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^1H NMR Study of Molecular Dynamics of 4-apyH Cation under High Hydrostatic Pressure

W. MEDYCKI^a, J. ŚWIERGIEL^b, R. JAKUBAS^c
AND K. HÓLDERNA-NATKANIEC^{b,*}

^aInstitute of Molecular Physics, Polish Academy of Sciences
Smoluchowskiego 17, 60-179 Poznań, Poland

^bInstitute of Physics, Adam Mickiewicz University
Umultowska 85, 61-614 Poznań, Poland

^cFaculty of Chemistry, University of Wrocław
Joliot-Curie 14, 50-383 Wrocław, Poland

Polycrystalline $[4\text{-NH}_2\text{C}_5\text{H}_4\text{NH}] \text{SbCl}_4$ and $[4\text{-NH}_2\text{C}_5\text{H}_4\text{NH}] \text{SbCl}_6$ have been investigated by proton NMR methods between 120 K and 370 K under hydrostatic pressure of 0.1 and 520 MPa. Reduction in the dipolar second moment is interpreted in terms of cation reorientation. Activation energies characterizing the motion increase with increasing pressure.

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1. Introduction

The subject of our study are two ferroic crystals built of an almost planar cation of 4-aminopyridinium $[4\text{-NH}_2\text{C}_5\text{H}_4\text{NH}]^+$ denoted as $[4\text{-apyH}]^+$, tetrahedral $[\text{SbCl}_4]^-$ and octahedral $[\text{SbCl}_6]^-$ anions, respectively. Calorimetric measurements indicate a complex sequence of phase transitions in $[4\text{-NH}_2\text{C}_5\text{H}_4\text{NH}] \text{SbCl}_4$, denoted as $[4\text{-apyH}] \text{SbCl}_4$ at 304 K, 270.5/271 K, 248.5/250.5 K, and 240/245 K [1], and in $[4\text{-apyH}] \text{SbCl}_6$ at 305/380 K on cooling/heating, respectively. The crystal $[4\text{-apyH}] \text{SbCl}_4$ has revealed ferroelectric properties in the temperature range from 240 K to 270 K. In the crystal structure infinite chains formed by anions are packed

*corresponding author; e-mail: natkanie@amu.edu.pl

so as to make a rigid tunnel-like structure, wherein the planar cations are stacked. The phase transitions of these compounds may be correlated to the reorientations of cations, and the pyridine NH–Cl hydrogen bonds play an important role in the mechanism of phase transition.

Molecular dynamics in polycrystalline samples has been determined from the temperature dependences of the second moment of ^1H NMR line (M_2) at different values of hydrostatic pressure.

2. Experimental

The proton magnetic resonance studies were performed on a laboratory made spectrometer operating in the double modulation system at 25 MHz. The coil from the resonance circuit was placed in the high pressure chamber cooperating with the high pressure helium compressor. The value of hydrostatic pressure was changed up to 520 MPa, and controlled by the analysis of the manganin resistor.

The temperature of the sample could be changed within the range of 100–400 K and stabilized to the accuracy of ± 0.5 K at any chosen value.

3. Results and discussion

The $[4\text{-apyH}]^+\text{SbCl}_4$ and $[4\text{-apyH}]^+\text{SbCl}_6$ were subjected to ^1H NMR studies. The second moment was determined from the derivative of absorption NMR line. The measurements were performed on heating the samples. Figure 1a and b shows the temperature dependence of the second moment of ^1H NMR lines at the pressure of 0.1 and 520 MPa.

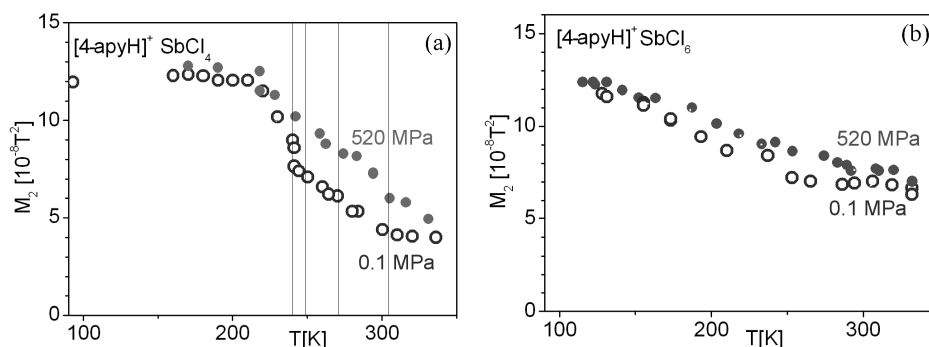


Fig. 1. Temperature dependence of the second moment of ^1H NMR line of $[4\text{-apyH}]^+\text{SbCl}_4$ (a) and $[4\text{-apyH}]^+\text{SbCl}_6$ (b) at different hydrostatic pressures.

