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Study of phase transition properties in rochelle salt crystal

Muzaffar Iqbal Khan* & Trilok Chandra Upadhyay

Department of Physics, Hemvati Nandan Bahuguna Garhwal University, Srinagar 246 174, India

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The extra spin-lattice interactions terms, external electric field term, direct spin-spin interaction term and fourth-order phonon anharmonic terms have been added to two-sublattice pseudo-spin lattice couples mode(PLCM) model for Rochelle salt crystal. By applying the double-time thermal Green function method and using the modified model, theoretically, expressions for the shift, width, soft mode frequency, dielectric constant and loss tangent have been derived. By fitting model parameters values, temperature variations of the above quantities have been calculated for Rochelle salt crystal. We compare theoretical variations of soft mode frequency for Rochelle salt crystal, by getting correlated values of soft mode frequency from experimental data of dielectric constant. We compare our theoretical values for dielectric constant and loss tangent for Rochelle salt with the experimental result of Sandy and Jones [Phys Rev, 168(2), 481-493 (1968)]. Our theoretical results well agree with experimental data of others for Rochelle salt. Present expressions will also be useful for other similar crystals like sodium ammonium tartrate tetrahydrate ($NaNH_4C_4H_4O_6.4H_2O$) crystal, lithium ammonium tartrate monohydrate ($LiNH_4C_4H_4O_6.H_2O$) crystal and lithium thallium tartrate monohydrate ($LiTlC_4H_4O_6.H_2O$) crystal etc.

Keywords: Anharmonic, Soft mode frequency, Dielectric constant, Loss tangent, Rochelle salt

1 Introduction

Ferroelectric crystals are technologically much more important. These have so many peculiar properties like pyroelectric, piezoelectric, memory devices, electrooptical and display apart from being very high dielectric permittivity materials. Rochelle salt is a well-known classic ferroelectric material which shows ferroelectricity between two transition temperatures 255K and 297 K. Generally, it is accepted that Rochelle salt (RS) (sodium-potassium tartrate tetrahydrate $NaKC_4H_4O_6.4H_2O$) crystal has two-phase transition temperatures or curie points at $T_{c_1} = 255\,K\ (= -18\,°C)$ and $T_{c_2} = 297\,K (= 24\,°C)$. Ferroelectricity exhibits in a narrow temperature [illegible] paraelectric phase below 255 K and above 297 K[1]. Therefore, Rochelle salt crystal has two Curie points between which it possesses spontaneous polarization in the direction along a-axis[1,2]. In Between the phase transition temperatures, the ferroelectric phase is monoclinic crystal system with $P2_1$space group and below and above these transition temperatures exhibits paraelectric phase having orthorhombic crystal system with $P2_12_12_1$ space group[2,3]. Lattice parameters of Rochelle salt crystal in ferroelectric phase are, a = 11.869 Å, b = 14.316Å, c = 6.223Å for the monoclinic structure and paraelectric phase, a = 11.875(4) Å,b = 14.266(8) Å, c = 6.209(7) Å, $\alpha = \beta = \gamma = 90^0$ for the orthorhombic structure. Its unit cell contains four (Z=4) formula and unit cell have volume V=1.051(1) nm^3 [2,4].

Experimentally, complex dielectric properties of Rochelle salt crystal haven been studied by Sandy and Jones[5]. Optical studies of Rochelle salt for understanding their physical properties have been done by Kobayashi *et al.*[6]. Infra-red (IR) spectra of composite heterostructures with complex molecular ferroelectric structures (triglycine sulphate and [illegible] d by Popravko *et al.*[7]. The crystal structure of the high-temperature paraelectric phase of Rochelle salt has been studied by Frode *et al.*[8] using synchrotron X-ray diffraction. The time dependence of remnant polarization under the influence of applied transverse DC electric field have been studied by Kikuta *et al.*[9] and confirmed that the remnant polarization decreases with time dependence under the applied transverse DC electric field. They also obtained that stronger applied transverse electric field causes a faster reduction in remnant polarization. Study of dielectric properties of composite structures based on porous aluminium with

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*Corresponding author
(E-mail:muzaffariqbalkhan786@gmail.com)

inclusions of TGS and RS ferroelectric crystals have been investigated by Golitsyna *et al.*[10].

