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Study of dielectric properties and thermal variations of rochelle salt crystal

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Considering modified two sub lattice pseudo spin lattice coupled-mode model with third-and fourth-order phonon anharmonic terms and double-time Green's function method Rochelle Salt has been investigated. Formulae for the shift, width, dielectric constant, soft mode frequency and loss tangent have been derived for Rochelle salt crystal. The numerical calculation has been done. Thermal variations of the above quantities have been obtained for Rochelle salt crystal. Our results have been compared with experimental results of other workers. Our results agree closely with those works.

Keywords: Phase transition, Shift, Width, Dielectric constant, Soft mode frequency, Loss tangent.

1 Introduction

The Sel de Seignette or Rochelle salt (sodium potassium tartrate tetrahydrate, $NaKC_4H_4O_6$ $4H_2O$) is ferroelectric discovered but compared to other H-bounded crystals, little theoretical work has been done on this classic salt. It is ferroelectric between 255K and 297K showing orthorhombic structures in paraelectric phases and monoclinic in the ferroelectric phase.

The theoretical studies of the ferroelectric transition of Rochelle salt were initiated by Muller[1] who correlated the physical properties of Rochelle salt. Mason[2] and Devonshire[3] developed theories based on atomic arrangements. They developed a single sublattice model. Mitsui[4] proposed a two-sublattice pseudospin model based on new information obtained from X-ray studies[5]. According to Mitsui's model[4], the ferroelectric dipole movement of the system arises from the ordering of protons in the hydrogen bond O_1-$(H_2O)_{10}$. The hydroxyl group $(OH)_5$ forms two sublattices and is the ordering element. Mitsui[4] assumed a complex local field and predicted two Curie points theoretically. Mitsui's model was further used by Sandy and Jones[6] to study the dielectric properties of Rochelle salt crystal. The occurrence of two transition points in Rochelle salt was explained by using pure pseudospin model by Zeks *et al.*[7]. The study of dielectric properties and phase transition in Rochelle salt crystal was carried out by Konsin[8] using two sublattice pseudospin model.

Chaudhuri *et al.*[9] have used a two-sublattice pseudospin-lattice coupled-mode model along with a fourth-order phonon anharmonic interaction term to explain ferroelectric transition and dielectric properties of Rochelle salt crystal. They have not considered third-order phonon anharmonic term. Moreover, they decoupled the correlations in the very beginning. Due to this reason, some important interactions disappeared from their expressions.

Iwata *et al.*[10], have used split-atom model for Rochelle salt crystal. Levitskii and Sokolovskii[11] have used modified Mitsui model to include piezoelectric coupling to the external field. Stasyuk and Velychko[12] have used a four-sublattice pseudospin model to study the dielectric susceptibility and thermal properties of Rochelle salt crystal which is a generalization of Mitsui's model. This model is more suitable for the description of mixed system RS_{1-x} - ARS_x. The dielectric properties of Rochelle salt were experimentally studied by Valasek[13], Sandy and Jones[6], Frazer *et al.*[14]., Blinc *et al.*[15], Bjorkstam and Wilmorth[16], Akao and Sasaki[17] and Harioka and Abe[18]. Kamba *et al.*[19] have studied far infrared red reflectivity and Raman spectroscopy in Rochelle salt. Volkov *et al.*[20] have made microwave dielectric measurements in Rochelle salt. Hlinka *et al.*[21] have made inelastic neutron scattering studies in Rochelle salt crystal. In the present study, a two-sublattice pseudospin- lattice coupled-mode model[9] along with third-and fourth-order phonon anharmonic interaction terms[22] for Rochelle salt has been used.

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By applying double-time thermal Green's function method[23] expressions for the shift, width; renormalized soft mode frequency, dielectric constant and loss tangent (microwave absorption) have been evaluated. By using model values of various physical quantities, values of soft mode frequency, dielectric constant and microwave absorption for different temperatures have been calculated and compared with experimental results of Sandy and Jones[6].

2 Theory

2.1 Model Hamiltonian

For Rochelle salt, the protracted two-sublattice pseudospin lattice coupled-mode model[5], along with third-and fourth-order phonon anharmonic contact terms[22] is expressed as:

