Study of Ferroelectric Properties of Hydrogen Bonded Rubidium Dihydrogen Arsenate (RdA) Crystal

Pawan Singh1* • Trilok Chandra Upadhya1 • Muzaffar Iqbal Khan1 • Sidharth Kashyap1

1Department of Physics, H.N.B Garhwal University (A Central University) Srinagar (Garhwal) Uttarakhand 246174, India.

*Corresponding Author E-mail ID: pawansingh4853@gmail.com

Received: 29.8.2021; Revised: 18.11.2021; Accepted: 19.112021
©Society for Himalayan Action Research and Development

Abstract: A simple pseudospin lattice coupled mode model with addition of third and fourth-order phonon anharmonic interactions terms, direct spin-spin interactions terms and external electric field term has been considered for investigation of transition phenomena and dielectric properties of hydrogen bonded ferroelectric crystal Rubidium dihydrogen arsenate (RDA). A double-time thermal dependent Green’s function method has been used for derivation of response function. From response function shift, width and soft mode frequency have been derived for RDA crystal. Response function is also related to dielectric constant which has been obtained in present paper. By fitting model values of different parameters in obtained expressions, the temperature variations of normal mode frequency, dielectric constant, and loss tangent have been calculated numerically for RDA crystal. Our theoretical results are compared with experimental results. It is observed that our theoretical results agree with experimental results. Therefore, it can be concluded that the modified pseudo-spin lattice coupled mode model with the simplest approximation is quite suitable to explain the transition and dielectric properties of RDA crystal.

Keywords: Normal Mode Frequency, Dielectric Constant, Dielectric, Ferroelectrics, Loss Tangent

Introduction

Rubidium dihydrogen phosphate (RDA) is a ferroelectric crystal that undergoes a ferroelectric phase transition at 110.25K. This crystal remains orthorhombic below Tc and tetragonal above Tc. The lattice parameters of tetragonal RbH2AsO4 are \( a = 7.7933 \text{ Å}, b = 7.7933 \text{ Å}, c = 7.466 \text{ Å}, \beta = 90^\circ \) with space group \( \text{P4}_2 \text{d} \) and in orthorhombic crystal system the space group is \( \text{Pdd}2 \) (Mitsui et. al., 2005). Since the discovery of ferroelectricity, KDP and its isomorphous (e.g. RDP, KDA, RDA) have attracted the interest of many theoretical and experimental researchers, possibly because of their relatively simple structure and very interesting properties related to hydrogen bond system. A most apparent feature in the progress of physics on this KDP-type crystal is the close interplay between theory and experiment which makes major progress in the microscopic understanding of their properties. Many theoretical and experimental works have been done in field of dielectric and ferroelectric properties of RDA crystal. Starting from experimental work, RbH2AsO4 (RDA) crystal’s phase behavior of above room temperature by different experimental techniques (Toriijano et. al., 2000). (Kahol and Dalal, 1994) have studied the Electron spin resonance spectra of \( \text{AsO}_2^4^- \) center in RDA and deuterated RDA crystals. (Truesdale et al., 1980) have studied the hysteresis effects in X-ray irradiated KDP, deuterated-KDP, and RDP ferroelectric...
single crystals through electron spin resonance. (Adhav, 1969) has studied the physical properties of single crystals of deuterated and undeuterated RbH₂AsO₄. (Kamysheva et al., 1974) have investigated the dielectric and pyroelectric properties of RbH₂AsO₄ single crystal in the ferroelectric phase. (Leung et al., 1973) have studied the behavior of soft mode in RbH₂AsO₄ single crystal. (Tornberg and Lowndes, 1973) have done Raman Spectra of RbH₂AsO₄ and presented it as a function of temperature for the paraelectric phase. (Pimienta et al., 1998) have studied optical-coupled soft mode in ferroelectric rubidium dihydrogen arsenate (RbH₂AsO₄) crystal by experimental techniques of Raman-scattering. Much theoretical work has been done to study the dielectric and ferroelectric transition of RDA crystal. (Slater, 1941) proposed a statistical treatment of phase transition in KDP crystal. Cochran has proposed a fundamental novel idea of soft mode in the theory of ferroelectric phase transition. Cochran has studied the phenomenon of ferroelectric in pseudo-cubic crystals in terms of normal modes of vibration. The study of dielectric and ferroelectric properties of RDA crystal by PLCM model was initiated by (Ganguli et al., 1980) by employing Green’s function theory of (Zubarev, 1960), they have decoupled correlation at an early stage. So they were not able to obtain convincing and precise results.

In the present work, we have considered the effect of third and fourth-order anharmonic interactions with some additional terms in our Hamiltonian. We have derived different expressions for soft mode frequency, dielectric constant, and loss tangent. We have numerically calculated values of soft mode frequency, dielectric constant, and loss tangent by fitting our model values in our derived expressions. We have also compared our numerically calculated data to the experimental data of (Blinc et. al., 1973).

