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

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The temperature dependences of \(T_1\) and \(T_2\) of \(^{81}\text{Br}\) and \(^{121}\text{Sb}\) 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\(_2\)PyHSbBr\(_4\)). The temperature dependence of \(T_1\) of \(^{81}\text{Br}\) and \(^{121}\text{Sb}\) 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\(_2\)PyH 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\(_2\)PyHSbBr\(_4\); Phase Transition; \(^{81}\text{Br}\) NQR, \(^{121}\text{Sb}\) 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\(_5\)H\(_5\)NHShX\(_4\) (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 ShX\(_4\)\(^-\) 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\(_5\)H\(_5\)NH\(^+\) by 4-NH\(_2\)C\(_4\)H\(_5\)NH\(^+\) 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 \pm 1) K \((T_c)\) in our previous experiment \([7]\). The \(^1\text{H}\) NMR spectra showed a sharp motional narrowing in RTP. The nuclear spin-lattice relaxation time \((T_1)\) of \(^1\text{H}\) NMR exhibited a jump at \(T_c\). These observations indicated the occurrence of a reorientational motion of the 4-NH\(_2\)PyH cations in accordance with the disordering of the cation in RTP.
In 4-NH₂PyHSbBr₄ in RTP, distorted SbBr₆ 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 ⁸¹Br NQR lines (ν₀₁ = 132.71, ν₀₂ = 115.38, ν₀₃ = 61.54 and ν₀₄ = 59.31 MHz at 77 K) and two Sb NQR lines (μ₅₁ = 53.78 and μ₅₂ = 33.76 MHz at 77 K) were found for the LTP, while a single ⁸¹Br NQR line was observed at T > 276 K (ν₁ = 121.80 MHz at 300 K).

In the present study, the temperature dependence of Tᵰ and the spin-spin relaxation time (Tₛ) 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 Tᵰ and Tₛ of Sb and Br NQR.

2. Experimental

The crystals of 4-NH₂PyHSbBr₄ were obtained from a concentrated hydrobromic acid solution containing stoichiometric amounts of Sb₂O₃ and 4-NH₂C₅H₄NHBr. The latter was obtained by adding hydrobromic acid to an aqueous solution of 4-NH₂C₅H₄N. 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. Tᵰ and Tₛ of Br and Sb NQR were measured with a conventional pulse spectrometer. Tᵰ was determined by the echo sequences 90°-t₁-90°-t₂-180°, and Tₛ by the pulse sequence 90°-t-180°.

3. Results and Discussion

The two resonance frequencies of Sb NQR in 4-NH₂PyHSbBr₄ are similar to those of ¹²¹Sb NQR in C₅H₅NHSbBr₄ [3]. Then, as a trial, we assigned both of the observed frequencies (μ₅₁ = 53.78 MHz and μ₅₂ = 33.76 MHz at 77 K) to those from ¹²¹Sb NQR (I = 5/2), resulting in the quadrupole coupling constant (e²Q/Qₐ/h) and asymmetry parameter (η) of 186.2 MHz and 0.461, respectively [9 - 11]. The values of the three resonance frequencies of ¹²¹Sb 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, μ₅₁ and μ₅₂ can be assigned unambiguously to the transitions ±3/2 - ±3/2 and ±3/2 - ±1/2 of ¹²¹Sb NQR, respectively.

Figure 1 shows the temperature dependence of Tᵰ of ⁸¹Br and ¹²¹Sb NQR in 4-NH₂PyHSbBr₄. The lines inserted in the figure are the calculated straight lines of (1) and the curves are obtained by using the T² law (see text).

![Temperature dependence of T₁ of ⁸¹Br and ¹²¹Sb NQR in 4-NH₂PyHSbBr₄. The lines inserted in the figure are the calculated straight lines of (1) and the curves are obtained by using the T² law.](image-url)
The $T_1$ vs. $1/T$ curves in the region between 120 and 140 K can be described by the equation \[ T_1 = b \exp(-E_a/RT). \] (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 $\nu_{B1}$, $E_{aB2} = 15.0$ kJ/mol for $\nu_{B2}$, $E_{aB3} = 16.6$ kJ/mol for $\nu_{B3}$, $E_{aB4} = 16.7$ kJ/mol for $\nu_{B4}$. The $T_1$ values of the two Sb NQR also decrease exponentially with a larger activation energy than those of Br above 120 K: $E_{aS1} = 21.7$ kJ/mol for $\nu_{S1}$, $E_{aS2} = 21.6$ kJ/mol for $\nu_{S2}$. These behaviors are attributable to the modulation effect caused by the reorientation of the 4-NH$_2$PyH 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$_2$PyH 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$_2$PyH 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$_2$PyH cations.

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