$$H = -2\Omega\sum_i \left(S_{1i}^x + S_{2i}^x\right) - \sum_{ij} J_{ij}\left[\left(S_{1i}^z + S_{2i}^z\right) + \left(S_{1i}^z + S_{2i}^z\right)\right] - \sum_{ij} K_{ij}\left(S_{1j}^z S_{2i}^z\right) - \Delta\sum_i \left(S_{1i}^z + S_{2i}^z\right) - \sum_{ij} V_{ik} S_{1i}^z A_k - \sum_{ik} V_{ik} S_{2i}^z A_k^+ + \frac{1}{4}\sum_k \omega_k \left(A_k A_k^+ + B_k B_k^+\right) + \sum_{k_1 k_2 k_3} V^{(3)}\left(k_1, k_2, k_3\right) A_{k_1} A_{k_2} A_{k_3} + \sum_{k_1 k_2 k_3 k_4} V^{(4)}\left(k_1, k_2, k_3, k_4\right) A_{k_1} A_{k_2} A_{k_3} A_{k4} \quad \ldots (1)$$

where Ω is proton tunneling 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[24]. J_{ij} describes interactions of the diploes fitting to the same and K_{ij} to the different sublattices.

2.2 Green's function, shift and width

The given below Zubarev[23], the evaluation of Green's function (GF)

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

Considering time t and t', differentiating Eq. (2) twice using the model Hamiltonian (Equation 1), applying Fourier transformation and Dyson's equation, one gets:

$$\hat{\Omega}^2 = a^2 + b^2 - bc$$

where $a = 2J_0\left\langle S_1^x\right\rangle + K_0\left\langle S_2^x\right\rangle + \Delta$ and $b = 2\Omega$ and $c = 2J\left\langle S_1^x\right\rangle + K\left\langle S_2^x\right\rangle$ One obtains Shift and width as:

Shift

$$\Delta_s(\omega) = \frac{a^4}{2\Omega\left(\omega^2 - \widetilde{\Omega}^2\right)} + \frac{b^2c^2}{2\Omega\left(\omega^2 - \widetilde{\Omega}^2\right)} + \frac{V_k^2 N_k a^2}{2\Omega\left(\omega^2 - \widetilde{\Omega}^2\right)} \quad \ldots (3)$$

Width

$$\Gamma_s(\omega) = \frac{\pi a^4}{4\Omega\widetilde{\Omega}}\left[\delta\left(\omega - \widetilde{\Omega}\right) - \delta\left(\omega + \widetilde{\Omega}\right)\right] + \frac{\pi b^2 c^2}{4\Omega\widetilde{\Omega}}\left[\delta\left(\omega - \widetilde{\Omega}\right) - \delta\left(\omega + \widetilde{\Omega}\right)\right] + \frac{\pi V_k^2 N_k a^2}{4\Omega\widetilde{\Omega}}\left[\delta\left(\omega - \widetilde{\Omega}\right) - \delta\left(\omega + \widetilde{\Omega}\right)\right] \quad \ldots (4)$$

The frequency $\hat{\Omega}$ is given by:

$$\hat{\Omega}^2 = \widetilde{\Omega}^2 + 2\Omega\Delta_{s-p}(\omega) \text{ and } \widetilde{\widetilde{\Omega}}^2 = \widetilde{\Omega}^2 + 2\Omega\Delta_s(\omega)$$

2.3 Soft mode frequency, transition temperatures, dielectric constant and loss tangent

Solving Green's function self consistently, one obtains renormalized frequency:

$$\hat{\Omega}_-^2 = \frac{1}{2}\left[\left(\widetilde{\widetilde{\omega}}_k^2 + \widetilde{\widetilde{\Omega}}^2\right) \pm \left\{\left(\widetilde{\widetilde{\omega}}_k^2 - \widetilde{\widetilde{\Omega}}^2\right)^2 + 8V_{ik}^2\left\langle S^x\right\rangle\right\}^{\frac{1}{2}}\Omega\right] \quad \ldots (5)$$

Where $\hat{\Omega}$ is the soft mode frequency which critically depends on temperature and is dependable for phase transition with $J^* = (J + K)$

$$(J+K)^* = (J+K) + \frac{V_{ik}^2\widetilde{\widetilde{\omega}}_k^2}{[\widetilde{\widetilde{\omega}}_k^4 + 4\omega_k\Gamma_k^2]}, \quad \ldots (6)$$

And

$$\eta^2 = (2J + K + 4\Omega^2 + \Delta^2) \quad \ldots (7)$$

The crystal response to the electromagnetic field is given by electrical filed and electrical susceptibility using Kubo's [25] and Zubarev's [23] formalisms is

expressed as $\varepsilon(\omega) = 1 + 4\pi\chi$, the expression for the dielectric constant following:

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

The power dissipation can suitably be expressed in dielectrics as a tangent loss. Using Eq. (8) one obtains: $\tan\delta = \dfrac{\varepsilon''}{\varepsilon'} = \dfrac{-2\Omega\Gamma(\omega)}{\left(\omega^2 - \hat{\Omega}^2\right)}$ … (9)

By using relation $\hat{\Omega}^2 = k(T - T_c)$, $\Gamma(\omega)$ i.e. $\Gamma(\omega) = \Gamma_s + \Gamma_{s-p}$, one may write a polynomial equation for loss tangent from Eq. (9) as $(T - T_c)\tan\delta = A + BT + CT^2$ ... (10)

Where A, B and C are constants. A stands for impurity in the crystal which is zero for pure crystal, B is due to third-order phonon anharmonic interaction and C is due to fourth-order phonon anharmonic interaction.

