CHAPTER - SIX

(VI)

STUDY OF PHASE TRANSITIONS IN AMMONIUM HYDROGEN DI-CHLOROACETATE $NH_4H(ClCH_2COO)_2$ AND ITS DEUTERATED FORM $ND_4D(ClCH_2COO)_2$ *

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6.1. INTRODUCTION

Ammonium monochloro-acetate $[ClCH_2COONH_4]$ (abbreviated as AHCA) crystallises in two forms. Form I is orthorhombic with space group $P2_12_12_1$ and form II is monoclinic with space group $C_{2/c}$, at room temperatures. Form II exhibited ferroelectricity below $T_C = 120°K$ [1]. The appearance of ferroelectricity in AHCA and its deuterated salt $ND_4D(ClCH_2COO)_2$ (abbreviated as ADCA) is very interesting. Deutero-ammonium deuterium bis-(chloro-acetate) has a ferroelectric phase transition at $T_{CD} = 130°K$ [1]. This shift of transition temperature on deuteron indicates the importance of hydrogen bonds associated with the dimer anion in the ferroelectric phase transition.

The crystal structure of ammonium hydrogen dichloro-acetate $[NH_4H(ClCH_2COO)_2]$ has been determined by Ichikawa [2] with the three-dimensional X-ray analysis at room temperature (i.e. in the paraelectric phase). The crystals are monoclinic with the space group $C_{2/c}$ and cell dimensions are as follows.

$a = 10.521$ Å

$b = 11.576$ Å

$c = 8.387$ Å

$\beta = 119.48°$

$Z = 4$

According to their studies ammonium ion lies on a two-fold axis and makes a hydrogen bond with an oxygen atom from each of six different chloroacetate residues. The acidic hydrogen atom is involved in a very short hydrogen bond O ··· O = 2.432±0.005 Å, which connects two chloroacetate residues across /1 a centre of symmetry (figure (6.1)). This signifies that in the paraelectric phase the chloroacetate radicals CA_1 and CA_2 7/2 (Fig.(6.2)) are crystallographically equivalent and are connected by a short O-H···O hydrogen bond across the centre of symmetry. The problem of the symmetrical OHO bond is interesting, /4 since a model of order-disorder type is accepted in most hydrogen-bonded ferroelectrics.

The crystal structure of the ferroelectric phase, below 120°K of AHCA was also determined by Ichikawa [3]. The symmetry of the crystal changes from $C_{2/c}$ to C_c. At the transition, the two acid radicals become non-equivalent. So in the low-temperature phase, it is revealed that the dimeric anion loses its centre of symmetry and the chlorine sites, at the ends of the anion, become crystallographically inequivalent [3].

From the detailed study of nuclear quadrupole reasonance [4] it also follows that all chlorine atoms in this crystal are equivalent at room temperature but there are two inequivalent chlorine sites in the low temperature phase which supports the X-ray analysis [2,3].

/2 Along the ferroelectric axes [102] the dielectric 2
/8 constants obey the Curie-Weiss law with a Curie-Weiss constant 6

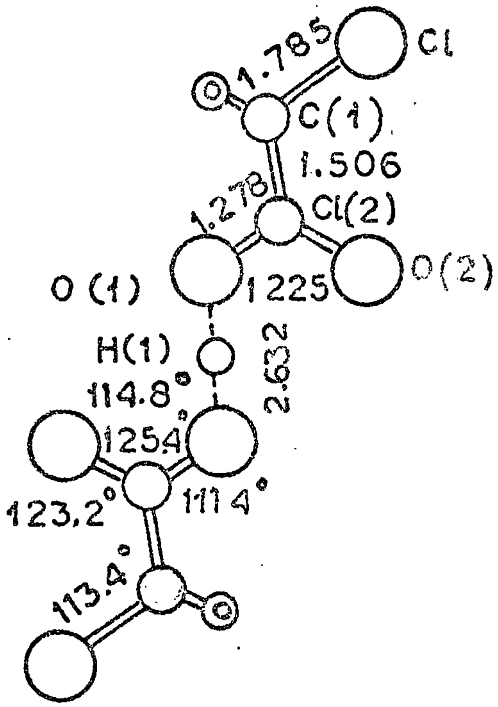

Fig.(6.1)