Model Hamiltonian and Method of Calculation

We have used the modified Pseudo-spin lattice coupled model (Ganguli et al., 1980) by adding terms given in Eq. (2)

\[ H = -2\Omega \sum S^x_i - \frac{1}{2} \sum_j J^S_i S^z_j + \frac{1}{4} \sum k \omega_k \left( A_k^x A_k + B_k^z B_k \right) - \sum_{ik} V^S_{ik} S^z_i A_k \]  

We have added third and fourth order anharmonic terms and some other terms in \( H_1 \)

\[ H_2 = \sum_{k,k,k_1} V^{(3)} \left( k_1, k_2, k_3 \right) A_{k_1} A_{k_2} A_{k_3} + \sum_{k,k,k_1} V^{(4)} \left( k_1, k_2, k_3, k_4 \right) A_{k_1} A_{k_2} A_{k_3} A_{k_4} \]

\[-\sum_{ik} V_{ik} S^x_i A_k - \sum_{ik} V_{ik} S^y_i A_k + \frac{1}{2} \sum_{ij} B_{ij} S^x_i S^x_j - \sum_{ik} V_{ik} S^z_i A_k^2 - 2\mu E \sum S^z_i \]  

Where \( \Omega \) represents proton tunnelling frequency between double-well potential O-H---O bonds, \( S^L (L = x, y, z) \) is the \( L^{th} \) component of the pseudo-spin variable. \( A_k \) and \( B_k \) both represent a
position and momenta coordinates. $J_{ij}$ and $V_{ik}$ represents exchange interaction constant and spin-lattice interaction constant respectively. $V^{(3)}(k_1, k_2, k_3)$ and $V^{(4)}(k_1, k_2, k_3, k_4)$ terms represent anharmonic interactions of third and fourth order. $B_0$ represents interaction of the transverse field with one proton to another proton. We have considered the total Hamiltonian by adding equations given by Eq. (1) and Eq. (2):

$$H = H_1 + H_2$$ (3)

We are using the method of double time temperature dependent Green’s function which was proposed by (Zubarev, 1960). Accordingly, for any two operators $A$ and $B$, this is defined as

$$G(t-t') = \langle\langle A(t); B(t')\rangle\rangle = -i\theta(t-t')\langle\langle A(t); B(t')\rangle\rangle$$ (4)

Differentiating twice equation (3) with respect to time $t$ and $t'$, with help of Hamiltonian used given by equation (2) and after Fourier transformation, setting equation (3) into Dyson’s equation framework, Green’s function is obtained as

$$G_{ij}(\omega) = G_{ij}^0(\omega) + G_{ij}^0(\omega)\tilde{P}(\omega)G_{ij}^0(\omega)$$ (5)

Where $G_{ij}^0(\omega)$ is given as

$$G_{ij}^0(\omega) = \frac{\Omega\langle S_i^z \rangle}{\pi(\omega^2 - 4\Omega^2)}$$ (6)

Now, getting the final form of $G(\omega)$

$$G(\omega) = \frac{\Omega\langle S_i^z \rangle \delta_{ij}[(\omega^2 - \hat{\Omega}^2) + 2i\Omega\Gamma(\omega)]^{-1}}{\pi}$$ (7)

Eqns. (8-11) relates pseudo-spin frequency, modified pseudo-spin frequency and soft mode frequency and are given as-

$$\hat{\Omega} = \hat{\Omega}^2 + \Delta(\omega)$$ (8)

$$\hat{\Omega}^2 = a^2 + b^2 - bc$$ (9)
\begin{equation}
a = J_y \langle S_i^z \rangle - B_y \langle S_i^z \rangle + 2E\mu \tag{10}
\end{equation}

\begin{equation}
b = 2\Omega \tag{11}
\end{equation}

\begin{equation}
c = J_y \langle S_i^x \rangle - B_y \langle S_i^x \rangle \tag{12}
\end{equation}

\(\tilde{\Omega}\) is modified soft mode frequency which is given by Eq. (12) and we compute soft mode frequency using Eq.(8).

\begin{equation}
\tilde{\Omega}^2 = \bar{\Omega}^2 + \left\{ a^4 + b^2c^2 + \frac{1}{4} a^2J_y^2 \langle S_i^z \rangle^2 + 4b^2J_y^2 \langle S_i^z \rangle^2 + J_y^2V_{ik}^2 N_k \langle S_i^x \rangle^2 + a^2V_{ik}^2 N_k + b^2V_{ik}^2 N_k + \frac{4\Omega V_{ik}^2 N_k a^2}{b} + 4\Omega^2 B_{ik}^2 \langle S_i^x \rangle \langle S_i^x \rangle N_k + 2\mu^2 E^2V_{ik}^2 N_k a^2 \right\} \tag{13}
\end{equation}