Dynamic pair correlation functions of disorder Ising and Mitsui models have been theoretically studied by Levitskii and Sokolovskii[11]. Theoretical description of phase transitions and dielectric properties of RS crystal beyond the Mitsui model have been studied by Stasyuk and Velychko[12]. The effect of hydrostatic pressure on thermodynamically properties of Rochelle salt crystal was theoretically studied within the framework of the Mitsui model by Levitskii *et al.*[13]. Miga *et al.*[14] have measured the second and third-order dielectric susceptibilities of Rochelle salt crystal. Moina[15] has measured theoretically the static thermodynamic properties, dynamic linear and non-linear susceptibilities and piezoelectric coefficients of Rochelle salt crystal. Kim *et al.*[16] have studied quantized polarization in a ferroelectric Rochelle salt crystal.

Ferroelectric phase transitions and dielectric properties in Rochelle salt and its deuterated form by using pseudo-spin lattice coupled mode (PLCM) model have been studied by Chaudhari *et al.*[17], but they could not use third-order anharmonic interactions term in their calculations and decoupled correlations at an early stage. Kandpal and Upadhyay[18], Rawat and Upadhyay[19] have studied ferroelectric and dielectric properties of RS crystal using pseudo-spin lattice coupled mode (PLCM) model, but they could not consider extra-spin lattice interactions terms. In this paper, we considered two sub-lattice PLCM model with third and fourth-order anharmonic interactions terms, spin- spin-lattice interactions term, extra interaction (direct coupling) term and external electric field term to get betters results. Our theoretical results compare with the experimental results of Sandy and Jones[5].

2 Theory and Calculations

Two sublattice pseudo-spin lattice coupled mode (PLCM) modelHamiltonian[17] is modified by adding cubic and quadric phonon anharmonic interactions terms for Rochelle salt (RS) crystal. The thermal Green function[20] $G_{ij}(t-t') = \ll S^z_{1i}(t); S^z_{1j}(t') \gg = -\theta(t-t')\langle[S^z_{1i}(t), S^z_{1j}(t')]\rangle$ evaluated with the help of modified Hamiltonian[17]. The final evaluated expression for thermal Green function[20] by applying symmetric decoupling scheme given as,

$$G_{ij}(\omega) = \frac{\Omega\langle S^x_{1i}\rangle\delta_{ij}}{\pi[\omega^2 - \hat{\Omega}^2 - 2i\Omega\Gamma(\omega)]} \quad ...(1)$$

The equation (1) is in the final form of the Green function in which we have,

$$\hat{\Omega}^2 = \tilde{\tilde{\Omega}}^2 + \Delta_{s-p}(\omega) \quad ...(2)$$

Where

$$\tilde{\tilde{\Omega}}^2 = \tilde{\Omega}^2 + \Delta_s(\omega) \quad ...(3)$$

$$\tilde{\Omega}^2 = a^2 + b^2 - bc \quad ...(4)$$

Where

$$a = 2J_{ij}\langle S^z_{1i}\rangle + K_{ij}\langle S^z_{1i}\rangle + \Delta - 2B_{ij}\langle S^z_{1i}\rangle + 2\mu E \quad ...(5)$$

$$b = 2\,\Omega \quad ...(6)$$

where Ω is the tunnelling frequency and

$$c = 2J_{ij}\langle S^x_{1i}\rangle + K_{ij}\langle S^x_{1i}\rangle - 2B_{ij}\langle S^x_{1i}\rangle \quad ...(7)$$

Also $\langle S^z_1\rangle = -S^z_2 \neq 0, T < T_c$ ...(8)

where, $\tilde{\Omega}$ *and* $\tilde{\tilde{\Omega}}$ is the pseudospin frequency and $\hat{\Omega}$ is the modified frequency.

In Eqs. (1) & (2), $\Gamma(\omega)$ and $\Delta(\omega)$ are the width and shift of response function. Their values have been given in our earlier paper[17-19] on Rochelle salt (RS) crystal.

