Applied Innovative Research
Vol. 2, September 2020, pp. 208-212

Theoretical investigation of structural phase transition and microwave dielectric properties in triglycine sulphate (TGS) crystal

Muzaffar Iqbal Khan*, Pawan Singh & T C Upadhyay

Department of Physics, H N B Garhwal University (A Central University) Srinagar (Garhwal) -246 174, India

Received 7 September 2020

By using the extended two sublattice pseudospin coupled mode (PLCM) model by summing third-order and fourth-order anharmonic interactions as well as extra spin lattice interactions, direct spin-spin interaction and electric field terms is considered for triglycine sulphate crystal (TGS) crystal. With the help of double-time thermal dependent Green's function method and Dyson's equation, expressions for soft mode frequency dielectric constant and loss tangent for triglycine sulphate crystal. By fitting the model values in the theoretical expressions, thermal variations of soft mode frequency, dielectric constant and loss tangent are calculated and compare well with the experimental data of Bye *et al*.

Keywords: Anharmonic interactions, Green function method, Triglycine sulphate

Introduction

Ferroelectric materials have great applications in memory devices, pyroelectric and infrared detectors, transducers, display devices, capacitors, piezoelectric devices etc. Triglycine sulphate (TGS) crystal is one of the pyroelectric materials, used as laser and transducer material and storage devices and one of the rare ferroelectrics which show isostructural phase transition. TGS received universal attention ever since Mathias *et al.*[1] have discovered its ferroelectric phase transition properties. The crystal structures are easily grown from aqueous water solution. It is uniaxial ferroelectric material with transition temperature 322K[1,2]. The crystal structure is monoclinic system in both polar and non-polar phases. The transition is second-order and order-disorder type ferroelectrics. Below the transition temperature (T_c) the space group of the TGS crystal is P_{2_1} of monoclinic structure and above the transition temperature(T_c), it possesses the P_{2_1}/m which is centrosymmetric and thus is non-piezoelectric material[1,2]. After a transition mirror plane disappears and crystal belongs to isostructural phase transition. Triglycine sulphate crystal and its isomorphs such as TGSe, TGBe etc are very similar in their essential character to KDP-type crystal. The temperature expansion is also an important thermodynamic property of crystals, since it is a result of the interactions and excitation of their constituent elements. The spontaneous polarization arises parallel to b-axis of the monoclinic system. This b-axis cut plates of triglycine sulphate crystals are used for room temperature infrared detectors, radiation monitoring, earth exploration and astronomical telescopes. The dielectric properties, transition temperature and Curie-Weiss are not greatly affected by its deuteration showing that tunnelling effect is present in TGS crystal.

Experimental explanations on TGS crystal have carried by Hoshino *et al.*[3] and determined the crystal structure of TGS by means of X-ray diffraction. Pasalov *et al.*[4] have studied the hysteresis loop measurements in TGS. Chan *et al.*[5] have explained the domain wall motion in triglycine sulphate crystal by using a pyroelectric probe. Sun *et al.*[6] have done the study of growth and pyroelectric properties of pure and doped TGS crystals. Lal and Batra[7] have studied the crystal structure growth and characterization studies on TGS crystal. Yamaguchi *et al.*[8] have done dilatometer studies on TGS down to cryogenic temperatures. Arago and Gonzalo[9] have studied the crystal growth and characterization of triglycine sulphate crystal. Alexandru and Berbecaru[10] have grown pure and doped triglycine sulphate crystals and studied its ferroelectric properties. Costache *et al.*[11] explained the pyroelectric properties of pure and doped TGS crystals. Dolino *et al.*[12] have done second harmonic generation studies experimentally in TGS crystal. Hill and Ichiki[13] have studied the polarization relaxation experimentally in TGS crystal. Aravazhi

