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Study of Ferroelectric Mode Frequency, Dielectric Constant and Loss Tangent in Triglycine Sulphate Crystal

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ABSTRACT

Considering two sub lattice pseudospin lattice coupled mode model and adding third and fourth-order phonon anharmonic interaction terms and extra spin-lattice interaction term and using double time thermal Green's function method expression for ferroelectric mode frequency, dielectric constant and loss tangent have been derived for TGS crystal. Model value have been fitted in expression and thermal dependence of above quantities have calculated for TGS crystal. Theoretical results have been compared with experimental results of others, which show good agreement.

Keywords: ferroelectric dielectric constant, anharmonic interaction , pseudospin phonon interaction.

1. INTRODUCTION

Ferroelectric crystals are special dielectrics which show spontaneous electric polarization which is reversible by stress or electric field. They find potential applications in technology due to their peculiar properties. They are used in memory devices, capacitors, optical modulators, infrared detectors etc. Triglycine sulphate $(NH_2CH_2COO)_3H_2SO_4$ crystal undergoes order-disorder phase transition at 49 ^{0}C[1]. This crystal is monoclinic in both ferroelectric and paraelectric phases. At a room temperature, a TGS crystal is white colored (transparent) and of dimensions of a = 9.15 Å, b = 12.69 Å, c = 5.73 Å, β = 105.4^0. At higher temperature these parameters are a = 9.320 Å, b = 7.277 Å, c = 8.970 Å and β = 114.91^0. TGS is interesting material for its wide range of applications. TGS found many applications in pyroelectric videocon tubes operating at room temperature and in fabrication of infrared detectors, capacitors, transducers and sensors.

Extensive experimental studies on TGS crystal have been carried out by many experimentalists. Batra and Lal[2] have done crystal growth study. Prasolve *et al.*[3] have done dielectric hysteresis loop study of TGS crystal. Beige *et al.*[4] have made experimental study of chaos near T_c in TGS crystal. Electric and mechanical properties have been studied by Murlidharan *et al.*[5]. Marciniszyn[6] has made application of TGS crystal for quartzite porous matrix. Khanum and Podder[7] have done synthesis, growth and electrical transport properties studies on pure and $LiSO_4$ doped TGS crystal. Deepti and Shanti[8] have made structural and optical studies on KDP-doped TGS crystal. Zolfagharien and Dizaji[9] have done growth and characterization of TGS single crystal doped with $NiSO_4$ grown by Sankaranarayanan-Ramasamy method. Pandian *et al.*[10] have studied crystal growth conditions of pure TGS crystal.

Theoretical studied on TGS crystal were initiated by Blinc *et al.*[11] who used Ising model. Chaudhuri *et al.*[12] have considered a two-sub lattice pseudo spin model. They have used Green's function method and obtained ferroelectric mode frequency, susceptibility, dielectric constant and transition temperature. These authors[13] have not considered third order phonon anharmonic interaction and extra spin lattice interaction term. They have decoupled the correlation at an early stage. So that they could not produce better and convincing results.

In the present work, the two sub-lattice coupled mode model with third and fourth-order phonon anharmonic interaction terms and extra spin-lattice interaction term has been considered. We have decoupled the correlations at proper stage. By using modified model and double-time thermal Green's function method, expressions for width, shift, renormalized soft mode frequency, transition temperature, dielectric constant and loss tangent have been obtained. By fitting model values of various quantities in derived formulae, their thermal variations have been calculated. The theoretically calculated values for ferroelectric mode frequency have been compared with correlated values of ferroelectric mode frequency obtained from experimental results of dielectric constant for TGS crystal reported by Stankowaska et al[14]. Theoretical results for dielectric constant and loss tangent for TGS crystal have been compared with experimentally reported results of Stankowaska *et al.*[14].