After solving Eq. (2) self consistently, we obtained final expression for modified soft mode frequency as:

$$\begin{aligned}\hat{\Omega}^2 = \frac{\left(\omega_k^2 + \tilde{\tilde{\Omega}}^2\right)}{2} &\pm \frac{1}{2}\Bigg\{\left(\omega_k^2 + \tilde{\tilde{\Omega}}^2\right)^2 + 4\{8aV_{ik}^2\langle S^z_{1i}\rangle\omega_k \\ &- 2bV_{ik}^2\langle S^x_{1i}\rangle\omega_k - 4bV_{ik}^2\langle S^z_{1j}\rangle\omega_k \\ &+ \frac{8V_{ik}^2J_{ij}^2\langle S^x_{1i}\rangle\langle S^z_{1j}\rangle^2\omega_k}{b} \\ &+ \frac{2V_{ik}^2K_{ij}^2\langle S^x_{1i}\rangle\langle S^z_{1j}\rangle^2\omega_k}{b} \\ &+ 12V_{ik}^2J_{ij}\langle S^x_{1j}\rangle\langle S^z_{1j}\rangle\omega_k \\ &- 2V_{ik}^2\langle S^z_{1j}\rangle\langle S^z_{2j}\rangle\omega_k \\ &+ \frac{8V_{ik}^2B_{ij}^2\langle S^z_{2j}\rangle^2\omega_k}{b} \\ &- \frac{16\mu EV_{ik}^2B_{ij}\langle S^x_{1j}\rangle\langle S^z_{1j}\rangle\omega_k}{b} \\ &+ \frac{8\mu^2E^2V_{ik}^2\langle S^x_{1j}\rangle\omega_k}{b} \\ &+ \frac{2\Delta^2V_{ik}^2\langle S^x_{1i}\rangle\omega_k}{b} + \ldots\ldots\}\Bigg\}^{\frac{1}{2}}\end{aligned} \quad ...(9)$$

We obtain the expression for dielectric constant (ε) for RS crystal as given below

$$\varepsilon = -\frac{8\pi N\mu^2\langle S_{1i}^{x}\rangle\left(\omega^2-\hat{\Omega}^2\right)}{\left[\left(\omega^2-\hat{\Omega}^2\right)^2+4\Omega^2\Gamma^2(\omega)\right]} \qquad ...(10)$$

where N is denoting the numbers of dipoles in the unit cell with dipoles moment mu.The dielectric loss tangent expression for Rochelle salt crystal obtained as given below:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = -\frac{2\Omega\Gamma(\omega)}{\left(\omega^2-\hat{\Omega}^2\right)} \qquad ...(11)$$

where, ε' is the real part and ε'' is the imaginary part of the dielectric constant. By putting model values for RS crystal of various physical parameters in Eqs. 9-11 from literature, thermal variations of above quantities are obtained (soft mode frequency, dielectric constant and dielectric loss tangent). These are shown in Figs 1-3. Theoretical results have been compared with experimental data of Sandy and Jones[5].

3 Results and Discussion

In the present paper, by fitting the various model parameters values for Rochelle salt crystal in the derived expressions for Rochelle salt (RS) crystal. By using various model parameters values obtained from the literature in Table 1, we get the thermal dependence of soft mode frequency, dielectric constant and dielectric tangent loss.

In our calculations throughout our fitting of experimental data with theoretical expressions, we used $N=3.8\times10^{21}\text{cm}^{-3}$ and $\mu=1.51\times10^{-18}$(esu). By using the values of various parameters for Rochelle salt crystal in the expressions obtained in Equations (9), (10) and (11), we get temperature dependence of soft mode frequency, dielectric constant and loss tangent have been calculated. Our theoretical result are well comparing with experimental data of Sandy and Jones[5] for Rochelle salt crystal shown in Figs (1-3).

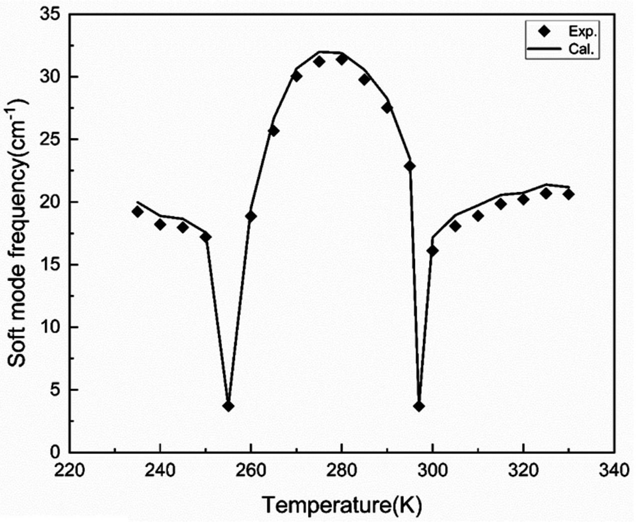

Fig. 1 — Temperature dependence of soft mode frequency in Rochelle salt. (— present calculation, ◆ Correlated values with experimental data of Sandy and Jones[5] for dielectric constant).