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

et al.[14] studied the dielectric constant and loss tangent experimentally in TGS crystal. Beeman[15] has explained the pyroelectric properties of triglycine sulphate crystal. Shreekumar and Philip[16] have studied ultrasonic study of pure and doped triglycine sulphate crystals. Tello and Hernandez[17] have applied tunnelling model to explain the phase transition mechanism in TGS crystal. Gonzalo[18] explained the phase transition in TGS crystal by using Ising model. Bye *et al.*[19] have measured dielectric constant and spontaneous polarization of TGS crystal in the presence of external applied electric field. Blinc *et al.*[20] have studied the ferroelectric properties of triglycine sulphate crystal by using pseudospin model Hamiltonian. Chaudhuri *et al.*[21] have used two sublattice Mitsui model[22] along with third and fourth-order anharmonic interaction terms. However due to an early decoupling of correlations they could not find better results to define ferroelectric properties and dielectric properties of TGS crystal. Ganguli *et al.*[23] studied the Green function theory of phase transition in H-bonded ferroelectric crystals with pseudospin lattice coupled mode (PLCM) model Hamiltonian. Chaudhuri *et al.*[24] studied the ferroelectric phase transitions in the Rochelle salt (RS) crystal with two sublattice PLCM model Hamiltonian. Chaudhuri *et al.*[25] studied the Green function theory of phase transition in H-bonded LHP-type ferroelectrics with PLCM model Hamiltonian.

In the present study, we have extended the two sublattice pseudospin lattice coupled (PLCM) model[21] by summing third- and fourth-order anharmonic interaction terms[26-29]along with third-order and fourth-order anharmonic interactions as well as extra spin lattice interactions, direct spin-spin interaction and electric field terms is considered for TGS crystal. Theoretical expressions for soft mode frequency, dielectric constant and loss tangent have been derived by using the double time temperature dependent Green's function method[30]. By fitting the model values in these expressions from literature[21], the temperature dependences of these quantities have been calculated. The theoretical thermal variations of soft mode frequency, dielectric constant and loss tangent are well agreed with the experimental data of Bye *et al.*[19].

Theory (Numerical Calculations and Results)

For TGS crystal we have used extended two sublattice PLCM model by adding third- and fourth-order anharmonic interactions terms along with extra spin lattice interactions, direct spin-spin interaction and electric field terms is considered. Following the Zubarev[30], we consider the evaluation of Green's function theory

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

where $\theta(t-t')$ is unit step function which is zero for $t < t'$ and unity for $t > t'$. The angular bracket $\langle \ldots \rangle$ denotes the ensemble average over a grand canonical ensemble. Differentiating Green's function Eq. (1) twice with respect to time t and time t' respectively by using the modify model Hamiltonian[21]. Apply the Fourier transform in the Dyson's equation we get final expression for Green's function by applying the symmetric decoupling scheme expressed as:

$$G_{ij}(\omega) = \frac{\Omega\langle S_{1i}^{x}\rangle\delta_{ij}}{\pi[\,\omega^2 - \widehat{\Omega}^2 - 2i\Omega\Gamma(\omega)]} \quad \ldots (2)$$

Solving the Eq. (2) self consistently we get the final expression for Green's function as in the form:

$$\widehat{\Omega}^2 = \widetilde{\widetilde{\Omega}}^2 + \Delta_{s-p}(\omega) \quad \ldots (3)$$

where

$$\widetilde{\widetilde{\Omega}}^2 = \widetilde{\Omega}^2 + \Delta_{s}(\omega) \quad \ldots (4)$$

$$\widetilde{\Omega}^2 = a^2 + b^2 - bc \quad \ldots (5)$$

where

$$\mathrm{a} = 2J_{ij}\langle S_{1i}^{z}\rangle + K_{ij}\langle S_{1i}^{z}\rangle - 2B_{ij}\langle S_{1i}^{z}\rangle + 2\mu E \quad \ldots (6)$$

$$\mathrm{b} = 2\,\Omega \quad \ldots (7)$$

where Ω is the phonon tunnelling frequency and

$$\mathrm{c} = 2J_{ij}\langle S_{1i}^{x}\rangle + K_{ij}\langle S_{1i}^{x}\rangle - 2B_{ij}\langle S_{1i}^{x}\rangle \quad \ldots (8)$$

Also

$$\langle S_1^z\rangle = -S_2^z \neq 0, T < T_c \quad \ldots (9)$$

where, $\widetilde{\Omega}$ and $\widetilde{\widetilde{\Omega}}$ is the first and second pseudospin frequency and $\widehat{\Omega}$ is the third and final modified frequency.

In equations (2) and (3), $\Gamma(\omega)$ and $\Delta(\omega)$ are the width and shift of response function.