The expression for dielectric constant is obtained as;

\begin{equation}
\varepsilon(\omega) - 1 = (-8\pi N \mu) \langle S_i^z \rangle (\omega^2 - \tilde{\Omega}^2) \left[ (\omega^2 - \tilde{\Omega}^2)^2 + 4\Omega^2 \Gamma^2 \right]^{-1} \tag{14}
\end{equation}

And, the dissipation of power loss at microwave frequencies \(\omega \square \tilde{\Omega}\), loss tangent can be defined as

\begin{equation}
\tan \delta = \frac{2\Omega \Gamma(\omega)}{\Omega^2} \tag{15}
\end{equation}

**Results**

We have used various model values (given in Table 1.) of different physical quantities for RDA crystal from literature\(^1\). We have calculated temperature dependence of soft mode frequency, dielectric constant, and loss tangent. We have shown our theoretically derived results in Figures (1-3). For validation, we have compared our calculated results with experimental values of (Blinc et. al., 1973).
Fig. 1. Temperature dependence of soft mode frequency in RDA crystal. (—Calculated, ● Correlated Experimental values). For validation, it is compared with (Bline et. al., 1973).

Fig. 2. Temperature dependence of Dielectric constant in RDA crystal. (—Calculated, ● Correlated Experimental values). For validation, it is compared with (Bline et. al., 1973).

Fig. 3. Temperature dependence of loss tangent in RDA crystal. (—Calculated, ● Correlated Experimental values). For validation, it is compared with (Bline et. al., 1973).
Table 1. Model values of Physical quantities for RDA crystal (Ganguli et al., 1980).

<table>
<thead>
<tr>
<th>$\Omega$ (cm$^{-1}$)</th>
<th>$J$ (cm$^{-1}$)</th>
<th>$J'$ (cm$^{-1}$)</th>
<th>$T_c$ (K)</th>
<th>$V_{ik}$ (cm$^{-1}$)</th>
<th>$\omega_k$ (cm$^{-1}$)</th>
<th>$\mu \times 10^{16}$ (esu-cm)</th>
<th>$N \times 10^{-22}$ (cm$^{-3}$)</th>
<th>$B_{ij}$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>238.8</td>
<td>321.50</td>
<td>110.25</td>
<td>14.66</td>
<td>26</td>
<td>1.5</td>
<td>0.76</td>
<td>0.918</td>
</tr>
</tbody>
</table>

Discussion and conclusion

Earlier authors have decoupled the correlations function at an early stage and hence some important interactions result were not included in their calculations and results. We have added higher order interaction terms i.e. third and fourth order anharmonic interaction terms and some other interaction terms to study different kinds of interactions in our results. In fig.1, the soft mode frequency goes to a minimum value at the transition point of RDA crystal and then increases which is following Cochran’s suggested theory. In fig.2, the dielectric constant first increases, and then it becomes large at near $T_c$ and then decreases. Similarly, in fig.3, the loss tangent shows its behavior. The present study shows that the pseudospin-lattice coupled mode model along with higher order anharmonic terms i.e. third and fourth-order phonon anharmonic interaction terms and some spin-lattice interaction terms can explain the temperature dependence of ferroelectric mode frequency, dielectric constant, and loss tangent in RDA crystal. We have also shown that our obtained results agree with the experimental results of (Blinc et al., 1973). This theoretical investigation may also be useful for other hydrogen-bonded ferroelectric like KH$_2$PO$_4$, RbH$_2$AsPO$_4$, CsH$_2$PO$_4$, and CsH$_2$AsO$_4$.

Acknowledgment

Authors are thankful to well-known physicist Prof. B.S Semwal (Ex HoD) for his valuable suggestions and we are also obliged to Prof. R. P Gairola, Prof. U.C Naithani, Prof. R.C Dimri (Dean, School of Science), Prof. S.C Bhatt(Ex-HoD, Physics ), Prof. P. D. Semalty (convener & HoD), Prof. O.P.S. Negi (VC-UOU)), Prof. H.C Chandola (HoD, K.U), Prof. Mahavir Singh, and Dr. Manish Uniyal for their encouragement. They are also thankful to Dr. Aanchal Rawat and colleagues for their suggestions and interest in the presented work. One author (Pawan Singh) thankful to UGC New Delhi and H.N.B. Garhwal University for providing a research fellowship.

References


Kahol PK and Dalal NS (1994) Electron Spin Resonance line shape studies of the AsO$_4$ center in RbH$_2$AsO$_4$, RbD$_2$AsO$_4$ and dipolar glass Rb$_{1-x}$(NH$_4$)$_x$H$_2$AsO$_4$. *Ferroelectrics.* 156(1): 3030-308.


