

^1H NMR Study on the Motion of NH_4^+ in Ferroelectric $\text{NH}_4\text{H}(\text{ClH}_2\text{CCOO})_2$ and Mixed $(\text{NH}_4)_{1-x}\text{Rb}_x\text{H}(\text{ClH}_2\text{CCOO})_2$ ($x = 0.15$)

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Temperature-dependent proton NMR relaxation time measurements have been performed at 60 MHz in order to study the NH_4^+ dynamics in ferroelectric $\text{NH}_4\text{H}(\text{ClH}_2\text{CCOO})_2$ and mixed $\text{Rb}_x(\text{NH}_4)_{1-x}(\text{ClH}_2\text{CCOO})_2$, where $x = 0.15$. The data indicate that the dominant relaxation mechanism for the NMR spin-lattice relaxation time T_1 in both crystals involves simultaneous NH_4 group reorientation about their C_2 and C_3 symmetry axis in the paraelectric phase. Details of the NH_4^+ reorientation have been inferred from analysis of temperature dependence of T_1 assuming the Watton model. The activation parameters of the motions have been determined. It has been found that the substitution of Rb does not change the activation parameters of the NH_4 group dynamics.

Key words: Ferroelectrics; Phase Transition; NMR.

Introduction

Paraelectric ammonium hydrogen bis-chloroacetate (AHCA) crystallizes in the monoclinic symmetry space group $C2/c$. The low-temperature phase transition at 120 K leads to a ferroelectric phase with the space group Cc [1, 2]. The crystal structure of AHCA involves a network of N-H...O type hydrogen bonds connecting bis-chloroacetic anions with NH_4^+ cations. Ichikawa [1, 2] has studied the crystal structure of AHCA in both phases and has found a displacement of the atoms in the dimeric anions and of the ammonium cations relative to the anions. The results of numerous experimental studies [3 - 6] and the analysis of our previous high pressure results (NQR [7 - 9], dielectric [10]) have shown the importance of hydrogen bonds associated with the dimer anion in the ferroelectric phase transition in chloroacetates. The mechanism of the phase transition seems to be well described by means of a phenomenological explanation with a pseudo-spin-lattice coupled-mode model [11]. Our crystal, compared to KH_2PO_4 , is a special case of a hydrogen bonded ferroelectric crystal. The hydrogen bonds in AHCA are very short.

Therefore the order and disorder states are almost equivalent. That is why the symmetrical double-well hydrogen bond potential hill is very small and behaves approximately as a single minimum. The pseudospin formalism is phenomenologically applicable, but the double-well potential of the hydrogen bonds behaves like a single-well potential [11]. The molecular mechanism of the phase transition in AHCA seems to be still unclear.

To get more information we studied the cation effect on the symmetry of the hydrogen bonds in acidic chloroacetic salts [12]. It was found that in the large family of acidic salts of monocarboxylic acids only those containing NH_4^+ and $\text{N}(\text{CH}_3)_4^+$ cations exhibit ferroelectric properties. The differences between the ferroelectric and paraelectric phases were also reflected in the Raman and IR spectra for some internal vibration bands of the ammonium and tetramethylammonium cations. It was, therefore, suggested that the transition in chloroacetates occurs due to a modification of hydrogen bonds at low temperatures, with probably at the same time "freezing out" relatively free ammonium rotation. Within this hypothesis, the transition should be of order-disorder type with ro-

Table 1. The ferroelectric phase transition temperatures of AHCA and mixed crystals derived from dielectric measurements [15].

	x [%]	T_c [K]	$T_{c\text{AHCA}} - T_c$ [K]
$\text{NH}_4\text{H}(\text{ClH}_2\text{CCOO})_2$	–	119.7	–
$\text{Rb}_x\text{NH}_{4(1-x)}\text{H}(\text{ClH}_2\text{CCOO})_2$	5	110.4	9.3
$\text{Rb}_x\text{NH}_{4(1-x)}\text{H}(\text{ClH}_2\text{CCOO})_2$	15	98.2	21.5
$\text{K}_x\text{NH}_{4(1-x)}\text{H}(\text{ClH}_2\text{CCOO})_2$	15	105.5	14.2

