J. Mountain Res. P-ISSN: 0974-3030, E-ISSN: 2582-5011 DOI: https://doi.org/10.51220/jmr.v16i2.16
Vol. 16(2) Special Issue ICRAMS-2021, (2021), 121-128

Investigation Of Ferroelectric Properties of Rochelle Salt Type Crystals Using A Modified Model

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Received: 8.8.2021; Revised: 28.8.2021; Accepted: 19.10.2021

Abstract: Rochelle salt type crystals show ferroelectricity. Previously suggested model is little modified to explain ferroelectric behaviour of three crystals. Simple Green's function approach is used to obtain normal mode frequency formula. This frequency is calculated for different temperatures for Rochelle salt crystal. Theoretical results are compared with others experimental data formulae for dielectric constant and spontaneous polarization are obtained. Values are calculated for Rochelle salt crystal and compared with experimental data of F. Sandy and R. V. Jones (1968).
Keyword: Green function • Tangent Loss • Ferroelectricity • Spontaneous Polarization.

Introduction

Rochelle salt is earliest known ferroelectric crystal. Ferroelectric crystals show spontaneous polarization which is reversible by stress or electric field. Most of ferroelectric crystals have important applications in electronics technology. So, their investigation is useful both from theoretical as well as technological applications.

The Rochelle salt type crystals are Deuterated Rochelle salt, Lithium ammonium tartrate monohydrate (LAT), Tetramethylammonium trichloro mercurate, Lithium thallium tartrate (LTT), Potassium nitrate, Sodium nitrate, Colemanite, Thiourea etc.

Shirane et al (1955) described that Rochelle salt shows ferroelectricity between 255 K and 297 K. It is orthorhombic in paraelectric and monoclinic in ferroelectric state already investigated by Valasek (1921). Theoretical work has been done earliest by Mueller (1935) from study of Properties of Rochelle salt, Mason (1947), Devonshire (1957) and Mitsui (1958) has given two sub lattice pseudospin model for these crystals. Chaudhuri et al (1980) have added pseudospin-lattice and a fourth-order phonon anharmonic term in this model. Experimentally a large worker has investigated these crystals in recent past are Sandy and Jones (1968), Blinc et al(1964), Akao and Sasaki (1955), Kamba et al(1995), Volkov et al(1985) and Hlinka et al(2001) have particular made dielectric, X-ray analysis, neutron scattering and crystal growth of these crystals. The investigated phase transition properties of Rochelle salt also studied by Rawat and Upadhyay (2019) & Khan and Upadhyay (2020). A synthesis for clarifying phase transition anomalies using ferroelectric nanocomposite from cellulose nanoparticles (CNP) and Rochelle salt (RS) at different composition mass ratios performed by Hoai Thuong Nguyen & Bich Dung Mai(2019). The effect of carbonization on pre-carbonized cellulose nanoparticles at different temperatures on the phase transition and conductive properties of nanocomposites with Rochelle salt investigated by Hoai Thuong Nguyen (2021).

In present work, we shell modify Chaudhuri's model by adding third order phonon anharmonic terms. We shell use simple Green Function approach to obtain normal mode frequency formula. Dielectric constant and spontaneous electric polarization numerical calculations are done to obtain thermal variations of soft mode frequency, dielectric constant and spontaneous polarization for Rochelle salt crystal.

Theoretical Calculation

We modify Chuadhari's[7] model as following –

$$H = -2\Omega \sum_i (S_{1i}^x + S_{2i}^x) - \sum_{ij} J_{ij}[(S_{1i}^z + S_{2i}^z) \quad + (S_{1i}^z + S_{2i}^z)] - \sum_{ij} K_{ij}\left(S_{1j}^z S_{2i}^z\right)$$

$$-\Delta \sum_i (S_{1i}^z + S_{2i}^z) \quad - \sum_{ij} V_{ik} S_{1i}^z A_k - \sum_{ik} V_{ik} S_{2i}^z A_k^+$$

$$+\frac{1}{4}\sum_k \omega_k (A_k A_k^+ + B_k B_k^+) \quad + \sum_{k_1 k_2 k_3} V^{(3)}\left(k_1, k_2, k_3\right) A_{k_1} A_{k_2} A_{k_3}$$

$$+\sum_{k_1 k_2 k_3 k_4} V^{(4)}\left(k_1, k_2, k_3, k_4\right) A_{k_1} A_{k_2} A_{k_3} A_{k_4} \quad \ldots (1)$$

where Ω is proton tunnelling frequency, S_z and S_x are components of pseudospin variable of S, V_{ik} is spin-lattice interaction, A_k and B_k are positions and momentum operators, ω_k is harmonic phonon frequency $V^{(3)}$ and $V^{(4)}$ are third-and fourth-order atomic force constants, defined by Born and Huang (1954). J_{ij} describes interactions of the diploes fitting to the same and K_{ij} to the different sublattices.

