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# Ferroelectric Phase Transition and Dielectric Response of Triglycine Sulphate Crystal and its Isomorphs†

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Considering two sublattice pseudospin lattice coupled mode model of Chaudhuri *et al.* along with third and fourth-order phonon anharmonic interaction terms is considered for triglycine sulphate crystal and its isomorphs. With the help of double-time temperature dependent Green's function method, expressions for shift, width, soft mode frequency, dielectric constant and loss tangent are derived. By fitting model values in the theoretical expressions, temperature dependence of soft mode frequency, dielectric constant and loss tangent have been calculated. The theoretical results compare well with experimental results of Aravazhi *et al*.

**Key Words: Anharmonic interactions, Ferroelectrics, Dielectrics, Green's function, Soft mode, Pseudospin-lattice.**

## INTRODUCTION

The ferroelectric nature of triglycine sulphate $(CH_2NH_2COOH)_3H_2SO_4$ (TGS), was discovered by Matthias, Miller and Remeika[1]. Despite its complex chemical and crystallographic form it became the object of active research for two reasons; firstly, it is one of very few ferroelectrics known to exhibit a second order phase transition and hence to offer possibilities for observation of genuine critical phenomena very close to Curie temperature; secondly, it is uniaxial and has dielectric properties which are not grossly affected by deuteration.

Ferroelectric materials are widely used in memory devices, infrared and pyro-electric detectors, transducers, display devices, piezoelectric devices, capacitors *etc*. Triglycine sulphate $(CH_2NH_2COOH)_3H_2SO_4$ crystal is one of the best pyroelectric material but it is also being used as storage device and laser and transduser material. Large crystals are easily grown from water solution.

Experimental studies on triglycine sulphate crystal have been carried out by many researchers in past, Hoshino *et al*.[2] have determined detailed crystal structure of triglycine sulphate crystal by means of X-ray diffraction. Lal and Batra[3] have carried out detailed crystal growth and characterization studies on triglycine sulphate crystal. Doped triglycine sulphate crystal have been grown by Sun *et al.*[4]. Different modified crystals have been grown by Fang *et al.*[5]. Yamaguchi *et al*.[6] have made dilatometer studies on triglycine sulphate crystal down to cryogenic temperatures. Alexandru and Berbecaru[7] have grown pure and doped triglycine sulphate crystals and studied its ferroelectric properties. Prasolov *et al*.[8] have carried out hysteresis loop studies of triglycine sulphate crystal experimentally. Arago and Gonzalo[9] have carried out crystal growth studies of triglycine sulphate and deuterated triglycine sulphate crystals. Costache *et al*.[10] have studied pyroelectric properties of pure and doped triglycine sulphate crystals. Beerman[11] has studied pyroelectric properties of triglycine sulphate crystal. Shreekumar and Philip[12] have carried out ultrasonic study of pure and doped triglycine sulphate crystals. Aravazhi *et al*.[13] have measured dielectric constant and loss tangent of triglycine sulphate crystal.

Blinc *et al*.[14] have used pseudospin model to study ferroelectric transition of triglycine sulphate crystal. Chaudhuri *et al*.[15] have used two sublattice-model of Mitsui[16] (applied for Rochelle salt earlier) along with third and fourth order phonon anharmonic interaction terms. Ever since ferroelectricity was discovered in triglycine sulphate crystal by Mathias *et al.*[1] theoretical studies were initiated.

In the present study, we have extended two-sublattice pseudospin lattice coupled mode model by adding third-and fourth-order phonon anharmonic interactions terms[17-20] for triglycine sulphate crystal. Expressions for shift, width, soft mode frequency, dielectric constant and loss tangent have been derived using double time thermal Green's function method[21].

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Temperature dependence of these quantities have been calculated using model values from literature[20]. The theoretical variations of soft mode frequency, dielectric constant and loss tangent are compared with experimental results of Aravazhi *et al.*[13].

## THEORY

**Model Hamiltonian and Green's function:** For triglycine sulphate crystals two-sublattice pseudospin-lattice coupled mode model by adding third and fourth order phonon anharmonic interaction terms, which is expressed as:

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

$$- \sum_{ij} K_{ij}\left(S_{1i}^z S_{2i}^z\right) - \sum_{ij} B_{ij}\left(S_{1i}^z S_{2j}^z + S_{2i}^x S_{1j}^x\right) - \sum_{ik} V_{ik} S_{1i}^z A_k$$

$$- \sum_{ik} V_{ik} S_{2i}^z A_k^+ + \frac{1}{4}\sum_k \omega_k \left(A_k A_k^+ + B_k B_k^+\right) +$$

$$\sum_{k_1 k_2 k_3} V^{(3)}\left(k_1, k_2, k_3\right) A_{k_1} A_{k_2} A_{k_3}$$

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

where, $\Omega$ is proton tunnelling frequency, $S^z$ and $S^x$ are components of pseudospin variable, S and $J_{ij}$ is interaction constant between same lattice and $K_{ij}$ is interaction constant between different lattices, $V_{ik}$ is spin-lattice interaction and $A_k$ and $B_k$ are position and momentum operators, $\omega_k$ is harmonic phonon frequency $V^{(3)}$ and $V^{(4)}$ are third-and fourth-order atomic force constants[17].

