Bromine and Antimony NQR of 4-Aminopyridinium Tetrabromoantimonate(III)

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The temperature dependences of T_1 and T_2 of ^{81}Br and ^{121}Sb NQR have been measured in order to study the phase transition at $T_c = 224$ K as well as the crystal dynamics in 4-aminopyridinium tetrabromoantimonate(III) (4-NH_2PyHSbBr_4). The temperature dependence of T_1 of ^{81}Br and ^{121}Sb NQR follows the usual T^2 law in the range from 80 to 120 K. T_1 is dominated by fluctuations of the EFG at the Br and Sb nuclei due to lattice vibrations.

The T_1 vs. $1/T$ curves in the region between about 120 and 140 K can be described by exponential curves. The activation energies of motions obtained from these curves are similar to those from proton NMR. The exponential changes of T_1 of Br and Sb NQR are attributable to fluctuations caused by the thermal motion of 4-NH_2PyH cations.

Echo signals of Br and Sb NQR in the low temperature phase could not be detected at temperatures higher than 145 and 150 K, respectively, because the S/N ratios became poor owing to the very short T_2. The echo signals could also not be detected at temperatures above T_c because of the short T_2.

Key words: 4-NH_2PyHSbBr_4; Phase Transition; ^{81}Br NQR, ^{121}Sb NQR.

1. Introduction

Halogenoantimonates(III) and -bismuthates(III) with organic cations [1] have found much interest because many of them exhibit interesting physical properties such as ferroelectricity and ferroelasticity. Relatively few pyridinium compounds have, however, been investigated. $C_5H_5NHSbX_4$ (X = Cl and Br), abbreviated PyHSbX_4, has been found to undergo a unique second order phase transition [2 - 4]. In these crystals infinite chains formed by the SbX_4^- anions are packed so as to make a rigid tunnel-like structure wherein the planar cations are stacked [5, 6]. The phase transitions of these compounds have been correlated to the reorientations of the cations, and the N-H···X hydrogen bonds are known to play an important role in the mechanism of the phase transitions [4].

It is interesting to replace the $C_5H_5NH^+$ by 4-$NH_2C_5H_4NH^+$ because the size of the latter is considerably larger than that of the former, and moreover the amino group -NH_2 as well as the pyridine ring N-H of the 4-aminopyridinium ion can contribute to the formation of hydrogen bonds.

A phase transition from the low-temperature phase (LTP) to the room temperature phase (RTP) of 4-aminopyridinium tetrabromoantimonate(III)(4-NH_2-PyHSbBr_4) was confirmed to occur at (224 ± 1) K (T_c) in our previous experiment [7]. The ^{1}H NMR spectra showed a sharp motional narrowing in RTP. The nuclear spin-lattice relaxation time (T_1) of ^{1}H NMR exhibited a jump at T_c. These observations indicated the occurrence of a reorientational motion of the 4-NH_2PyH cations in accordance with the disordering of the cation in RTP.

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In 4-$NH_2PyHSbBr_4$ in RTP, distorted $SbBr_6$ octahedra share their two edges to result in an infinite chain structure [7]. Bridging and terminal bromine atoms are labeled as Br(1) and Br(2), respectively. The Br and Sb NQR spectra were obtained with a super-regenerative spectrometer. Four ^{81}Br NQR lines (ν_{B1} = 132.71, ν_{B2} = 115.38, ν_{B3} = 61.54 and ν_{B4} = 59.31 MHz at 77 K) and two Sb NQR lines (ν_{S1} = 53.78 and ν_{S2} =33.76 MHz at 77 K) were found for the LTP, while a single ^{81}Br NQR line was observed at $T > 276$ K (ν_{BR1} = 121.80 MHz at 300 K).

In the present study, the temperature dependence of T_1 and the spin-spin relaxation time (T_2) of Br and Sb NQR have been measured in order to study the phase transition at 224 K as well as the crystal dynamics and to discuss them on the basis of the temperature dependence of T_1 and T_2 of Sb and Br NQR.

2. Experimental

The crystals of 4-$NH_2PyHSbBr_4$ were obtained from a concentrated hydrobromic acid solution containing stoichiometric amounts of Sb_2O_3 and 4-NH_2-C_5H_4NHBr. The latter was obtained by adding hydrobromic acid to an aqueous solution of 4-NH_2C_5-H_4N. The C, H, and N analyses were consistent with the chemical formula, as shown by the corresponding ratios of the measured and calculated weight percent; found/calc; C: 11.11/11.19; H: 1.32/1.32; N: 5.20/5.22.