3 Mathematical Calculation and Results

By using model values of Physical quantities given by Chaudhuri *et al* 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 $\langle S_1^z \rangle, \langle S_2^z \rangle, \langle S_1^x \rangle, \langle S_2^x \rangle, \tilde{\Omega}, \tilde{\tilde{\Omega}}, \hat{\Omega}$ and dielectric constant ε across transition temperatures have been calculated .The values of shift, width, soft mode frequency, dielectric constant and loss tangent for different temperatures (240 K-340 K) have been shown in Table 1 & Figs (1 to 5) along with experimental data for dielectric constants of Kamba *et al.*[19], Sandy and Jones[6] & Chaudhuri B K *et al.*[9].

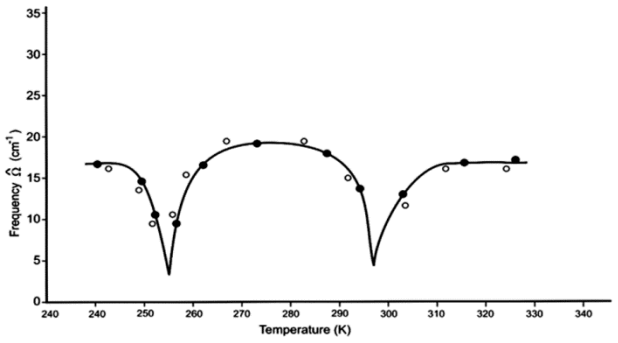

Fig. 1 — Temperature Dependence of Soft Mode Frequency ($\hat{\Omega}$) for Rochelle salt crystal [-Present Calculation, Experimental Data of Kamba et al[19], Calculation of Chaudhuri et al[9]].

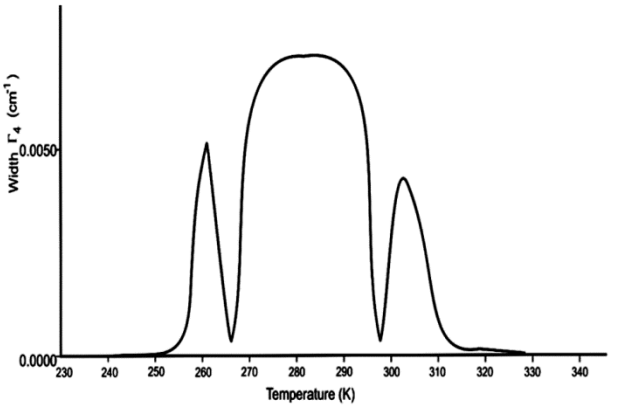

Fig. 2 — Temperature Dependence of Frequency Shift (Δ_4) in Rochelle salt crystal [-Present Calculation].

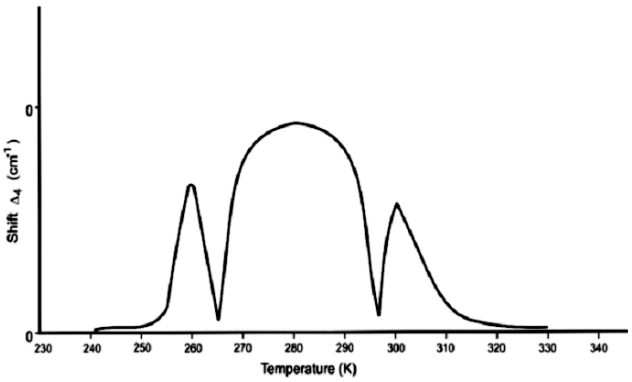

Fig. 3 — Temperature Dependence of Width (Γ_4) in Rochelle salt crystal [-Present Calculation].