After solving the calculations of equation (3), we obtained final expression for modified soft mode frequency ($\widehat{\Omega}$) as,

$$\widehat{\Omega}^2 = \frac{\left(\omega_k^2 + \widetilde{\widetilde{\Omega}}^2\right)}{2} \pm \frac{1}{2}\left\{\left(\omega_k^2 + \widetilde{\widetilde{\Omega}}^2\right)^2 + 4\{8aV_{ik}^2\langle S_{1i}^z\rangle\omega_k + 2bV_{ik}^2\langle S_{1i}^x\rangle\omega_k + 4bV_{ik}^2\langle S_{1j}^z\rangle\omega_k + \ldots\ldots\}\right\}^{\frac{1}{2}} \quad \ldots (10)$$

In the Eq. (10), $\widehat{\Omega}$ is the soft mode frequency which becomes zero at transition temperature causing phase transition in triglycine sulphate crystal.

Following the Zubarev[30], we obtained the dielectric permittivity (ε) for triglycine sulphate crystal as obtained by

$$\varepsilon = -\frac{8\pi N\mu^2\langle S_{1i}^x\rangle\left(\omega^2 - \widehat{\Omega}^2\right)}{\left[\left(\omega^2 - \widehat{\Omega}^2\right)^2 + 4\Omega^2\Gamma^2(\omega)\right]} \quad \ldots (11)$$

The loss of power in dielectric constant when it is exposed to an applied ac electric field called loss tangent expressed as

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = -\frac{2\Omega\Gamma(\omega)}{\left(\omega^2 - \widehat{\Omega}^2\right)} \quad \ldots (12)$$

where, ε' is the real part and ε'' is the imaginary part of the dielectric constant.

By fitting the model Hamiltonian values of various physical parameters from literature given in the Table (1), the temperature dependence of soft mode frequency, dielectric constant and loss tangent for triglycine sulphate crystal have been calculated and shown in Figs. (1-3).

where T_c is the Curie temperature or transition temperature and C is the Curie-Weiss constant, ω_k is the phonon frequency, $J_{ij}$and K_{ij} are the inter-sublattice and intra-sublattice interactions respectively, Ω is the tunnelling energy. A_k is the contribution of the anharmonic parameter, N is the number of unit cells in the crystal, V_{ik} represents the proton-lattice interaction constant. μ is the dipole moment along the direction of polarization axis. E is the applied electric field and B_{ij} is the corresponding direct coupling constant.

Our theoretical results are well comparing with experimental data of Bye *et al.*[19] for triglycine sulphate crystal shown in Figs. (1-3) show good agreement.

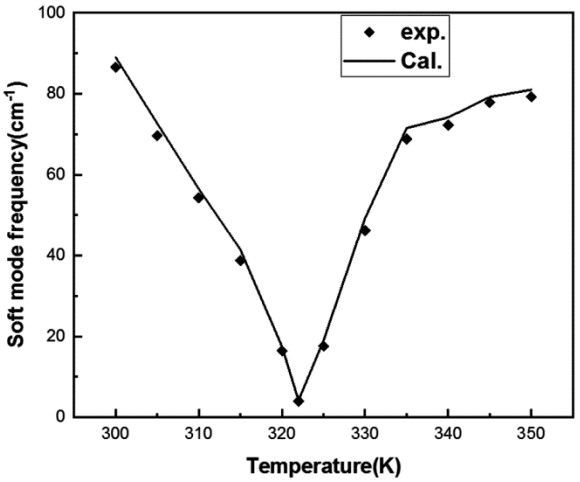

Fig. 1 — Calculated temperature dependence of soft mode frequency for TGS crystal compare with the correlations data of Bye *et al.*[19].

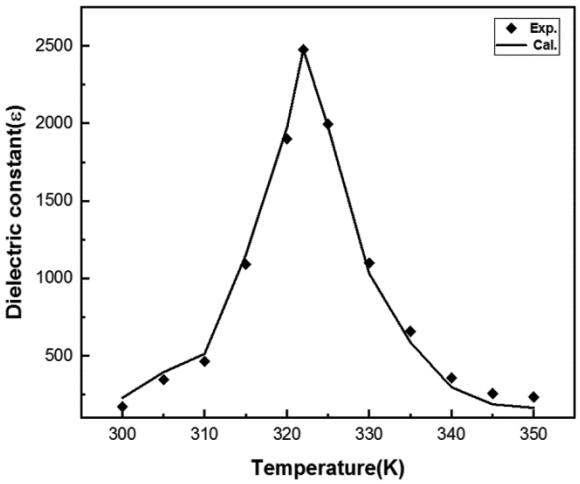

Fig. 2 — Calculated temperature dependence of dielectric constant for TGS crystal compare with experimental data of Bye *et al.*[19].

