Curie-point Behaviour of Partially Deuterated H- Bonded Ferroelectric Crystals

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Abstract

Using Green’s function method, modified Hamiltonian and G.A. Samara’s approximations, Curie-temperatures for various KDP-DKDP mixed Crystals are Calculated Considering Various Models of phase transition mechanism. The values thus obtained are compared with the results of others and the results thus obtained using PLCM model are found in quite agreement.

Keywords: Curie-temperature, ferro-electric crystals, Green’s function, Hamiltonian, Hydrogen Bonding, Pseudo-Spin lattice coupled-model, Tunneling Model.

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1. Introduction

Several models have been proposed to explain the mechanism of phase transition in hydrogen bonded ferro-electric crystals. Substitution of deuterium for hydrogen in these Type of crystals produces large isotope effect on ferro electric properties of these crystals. To obtain a full understanding of the role of the hydrogen bond in the phase transition, it is important to study variation of dielectric properties like Curie-point with the degree of deuteration (x). The mixed crystals K(H₁₋ₓDₓ)₂PO₄ is considered to be a random system where each hydrogen-bond is randomly occupied by a hydrogen or a deuterium. Tokunaga and Matsubara discussed transition temperature of these mixed crystals using tunneling model. The effect of random configuration was not taken into consideration by them. Transition temperature (T_c) shifts upwards as much as 100k on complete deutration. Although the effect of deuteration on T_c is known as the tetragonal isomorphs of KH₂PO₄. In KDP, the hydrogen bonds form a three
dimensional network in the crystal lattice. Deguchi et al.\textsuperscript{4} investigated the complex dielectric constant in partially deuterated CDP-DCDP crystals.

Chaudharia and Saha\textsuperscript{5} studied the properties of mixed KDP-DKDP crystals theoretically. In our earlier works\textsuperscript{6-8}, we have theoretically investigated the isotope-effect on Curie-constant, dielectric constant and sound attenuation in hydrogen-bonded ferro-electric crystals. The purpose of this paper is to investigate the Curie-point response of the mixed crystals $K_2(H_{1-x}D_x)PO_4$ using various models of phase transition and to analyse the results of various models.

**Theory**

In order-disorder model, total system is represented by proton or deuterium configurations. The Hamiltonian is of the typical order-disorder type and is given as–

$$H = -\sum_{ij} J_{ij} S_i^z S_j^z$$

(1)

Here, $S_i$ is the Ising operator and $J_{ij}$ is the general effective interaction between the $i$th and $j$th protons. In order-disorder model, the proton system plays the role of trigger. The mechanism of the dynamical interaction between the order-disorder proton system and $f$-mode was introduced\textsuperscript{9} so that the dielectric-dispersion in paraelectric phase can be accounted for. Since the crystal structure changes at the transition-point even in the order-disorder type, it is required to treat the relation between the order-disorder system and lattice instability.

The idea of the “Tunneling model” was introduced by Blinc\textsuperscript{10}. In this model, each proton on the corresponding hydrogen bond makes a tunneling motion between two equilibrium positions. The static effective interaction makes a tunneling particle stay at one side of two positions and the tunneling motion disturbs this inclination. The transition point is determined by balancing these two opposite inclinations. If the deuteron with its heavier mass is substituted for the proton, it reduces the frequency of the tunneling motion, disturbs less the localization of the proton and results in the larger Curie-temperature. The Hamiltonian is expressed in terms of the spin operators and obtained by adding the tunneling term $\left(-\sum \Omega S_i^x\right)$ to equation (1). The approximated form of the Hamiltonian is–

$$H = -\sum_i 2\Omega S_i^x - \sum_{ij} J_{ij} S_i^z S_j^z - \frac{1}{2} \sum B_{ij} S_i^z S_j^z$$

(2)

where $\Omega$ is the tunneling frequency. $B_{ij}$ is $10^{-1}$ to $10^{-2}$ times smaller than $\Omega$, so terms containing $B_{ij}$ is generally omitted. Large isotope effect of on $T_c$ is well accounted for this model i.e. it gives larger $T_c$ values for deuterated crystals as compared to undeuterated crystals.