tational disorder of protons as well as NH_4^+ ions in the high temperature phase. Unfortunately, contrary to expectations, NMR experiments carried out by Yamamoto at 10 MHz have not revealed any sign of a phase transition within experimental precision [13]. He has found that the onset of reorientation of the NH_4^+ ion in the AHCA crystal leads to the observed reduction of the proton second moment and gives rise to the minimum of T_1 . A single minimum of T_1 at 118 K was observed, i. e. very close to the ferroelectric phase transition temperature ($T_c = 120$ K). Therefore, the random reorientation of ammonium groups is the only mechanism being seen in the proton NMR relaxation experiments, especially near the T_1 minimum region. Probably this is why Yamamoto could not see any evidence of a phase transition in AHCA crystals. Therefore we have measured the temperature dependence of the ^1H NMR spin-lattice relaxation time of protons at 60 MHz. An increase in the resonance frequency from 10 to 60 MHz is expected to shift the T_1 minimum towards higher temperatures, beyond the range of the ferroelectric transition.

Recently, the results of dielectric measurements of mixed crystals $\text{K}_x(\text{NH}_4)_{1-x}\text{H}(\text{ClH}_2\text{CCOO})_2$ (abbreviated KAHCA) and $\text{Rb}_x(\text{NH}_4)_{1-x}\text{H}(\text{ClH}_2\text{CCOO})_2$ (abbreviated RbAHCA) have shown that substitution of K^+ or Rb^+ for the ammonium cations lowers considerably the ferroelectric phase transition temperature T_c [14], see Table 1. Additionally it was found from dielectric relaxation results [6, 15] that the relaxation soft mode, clearly evidenced in close vicinity of T_c in the paraelectric phase, was due to the NH_4^+ thermal motion.

To get more information about a role NH_4^+ ions in the ferroelectric phase transition mechanism, we have measured the temperature dependence of the ^1H NMR spin-lattice relaxation times of protons at 60 MHz in $(\text{NH}_4)\text{H}(\text{ClH}_2\text{CCOO})_2$ and mixed $\text{Rb}_x(\text{NH}_4)_{1-x}\text{H}(\text{ClH}_2\text{CCOO})_2$ ($x = 0.15$) over a wide range of temperature.

Experimental

The preparation of pure $\text{NH}_4\text{H}(\text{ClH}_2\text{CCOO})_2$ crystals was described in [16]. Mixed crystals were prepared by dissolving the parent compounds $\text{NH}_4\text{H}(\text{ClH}_2\text{CCOO})_2$ and Rb_2CO_3 with a small excess of ClCH_2COOH in ethanol solution. The resulting precipitate was washed with ethanol, and large single crystals of $\text{Rb}_x(\text{NH}_4)_{1-x}\text{H}(\text{ClH}_2\text{CCOO})_2$ ($x = 0.15$) were grown by controlled evaporation from ethanol solution. The ammonium concentration ($1 - x = 0.85$) was estimated using elemental analysis.

Polycrystalline samples of the dried substance were evacuated and sealed in glass tubes for NMR measurements. The proton spin-lattice relaxation times $T_1(^1\text{H})$ were measured with a home made pulse spectrometer at 60 MHz by a saturation method. The errors of the T_1 values were estimated to be 5%.

Results and Calculations

The proton spin-lattice relaxation time of AHCA plotted against the reciprocal temperature is shown in Figure 1. The magnetisation recovery from saturation was exponential within the whole temperature range. A single minimum of T_1 was observed at 130 K with a value of about 36.3 ms. The activation energy values determined from the slopes of $\ln T_1$ versus $1000/T$ at the low and high temperature sides of the T_1 minimum are nearly the same. Contrary to expectations, there is no evidence of a distinct anomaly in the vicinity of T_c .

Details of the ammonium ion reorientation have been inferred from an analysis of the T_1 minima taking into account simple model proposed by Watton [17, 18], wherein simultaneous NH_4^+ reorientation around the C_3 and C_2 axes was considered. We have used this model earlier for the interpretation of NMR results of other crystals. Assuming the Watton model, the intramolecular contribution to the NMR spin-lattice relaxation rate is given by

$$\frac{1}{T_1} = \frac{1}{6}\gamma^2\Delta M_2 \left[\frac{\tau_3}{1 + \omega_0^2\tau_3^2} + \frac{4\tau_3}{1 + 4\omega_0^2\tau_3^2} + \frac{3\tau}{1 + \omega_0^2\tau^2} + \frac{12\tau}{1 + 4\omega_0^2\tau^2} \right], \quad (1)$$

where $\tau^{-1} = 1.5(1/\tau_2 + 1/\tau_3)$ and the correlation times τ_2 and τ_3 , describing reorientations around the

Table 2. The activation energies, E_{a2} and E_{a3} , and the preexponential factors, τ_{02} and τ_{03} , for ammonium reorientation in AHCA and RbAHCA, derived from T_1 data.

