



# NMR study of ferroelastic phase transition of tetramethylammonium tetrabromocobaltate



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## ABSTRACT

Static and magic angle spinning (MAS) nuclear magnetic resonance (NMR) experiments were carried out on  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{14}\text{N}$  nuclei in order to understand the structural changes of the  $\text{N}(\text{CH}_3)_4$  groups in  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  near the ferroelastic phase transition temperature  $T_C$ . The two chemically inequivalent  $\text{N}(\text{CH}_3)_4$  groups were distinguished using  $^{13}\text{C}$  cross-polarization/(CP)MAS and  $^{14}\text{N}$  static NMR. The changes in chemical shifts, line intensities, and the spin-lattice relaxation time near  $T_C$  can be correlated with the changing structural geometry, which underlies the phase transition. The  $^{14}\text{N}$  NMR spectra indicated a crystal symmetry change at  $T_C$ , which is related to the ferroelastic domain with different orientations of the  $\text{N}(\text{CH}_3)_4$  groups. The ferroelastic domain walls were confirmed by optical polarizing microscopy, and the wall orientations were described by the Sapriel theory. The transition to the ferroelastic phase was found to be related to the orientational ordering of the  $\text{N}(\text{CH}_3)_4$  groups.

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## 1. Introduction

A large number of crystals of the  $[\text{N}(\text{CH}_3)_4]_2\text{MCl}_4$  ( $M = \text{Zn}, \text{Co}, \text{Cu}, \text{Mn},$  and  $\text{Cd}$ ) type undergo various successive structural phase transitions with decreasing temperature, including the incommensurate-commensurate phase transition [1–4]. The bromide compounds  $[\text{N}(\text{CH}_3)_4]_2\text{MBr}_4$  undergo the novel ferroelastic phase transition from the orthorhombic to monoclinic symmetry below room temperature, with anomalous behavior in the monoclinic [5–9]. Among these, bis(tetramethylammonium) tetrabromocobaltate (II)  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$ , undergoes a second-order phase transition at the transition temperature  $T_C = 287.6$  K, from an orthorhombic structure with the space group  $Pm\bar{c}n$  to a monoclinic one with the space group  $P12_1/c1$  [5,6,10]. In the high-temperature phase, the two inequivalent  $\text{N}(\text{CH}_3)_4$  cations and the  $\text{CoBr}_4$  anion are disordered symmetrically with respect to the mirror planes. The  $\text{CoBr}_4$  tetrahedron is only slightly distorted, while the distortions in the  $\text{N}(\text{CH}_3)_4$  tetrahedra are large. The  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  single crystal at room temperature (phase I) has an orthorhombic structure with lattice constants  $a = 12.683$  Å,

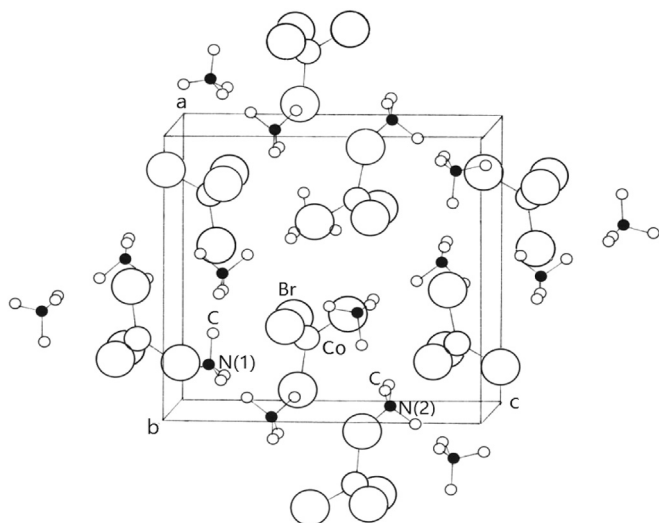
$b = 9.247$  Å,  $c = 16.052$  Å, and  $Z = 4$  [11]. The crystal structure of phase I is shown in Fig. 1 [11].