**Green's function, shift, width and soft mode frequency**: We consider the Green's function[26]

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

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

where, $\theta(t- t')$ is unit step function, which is zero for $t < t'$ and unity for $t > t'$. Differentiating twice Green's function with respect to time t and then with respect to time t' using model Hamiltonian (1), taking Fourier transform and setting it into Dyson's equation form

$$G_{ij}(\omega) = G_{ij}^0(\omega) + G_{ij}^0(\omega) P(\omega) G_{ij}^0(\omega) \quad (3)$$

Spin shift is obtained as:

$$\Delta_s(\omega) = \frac{a^4}{2\Omega\left(\omega^2 - \tilde{\Omega}^2\right)} + \frac{b^2c^2}{2\Omega(\omega^2 - \hat{\Omega}^2)} + \frac{V_{ik}^2 N_k a^2}{2\Omega\left(\omega^2 - \tilde{\Omega}^2\right)} \quad (4)$$

Spin-phonon shift is obtained as :

$$\Delta_{s-p}(\omega) = \frac{2V_{ik}^2\langle S_{1i}^x\rangle\omega_k\delta_{k-k}\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)^2 + 4\omega_k^2\Gamma_k^2(\omega)\right]} \quad (5)$$

Spin-width is obtained as :

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

$$+ \frac{V_{ik}^2 N_k a^2}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right] \quad (6)$$

Spin-phonon width is obtained as :

$$\Gamma_{s-p}(\omega) = \frac{4V_{ik}^2\langle S_{1i}^x\rangle\omega_k\delta_{k-k'}\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)^2 + 4\omega_k^2\Gamma_k^2(\omega)\right]} \quad (7)$$

In the above Eqns. (5) and (7), $\tilde{\tilde{\omega}}_k$ is renormalized phonon frequency and $\Gamma_k(\omega)$ is phonon width in the Green's function $G_{kk'}(\omega) = \langle\langle A_k; A^+_{k'}\rangle\rangle$ which is obtained as:

$$G_{kk'}(\omega) = \frac{\omega_k\delta_{kk'}}{\pi\left[\omega^2 - \tilde{\tilde{\omega}}_k^2 + 2i\omega_k\Gamma_k(\omega)\right]} \quad (8)$$

The Green's function (2) becomes

$$G_{ij}(\omega) = \frac{\Omega\langle S_{1i}^x\rangle\delta_{ij}}{\pi\left(\omega^2 - \hat{\Omega}^2 - 2\Omega i\Gamma(\omega)\right)} \quad (9)$$

where, $\hat{\Omega}^2 = \tilde{\tilde{\Omega}}^2 + 2\Omega\Delta_{s-p}(\omega)$ (10)

$$\tilde{\tilde{\Omega}}^2 = \tilde{\Omega}^2 + 2\Omega\Delta_s(\omega) \quad (11)$$

and

$$\tilde{\Omega}^2 = 4\Omega^2 + \frac{1}{\Omega\langle S_{1i}^x\rangle}\left\langle\left[F, S_{1i}^y\right]\right\rangle \quad (12)$$

In eqn. 12 sec term is evaluated using mean field approximation:

$$\frac{\langle S_{1i}^z\rangle}{a} = \frac{\langle S_{1i}^x\rangle}{b} = \frac{1}{2\tilde{\Omega}}\tanh\beta\frac{\tilde{\Omega}}{2} \quad (13)$$

which gives

$$\tilde{\Omega}^2 = a^2 + b^2 - bc \quad (14)$$

where, $a = 2J\langle S_1^z\rangle + K\langle S_2^z\rangle$, $b = 2\Omega + B\langle S_i^x\rangle$, i = 1 or 2 and

Solving Eq. (10) self consistently, one obtains soft mode frequency

$$\hat{\Omega}_\pm^2 = \frac{1}{2}\left(\tilde{\tilde{\omega}}_k^2 + \tilde{\tilde{\Omega}}^2\right) \pm \frac{1}{2}\left[\left(\tilde{\tilde{\omega}}_k^2 - \tilde{\tilde{\Omega}}^2\right)^2 + 8V_{ik}^2\langle S_{1i}^x\rangle\Omega\omega_k\right]^{1/2} \quad (15)$$

where, $\hat{\Omega}_-$ frequency is the soft mode frequency of triglycine sulphate crystal. This frequency is responsible for phase transition in triglycine sulphate crystal.