Crystal	Motion	E_a [kJ/mol]	τ_0 [s]
AHCA	C_2	8.9	$4.1 \cdot 10^{-13}$
	C_3	11.8	$1 \cdot 10^{-13}$
RbAHCA	C_2	8.7	$5.7 \cdot 10^{-13}$
	C_3	11.8	$1 \cdot 10^{-13}$

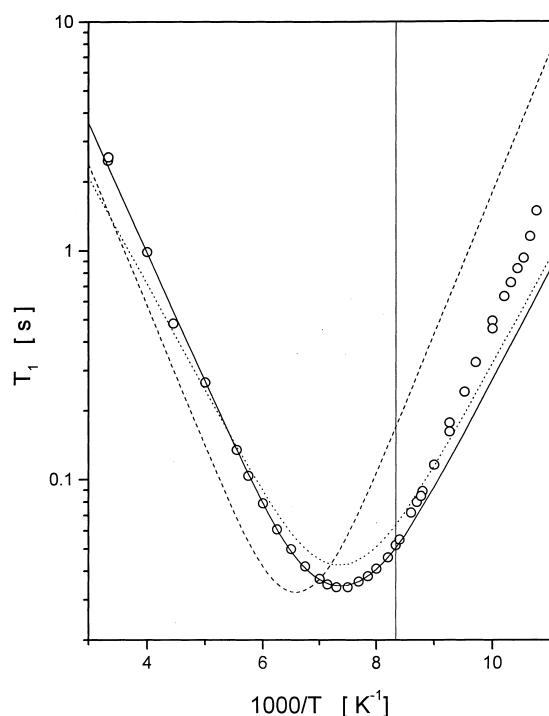


Fig. 1. The proton spin-lattice relaxation time in $\text{NH}_4\text{H}-(\text{ClH}_2\text{CCOO})_2$ plotted against the reciprocal temperature. The experiment was done at 60 MHz. The solid curve was obtained by fitting (1) to the T_1 data (see text). The broken lines indicate the contributions to T_1 from the C_2 (---) and C_3 (- - -) type of motion.

C_2 and C_3 axes, respectively, are related to the activation energies through the Arrhenius relation

$$\tau_{ci} = \tau_{0i} \exp(E_{ai}/RT),$$

where $i = 2$ or 3 and indicates type of motion.

A graphic illustration of the best fit is given by the solid line in Figure 1. The activation energies E_{ai} and preexponential factors τ_{0i} obtained from the fitting procedure are given in Table 2.

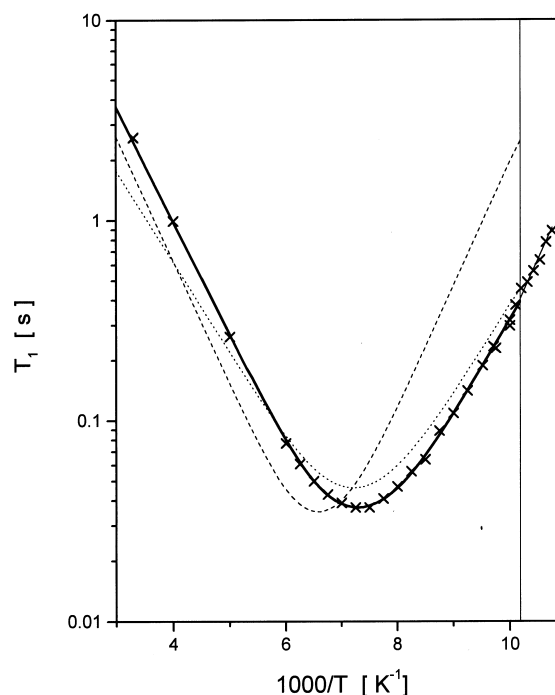


Fig. 2. The temperature dependence of the ^1H NMR spin-lattice relaxation in mix $\text{Rb}_x(\text{NH}_4)_{1-x}\text{H}(\text{ClH}_2\text{CCOO})_2$ crystal, where $x = 0.15$ (abbreviated RbAHCA). The experiment was done at 60 MHz. The solid curve was obtained by fitting (1) to the T_1 data. The broken lines indicate the contributions to T_1 from the C_2 (---) and C_3 (- - -) type of motion.