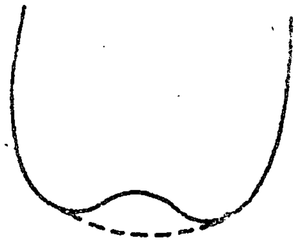

Fig.(6.2)

Fig.(6.1). Bond distances (in angstroms) and bond lengths in the AHCA chloroacetate residue indicating the dimeric structure of AHCA connecting the hydrogen bonds O-H•••O [3].

C(1) C(2) O(1) = 111.4°

C(1) C(2) O(2) = 123.2° .

Fig.(6.2). Nature of the symmetric double well potential.

of 44°C . The direction of the O-H···O hydrogen bond coincides roughly with the direction of the sponteneous polarization. At the Curie-point, sponteneous polarization jumps to about 0.05 $\mu c/cm^2$ and reaches 0.18 $\mu c/cm^2$ at -195°C [1] . The discontineous changes in the sponteneous polarization and the dielectric constant suggest that the phase transition is of the first order in nature. Chihara et al. [4] also pointed out that the separation between the quadrupole resonance lines is proportional to the sponteneous polarization which can serve as the order parameter.

Considering the features for the transition of ADCA or AHCA viz.

i) the transition temperature becomes 10° higher upon deuteration,

ii) the sponteneous polarization is small

iii) differential thermal analysis shows that the transition is accompanied with a small thermal anomaly over a very broad temperature region

iv) the NQR doublet spacing shows a large effect of deuteration (by a factor of 2.17), Chihara et al [4] suggested the possibility of an order-disorder or a displacive type of mechanism. They also proposed that the hydrogen bond has a double-well minimum potential, (figure (6.2)) one deeper than the other in the low temperature phase. In the high temperature phase protons will see, as also observed from X-ray studies [2,3], a symmetric double-well minimum potential, and

/2

the protons rapidly tunnel between these minima which are separated by a low and close potential barrier. The mechanism, therefore, now becomes that of an order-disorder Ising spin system. Hence the usual pseudo-spin model [6,7,8] seems to be applicable.

But from their (Chihara et al.) recent calorimetric studies [5] Chihara et al. discarded this possibility on the grounds that the observed entropy is small compared to the value of $R\ln 2$ predicted from the order-disorder model. They rejected the possibility of a double-well potential as the O-H···O distance (2.432 Å) at room temperature is inadequate for a double-well potential approximation. They also pointed out that the entropy of transition as well as the jump of the heat capacity is too large for a displacive type of transition.

Raman and infrared spectra of AHCA and DADCA showed that the ammonium ions are distorted even in the high temperature phase and the distortion becomes larger below T_c [7].

However, from the work of Elliott [9] and Larkin and Vask [10] we find that an Ising model in a transverse field coupled with proton-lattice interactions is suitable for describing many kinds of phase transitions in crystals assuming small displacement of ions or groups in the lattice. Thus it may appear suitable to apply the coupled pseudo-spin-lattice model to the present salt.

The purpose of this chapter is to extend the pseudo-spin model [11] for the explanation of the anomalous dielectric behavior of AHCA and ADCA. It has been shown for the first time that such a model can very well explain the anomalous dielectric as well as ferroelectric behavior of these salts.