**Dielectric constant and loss tangent:** The response of a dielectric crystal to electric field is expressed by electric susceptibility ($\chi$).

$$\chi = -\lim_{X\to 0} 2\pi N\mu^2 G_{ij}(\omega + iX) \text{ and } \epsilon = 1 + 4\pi\chi \quad (16)$$

we obtain dielectric constant is obtained as:

$$\epsilon = \left(-8\pi N\mu^2\right)\langle S_1^x\rangle\left(\omega^2 - \hat{\Omega}^2\right)\left[\left(\omega^2 - \tilde{\tilde{\Omega}}^2\right)^2 + 4\Omega^2\Gamma^2\right]^{-1} \quad (17)$$

and tangent loss is expressed as:

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \tag{18}$$

By using Eq. (17) and (18) we obtain expression for loss tangent

$$\tan\delta = -\frac{2\Omega\Gamma(\omega)}{\left(\omega^2 - \hat{\Omega}^2\right)} \tag{19}$$

At microwave frequencies $\omega \ll \hat{\Omega}$, so Eqn. (19) reduces to

$$\tan\delta = \frac{2\Omega\Gamma(\omega)}{\left(\hat{\Omega}^2\right)} \tag{20}$$

## RESULTS AND DISCUSSION

**Numerical calculation:** By using model values in theoretical expressions for $\hat{\Omega}$, $\epsilon$ and tanδ are obtained and shown in Figs 1-3. Present obtained variations are compared with experimental data of Aravazhi *et al.*[13], which shows a good agreement (Tabele-1).

The study of ferroelectric crystals reveals about inter- and intra molecular interactions, molecular motion and conformational changes in macromolecules. In this paper, by modifying two sublattice pseudospin lattice coupled mode model for triglycine sulphate crystals, by adding third-and fourth order phonon anharmonic interaction terms expressions for shift, width, soft mode frequency, dielectric constant and loss tangent have been evaluated. Using model values given by Chaudhuri *et al.*[15], temperature dependence of shift, width, soft mode frequency, dielectric constant and tangent loss have been obtained for triglycine sulphate crystal.

TABLE-1
MODEL VALUES OF PHYSICAL PARAMETERS FOR TRIGLYCINE SULPHATE CRYSTAL[13]

| $\omega^2_k$ ($cm^{-2}$) | Ω ($cm^{-1}$) | J ($cm^{-1}$) | K ($cm^{-1}$) | B | $V_{ik}$ ($cm^{-3/2}$) | $T_c$ (K) ($cm^{-1}$) | C (K) | Nμ ($10^{18}$esu) | $A_k$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.59 | 0.10 | 340 | 0 | 0 | 10 | 49.410 | 3007 | 2.22 | 10.2 |

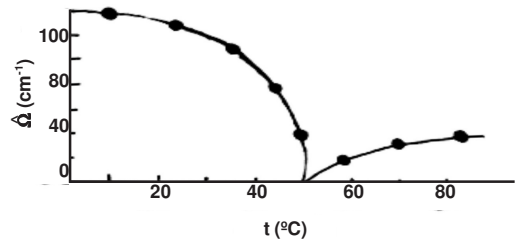


Fig. 1. Calculated temperature dependence of soft mode frequency in triglycine sulphate crystal: (present calculation-experiment[13]•)

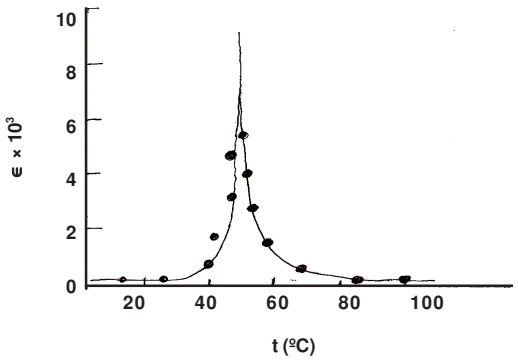


Fig. 2. Calculated temperature dependence of dielectric constant in triglycine sulphate crystal:(present calculation-experiment[13]•)

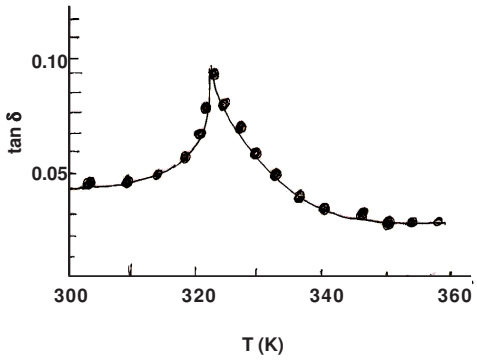


Fig. 3. Calculated temperature dependence of tangent loss in triglycine sulphate crystal : (present calculation- experiment[13].)

### Conclusion

Present study reveals that the two sublattice pseudospin-lattice coupled mode model along with third and fourth order phonon anharmonic interaction tearms explains well the temperature dependence of soft mode frequency, dielectric constant and loss tangent in triglycine sulphate crystal. Theoretical results fairly agree with experimental results of Aravazhi *et al.*[13].

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