2. THEORY

For TGS crystal, the modified two sub-lattice pseudospin lattice coupled mode model, along with third and fourth-order phonon anharmonic interaction terms as well as extra spin lattice interaction term is expressed as

$$H_1 = -2\Omega\sum_i (S_{1i}^X + S_{2i}^X) - \sum_{ij}[J_{ij}(S_{1i}^Z S_{1j}^Z + S_{2i}^Z S_{2j}^Z) + K_{ij} S_{1i}^Z S_{2j}^Z]$$
$$- \sum_k V_{ik}(S_{1i}^Z A_k + S_{2j}^Z A_k^+) + \tfrac{1}{4}\sum_k \omega_k (A_k^+ A_k + B_k^+ B_k) \tag{1}$$

where s_α^m(m=x,y,z) is mth component of the Pseudospin variable S, Ω is proton tunneling frequency, J_{ij} and K_{ij} are respectively coupling constants of coupling within same lattice and different lattices. V_{ik} is spin lattice interaction constant, ω_k is phonon frequency, A_k and B_k are operators corresponding to position and momenta.

We shall add third and fourth order phonon anharmonic interactions terms

$$H_2 = \sum_{k_1k_2k_3} V^{(3)}(K_1, K_2, K_3) A_{k_1} A_{k_2} A_{k_3} + \sum_{k_1k_2k_3k_4} V^{(4)}(K_1, K_2, K_3, K_{4,}) A_{k_1} A_{k_2} A_{k_3} A_{k_4}, \tag{2}$$

where $V^{(3)}(K_1, K_2, K_3)$ and $V^{(4)}(K_1, K_2, K_3, K_4)$ are third and fourth order atomic force constants.
we shall add

$$H_3 = -2\mu E \sum_i (S_{1i}^Z + S_{2i}^Z) - \sum_{ik} V_{ik} (S_{1i}^X A_k + S_{2i}^X A_k^+), \tag{3}$$

where μ is dopole moment of O-H---O bond and E external electric field. The first term describes effect of external electric field on crystal and the second term describes the modulation of the distance between the two equilibrium sites in the O-H---O bonds. This term provides an indirect coupling between tunnelling motion of one proton and another proton. This modulates Ω by non-polar optic phonon.
we shall consider the total Hamiltonian

$H = H_1 + H_2 + H_3$

3. GREEN'S FUNCTION, SHIFT, AND WIDTH

Following Zubarev[14], we consider the Green's function

$$G_{ij}(t-t') = \langle\langle S_{1i}^z(t); S_{1j}^z(t') \rangle\rangle \;, \; = -i\theta(t-t') \langle [S_{1i}^z(t); S_{1j}^z(t')] \rangle \tag{4}$$

In Eq. (4) S_{1i}^z is spin variable, θ is step function, θ=0 for t< t' and θ=1 for t> t'. Differentiating Green's function Eq. (4) two times with respect to times t and t' respectively, Fourier transforming and writing in Dyson's equation form we obtain

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

Where $G_{ij}^0(\omega)$ is unperturbed Green's function, and $\tilde{P}(\omega)$ is polarization operator. These are given as

$$G_{ij}^0(\omega) = \frac{\Omega \langle S_{1i}^x \rangle \delta_{ij}}{\pi [\omega^2 - 4\Omega^2]} \;, \tag{6}$$

$$\tilde{P}(\omega) = \pi i \frac{\langle [F_{1i}; S_{1j}^y] \rangle}{\Omega \langle S_{1i}^x \rangle^2} + \frac{\pi^2}{\Omega^2 \langle S_{1i}^x \rangle^2} \langle\langle F_{1i}; F'_{1j} \rangle\rangle \tag{7}$$

Where

$$F(t) = 2\Omega V_{ik} A_k S_{1i}^z \delta_{ij} - 2\Omega J_{ij} (S_{1i}^z S_{1i}^x \delta_{ij} + S_{1i}^x S_{1j}^z) - V_{ik} A_k J_{ij} (S_{1i}^z S_{1i}^x \delta_{ij} + S_{1i}^x S_{1i}^z) - 2\Omega K_{ij} S_{1i}^x S_{2j}^z$$
$$- V_{ik} A_k K_{ij} S_{1i}^x S_{2j}^z - 2\Omega V_{ik} A_k S_{1i}^x - V_{ik}^2 A_k^2 (S_{1i}^x - S_{1i}^z) - 4\Omega \mu E S_{i1}^x - 2\mu E V_{ik} A_k S_{i1}^x + 2\Omega V_{ik} A_k S_{i1}^x V_{ik} A_k S_{i1}^z \tag{8}$$