6.2. THEORETICAL CALCULATION

Considering the anharmonic contribution of the lattice vibration, the proton-lattice coupled mode model can be written as (see chapter IIIA and IIIB)

$$\begin{aligned} H = & -2\Omega \sum_i X_i - \frac{1}{2} \sum_{i,j} J_{ij} Z_i Z_j \\ & - \sum_{i,\underset{\sim}{q}} V_{i\underset{\sim}{q}} Z_i Q_{\underset{\sim}{q}} \\ & + \sum_{\underset{\sim}{q}} \left(\frac{1}{2M}\right) P_{\underset{\sim}{q}} P_{-\underset{\sim}{q}} + \frac{1}{2} M\omega_{\underset{\sim}{q}}^2 Q_{\underset{\sim}{q}} Q_{-\underset{\sim}{q}} \\ & + \sum_{\underset{\sim}{q}_1,\underset{\sim}{q}_2,\underset{\sim}{q}_3,\underset{\sim}{q}_4} \Gamma_{\underset{\sim}{q}} (\underset{\sim}{q}_1,\underset{\sim}{q}_2,\underset{\sim}{q}_3,\underset{\sim}{q}_4)\, Q_{\underset{\sim}{q}_1} Q_{\underset{\sim}{q}_2} Q_{\underset{\sim}{q}_3} Q_{\underset{\sim}{q}_4} \end{aligned} \qquad \text{(VI-1)}$$

where Ω is the tunneling frequency, J_{ij} is the proton-proton interaction, $V_{i\underset{\sim}{q}}$ is the proton-lattice interaction. $Q_{\underset{\sim}{q}}$ and $P_{\underset{\sim}{q}}$ are the normal coordinates and the conjugate moments respectively. $\underset{\sim}{q}$ is the phonon wave vector with bare harmonic frequency $\omega_{\underset{\sim}{q}}$ and $\Gamma_{\underset{\sim}{q}}$ is the fourth order anharmonic part of the lattice vibrations. Without going into the details of the theoretical calculations which has been shown earlier (chapter IIIA and IIIB), only the working formula are presented here. Calculation of thermal Green's functions like $\langle\langle Q_q | Q_{-q} \rangle\rangle$ gives the energy spectrum from which the transition temperature T_c is obtained (as the soft mode frequency $\omega_{\underset{\sim}{q}} \to 0$, using ferroelectric instability condition)

$$\Omega / k_B T_C = \tanh^{-1}(4\Omega / J^*) \qquad \text{(VI-2)}$$

where,

$$J^* = J_o + \bar{V}^2(0)/(\omega_o^2 + \bar{\Gamma}(\underset{\sim}{q}, T_C))$$

$$\bar{V}(\underset{\sim}{q}) = \sum_{\underset{\sim}{q}} V_{\underset{\sim}{q}} \qquad \text{(VI-3)}$$

$\bar{\Gamma}(\underset{\sim}{q}, T_C)$ is the contribution from the anharmonic part of the Hamiltonian (equation (VI-1)) and J_o is the pure proton-proton interaction. The static susceptibility calculated from

$$\chi(\omega, \underset{\sim}{q}) = -\left(\frac{n\mu^2}{v_o}\right) \langle\langle Q_{\underset{\sim}{q}} | Q_{-\underset{\sim}{q}} \rangle\rangle \qquad \text{(VI-4)}$$

follows a Curie-Weiss law with Curie constant,

$$C = \frac{n\mu^2}{v_o}\left[\bar{\Gamma}_o^1 + \frac{k_B\, 8\Omega^2 \bar{V}^2(0)\left[1 - \tanh^2 \frac{\Omega}{k_B T_C}\right]}{k_B^2 T_C^2 \left[4\Omega + J_o \tanh\left(\frac{\Omega}{k_B T_C}\right)\right]^2}\right]^{-1} \qquad \text{(VI-5)}$$

