (C_{2h}^5 space group with $Z = 12$), with its unique axis parallel to the b -axis of phase I, and phase II is incommensurate, with lattice modulation in the c -direction. As the temperature increases, phase IV transforms into the other monoclinic phase, phase III, at $T_{C3} = 263$ K. At $T_{C2} = 291$ K, phase III transforms to the incommensurate phase II, and phase II transforms to

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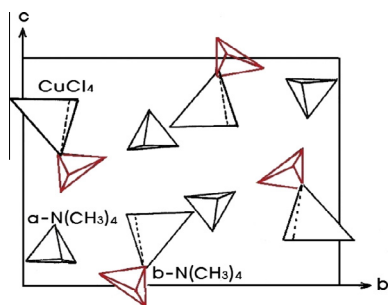


Fig. 1. Crystal structure of $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ in the paraelastic phase, containing two inequivalent kinds of tetramethylammonium ions, a- $\text{N}(\text{CH}_3)_4$ and b- $\text{N}(\text{CH}_3)_4$, and one kind of CuCl_4^{2-} ion. The hydrogen atoms of the CH_3 ion are not shown.

the commensurate phase I at $T_{C1} = 301$ K. These three phase transitions in $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ are ferroelastic–ferroelastic (T_{C3} , IV–III), ferroelastic–paraelastic (T_{C2} , III–II), and paraelastic–paraelastic (T_{C1} , II–I), respectively [6]. Phases III and IV are ferroelastic with a lattice constant ($c = 3c_0$) nearly triple that of the prototype phase [9], and show ferroelastic properties with different domain orientations. The ZnCl_4 ion and a- $\text{N}(\text{CH}_3)_4$ are positioned in a strongly correlated manner, while b- $\text{N}(\text{CH}_3)_4$ is less correlated to the other kind of ions [7].

Ferroelasticity was first recognized as a new property by Aizu in 1970 [10]. The ferroelastic domain occurs in all ferroelastic crystals as a consequence of the reduction in symmetry between the paraelastic and ferroelastic phases. When a ferroelastic crystal is heated, the ferroelasticity usually disappears at a specific temperature at which a structural phase transition between the ferroelastic and paraelastic phases takes place.

In the last two decades, $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ has been the subject of numerous scientific investigations on its thermal conductivity and dielectric properties [11,12], optical transmission and optical birefringence [13,14], phase transitions [15–17], and hydrostatic pressure effects [18–20]. Furthermore, the ^1H spin–lattice relaxation time in the laboratory frame, T_1 , near the phase transition temperatures of $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ crystals was discussed [21].

To better elucidate the nature of the phase transitions in these crystals and, in particular, to obtain a better understanding of their structural geometry, we measured the temperature dependence of the cross-polarization/magic angle spinning (CP/MAS) NMR spectrum and the nuclear spin–lattice relaxation times in the laboratory frame, T_1 , and in the rotating frame, $T_{1\rho}$, for ^1H and ^{13}C in $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$. Based on these results, we discuss the roles of two chemically inequivalent $\text{N}(\text{CH}_3)_4$ groups in the $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$. These investigations allow us to shed light on the role of the $\text{N}(\text{CH}_3)_4$ ions in the phase transition mechanism.

2. Experimental procedure

$[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ single crystals were grown through slow evaporation of an aqueous stoichiometric solution of $\text{N}(\text{CH}_3)_4\text{Cl}$ and CuCl_2 at room temperature. The $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ crystals obtained here were bright orange in color and hexagonal shape.

The spin–lattice relaxation time in the laboratory frame, T_1 , for ^1H was measured using a Bruker 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 to $\omega_0/2\pi = 200$ MHz. The ^1H NMR experiments were performed using a π – t – $\pi/2$ pulse sequence. MAS NMR experiments were performed using a Bruker DSX 400 FT NMR spectrometer at the Korea Basic Science Institute. The ^1H MAS NMR and ^{13}C CP/MAS NMR experiments were performed at the Larmor frequencies of 400.12 MHz and

100.61 MHz, respectively. The samples were placed in the 4 mm CP/MAS probe as powders, and the magic angle spinning rate was set at 10 kHz and 7 kHz for ^1H MAS and ^{13}C CP/MAS, respectively, to minimize the spinning sideband overlap. $T_{1\rho}$ was measured by varying the duration of a ^{13}C spin-locking pulse applied after the CP preparation period. The $\pi/2$ pulse times for ^1H and ^{13}C were 5 μs and 10 μs , respectively, according to the spin-locking field strength of 50 kHz and 25 kHz. The spin–lattice relaxation times in the rotating frame, $T_{1\rho}$, for ^1H and ^{13}C were measured by applying ^1H and ^{13}C spin-locking pulses. The temperature-dependent NMR measurements were carried out in the temperature range of 150–450 K.

3. Experimental results and discussion

Structural analysis for the protons in $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ was carried out using the MAS NMR method. Fig. 2 shows the ^1H MAS NMR spectrum of $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ at room temperature. The NMR spectrum consists of two peaks at chemical shifts of $\delta = 2.45$ ppm and $\delta = 6.80$ ppm. The spinning sidebands are marked with asterisks. The signals at chemical shifts of 2.45 and 6.80 ppm are assigned to the methyl protons, and they are clearly due to magnetically inequivalent sites. Here, two proton peaks at 2.45 and 6.80 ppm of a- $\text{N}(\text{CH}_3)_4$ and b- $\text{N}(\text{CH}_3)_4$ cannot be distinguished. Furthermore, the relative intensities of two ^1H signals increase abruptly as the temperature is raised, as shown in Fig. 3a. Here, the intensities of the two signals are the same within the error range. In addition, the ^1H signals discontinuously change near T_{C3} and T_{C1} , which indicates that the ^1H plays an important role in this phase transition temperature. In particular, the intensities change abruptly near T_{C1} . At phase transition temperature, the ordering of the methyl protons is obvious. Prompted by the result reported in the literature [22] that dynamic ordering of protons occurs in the material goes into the ferroelectric phase, the increase of the intensity of the signal from protons with temperature is related to the ordering of methyl protons. The ^1H chemical shift changes with increasing temperature as shown in Fig. 3b. The chemical shifts near T_{C3} also change abruptly, whereas those near T_{C1} and T_{C2} change more or less continuously.

For the protons in $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$, the spin–lattice relaxation times in the rotating frame $T_{1\rho}$ were also measured as a function of temperature. The nuclear magnetization recovery traces obtained for the protons were described by the following single-exponential function [23]: $S(t) = S_0 \exp(-t/T_{1\rho})$, where $S(t)$ is the magnetization at time t and S_0 is the total nuclear magnetization of ^1H at thermal equilibrium. The recovery traces showed slightly nonexponential decay due to the correction for the relative positions of the three protons in each CH_3 group, but the effects are

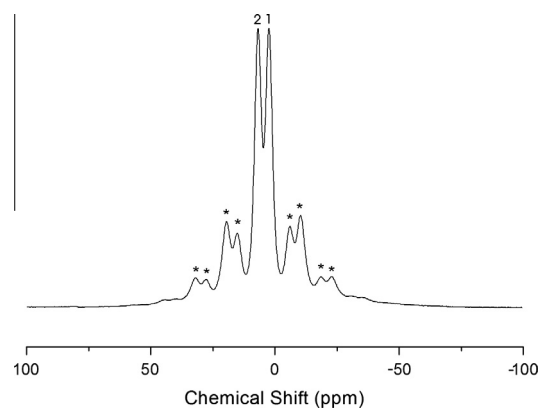


Fig. 2. Solid-state ^1H MAS NMR spectrum for $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ at room temperature.

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