The static and dynamical properties are examined on the basis of coupled Hamiltonian (coupled mode or PLCM model) and it is well established that proton system and optical phonon plays an essential part in ferroelectric phase transition.

The Hamiltonian of the coupled system\textsuperscript{6} is given as
Curie-point Behaviour of Partially Deuterated H- Bonded Ferroelectric Crystals

\[
H = -2\Omega \sum_i S_i^z - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z - \frac{1}{4} \sum_{ijkl} J_{ijkl} S_i^z S_j^z S_k^z S_l^z + \frac{1}{2m} \sum_{q} \frac{1}{2} (P_{ij}^q P_{ij}^q + \frac{1}{2} m \omega^2 Q_i^q Q_i^q) + \sum_{kq} V_{kq} S_k^z Q_q + \sum_{q_i q_j q_k q_l} A_{ijkl} Q_{q_i} Q_{q_j} Q_{q_k} Q_{q_l} \]  

The first term in equation (3) is due to tunneling, second and third terms are due to dipole and quadrupole (four-spin) interactions, fourth, term is phonon contribution, fifth is due to proton-lattice coupling and the last is fourth-order anharmonic interaction term which is essential for stabilization of lattice instability near phase transition. In short, we can write

\[H = H_1 + H_2 + H_3 + H_4 + H_5 + H_6.\] ...(4)

\[H_p = (H_1 + H_2 + H_3)\] is the defining Hamiltonian for pseudo-spin model. \(H_{pl}\) \((H_4 + H_5)\) represents the Hamiltonian representing proton-lattice coupling. \(H_a = H_6\) represents the Hamiltonian represing fourth-order anharmonicity in lattice vibration. The model representing equation(3) is proton-lattice (phonon) coupled mode (PLCM) model. The interaction \(J_{ij}\) between protons is decided into the direct one \(J_{ij}^1\) and the indirect one through the \(f\)-mode. \(S_i^z\) is called tunneling operator which measures the tunneling power of the proton between the hydrogen double well, \(S_i^z\) is half of the difference of occupation probability for the proton to be found in the two equilibrium positions of the hydrogen bond. The two body coupling \(J_{ij}\) (interaction between dipoles of same chain) is same for every pair of protons. The four-body coupling parameter \(J_{ijkl}\) refers to the four-Hydrogen bonds in Po_4 group in KDP and \(J_{ijkl} = \sum_{ijkl} J_{ijkl}^1\).

Expressions for calculations\(^{10}\) of Curie-point for crystals are as follows
1. in order–disorder model.
   \[J = 4K_BT_C\]
2. Tunneling Model-
   \[
   \frac{4\Omega}{J} = \tan h \left( \frac{\Omega}{K_BT_C} \right)
   \]
3. PLCM Model-
   \[
   \frac{4\Omega}{J^*} = \tan h \left( \frac{\Omega}{K_BT_C} \right)
   \]

Here,

\[J = \text{Proton–Proton and lattice interaction constant}\]
\[J^* = \text{PLCM model interaction constant which includes an harmonicity} \Omega \text{ the crystal vibration}\]
\[T_C = \text{Curie-temperature}\]
\[w = \text{tunneling Frequency}\]
\[K_B = \text{Boltzmann constant}\]
For evaluating $x$ and $J_x$, we have used the relations 3,11.