Following Zubarev (1960), we consider the evaluation of Green's function (GF)

$$G_{ij}(t - t') = \left\langle\left\langle S_{1i}^z(t); S_{1j}^z(t')\right\rangle\right\rangle$$

$$= -i\theta(t - t')\left\langle\left[S_{1i}^z(t); S_{1j}^z(t')\right]\right\rangle, \quad \ldots\ldots\ldots (2)$$

Differentiating Eq. (2) twice with respect to time t and t' using the model Hamiltonian (Eq. 1), taking Fourier transformation and applying Dyson's equation, one gets:

$$G_{ij}(\omega) = G^0(\omega) + G^0(\omega)\tilde{p}(\omega)G^0(\omega), \quad \ldots\ldots\ldots (3)$$

Where

$$G^0(\omega) = \frac{\Omega < S_{1i}^x > \delta_{ij}}{\pi(\omega^2 - 4\Omega^2)} \quad \text{……… (4)}$$

$$G_{ij}(\omega) = \frac{G^0(\omega)}{[1 - G^0(\omega)\tilde{P}(\omega)]}, \quad \text{…………. (5)}$$

and

$$\tilde{P}(\omega) = \frac{\pi i \langle [F(t) S_{1j}^y] \rangle}{\Omega \langle S_{1i}^x \rangle^2}$$

$$+ \frac{\pi^2}{\Omega^2 \langle S_{1i}^x \rangle^2} \langle \langle F_i(t); F_j'(t') \rangle \rangle, \quad \text{……….. (6)}$$

and

$$F(t') = 2\Omega J_{ij}(S_{1j}^x S_{1i}^z + S_{1j}^z S_{1i}^x) - 2\Omega K_{ij}(S_{1i}^x S_{2i}^z)$$

$$+ 2\Omega V_{ik} S_{1i}^x A_k + 2\Omega \Delta(S_{1i}^x + S_{2i}^z) + 2\Omega V_{ik} A_k^+ S_{2i}^x \quad \text{………. (7)}$$

The Green's Function (GF), Eq. (5) can be written as:

$$G(\omega) = \frac{\Omega \langle S_{1i}^x \rangle \delta_{ij}}{\pi[\omega^2 - \hat{\Omega}^2 - \tilde{\tilde{P}}(\omega)]}, \quad \text{………..(8)}$$

where renormalized frequency $\hat{\Omega}$, in lowest approximation is given as:

$$\hat{\Omega}^2 = 4\Omega^2 + \frac{i}{\langle S_{1i}^x \rangle} \langle [F, S_{1i}^y] \rangle \quad \text{……….. (9)}$$

and polarization operator $\tilde{\tilde{P}}(\omega)$ is given as :

$$\tilde{\tilde{P}}(\omega) = \frac{\pi}{\Omega \langle S^x \rangle} \langle \langle [F_i(t);] F_j'(t') \rangle \rangle \quad \text{……….. (10)}$$

so that

$$\widehat{\Omega}^2 = a^2 + b^2 - bc \qquad \text{……….. (11)}$$

with

$$a = 2J_0\langle S_1^x\rangle + K_0\langle S_2^x\rangle + \Delta \qquad \text{……….. (12)}$$

$$b = 2\Omega \qquad \text{……….. (13)}$$

and

$$c = 2J\langle S_1^x\rangle + K\langle S_2^x\rangle \qquad \text{……….. (14)}$$

Putting values of $\tilde{\tilde{P}}(\omega)$ in Eq. (8), Green's function finally becomes:

$$G(\omega) = \frac{\Omega\langle S_{1i}^x\rangle\delta_{ij}}{\pi[\omega^2 - \widehat{\Omega}^2 - 2i\Omega\Gamma(\omega)]} \qquad \text{……………… (15)}$$