The NMR line narrows nearly continuously from 12 to $4 (\times 10^{-8} \text{ T}^2)$ in the temperature range of 200–310 K for $[4\text{-apyH}]^+\text{SbCl}_4$, and from 12 to $7 (\times 10^{-8} \text{ T}^2)$ in the range of 125–300 K for $[4\text{-apyH}]^+\text{SbCl}_6$. The hydrostatic pressure of 520 MPa

caused a shift of the temperature dependence of second moment towards higher temperatures.

Since the crystal's structure is known, a theoretical value of the second moment could be calculated using the dipolar theory of van Vleck for rigid structure. The experimental results are discussed in terms of the theory of dipolar interactions [2, 3]. The possibility of the amino group reorientation about its C₂ axis, the stochastic in-plane jumps over three inequivalent barriers [4] and pseudohexagonal reorientation between six equivalent wells of the [4-apyH]⁺ cations is analysed. The second moment decreased from 9.5 calculated for the rigid structure to 9.0 and then 2.3 (in 10⁻⁸ T²), on subsequent onset of internal rotations.

The NMR spectrum of [4-apyH] SbCl₄ is narrowing above the phase transition temperature from polar (V) to ferroelectric (IV) state at 240 K. However, in [4-apyH] SbCl₆ the onset of cation reorientation is observed just close to 125 K in the low-temperature phase. The activation energy of this process can be estimated, within the 20% error, from the Waugh–Fiedin dependence $E_a \approx 37 T$ [5], where T is the transition temperature, found as that corresponding to the point in the middle of the section of the temperature changes in the second moment. At atmospheric pressure E_a is estimated as 8.8 and 7.2 kcal/mol for [4-apyH] cation connected with tetrahedral and octahedral anion, respectively. Under the pressure of 520 MPa the height of the barrier for the cation reorientation increases to 10.4 and 8.2 kcal/mol in the samples studied, respectively [4, 6].

On heating, the crystal structures of both samples change from monoclinic $P2_1/c$ in the low-temperature phase to C_2/c in the high-temperature phase, but

TABLE

Comparison of the hydrogen bond length (in Å) of [4-apyH] SbCl₄ and [4-apyH] SbCl₆.

Hydrogen bond (atoms notation as in [1])	[4-apyH] SbCl ₄ ⁻	[4-apyH] SbCl ₄ ⁻	[4-apyH] SbCl ₆
	$T = 100$ K [1]	$T = 258$ K [1]	$T = 293$ K [1]
N(1)–H–Cl	3.272	3.280	3.563
		3.286	
N(5)–H–Cl	3.514	3.516	3.807
	3.524	3.611	
		3.703	
		3.483	
		3.519	
		3.652	

in a different way [1, 4, 6]. In particular, [4-apyH] SbCl₄ shows a number of phase transitions that seem not to affect the nearly continuous character of changes in the second moment of NMR line observed under the atmospheric pressure and under 520 MPA. The external stress induces changes in many properties of the material, among others in the thermodynamic properties, crystalline structure, and hence a shift in the phase transition temperatures. In both compounds of the same cation [4-apyH] with inorganic anions: SbCl₄ and SbCl₆, the effect of pressure on the phase transition temperatures has not been recognised yet.

In the crystal structure of the samples studied, the 4-apyH organic cation is connected with inorganic anion by the hydrogen bond NH–Cl. As follows from the data collected in the Table, the hydrogen bonds in the crystal of [4-apyH] SbCl₆ salt are weaker.

4. Conclusions

The effect of high hydrostatic pressure on internal dynamics of the cation has been observed by NMR continuous wave study. The weaker hydrogen bonds in [4-apyH] SbCl₆ seem to be a reason for a higher mobility of its [4-apyH]⁺ cation. The intermolecular interaction has been shown to influence the activation energy of the cation in-plane reorientation.

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