The NQR spectra were recorded between 31 and 140 MHz by the cw method using a super-regenerative spectrometer [8]. The NQR measurements were carried in the temperature range 77 to 400 K. T_1 and T_2 of Br and Sb NQR were measured with a conventional pulse spectrometer. T_1 was determined by the echo sequences 90°-t_1-90°-t_2-180°, and T_2 by the pulse sequence 90°-t-180°.

3. Results and Discussion

The two resonance frequencies of Sb NQR in 4-$NH_2PyHSbBr_4$ are similar to those of ^{121}Sb NQR in $C_5H_5NHSbBr_4$ [3]. Then, as a trial, we assigned both of the observed frequencies (ν_{S1} = 53.78 MHz and ν_{S2} = 33.76 MHz at 77 K) to those from ^{121}Sb NQR ($I = 5/2$), resulting in the quadrupole coupling constant (e^2Qq/h) and asymmetry parameter (η) of 186.2 MHz and 0.461, respectively [9 - 11]. The values of the three resonance frequencies of ^{123}Sb NQR ($I = 7/2$), estimated from these values, are 49.74, 31.54, and 26.74 MHz. In the present work we could detect a resonance line of 49.74 MHz at 77 K using the super-regenerative spectrometer, although it was very weak owing to line broadening, so that a very careful measurement was needed. Thus, ν_{S1} and ν_{S2} can be assigned unambiguously to the transitions ±5/2 - ±3/2 and ±3/2 - ±1/2 of ^{121}Sb NQR, respectively.

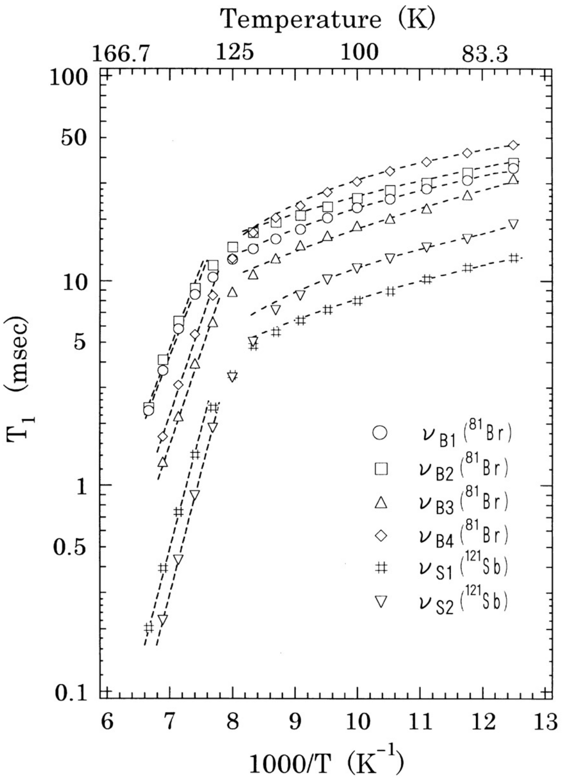

Fig. 1. Temperature dependence of T_1 of ^{81}Br and ^{121}Sb NQR in 4-$NH_2PyHSbBr_4$. The lines inserted in the figure are the calculated straight lines of (1) and the curves are obtained by using the T^2 law (see text).

Figure 1 shows the temperature dependence of T_1 of ^{81}Br and ^{121}Sb NQR. Four Br NQR lines could be unambiguously assigned to ^{81}Br by the observation of the corresponding ^{79}Br lines. All of the recovery curves of nuclear magnetizations of ^{81}Br and ^{121}Sb NQR can be described by an exponential function within errors.

Between 80 and 120 K, the temperature dependence of T_1 of ^{81}Br and ^{121}Sb NQR followed the usual T^2 law [12]. T_1 in this temperature region is considered to be dominated by fluctuations of the EFG at the Br and Sb nuclei due to lattice vibrations [3, 12].