Since the activation parameters for the C_3 and C_2 type of motion in AHCA do not differ very much therefore, according to the Watton model a single T_1 minimum has been observed. The relaxation then appears as that of a single process, but with different activation energies on the high and low temperature side of the minimum. The high temperature relaxation is dominated by the threefold reorientation, while the low temperature relaxation is dominated by the twofold one [17, 18].

In order to study the NH_4^+ cation dynamics in mixed $\text{Rb}_x(\text{NH}_4)_{1-x}\text{H}(\text{ClH}_2\text{CCOO})_2$ (abbreviated RbAHCA) crystal, where $x = 0.15$, we have measured the temperature dependence of the proton NMR spin-lattice relaxation time. The experiment was done at 60 MHz, as previously. The results are shown in Figure 2. The temperature variation of the proton spin-lattice relaxation time of RbAHCA shows a single minimum at $T_{\text{min.}} = 138$ K with a value 37 ms. The difference in the slopes of the $\ln T_1$ vs. $10^3/T$ curve at the low and high temperature sides of the T_1 mini-

imum was about 26%. Additionally, the potential barrier hindering NH_4 rotation in the ferroelectric phase obtained from the slope of the T_1 versus $10^3/T$ curve is higher, $E_a = 12.5$ kJ/mol, than that in the paraelectric one, i. e. 8.9 kJ/mol. Below that, the ferroelectric phase transition temperature, $T_c = 98.2$ K, found previously with DSC and dielectric measurements in the salt studied [15], the slope of the T_1 vs. $10^3/T$ curve was changed. In the analysis of the experimental results, the same Watton model for the motion of the ammonium groups was taken into account. The results of the fitting procedure are given in Table 2.

Discussion

The results of our NMR study, carried out for AHCA and mixed RbAHCA crystals, have shown that the activation parameters for the ammonium cation motion in investigated crystals are the same in the paraelectric phase (Table 2). This suggests, that substitution Rb^+ for ammonium cations does not affect the motion of the ammonium groups [1, 2]. The relaxation, interpreted in terms of the Watton model, then appears as that of a single process, but with different activation energies on the high and low temperature side of the minimum. The high temperature relaxation is dominated by a threefold reorientation, while the low temperature relaxation is dominated by a twofold one [17, 18]. A possibility that some motion of the ammonium cations may be playing a role in the transition seems to be ruled out because our proton NMR study indicated no discontinuous change at the transition temperature in the temperature dependence of T_1 . However, the potential barrier hindering NH_4 rotation in the ferroelectric phase of AHCA, obtained from the slope of the T_1 versus $10^3/T$, is higher ($E_a = 11.3$ kJ/mol) than that extrapolated from paraelectric phase (8.9 kJ/mol), which can be assigned to the structural phase transition changing the barriers for the ammonium group motion. The small effect of phase transition on the temperature dependence of proton NMR relaxation suggests that changes in the mode of motion of NH_4^+ , if any, do not seriously participate in the critical phenomenon near T_c . The results

confirmed in a way those reported by Yamamoto [13]. The random reorientation of the NH_4 groups is the only mechanism being clearly seen by the proton NMR relaxation experiment, especially near the T_1 minimum region.

On the other hand, the replacement Rb^+ for ammonium cations shifts T_c towards the lower temperatures, therefore destroys the ferroelectric phase probably due to breaking up the coupling between protons and ammonium ions via chloroacetic anions. In the ferroelectric phase of RbAHCA the cations experience a higher potential energy hindering their motion, $E_a = 12.5$ kJ/mol below T_c . Our NMR investigations confirmed the difference in mobility of the NH_4 groups in the paraelectric and ferroelectric phases. This means that the ammonium cations, in a way, are involved in the ferroelectric phase transition. However, the question about what mode of motion is the soft one near T_c seems to be still open.

It should be emphasised that the fast reorientations of the NH_4 groups mask the movement of the protons in the hydrogen bonds effectively enough, so that we are not able to say anything about the shape of the potential barriers in these bonds and their change at the phase transition.

Conclusions

1. The dominant relaxation mechanism for T_1 in both crystals can be attributed to simultaneous NH_4^+ cations reorientation around their C_2 and C_3 symmetry axes.
2. The activation parameters for the ammonium cation motions in both investigated crystals have the same values. This suggests that substitution Rb^+ for ammonium cations does not affect the motion of the ammonium groups.
3. On the other hand, substitution Rb^+ for ammonium cations in the investigated crystals lowers T_c . Our NMR studies evidence the difference in the mobility of the NH_4 groups in the two phases, the paraelectric and ferroelectric one in both crystals.
4. The question, which mode of motion is the soft one, seems to be still open.

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