The second term of $\tilde{P}(\omega)$ contains higher order Green functions $\langle\langle F_{1i};F'_{1j}\rangle\rangle$, which are like <<ab,cd>>, <<abc,def>>. These are decoupled into simpler ones and then solved. In this way $\tilde{P}(\omega)$ is evaluated. Eq. (5) gives Green's function finally as

$$G_{ij}(\omega)=\frac{\Omega\langle S_i^x\rangle\delta_{ij}}{\pi\left[\omega^2-\tilde{\Omega}^2-\tilde{P}(\omega)\right]} \tag{9}$$

where

$$\tilde{\Omega}^2=a^2+b^2-bc \tag{10}$$

$$a=2J_0\langle S_1^z\rangle+K_0\langle S_2^z\rangle, \tag{11}$$

$$b=2\Omega \tag{12}$$

$$c=2J_0\langle S_1^z\rangle+K_0\langle S_2^x\rangle \tag{13}$$

Putting the value of $\tilde{P}(\omega)$ into Eq. (9) and resolving into real $\Delta(\omega)$ and imaginary $\Gamma(\omega)$ parts we obtain

$$\Delta(\omega)=\frac{a^4}{\omega^2-\tilde{\Omega}^2}+\frac{b^2c^2}{\omega^2-\tilde{\Omega}^2}+\frac{8\Omega^2V_{ik}^2N_k}{\omega^2-\tilde{\Omega}^2}+\frac{V_{ik}^2J_{ij}^2N_k\langle S_{i1}^x\rangle^2}{\omega^2-\tilde{\Omega}^2}+\frac{V_{ik}^2K_{ij}^2N_k\langle S_{i1}^x\rangle^2}{\omega^2-\tilde{\Omega}^2} \tag{14}$$

$$\Gamma(\omega)=\frac{a^4}{2\tilde{\Omega}^2}\left[\delta(\omega-\tilde{\Omega})-\delta(\omega+\tilde{\Omega})\right]+\frac{b^2c^2}{2\tilde{\Omega}}\left[\delta(\omega-\tilde{\Omega})-\delta(\omega+\tilde{\Omega})\right]$$

$$+\frac{8\Omega^2V_{ik}^2N_k}{2\tilde{\Omega}}\left[\delta(\omega-\tilde{\Omega})-\delta(\omega+\tilde{\Omega})\right]+\frac{V_{ik}^2J_{ij}^2N_k\langle S_{1i}^x\rangle^2}{2\tilde{\Omega}}\left[\delta(\omega-\tilde{\Omega})-\delta(\omega+\tilde{\Omega})\right] \tag{15}$$

In Eq. (14) & (15) $\tilde{\tilde{\omega}}_k$ is modified phonon frequency, $\Delta_k(\omega)$is phonon shift and $\Gamma_k(\omega)$ is phonon width. They are obtained by solving phonon Green's function $\langle\langle A_k;A_{k'}^+\rangle\rangle$ by using phonon Hamiltonian only. These are obtained as

$$\Delta_k(\omega)=18P\sum_{k_1k_2}\left|V^{(3)}(k_1,k_2,-k)\right|^2\frac{\omega_{k_1}\omega_{k_2}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}}$$

$$\left\{(n_{k_1}+n_{k_2})\frac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}}{\omega^2-(\tilde{\omega}_{k_1}+\omega_{k_2})^2}+(n_{k_1}-n_{k_2})\frac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}}{\omega^2-(\tilde{\omega}_{k_1}+\omega_{k_2})^2}\right\}+48P\sum_{k_1k_2k_3}\left|V^{(4)}(k_1,k_2,k_3,-k)\right|^2$$

$$\frac{\omega_{k_1}\omega_{k_2}\omega_{k_3}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}\tilde{\omega}_{k_3}}\left\{\begin{array}{l}(1+n_{k_1}n_{k_2}+n_{k_2}n_{k_3}+n_{k_3}n_{k_4})\dfrac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3}}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2}\\+3(1-n_{k_1}n_{k_2}+n_{k_2}n_{k_3}-n_{k_3}n_{k_4})\dfrac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3}}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2}\end{array}\right\}$$