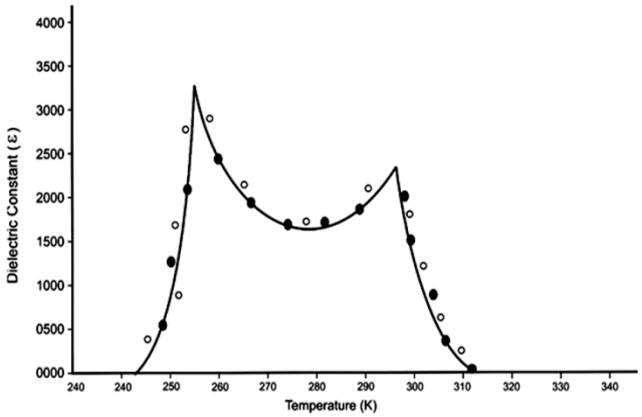

Fig. 4 — Temperature Dependence of Dielectric Constant (∈) in Rochelle salt crystal [-Present Calculation, Experimental Data of Sandy & Jones [6], Calculation of Chaudhuri *et al*[9]].

Table 1 — Calculated values of soft mode frequency ($\hat{\Omega}$), frequency shift (Δ_4), width (Γ_4) dielectric constant ($\in$), loss tangent (δ) for rochelle salt crystal.

Temperature (K)	Soft mode Frequency $\hat{\Omega}$ (cm-^{1})	Frequency Shift (Δ_4) (cm-^{1})	Width Γ_4 (cm-^{1})	Dielectric constant ($\in$)	loss tangent (δ)
240	17.103816264803	0.0000365411	0.0000465588	14.7906827675	0.313953
245	17.0990905517	0.0000730823	0.0000931176	29.5977187282	0.3142
250	17.0755398039	0.0001096234	0.0001396765	44.5191269141	0.31657
255	3.7575357490	0.0004019525	0.0005121470	3371.0151967310	0.624808
260	19.0906038223	0.0040195246	0.0051214704	1836.62342	0.296803
265	19.1126992126	0.0003654113	0.0004655882	1528.2680	0.313874
270	19.1043127590	0.0047503472	0.0060526468	1541.1850266132	0.295833
275	19.1087349513	0.0051157585	0.0065182350	1658.9696083570	0.325901
280	19.1028409321	0.0054811699	0.0069838232	1778.5644516823	0.313741
285	19.1011803281	0.0058465812	0.0074494114	1897.4652929107	0.316407
290	19.0730510250	0.0062119925	0.0079149997	2022.0078978758	0.323573
295	16.8199105039	0.0007308226	0.0009311764	1754.8265	0.342428
297	4.5577658227	0.0003650459	0.0004651226	2080.8258805072	0.594073
300	16.6554231632	0.0032887019	0.0041902939	1403.8006345139	0.362204
305	16.7209169117	0.0025578793	0.0032591175	1083.3084477409	0.352276
310	16.9718939202	0.0003654113	0.0004655882	150.2151203980	0.321152
315	16.9404502748	0.0001461645	0.0001862353	60.3093099704	0.319237
320	16.9581451647	0.0001096234	0.0001396765	45.1376375634	0.318606
325	16.9813469241	0.0000730823	0.0000931176	30.0095852977	0.317903
330	16.9935226727	0.0000365411	0.0000465588	14.9832986788	0.317353

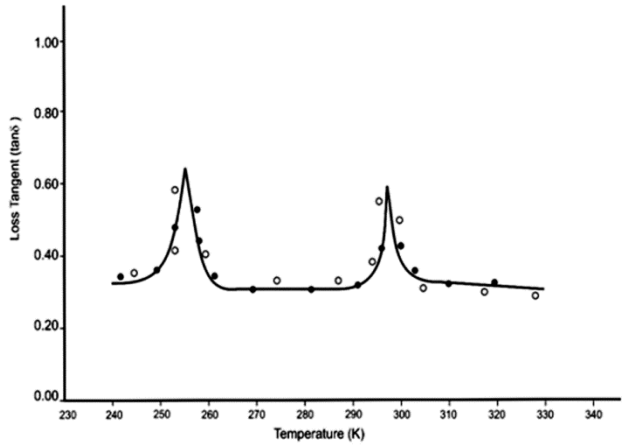

Fig. 5 — Temperature Dependence of Loss Tangent ( ) in Rochelle salt crystal [-Present Calculation, Experimental Data of Sandy & Jones [6], Calculation of Chaudhuri *et al*[9]].

4 Conclusions

By using this model, the results obtained agree with the experimental results of Sandy and Jones' for dielectric constant and loss tangent of Rochelle salt crystal. The present study shows that both inter-and inter-chain interactions are important in Rochelle salt for the explanation of low values of tunnelling frequency. The spin-lattice interaction containing phonon-anharmonic interactions as well explains the occurrence of two transition temperatures in Rochelle salt. The phonon anharmonic interactions contribute to explain the stabilization of paraelectric phases and the temperature dependence of dielectric constant, loss tangent and the soft mode frequency. The present model may also apply to other crystals such as $PbHPO_4$, $C_4O_4H_2$, and TGs etc. with slight modifications if any.

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