The quantities $n_{ks} = coth\frac{\tilde{\omega}_{ks}}{k_B T}$ where k_BBoltzmann's constant temperature and s is numerical index s=1, 2, 3, 4: the frequency $\widehat{\Omega}$ is given by:

$$\widehat{\Omega}^2 = \tilde{\Omega}^2 + 2\Omega\Delta_{s-p}(\omega) \qquad \text{……. ……..… .. (16)}$$

and

$$\tilde{\tilde{\Omega}}^2 = \tilde{\Omega}^2 + 2\Omega\Delta_s(\omega) \qquad \text{………………. (17)}$$

2.2 Soft Mode Frequency and Transition Temperatures

Solving Eq. (10) self consistently, one obtains renormalized frequency:

$$\widehat{\Omega}_-^{\ 2} = \frac{1}{2}\left[\left(\tilde{\tilde{\omega}}_k^2 + \tilde{\tilde{\Omega}}^2\right) \pm \left\{\left(\tilde{\tilde{\omega}}_k^2 - \tilde{\tilde{\Omega}}^2\right)^2 + 8V_{ik}^2\langle S^x\rangle\right\}^{\frac{1}{2}}\Omega\right] \qquad \text{……….. (18)}$$

The frequency $\widehat{\Omega}$ is the soft mode frequency which critically depends on temperature and is responsible for phase transition.

2.3 Dielectric Constant and Loss Tangent

The expression for dielectric constant can be expressed as $\varepsilon(\omega)\rangle\rangle 1$ is following:

$$\varepsilon(\omega)1 = -\ 8\pi N\mu^2\langle S_1^x\rangle\left(\omega^2 - \widehat{\Omega}^2\right)\left[\left(\omega^2 - \widehat{\Omega}^2\right)^2 + 4\Omega^2\Gamma^2(\omega)\right]^1 \qquad \text{(19)}$$

2.4 Spontaneous Polarization

The Spontaneous Polarization (Ps) is given by Halblutzel[16]

$$Ps = 2N\mu(\langle S_1^z\rangle + \langle S_2^z\rangle) \qquad \text{(20)}$$

Putting the values of $N\mu$ and $\langle S_1^z\rangle$ and $\langle S_2^z\rangle$ we obtain the value of Ps for Rochelle salt. We compare our results with Sandy and Jones (1968). A good agreement is obtained.

3. Numerical Calculation and Results

By using model values of Physical quantities, the thermal variations of soft mode frequency, dielectric constant and spontaneous polarization are shown in Fig. 1, 2 and 3. Fig 1. reveals that the electrical permittivity first increases by increasing the temperature and then decreases and reaches a minimum value at 0K and follow a same pattern for further temperature. Fig 2. Shows that soft mode frequency increases with increasing temperature and reaches a maximum value near transition temperature, after that decreases and then slightly increases which strictly follow the Cochran's behaviour. Fig 3. Shows that the spontaneous polarization first increases by increasing temperature and reaches a maximum value 2.5 near transition temperature and then decreases. The constant values given by Chaudhuri et al (1980) T_{c1} = 255-2K, T_{c2} = 296.9K, C_1 = 1830K, C_2= 2248K, η = 5.51 cm^{-1}, Δ = 0.678 cm^{-1}, Ω^2 (J'+K') * = 2738cm^{-3}, Ω^2 (J+K) = 2340 cm^{-1}, Δ=0.678 cm^{-1}, $\omega_k^2 = 520 cm^{-1}$, $\Omega V_{ik} = 20.92K$, $A_0k_BX10^{17}$=5.737 prg/K, N=3.8x10^{21} cm^{-3}, μ=1.51X10^{18} esu.

The temperature dependence of $\langle S_1^z\rangle, \langle S_2^z\rangle, \langle S_1^x\rangle, \langle S_2^x\rangle, \widetilde{\Omega}, \widetilde{\widetilde{\Omega}}, \widehat{\Omega}$ and permittivity (Ɛ) across Tc have been calculated.

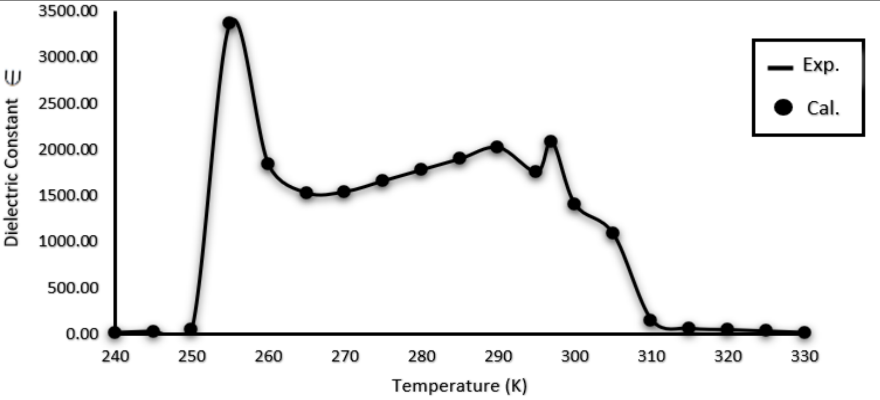

Fig. 1, Calculated Temperature difference of dielectric constant of RS ━ ; exp.8 . ●

