# The Proton Motion Effect in the Ferroelectric Phase of $NH_4H(ClCH_2COO)_2$ *

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The effects of pressure up to $3 \cdot 10^2$ MPa on the $^{35}Cl$ NQR line splitting in the ferroelectric phase of $NH_4H(ClCH_2COO)_2$ was studied from 77 K to $T_c$. The results are interpreted in terms of the so called pseudo-spin-lattice coupled mode model. A correlation was found between the magnitude of the $^{35}Cl$ NQR line splitting and the pseudo-spin component $\langle S_z \rangle$ (the order parameter of the applied model).

## Introduction

The appearance of ferroelectricity in ammonium hydrogen di-chloroacetate (abbreviated as AHCA), $NH_4H(ClCH_2COO)_2$, is very interesting. The crystal is composed of $NH_4^+$ ions and chloroacetate anions $H(ClCH_2COO)_2^-$ in which the two chloroacetate radicals are kept together by a short hydrogen bond (0.2457 nm). AHCA crystallizes with the space group C2/c in the paraelectric and Cc in the ferroelectric phase [1, 2]. In the paraelectric phase the nitrogen atom of the $NH_4^+$ group lies on the twofold axis. The chloroacetate radicals are crystallographically equivalent and are connected with a hydrogen bond across the center of symmetry [1]. The crystal exhibits ferroelectricity below 120 K. In the ferroelectric phase the dimeric anion loses its center of symmetry and the chlorine sites at the ends of the anion become crystallographically inequivalent [2]. The nitrogen atom of the $NH_4^+$ ion is shifted by 0.024 nm along the c axis of the crystal. The direction of spontaneous polarization coincides with that of the hydrogen bond direction (120).

Chihara et al. [3, 4] have presented a series of papers reporting $^{35}Cl$ NQR studies of this compound and its deuterated analog. It was found that a single resonance line in the high temperature paraelectric phase splits into a pair in the ferroelectric phase. The separation between the quadrupole resonance lines is proportional to the spontaneous polarization which can be considered as the order parameter.

Neither the crystallographic [1, 2] nor the NQR [3, 4] investigations answer the question whether we have an order-disorder or displacive type of transition.

The presence of a short hydrogen bond and the effect of deuteration (deuteration shifts the transition temperature to 130 K [3]) suggest an order-disorder type of transition. Chihara proposed that the hydrogen bond has a double well minimum potential. In the high temperature phase the protons rapidly tunnel between these minima which are separated by a low and narrow potential barrier. Therefore the mechanism becomes an order-disorder Ising spin system. From their calorimetric studies, however, Chihara and Inaba [5] discarded this possibility because the observed entropy is small compared to R ln 2 predicted from the order-disorder model.

In a previous paper we have studied the pressure dependence of the $^{35}Cl$ NQR in AHCA [6], determining $dT_c/dp$ and evaluating, on the basis of the Blinc pseudo-spin model, the proton tunneling energy $\Omega$, the dipole-dipole interaction $J$ and the pressure dependences of these parameters.

We also have pointed out that the pseudo-spin lattice coupling mode model is phenomenologically applicable to AHCA and that the proton motion in hydrogen bridges plays a primary role in the ferroelectricity of AHCA crystal.

In the present work we search for the correlation between the pressure and temperature dependence of the separation of the $^{35}Cl$ NQR lines and the

microscopic parameters $\Omega$ and $J$ characterizing the dynamic properties of the hydrogen bonds of the AHCA crystal.

## Experimental Details

The NQR measurements were carried out with an ISSz 1–2 type pulse spectrometer.

Polycrystalline AHCA used in the present study was the same as prepared previously [6].

For the details of our pressure device we refer to [7].

## Results and Discussion

The pressure dependence of the $^{35}Cl$ NQR line splitting in AHCA at various temperatures is shown in Figure 1. An increase in pressure lowers the NQR

