

Deuteration Effect on Curie-temperature of Deuterated $K(H_{1-x}D_x)_2PO_4$ Crystal

Paper Submission: 15/01/2021, Date of Acceptance: 26/01/2021, Date of Publication: 27/01/2021



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Abstract

Taking modified Hamiltonian and retarded Green's function method, Curie-temperatures for various partially deuterated $K(H_{1-x}D_x)_2PO_4$ hydrogen bonded ferroelectric crystals are evaluated using pseudo spin lattice coupled mode (PLCM) model. These results are quantitatively and qualitatively much better than the theoretically obtained results based on order-disorder and tunneling models used by others.

Keywords: Curie-point, Hydrogen bond, Hamiltonian and Green's function, PACS: 77.80 Bh, 77.84 Fa

Introduction

There has been a great deal of interest, both theoretical and experimental in phase transition of partially deuterated H-bonded ferroelectrics. KDP (KH_2PO_4) type ferroelectrics with a general formula MH_2XO_4 where $M = K, Rb, Cs...$ and $X = P, As$ are classical examples of crystals having order-disorder type phase transition. Deuteration of a hydrogen bond by replacing (H) with deuterium (D) can cause geometric changes (δ distance between the two equilibrium m positions of potential well; $2R$ is O—H---O hydrogen bond length) in the hydrogen bond known as the geometrical isotope effect. There is usually large isotope effect associated with the ordering of protons. In in order-disorder type ferroelectrics like KDP, the four hydrogen bonds usually appear as a group and everyone is an equivalent to another.

In PLC model of phase transition, the effect of deuteration on spontaneous polarization (P_s) enter via tunneling frequency Ω as well as the coupling parameter G and can be accounted for qualitatively [1]. Understanding the geometric isotope effects on global structures and bulk properties is of great importance to study structure properties relationships of hydrogen bonded system [2].

Some hydrogen bonded crystals exhibit a very remarkable isotope effect (physical isotope effect) on T_c . What conditions are required for its occurrence and what role does the hydrogen bond play in structural phase transition? The isotope effect on physical quantities (like spontaneous polarization, Curie temperature etc.) and the phase transition mechanism are expected to be closely connected with the nature of the hydrogen bond. Curie-points for KH_2PO_4 , and KD_2PO_4 are 123 K and 230 K respectively.

In this paper we have calculated Curie-points for various concentrations (x) for $K(H_{1-x}D_x)_2PO_4$ hydrogen bonded ferroelectric crystals using PLCM model of phase transitions. Thus the results obtained are compared with the theoretical and experimental results of others.

Theory

The total Hamiltonian [3,4] in the pseudo spin lattice coupled mode (PLCM) model containing fourth-order anharmonic term can be written as

$$H = H_P + H_L + H_{PL} + H_A \quad (1)$$

Where the pseudo spin Hamiltonian H_P for a system of interacting hydrogen bonds including four spin interaction can be given as

$$H_P = -2\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z - \frac{1}{4} \sum_{ijkl} J_{ijkl} S_i^z S_j^z S_k^z S_l^z \quad (1a)$$

(1a)

H_L is Hamiltonian for the pure lattice system and can be described as

$$H_L = \frac{1}{2} \sum_q [(P_q P_{-q})/M + M\omega_q^2 (Q_q Q_{-q})]. \quad (1b)$$

(1b)

H_{PL} is the Hamiltonian describing the interaction between Proton tunneling mode and the lattice vibration and is given by

$$H_{PL} = -\sum_q V_{iq} S_i^z Q_q - \frac{1}{2} \sum_{q,p} R(q,p) Q_q Q_p S_{p-q}^z - \frac{1}{3} \sum_{q,p,r} T(q,p,r) Q_q Q_p Q_r S_{p-q-r}^z \quad (1c)$$

H_A is the contribution from third and fourth order anharmonic interactions of phonons (because at least 4th order anharmonicity is required to consider the stabilization of the lattice at curie phase transition) and may be expressed as

$$H_A = \sum_{q_1,q_2} B(q_1,q_2) Q_{q_1} Q_{q_2} Q_{q_3} + \sum_{q_1,q_2,q_3,q_4} A(q_1,q_2,q_3,q_4) Q_{q_1} Q_{q_2} Q_{q_3} Q_{q_4} \quad (1d)$$