Table 1 — Shows model values of various physical parameters for triglycine sulphate[21].

T_c (K)	C (K)	ω_k^2 (cm^{-2})	J_{ij} (cm^{-1})	K_{ij} (cm^{-1})	Ω (cm^{-1})	B_{ij} (cm^{-1})	V_{ik} $(cm^{3/2})$	$N_k(at\ T_c)$
322	3280	0.59	340	0	0.10	0.6	10	2.22
$N(cm^{-3})$	$\mu(esu)$	E (kV/cm)	$2\mu E$ (kJ/cm^3)	A_k				
3.8×10^{22}	1.51×10^{-18}	1	0.553	10.2				

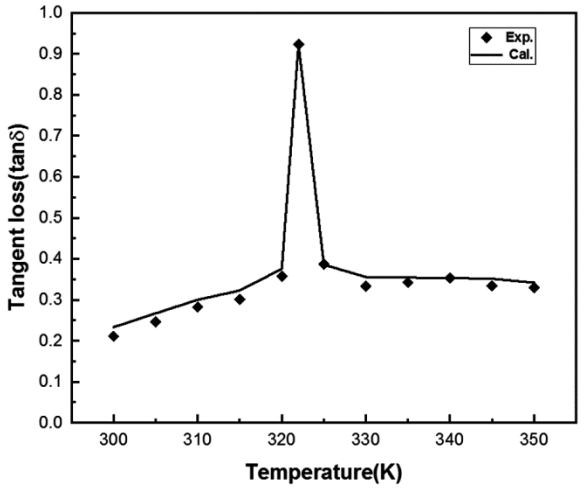

Fig. 3 — Calculated temperature dependence of tangent loss for TGS compare with experimental data of Bye *et al.*[19].

Discussion

In this paper, for TGS modifying the two sublattice PLCM model Hamiltonian by adding third- and fourth-order Phononanharmonic interaction terms along with extra spin lattice interactions, direct spin-spin interaction and electric field terms, expressions for soft mode frequency dielectric constant and loss tangent have been evaluated. By fitting the model values of various parameters given by Chaudhuri *et al.*[21], thermal dependence of soft mode frequency, dielectric constant and loss tangent have been obtained for TGS. Earlier workers[27-29] has not considered phonon anharmonic interactions as well as extra terms and two-sublattice pseudospin model. Only a rear authors[27-29] have used two sublattice model, with third anharmonic interactions terms but not get better results as they have decoupled the correlations at early stage. As a result some important interactions disappeared. Our calculated results compare well with experimental data of Bye *et al.*[19]. It can be seen from the expressions that soft mode frequency is the same as the initial frequency of Chaudhuri *et al.*[21]. However, our soft mode frequency, contain extra terms like $\Delta_s(\omega)$ same as Chaudhuri *et el.*[21]. Soft mode frequency like the term $\Delta_{s-p}(\omega)$. But our soft mode frequency contains the extra term in $\widetilde{\widetilde{\omega}}_k$ and $\Gamma_k(\omega)$. These extra terms are due to the term $|V^3(k_1, k_2, -k)|^2$ given in $\Delta_k(\omega)$ and $\Gamma_k(\omega)$. These terms differentiate our expressions with Chaudhuri *et al.*[21]. The calculated values of soft mode frequency,dielectric constant and loss tangent are in good agreement with experimental data. Similar way the thermal variations of soft mode frequency, dielectric constant and loss tangent can be calculated for isomorphs and its deuterated families of TGS-type crystals. Loss tangent can be explained, a transverse radiation field derives the low-lying transverse mode of the material in a forced vibration. Due to anharmonic interactions terms, decay processes take place such as third order interaction leads to the decay of a virtual phonons or the phonon may be destroyed by scattering a temperature excited phonon. Same process occurs for the fourth-order and higher order anharmonic interactions. We have been done modelling and fitted well our theoretical results for soft mode frequency, dielectric constant and dielectric tangent loss with experimental data of Bye *et al.*[19]. From Fig. (1), we find that the soft mode frequency decreases as the value of temperature of increases and become minimum at T_c(soften) and then increases as the value of temperature of increases. In Fig. (2), the value of dielectric constant increases as the temperature increases and become maximum at T_c and from Fig. (3) the dielectric tangent loss has shown almost same behaviour as dielectric constant.