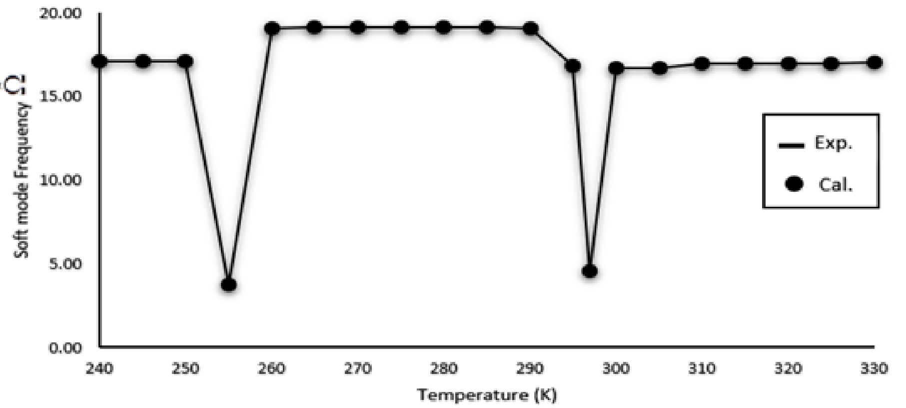

Fig-2, Calculated Temperature difference of soft mode frequency in RS ━ ; exp.8 . ●

Table 1- Calculated temperature dependence of Spontaneous Polarization in Rochelle salt

T(K)	$Ps \times 10^7 (c/cm^2)$
250	0.0
255	0.0
260	1.5
265	2.0
270	2.4
275	2.5
280	2.4
285	2.2
290	2.0
295	1.5
297	0.0
300	0.0

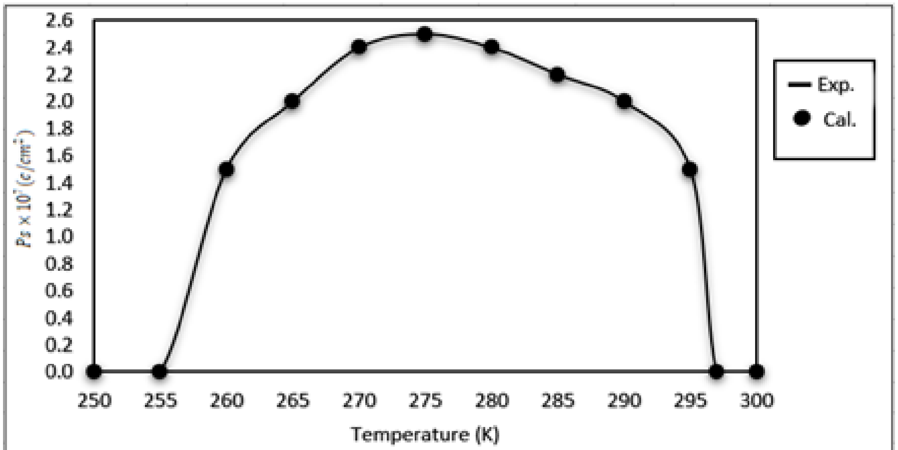

Fig-3, Spontaneous Polarization for Rochelle Salt- J.Hablutzel et al

4. Conclusion

In this paper, present work reveals that the two-sublattice PLCM model along with a third- and fourth-order phonon anharmonic interaction terms. These extra interaction terms play an important role to explain well the thermal dependence physical quantities of soft mode frequency, dielectric constant and spontaneous polarization in Rochelle salt crystal.

Acknowledgement

The authors are thankful Prof. S.C. Bhatt, Prof. P.D. Semalty, Prof. Mahavir Singh (Shimla), Prof. L.P. Purohit (Haridwar), Prof. R.K. Shukla (Lucknow), Prof.N.S. Negi (Shimla)and Dr. Manish Uniyal for their kind encouragement and Mr. Kuldeep Singh (Research Scholar) for help.

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