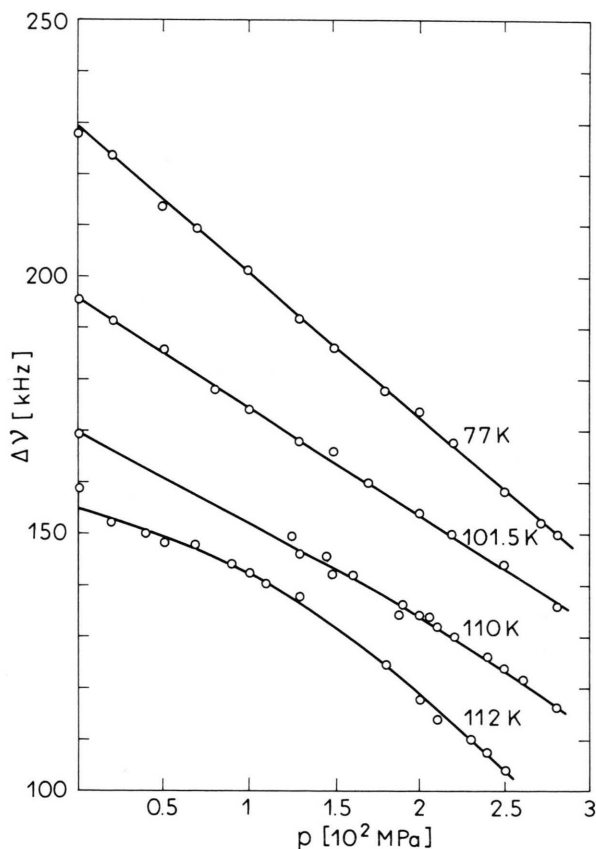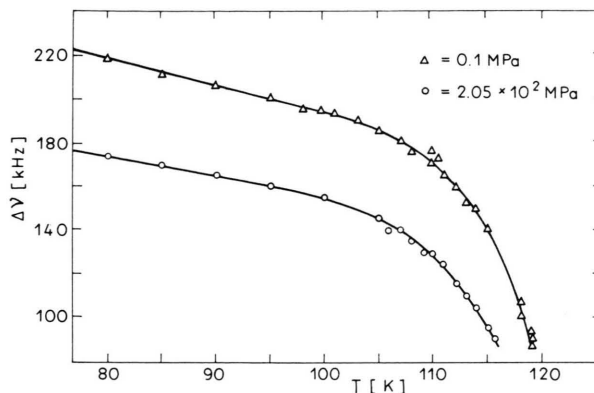Fig. 2. The NQR line splitting in AHCA vs. temperature at pressures of 0.1 MPa and $2.05 \times 10^2$ MPa.
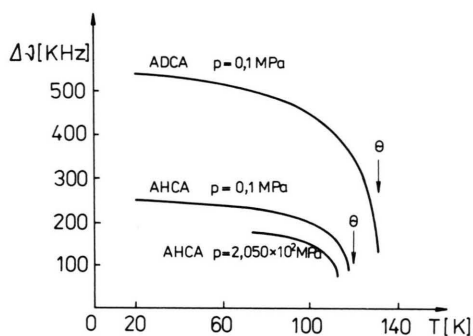
Fig. 3. The NQR line splitting vs. temperature for AHCA and ADCA at atmospheric pressure (part of results are taken from literature [3]) and for AHCA at $2.05 \times 10^2$ MPa.

Fig. 1. The pressure dependence of the $^{35}Cl$ NQR line splitting for AHCA at 77 K, 101.5 K, 110 K and 112 K.

line splitting, the effect is stronger in the vicinity of the phase transition. Figure 2 shows the NQR line splitting in AHCA vs. temperature measured isobarically at pressures of 0.1 MPa and $2.05 \cdot 10^2$ MPa. Increase in pressure lowers the NQR line splitting and the point of its disappearance is shifted downward with the slope $dT_c/dp = -1.95 \cdot 10^{-2}$ deg/MPa.

It is noteworthy that high pressure has an effect contrary to that of deuteration. Figure 3 shows the NQR line splitting vs. temperature in the polar phase of AHCA and ADCA measured at atmospheric pressure (part of the results are taken from literature [3]) as well as $\Delta\nu_{NQR}$ vs. temperature measured by us at a pressure of $2.05 \cdot 10^2$ MPa. Deuteration shifts $T_c$ upwards ($T_c^D = 131$ K) and enhances the NQR line splitting. The high pressure acts in a way to destroy the ferroelectric phase in AHCA.
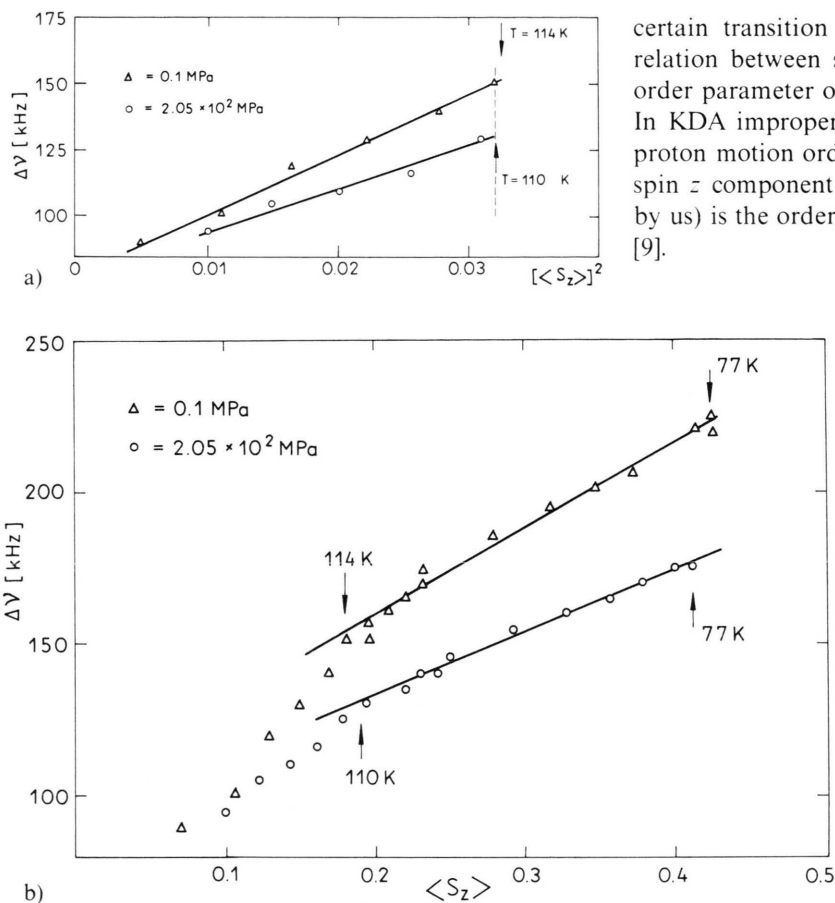
a)