The ferroelectric soft mode frequency goes to a minimum value at transition temperatures(T_{c1} and T_{c2}) as shown in Fig. 1.The dielectric constant shows the maximum value at the Curie temperatures(T_{c1} and T_{c2}) and then decreases with increasing temperature. The similar result is obtained for dielectric tangent loss. Our theoretical dielectric constant thermal variations are compared with the experimental data of Sandy and Jones[5] which shows a

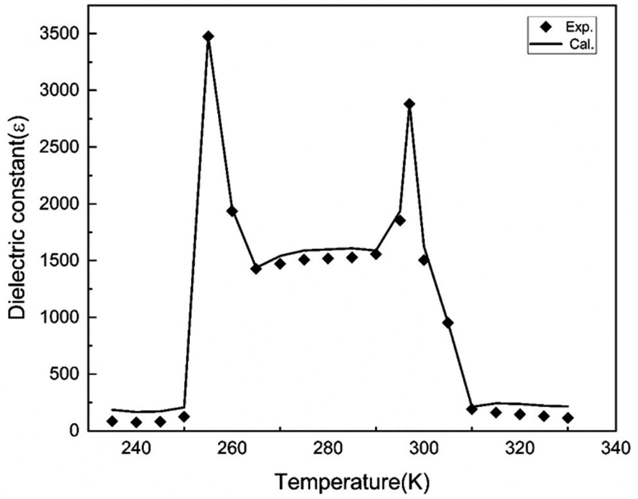

Fig. 2 — Temperature dependence of dielectric constant in Rochelle salt. (—present calculation, ◆ experimental data of Sandy and Jones[5]).

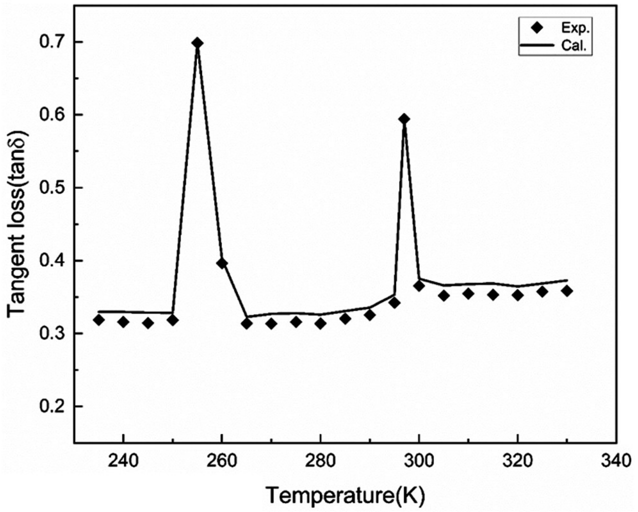

Fig.3 — Temperature dependence of tangent loss in Rochelle salt. (—present calculation, ◆ experimental data of Sandy and Jones[5]).

Table 1 — Shows model values of various physical quantities for Rochelle salt[17].

Ω $(\mathrm{cm}^{-1)}$	V_{ik} $(cm^{-3/2})$	J_{ij} (cm^{-1})	K_{ij} (cm^{-1})	T_{c1} (K)	T_{c2} (K)	C_1 (K)	C_2 (K)	Δ (cm^{-1})	ω_k^2 (cm^{-2})
1.820	11.558	354.701	351.735	255	297	1830	2248	0.678	5.20

good agreement. The thermal variation of soft mode frequency is compared with the correlated values obtained from the dielectric data of Sandy and Jones[5].

4 Conclusions

In the present work, our study shows the modified PLCM model (two-sublattice pseudospin lattice coupled-mode model) with the addition of third and fourth-order anharmonic interaction terms, extra spin-lattice interactions terms, spin-spin interaction term and applied external field term explains quantitatively the dielectric and ferroelectric behaviours of Rochelle salt crystals. Obtained theoretical results well agree with experimental data of Sandy and Jones[5]. Present theory model has also applicability for similar other crystals such as TGS, LHP and CDP. The calculations on these crystals are in progress in our laboratory.

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