$$x = (1-x) H 
J_x = (0.61 + 0.39x)J_D 
J_x^* = (0.69 + 0.31x)J_D^*$$

Theoretically calculated values for $x$, $J_x$ and $J_x^*$ are given in table 1.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$(\text{cm}^{-1})$</th>
<th>$J_x$ $(\text{cm}^{-1})$</th>
<th>$J_x^*$ $(\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>82</td>
<td>287.92</td>
<td>441.6</td>
</tr>
<tr>
<td>0.1</td>
<td>73.8</td>
<td>306.328</td>
<td>461.44</td>
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<td>0.2</td>
<td>65.6</td>
<td>324.736</td>
<td>481.28</td>
</tr>
<tr>
<td>0.3</td>
<td>57.11</td>
<td>343.144</td>
<td>501.12</td>
</tr>
<tr>
<td>0.4</td>
<td>49.2</td>
<td>361.552</td>
<td>520.96</td>
</tr>
<tr>
<td>0.5</td>
<td>41.0</td>
<td>379.96</td>
<td>540.8</td>
</tr>
<tr>
<td>0.6</td>
<td>32.8</td>
<td>398.368</td>
<td>560.64</td>
</tr>
<tr>
<td>0.7</td>
<td>24.6</td>
<td>416.776</td>
<td>580.48</td>
</tr>
<tr>
<td>0.8</td>
<td>16.4</td>
<td>435.184</td>
<td>600.32</td>
</tr>
<tr>
<td>0.9</td>
<td>8.2</td>
<td>453.592</td>
<td>620.16</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5(Ref.11)</td>
<td>472</td>
<td>640</td>
</tr>
</tbody>
</table>

2. Calculation
Using expressions for the said three models of phase transition we have calculated Curie-points for the KDP-DKDP system. The results are given in table 2.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Order-Disorder Model</th>
<th>Tunning Model</th>
<th>PLCM Model</th>
<th>Results Available</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>103.5886</td>
<td>-</td>
<td>123.36</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>110.2115</td>
<td>53.226</td>
<td>140.1658</td>
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<tr>
<td>0.2</td>
<td>116.8344</td>
<td>84.190</td>
<td>154.3758</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>123.4572</td>
<td>-</td>
<td>167.02652</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>130.0801</td>
<td>116.02278</td>
<td>187.4344</td>
<td></td>
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<tr>
<td>0.5</td>
<td>136.703</td>
<td>127.7466</td>
<td>194.5733</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>143.3259</td>
<td>137.98556</td>
<td>197.9679</td>
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</tr>
<tr>
<td>0.7</td>
<td>149.9488</td>
<td>-</td>
<td>206.8272</td>
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</tr>
<tr>
<td>0.8</td>
<td>156.5716</td>
<td>151.6235</td>
<td>215.1088</td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>163.1945</td>
<td>162.9054</td>
<td>222.91028</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>169.8174</td>
<td>169.817392</td>
<td>230.26087</td>
<td></td>
</tr>
</tbody>
</table>
3. Discussion

Our results (PLCM model) show $T_C^D / T_C^H \approx 1.837$ which is close to experimental result 1.827 of others. Order-disorder and tunneling models fail to give experimental values of $T_c$. It is clear that PLCM model is best suitable for explaining the Curie-point behavior of hydrogen bonded ferro-electric crystals. It is investigated that deuteration has large effect on $T_c$ of KDP Type crystal.

Deuteration verses Curie-point curve is shown in figure (1). It may be concluded that expression for transition temperature character can be used for other hydrogen bonded mixed ferro-electric crystals. For a mixed $K_2(H_1-xD_x)2PO_4$ system, the above calculations (PLCM model) indicate that Curie-temperature is a function of concentration of H and D atoms. It is evident that in this system, the nature of phase transition not only depends on the ratio of $\Omega / \Omega$ but also depends on relative concentration of H and D. Thus the H atoms or D atoms (in pure KDP or in pure DKDP) just behaves as impurity in a pure crystal.

Tunneling model provides a qualitative explanation for the mass dependence of $T_c$ on the basis of the change in tunneling frequency. In the mixed crystals, the tunneling frequency $(\Omega_r)$ takes a random value according as each hydrogen-bond is occupied by a hydrogen or deuterium atom. In our investigation, for three-dimensional random bond crystals as $K_2(H_1-xD_x)2PO_4$, the function $T_c(x)$ is nearly linear. Pseudo-spin lattice coupled mode indicates that not only does the tunneling frequency $(\Omega_r)$ decreases with on deuteration, but also the interaction parameter (including an-harmonicity in the

![Graph showing $T_c$ vs $x$](image-url)

**Fig. 1:** $T_c$ of the mixed crystals.
crystal) J* increases on deuteration. One must consider the Proton-deuteron interaction $J_{HD}$ in addition to proton-proton interaction $J_{HH}$ and deuteron-deuteron interaction $J_{DD}$.

Thus the pseudo-spin lattice coupled mode model provides the basis to account for the changes in the dynamics with deuteration.

References