$$\Gamma_k(\omega) = 9\pi \sum_{k_1 k_2} \left| V^{(3)}(k_1, k_2, -k_3) \right|^2 \frac{\omega_{k_1}\omega_{k_2}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}}$$

$$\left\{ (n_{k_1} + n_{k_2}) \left[\delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta(\omega - \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}) \right] + (n_{k_2} - n_{k_1}) \left[\delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) \right] \right\}$$

$$+ 48\pi \sum_{k_1 k_2 k_3 k_4} \left| V^{(4)}(k_1, k_2, k_3, -k_4) \right|^2 \begin{Bmatrix} (1 + n_{k_1} n_{k_2} + n_{k_2} n_{k_3} + n_{k_3} n_{k_4}) \left[\delta(\tilde{\omega} + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}) - \delta(\tilde{\omega} - \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}) \right] \\ + 3(n_{k_1} n_{k_2} + n_{k_2} n_{k_3} - n_{k_3} n_{k_4}) \left[\delta(\tilde{\omega} + \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}) - \delta(\tilde{\omega} - \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}) \right] \end{Bmatrix} \tag{17}$$

4. FERROELECTRIC MODE FREQUENCY

By putting the above values of into Eq. (9) the Green function finally becomes

$$G_{ij}(\omega) = \frac{\Omega \left\langle S_i^x \right\rangle \delta_{ij}}{\pi \left[\omega^2 - \tilde{\Omega}^2 + 2i\Omega\Gamma(\omega) \right]}. \tag{18}$$

Where

$$\hat{\Omega}^2 = \tilde{\tilde{\Omega}}^2 + \Delta_{s-p}(\omega) \tag{19}$$

$$\tilde{\tilde{\Omega}}^2 = \tilde{\Omega}^2 + \Delta_s(\omega) \tag{20}$$

Solving Eq. (16) we obtain

$$\hat{\Omega}^2 = \frac{1}{2} \left[\left(\tilde{\tilde{\Omega}}^2 + \tilde{\tilde{\omega}}_k^2 \right) \pm \left\{ \left(\tilde{\tilde{\omega}}_k{}^2 - \tilde{\tilde{\Omega}}^2 \right)^2 + 8V_{ik} \left\langle S_i^x \right\rangle \Omega + \ldots\ldots\ldots \right\}^{\frac{1}{2}} \right]. \tag{21}$$

The frequency $\hat{\Omega}$ is ferroelectric mode frequency of TGS crystal.

5. DIELECTRIC CONSTANT AND LOSS TANGENT

The response of ferroelectric or dielectric crystal to electric field is expressed by susceptibility. This is related to Green's function as

$$\chi = -\lim_{x \to 0} 2\pi\chi N \mu^2 G_{ij}(\omega + ix) \tag{22}$$

Where N is number of dipoles with dipole moment in crystal. The dielectric constant is related to χ as

$$\varepsilon = 1 + 4\pi\chi \tag{23}$$

For ferroelectric crystals $\varepsilon >> 1$

$$\varepsilon = 4\pi\chi \tag{24}$$

From Eq. (18), (22) and (23) we obtain

$$\varepsilon(\omega) - 1 = \frac{8\pi N\mu^2\Omega\langle S_{1i}^x\rangle\delta_{ij}\left(\omega^2 - \hat{\Omega}^2\right)}{\left[\left(\omega^2 - \hat{\Omega}^2\right)^2 + 2\Omega^2 i\Gamma^2(\omega)\right]} \tag{25}$$

Where $\varepsilon(\omega) >> 1$

Eq. (25) shows that dielectric constant depends on tunneling frequency of proton, ferroelectric mode frequency $\hat{\Omega}$ (inversely).