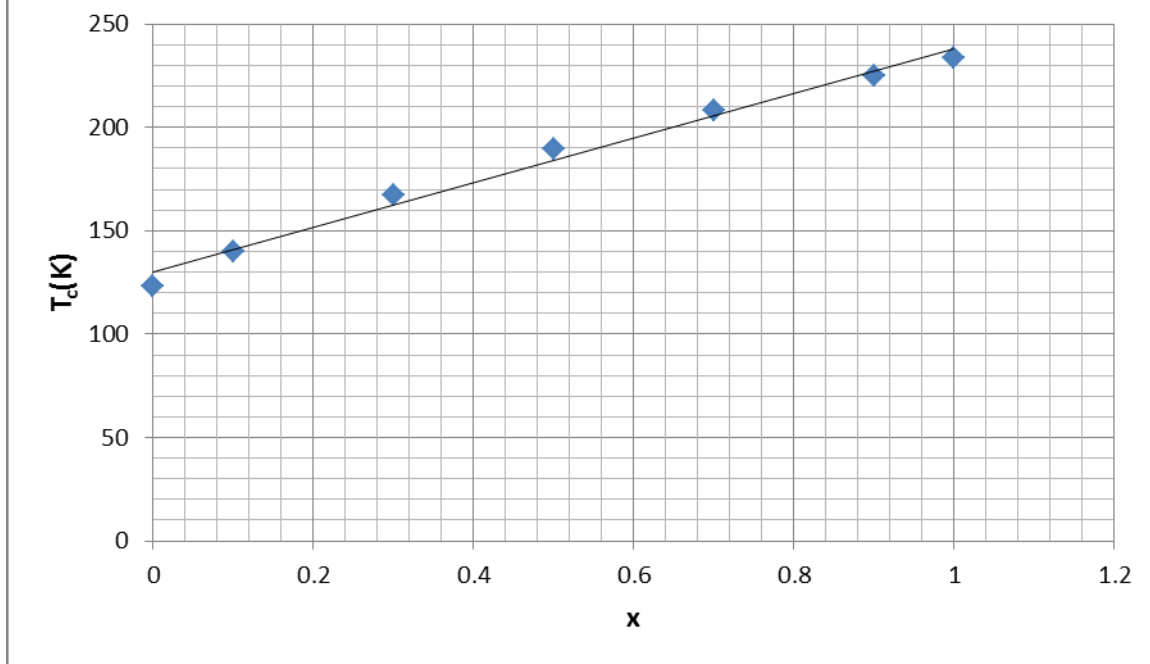
All terms have same meaning as given in reference [3,4] and references cited therein Green's function for the study of dynamical properties can be written as

$$G_q^{\Theta\Theta}(t-t') = \langle\langle Q_q(t) | Q_{-q}(t') \rangle\rangle \quad (2)$$

Using required equation of motion and decoupling scheme [5] gives the expression for Curie

Table (1)

x	0.0	0.1	0.3	0.5	0.7	0.9	1.0
$T_c(K)$	123.2	140.2	167.4	189.3	208.3	225.1	233.8



In Fig.(1), we have drawn a graph between T_c (K) v/s x.

Conclusion

The values calculated by us using PLCM model are in qualitative agreement with the results of others [7,8]. The T_c in KDP increases approximately 1.1K for each one percent increase in deuteration. There is almost 87% increase in T_c on complete deuteration.

References

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transition temperature and shows the softening of the mixed mode when $\omega_2 \rightarrow 0$ (lattice instability condition) and can be expressed as

$$\frac{4\Omega}{j\phi} = \tan h (\Omega/K_B T_C) \quad (3)$$

For a mixed crystal like $K(H_{1-x}D_x)_2PO_4$ equations(3) can be readjusted as

$$4 \Omega_A/J_{OA} = \tan h (\Omega_A/K_B T_C) \quad (4)$$

Here $\Omega_A = x \Omega_H + (1-x) \Omega_D$, (4a)

And $J_{OA} = x J_{OH} + (1-x) J_{OD}$ (4b)

Curie-temperature calculation

The values of Ω_H , Ω_D , J_{OH} and J_{OD} are taken from the reference [6] as

Ω_H	Ω_D	J_{OH}	J_{OD}
82 cm^{-1}	0.4858 cm^{-1}	440.86 cm^{-1}	645.46 cm^{-1}

Using these values in equation (4), we have calculated the T_c for various concentrations x for the crystal $K(H_{1-x}D_x)_2PO_4$, and the values are summarized in Table(1).

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