In equation (VI-5) we have put $\bar{\Gamma}(\underset{\sim}{q}=0, T = T_C) = k_B T_C \bar{\Gamma}_o' = \bar{\Gamma}_o' T_C$ (where $\bar{\Gamma}_o' = k_B \bar{\Gamma}_o(0, T_C)$). k_B is the Boltzman constant, T is the absolute temperature, 'n' is the number of pseudo-spins in the unit cell of volume v_o, and μ is the dipole moment along the direction of spontaneous polarization. The dielectric constant ε is calculated from the relation,

$$\varepsilon = 1 + 4\pi\chi \qquad \text{(VI-6)}$$

The calculated and observed [1] dielectric constants (ε) /3 at different temperature are shown in figure (6.3). Experimental data of dielectric constant are fitted with the present theory taking $T_c = 120^oK$ [4] instead $T_c = 128^oK$ [1]. Later findings /b of Chihera et al. [4] and Chihara and Inaba [5] indicate that the transition temperature should be 120^oK. Proper temperature corrections in the dielectric constant data have also been made before fitting with the theory.

6.3. RESULTS AND DISCUSSION

Since none of the model parameters (Ω, V_o, J^*, $\overline{\Gamma}_o'$) are known we simply vary these parameters and fit the transition temperature T_c (equation (VI-2)) and the Curie constant C (equation (VI-5)) for a single set of the parameters in table (VI.1). For a particular value of Ω the value of J^* becomes fixed (from equation (VI-2)). As our purpose is to fit the experimental data of T_c and C, we put a fixed value of $\overline{\Gamma}'(0,T_c) = 5.0\times10^{-19}$ erg K^{-1}, calculated for hydrogen-bonded /a ferroelectric systems like KDP(KH_2PO_4) and vary Ω (for different sets) to find $\overline{V}_o$. Further since J_o is also unknown we take $J_o \simeq 0.75\, J_o^*$ as is true for KDP type crystals [12].

It may be concluded from the good fitting of the experimental data of Curie constant, transition temperature /3 and the dielectric constants (figure (6.3)) that the pseudo-spin lattice coupled mode (PLCM) model is phenomenologically

TABLE (VI.1)

Pseudo-spin model parameters and other constants for $NH_4H(C\ CH_2COO)_2$ AHCA single crystal.

$P_s = 0.18\ \mu c\ cm^{-2}$; $C = 317/4\pi\ K$

$\frac{n\mu^2}{v_o} = 1.6151 \times 10^{-16}$; $n = 4$

$v_o = 881.49 \times 10^{-24}\ cm^3$; $\mu = 0.2 \times 10^{-18}$ esu-cm.

 cm^{-1}	J^* cm^{-1}	J_o cm^{-1}	V_o cm^{-1}	$_o$ erg K^{-1}
0.1	284.697	213.552	5.5710	0.05×10^{-17}
15.0	288.884	216.663	5.6091	0.05×10^{-17}
25.0	296.295	222.221	5.8900	0.05×10^{-17}
49.0	328.301	246.225	6.9170	0.05×10^{-17}
50.0	330.045	247.534	6.9670	0.05×10^{-17}
75.0	383.005	287.254	8.9150	0.05×10^{-17}
80.0	395.560	296.670	9.4232	0.05×10^{-17}
100.0	451.238	338.429	11.9752	0.05×10^{-17}