b)

Fig. 4. The NQR line splitting vs. $\langle S_z \rangle$, a) in the critical fluctuations region, b) far from critical fluctuations region.

certain transition parameters [8]. In addition, the relation between spontaneous polarization and the order parameter of the phase transition is linear [9]. In KDA improper type ferroelectrics the degree of proton motion ordering (the mean value of pseudo-spin $z$ component $\langle S_z \rangle$ in the Blinc model applied by us) is the order parameter of the phase transition [9].

The isotope and pressure effects create a further evidence of the decisive role of the hydrogen bonds in the ferroelectric phase transition in AHCA.

On the basis of the pressure dependence of the ³⁵Cl NQR in AHCA one can suggest that, similar to KDA (KH₂AsO₄), AHCA crystal belongs to the group of improper ferroelectrics with the phase transition initiated by ordering of the proton motion in the hydrogen bonds.

Improper ferroelectricity seems very probable because the heat capacities show a lambda-shape anomaly with an entropy of transition of about 0.5 R ln 2. It is only half of what one would expect for a simple order-disorder transition and it is too large for a displacive type of transition [5]. The Curie-Weiss constant for AHCA is also very small ($C = 80$ K) [10].

In improper ferroelectrics the polarization is not the order parameter of the phase transition and arises spontaneously only due to coupling with

Chihara has drawn attention to the fact that the separation between the NQR resonance lines in AHCA is proportional to the spontaneous polarization $P_s$ [3]. Because of that we searched for the correlation between the ³⁵Cl NQR line splitting in AHCA and $\langle S_z \rangle$.

The mean value of the pseudo-spin component $\langle S_z \rangle$ is an implicit function of the temperature $T$, tunneling energy $\Omega$, and dipole-dipole interaction $J$ [9]:

$$\sqrt{(2\Omega)^2 + (J\langle S_z \rangle)^2}$$
$$= \frac{1}{2} J \, \mathrm{tgh} \, \frac{\sqrt{(2\Omega)^2 + (J\langle S_z \rangle)^2}}{2 k T}. \quad (1)$$

Using (1) we calculated the temperature dependence of $\langle S_z \rangle$ for various values of pressure. The values of $\Omega(p)$ and $J(p)$, given in [6], were taken for the calculations. The theoretical relationships $\langle S_z \rangle$ $(\Omega, J, T)$ obtained by us were compared with the

experimental relation $\Delta\nu_{NQR}$ derived from our NQR studies. Results are shown in Figure 4.

In the critical fluctuation region ($T_c - T < 5$ K) the $^{35}$Cl NQR line splitting in AHCA is proportional to the square of the order parameter $\langle S_z \rangle$, see Figure 4a.

The critical fluctuations region is extensive. The dimension of this region has been already confirmed by investigation of dielectric [10] and quadrupole relaxation [4].

The hydrogen bond in AHCA is very short. If the two minima potential exists, for such a short bond the minima are separated by a low barrier. Hence, the tunneling frequency of the proton should be rather low and the proton-lattice coupling weak. As a consequence of this the critical fluctuations region can be extensive.

Far from the critical fluctuations region ($T_c - T > 5$ K) a linear relation between the $^{35}$Cl NQR line splitting and $\langle S_z \rangle$ occurs (Figure 4b). On the grounds that, the NQR line splitting in the polar phase of AHCA is proportional to the spontaneous polarization; a linear relation between $P_s$ and $\langle S_z \rangle$ is expected.

## Conclusion

In conclusion we suggest that AHCA crystal belongs to the group of improper ferroelectrics with the phase transition initiated by ordering of proton motion in hydrogen bonds. The most adequate model for the phase transition is the so called pseudo-spin lattice coupled mode model. The degree of proton motion ordering, characterized by $\langle S_z \rangle$, is the order parameter of the phase transition.

The present investigation is in no way complete. For better understanding of the mechanism of the phase transition in this crystal, and for the verification of the model parameters further NQR studies of deuterated salt will be highly interesting.

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