$[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  has been studied by several experimental methods near the phase transition temperature [5–11]. Its structure and phase transition have been determined by X-ray diffraction [6,11] and dielectric measurements [10], respectively. Recently, static nuclear magnetic resonance (NMR) and magic angle spinning (MAS) NMR measurements of the chemical shifts and spin-lattice relaxations in the rotating frame were carried out for  $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$  [12], which is similar to  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  in crystal structure. Two chemically inequivalent sites,  $\text{N}(1)(\text{CH}_3)_4$  and  $\text{N}(2)(\text{CH}_3)_4$ , were determined using  $^{13}\text{C}$  cross-polarization (CP)/MAS NMR, and the behaviors of the two  $\text{N}(\text{CH}_3)_4$  groups were discussed [12]. However, the characteristic for the inequivalent  $\text{N}(\text{CH}_3)_4$  ions in phase I, and the ferroelastic property in phase II, have not been investigated by NMR methods in  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$ .

Here we studied the temperature dependency of the chemical shifts and intensities in  $^1\text{H}$  MAS and  $^{13}\text{C}$  CP/MAS NMR spectra of  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$ , in order to understand its structural change and the mechanism of the phase transition, with a focus on the role of  $\text{N}(\text{CH}_3)_4$  groups. The  $^1\text{H}$  spin-lattice relaxation time  $T_{1\rho}$  in the rotating frame was obtained to understand the molecular motion near  $T_C$ . The roles of the two chemically inequivalent  $\text{N}(\text{CH}_3)_4$

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**Fig. 1.** Crystal structure of  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  at room temperature. Two inequivalent tetramethylammonium ions,  $\text{N}(1)(\text{CH}_3)_4^+$  and  $\text{N}(2)(\text{CH}_3)_4^+$ , and one of the equivalent  $\text{CoBr}_4^-$  ions are shown. The hydrogen atoms on  $\text{CH}_3$  are not shown.

groups in  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  in each phase are discussed based on these results. Ferroelasticity was observed in the  $^{14}\text{N}$  static NMR spectra measured in the laboratory frame below  $T_C$ . The existence of ferroelasticity was confirmed by optical polarizing microscopy, and the domain wall orientation modeled with the Sapriel theory.

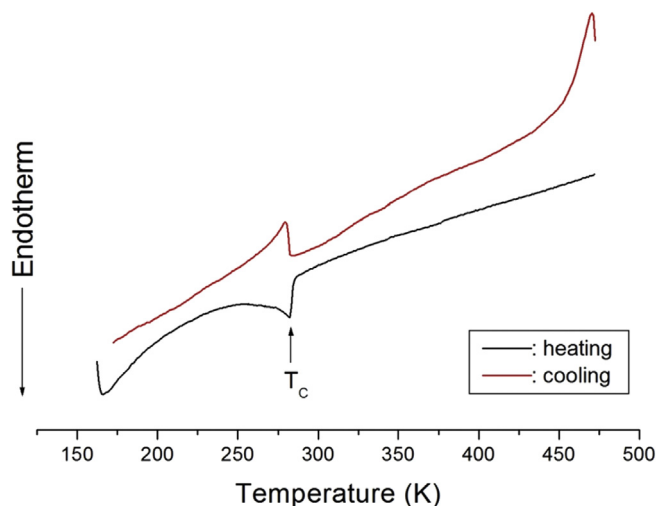
## 2. Experimental procedure

Single crystals of  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  were grown by slow evaporation from an aqueous solution which contained  $\text{CoBr}_2$  and  $\text{N}(\text{CH}_3)_4\text{Br}$  in stoichiometric molar ratio. The  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  crystals are blue and hygroscopic.

The structure of the crystal at room temperature was determined with an X-ray diffraction system at the Korea Basic Science Institute, Seoul Western Center. The single crystal was mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation source. Data collection and integration were performed with SMART (Bruker, 2000) and SAINT-Plus (Bruker, 2001) [13]. The phase transition temperature of the crystal was determined by differential scanning calorimetry (DSC) with a DuPont 2010 DSC instrument at a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ .

The MAS NMR experiments were performed using a Bruker DSX 400 FT NMR spectrometer at the Korea Basic Science Institute, Seoul Western Center. The magnetic field was 9.4 T, and  $^1\text{H}$  MAS NMR and  $^{13}\text{C}$  CP/MAS NMR experiments were performed at the Larmor frequencies of 400.13 MHz and 100.619 MHz, respectively. The powder samples were placed in a 4-mm CP/MAS probe. The MAS rate was set to 10 kHz for  $^1\text{H}$  MAS and  $^{13}\text{C}$  CP/MAS, to minimize spinning sideband overlap. The chemical shifts were relative to the reference signal of tetramethylsilane (TMS). The  $T_{1\rho}$  values for  $^1\text{H}$  were measured using  $\pi/2-t$  acquisition, by varying the duration of the spin-locking pulses. The  $\pi/2$  pulse width used for  $T_{1\rho}$  of  $^1\text{H}$  was 5  $\mu\text{s}$ , according to the spin-locking field at 50 kHz. The temperature-dependent NMR measurements were carried out in the range from 180 to 400 K. The temperature was controlled to an accuracy of  $\pm 0.5 \text{ K}$  by the nitrogen gas flow and heater current. The heating rate was  $1 \text{ }^\circ\text{C}/\text{min}$ , and maintained at a constant value for about 5 min before each NMR measurement.

The  $^{14}\text{N}$  static NMR spectra in the  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  single crystal



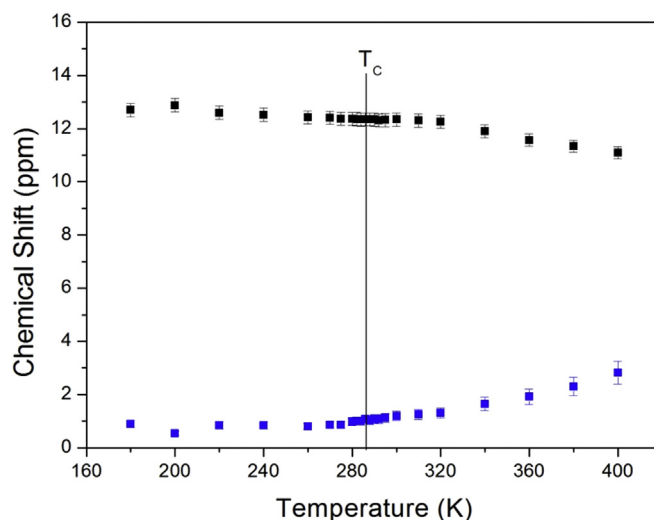
**Fig. 2.** DSC thermogram of the  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$ .

were measured using a Bruker DSX 400 FT NMR spectrometer. The static magnetic field was 9.4 T and the Larmor frequency was set to  $\omega_0/2\pi = 28.9 \text{ MHz}$ . The magnetic field was applied along the crystallographic  $c$ -axis. The  $^{14}\text{N}$  NMR experiments were performed using a one pulse sequence, and the chemical shifts were obtained relative to the reference signal of  $\text{NH}_4\text{NO}_3$ .

## 3. Results and discussion

The  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  crystal exhibits orthorhombic symmetry with cell parameters  $a = 12.677 \text{ \AA}$ ,  $b = 9.236 \text{ \AA}$ , and  $c = 16.052 \text{ \AA}$ , according to our X-ray diffraction results. These values are consistent with those reported by Nishihata and Sawada [11]. The DSC curve reveals an endothermic and an exothermic peak at 282 K during heating and cooling, as shown in Fig. 2. These peaks correspond to the ferroelastic phase transition at a temperature consistent with previous reports [5,6,10].

The NMR spectrum for  $^1\text{H}$  in  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  was recorded by MAS NMR at a frequency of 400.13 MHz. At room temperature, the spectrum consists of two peaks at chemical shifts  $\delta = 1.19 \text{ ppm}$  and



**Fig. 3.** Chemical shifts of  $^1\text{H}$  MAS NMR spectra in  $[\text{N}(\text{CH}_3)_4]_2\text{CoBr}_4$  as functions of temperature.

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