Conclusions

Present study explains that the two sublattice PLCM model along with third- and fourth-order anharmonic interaction terms along with extra spin lattice interactions, direct spin-spin interaction and electric field terms explains well the temperature dependence of soft mode frequency, dielectric constant and dielectric loss tangent in TGS crystal. Theoretical obtained results are in good agreement with experimental data of Bye *et al.*[19]. This theory may also applicable for KDP, RDP, LHP, RS and CDP etc. crystals.

Acknowledgment

The authors are very thankful to prof. B.S. Semwal, Prof. P.D. Semalty (HOD), Prof. S.C. Bhatt and Dr. Manish Uniyal for kind suggestions and encouragements in the work.

References

1 Mathias B T, Miller C E & Remeika, *Phys Rev*, 104 (1956) 449.
2 Nakamura E, et al., Ferroelectrics and Related Substances-Landolt-Bornstein New Series III/36C (Springer Berlin Heidelberg, New York, 2006).
3 Hoshino S, Okaya Y & Peninsky R, *Phys Rev*, 115 (1959) 323.
4 Pasalov B N, Palagin M Y & Gorbatenko V V, *Ferroelectrics*, 214 (1988) 325.
5 Chan T D, Xavier & Aremand H, *Ferroelectrics*, 33 (1981) 31.

6 Sun X,Wang M, Pan Q W, Shi W & Fang C S, *J Exp Indus Crystal*, 34 (1999) 1251.
7 Lal R B & Batra A K, *Ferroelectrics*, 142 (1993) 51.
8 Yamaguchi T, et al., *Ferroelectrics*, 337 (2006) 59.
9 Arago C & Gonzalo J A, *J of Physics C: Cond Mat*, 12 (2000) 3737.
10 Alexandru H V & Ciceron A B, *Ferroelectrics*, 202 (1997) 173.
11 Costache M, Matei I, Pintilie L, Alexandru H V & Berbecaru C, *J Optoelect Adv Mater*, 3 (2001) 75.
12 Dolino G, Lajzerowicz J & Vallade M, *Phys Rev B*, 2 (1970) 2194.
13 Hill R M & Ichiki S K, *Phys Rev*, 132 (1963) 1603.
14 Aravazhi S, Jayavel R & Subramanian C, *Ferroelectrics*, 200 (1997) 279.
15 Beerman H P, *Ferroelectrics*, 2 (1971) 123.
16 Shreekumar R & Philip J, *Ferroelectrics*, 160 (1994) 23.
17 Tello M J & Hernandeez E, *J Phys Soc Jap*, 35 (1973) 1289.
18 Gonzalo J A, *Phys Rev B*, 1 (1970) 3125.
19 Bye K L, Whipps P W & Keve E T, *Ferroelectrics*, 4 (1972) 253.
20 Blinc R, Detoni S & Pintar M, *Phys Rev*, 124 (1961) 1036.
21 Chaudhuri BK, Choudhary K R & Banerjees S, *Phys Rev B*, 38 (1988) 689.
22 Mitsui T, Phys Rev, 111 (1958) 1259.
23 Ganguli S, Nath D & Chaudhuri B K, *Phys Rev B*, 21 (7) (1980) 2937.
24 Chaudhuri B K, *et al.*, *J Phys Soc Jap*, 49 (2) (1980) 608.
25 Chaudhuri B K, Ganguli S & Nath D, *Phys Rev B*, 23 (5) (1981) 2308.
26 Semwal B S & Sharma P K, *Prog Theor Phys*, 51 (1974) 639.
27 Upadhyay T C & Semwal B S, *Ind J Pure Appl Phys*, 40 (2002) 615.
28 Upadhyay T C, *Ind J Pure Appl Phys*, 45 (2007)157.
29 Upadhyay T C & Gairola S, *Ind J Pure and Appl Phys*, 46 (2008) 727.
30 Zubarev D N, *Sov Phys Uspekhi*, 3 (1960) 320.