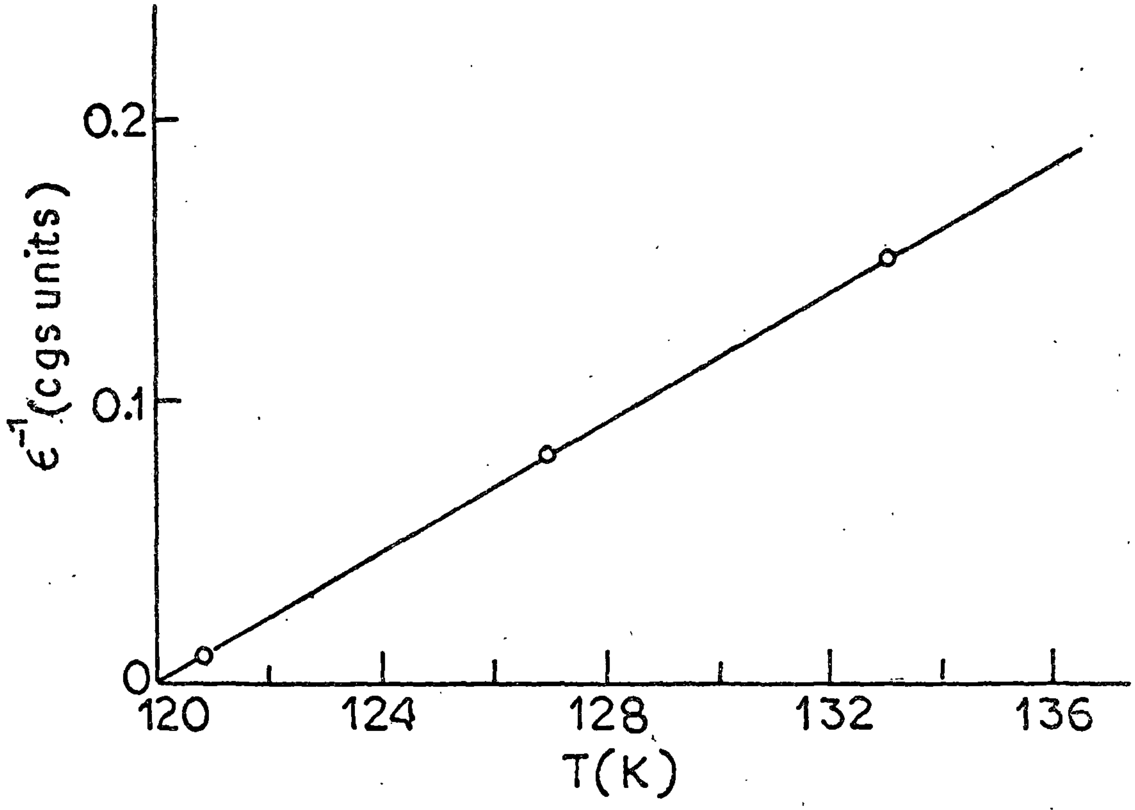

Fig. (6.3). Thermal variation of the inverse dielectric constant.

Contineous line - present theory;

circles - experimental.

We used T_c = 120°K instead of 128°K for the reason discussed in the text.

applicable for AHCA salt if the first suggestion of Chihara et al. [4] is correct. For finding the model parameters further elaborate IR and Raman studies may be fruitful. From these studies the O-H streching bonds, as were observed by Hadzi [13] in the KDP system can also be detected. One piece of evidence for the short hydrogen bonds, of course, comes [4] from the IR measurements of Chihara et al. [5] at 900 cm^{-1} and another at 850 cm^{-1}. We cannot, however, ascertain whether (900-800) = 50 cm^{-1} is equivalent to the separation 2Ω, if the procedure of Hadzi [13] is followed. It appears that Ω is very small for AHCA compared to KDP where $\Omega \sim 80$ cm^{-1} [12]. As a consequence, the order and the disorder states are almost equivalent. That is, the symmetrical double well potential hill is very small and behaves
/2 approximately as a single minimum (figure (6.2)) which was also pointed out by Ichikawa [3] from X-ray study. The present crystal is therefore a special case where the pseudo-spin formalism is phenomenologically applicable and the double well potential behaves as a single-well potential giving the appreciably low value of the observed entropy 2.90 JK^{-1} mol^{-1},
/ar compared to Rln2.

Here we would like to mention that for a deeper understanding of the mechanism of phase transition in this crystal, and for the verification of the model parameters calculated, further studies, both theoretical and experimental (IR and Raman) will be highly interesting. From this study with the pseudospin model a critical evaluation of the PLCM model will also be possible.

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