The T_1 vs. $1/T$ curves in the region between 120 and 140 K can be described by the equation [3, 12]

$$T_1 = b\exp(-E_a/RT). \qquad (1)$$

The slope of the ln (T_1) vs. $1/T$ curves in this temperature range gives activation energy of each Br site: E_{aB1} = 14.8 kJ/mol for ν_{B1}, E_{aB2} = 15.0 kJ/mol for ν_{B2}, E_{aB3} = 16.6 kJ/mol for ν_{B3}, E_{aB4} = 16.7 kJ/mol for ν_{B4}. The T_1 values of the two Sb NQR also decrease exponentially with a larger activation energy than those of Br above 120 K: E_{s1} = 21.7 kJ/mol for ν_{s1}, E_{s2} = 21.6 kJ/mol for ν_{s2}. These behaviors are attributable to the modulation effect caused by the reorientation of the 4-NH_2PyH cations, as mentioned below.

In the previous proton NMR experiment (carried out at 33 MHz) [7], it was found that the resonance line width decreased suddenly at T_c to 2.5 Oe due to motional narrowing of hydrogen atoms above T_c. The T_1 values of proton NMR in LTP decreased exponentially with an activation energy of 12.2 kJ/mol as the temperature increased. T_1 abruptly decreased around T_c, as the temperature increased. T_1 had a minimum at 236 K in RTP, and above this temperature it increased exponentially with an activation energy of 25.9 kJ/mol.

From the viewpoint of proton NMR, the 4-NH_2PyH cations are vibrating in LTP. In RTP, however, flipping or rotational motion of the NH_2 group around the C-N bond axis would be excited and the latter one seems to be responsible for the narrow line width of proton NMR. The disorder of the cations observed in the crystal structure analysis suggests that they also undergo a reorientational motion around a principal axis of inertia perpendicular to the pyridine ring. These imply that the hydrogen bonds between the 4-NH_2PyH cations and the bromine atoms in the anions become weak compared with those in LTP.

The activation energies derived from T_1 of ^{81}Br and ^{121}Sb NQR are comparable to that of proton NMR. Therefore, the T_1 behavior of Br and Sb NQR is attributable to the modulation effect caused by the fluctuations by thermal motions of 4-NH_2PyH cations.

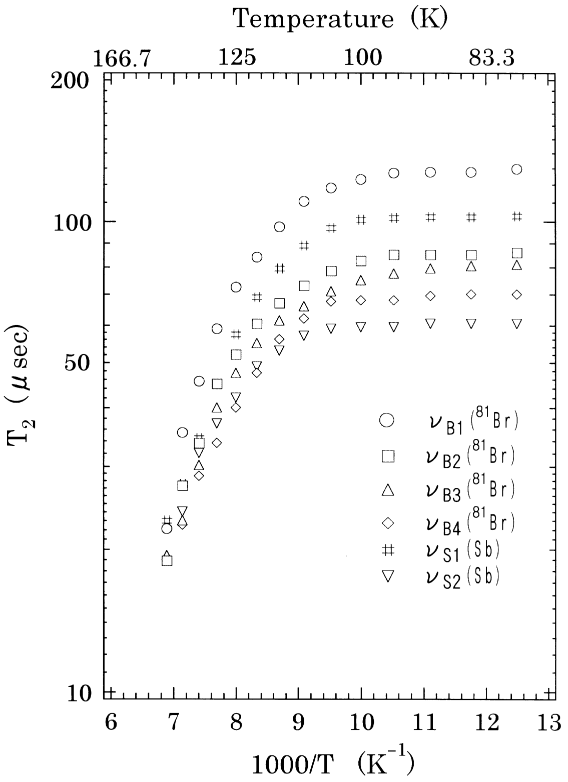

Fig. 2. Temperature dependence of T_2 of ^{81}Br and ^{121}Sb NQR in 4-NH_2PyHSbBr_4.

The reason why the activation energy of Sb atoms is higher than that of Br atoms may be due to other unknown vibrations coupled with the motions of 4-NH_2PyH cations.

Figure 2 shows the temperature dependence of T_2 of ^{81}Br and ^{121}Sb NQR. The T_2 values of ^{81}Br and ^{121}Sb NQR are rather short in the low temperature region and decrease with increasing temperature. Therefore, echo signals of ^{81}Br and ^{121}Sb NQR at temperatures higher than 145 and 150 K, respectively, could not be detected due to the poor S/N ratios caused by the very short T_2. The reason why echo signals could not be detected for ν_{BR1} (= 121.80 MHz at 300 K) in RTP is also considered to be attributable to short T_2.

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