The dissipation of electric field in dielectric crystal is expressed as loss tangent as

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{26}$$

Eq. (25) gives

$$\tan\delta = -\frac{2\Omega\Gamma(\omega)}{\omega^2 - \hat{\Omega}^2} \tag{27}$$

From Eqs. (25) and (27) one observes that dielectric constant and loss tangent depend on modified ferroelectric mode frequency. Hence, these depend upon tunneling frequency as well as anharmonic interaction terms.

Table-1: Model value of Physical quantities for TGS crystal

ω_k^2 (cm^{-2})	Ω(cm^{-1})	J(cm^{-1})	K	V_{ik}(cm$^{-3/2}$)	T_c(^{0}c)	C(^{0}c)	Nμ(10^{18}esu)	A_k
0.59	0.10	340	170	10	49	3007	2.22	10.2

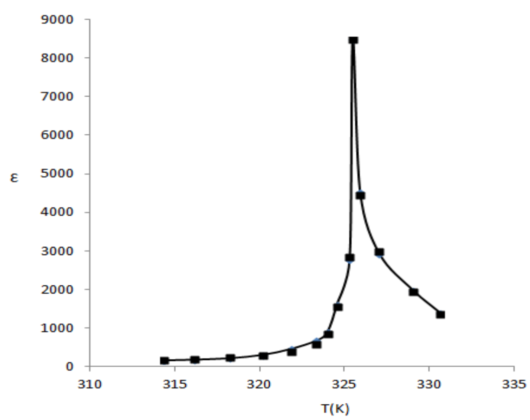

Fig.1 Calculated temperature dependence of dielectric constant in TGS crystal-Exp[14] ♦

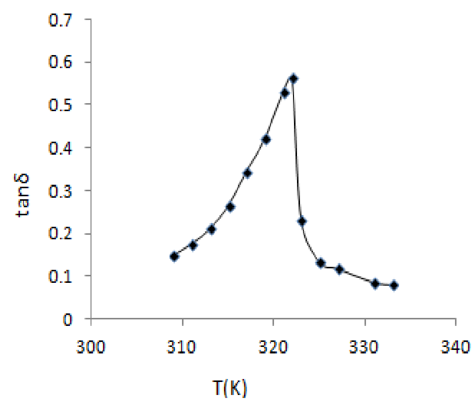

Fig.2 Calculated temperature dependence of Tangent loss in TGS crystal-Exp[14] ♦

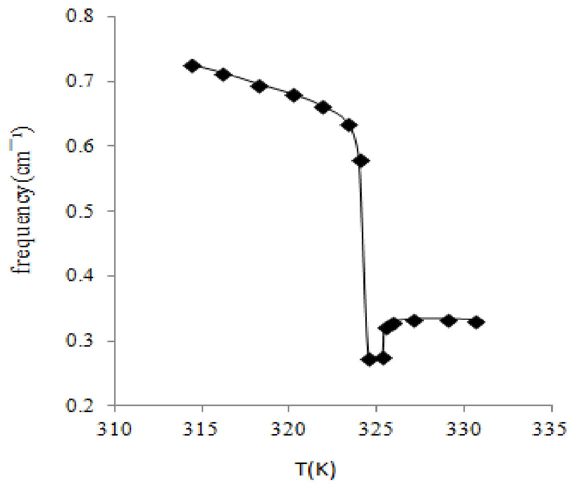

Fig. 3 Calculated temperature dependence of soft mode frequency of TGS crystal-Exp[14] ♦

6. RESULT AND DISCUSSION

By fitting model values of physical quantities Ω, J, K, V_{ik}, Nμ, T_c, ω_k (Table-1)in the expressions, (21) (23) and (26) we have calculated the temperature variations of shift, width, ferroelectric mode frequency, dielectric constant and loss tangent for TGS crystal. These are shown in fig 1-3. The theoretical variation of ferroelectric mode frequency are compared with values obtained by correlating experimental dielectric constant measurement data reported by Stankowaska *et al.*[14]for TGS crystal. The theoretical variation of dielectric constant are compared with experimental data for TGS crystal of Stankowaska *et al.*[14]. The Loss tangent values are compared with experimental data for TGS of Stankowaska *et al.*[14]. Theoretical results agree with experimental data for TGS crystal.

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