

Thermal Variation of Vibrational Frequency and Dielectric Constant in Triglycine Selenate Crystal

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ABSTRACT

Using the method of retarded double-time thermal Green's function with a two sub-lattice pseudospin lattice coupled mode (PLCM) model modified for triglycine selenate crystal with third and fourth-order phonon anharmonic interaction and extra spin-lattice coupling terms expressions for Shift, width, vibrational frequency and dielectric constant have been evaluated. Fitting the values of model parameters in expressions for vibrational frequency and dielectric constant for triglycine selenate crystal thermal dependence of these quantities have been obtained. Theoretical results compare well with experimental results of Polandov *et al.*¹⁵.

Keywords: vibrational frequency, dielectric constant, ferroelectrics, Green's function, triglycine selenate.

INTRODUCTION

Ferroelectric materials have attracted considerable interest due to their use in fabricating various optoelectronic and microelectronic devices like that capacitors, transducers, detectors, RAM, microactuators and microsensors. Ferroelectric materials are unusual dielectrics showing spontaneous electric polarization which is reversible by an external electric field. This property of showing spontaneous polarization persists in a limited temperature range. Above certain temperature material losses its ferroelectric properties and becomes paraelectric. Triglycine selenate $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SeO}_4$ is a well known ferroelectric material, belongs to the glycine salt family (TGS family: TGS, TGFB, TGSe). It undergoes a structural phase transition at about $T_c \sim 295.5\text{K}$. It belongs to space group symmetry $P2_1$ in the ferroelectric phase and $P2_1/m$ in the paraelectric phase. The lattice dimensions are $a=9.54\text{\AA}$, $b=12.92\text{\AA}$, $c=5.86\text{\AA}$ and $\beta=110^\circ$.

Ferroelectric TGSe crystallizes in a monoclinic structure¹. The influence of deuteration on TGSe crystal were studied by different methods Landau description, calorimetric study, Green's function method²⁻⁵, showing that the crystal does not show enormous change in the ferroelectric properties. The hysteresis loop of the ferroelectric triglycine selenate can be progressively suppressed in an inhomogeneous electric field not parallel to ferroelectric axis⁶. With increase in temperature, the peak of the imaginary part related to loss of the dielectric constant of ferroelectric TGSe shifts to the higher frequencies⁷. Electronic band structure, density of electronic states, dielectric functions of the ferroelectric TGSe, TGS and TGS crystals were studied by the ab initio method in the framework of the DFT (density functional theory)⁸. The paraelectric-ferroelectric phase transition of a highly pure TGSe crystal has been studied using a high sensitivity calorimetric technique⁹⁻¹⁰ and no evidence of latent heat has been found, under the influence of a weak electric field there is evidence of different specific heat behaviour on cooling and heating. Ferroelectric phase transition and thermal dependence of ordered parameters of TGSe crystals were also investigated by linear birefringence method¹¹⁻¹². The capability of a generalized pressure/temperature equation of state to describe phase transition in uniaxial ferroelectric TGSe, which shows a quasi-tricritical point¹³.

Theoretical studies of properties of TGSe type ferroelectrics have been carried out by Chaudhuri *et al.*,¹⁴. They have considered PLCM model. These authors have not considered third and fourth order phonon anharmonic interaction and extra spin-lattice coupling terms. Moreover, they have decoupled the correlations at an early stage. So that they could not produce better and convincing results. In the present study, we shall modify PLCM model by adding third and fourth-order phonon anharmonic interactions and extra spin-lattice coupling terms. This is an indirect coupling between tunneling motion of one proton and other proton. This modulates distance between two equilibrium sites in O-H...O bonds. This is modulation of Ω by non-polar phonons. By using double-time thermal Green's function method, expressions for vibrational frequency and dielectric constant have been derived to obtain thermal dependence of these quantities. Theoretical results will be compared with experimental and correlated experimental results of Polandov *et al.*¹⁵.

CALCULATION

In present study to explain dielectric behaviour of triglycine selenate crystal, the Hamiltonian used is

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

where Ω is proton tunneling frequency, J and K are coupling constants corresponding to coupling in same lattice and different lattices respectively, V_{ik} is spin-lattice interaction

constant, ω_k is phonon frequency S^z and S^x are components of pseudospin variable S , A_k and B_k are operators corresponding to position and momenta, $V^{(3)}(k_1, k_2, k_3)$ and $V^{(4)}(k_1, k_2, k_3, k_4)$ are third and fourth order atomic force constants.

We shall evaluate Green's function

$$\begin{aligned} G_{ij}(t-t') &= \langle\langle S_{1i}^z(t); S_{1j}^z(t') \rangle\rangle \\ &= -i\theta(t-t') \langle [S_{1i}^z(t); S_{1j}^z(t')] \rangle \end{aligned} \quad (2)$$

Differentiating Green's function with respect to times t and t' twice, then fourier transforming and putting into Dyson's equation form, we get a green function which contain higher order Green's function and simpler Green's function. Higher order Green's functions are evaluated by decoupling schemes while simple Green's function by Zeroth order approximation.

Finally we get the Green's function

$$G_{ij}(\omega) = \frac{\Omega \langle S_{1i}^x \rangle}{\pi[\omega^2 - \hat{\Omega}^2 - 2i\Omega\Gamma(\omega)]} \quad (3)$$

where

$$\hat{\Omega}^2 = a^2 + b^2 - bc + \Delta(\omega) \quad (4)$$

with

$$a = 2J \langle S_1^z \rangle + K \langle S_2^z \rangle \quad (5)$$

$$b = 2\Omega \quad (6)$$

$$c = 2J \langle S_1^x \rangle + K \langle S_2^x \rangle \quad (7)$$

width $\Delta(\omega)$ and corresponding shift $\Gamma(\omega)$ is obtained as

$$\begin{aligned} \Delta(\omega) &= \frac{a^4}{(\omega^2 - \tilde{\Omega}^2)} + \frac{b^2 c^2}{(\omega^2 - \tilde{\Omega}^2)} + \frac{V_{ik}^2 N_k a^2}{(\omega^2 - \tilde{\Omega}^2)} + \frac{8\Omega^2 V_{ik}^2 N_k}{(\omega^2 - \tilde{\Omega}^2)} + \frac{a^2 V_{ik}^2 J_{ij}^2 N_k \langle S_1^z \rangle^2}{\Omega b (\omega^2 - \tilde{\Omega}^2)} + \frac{2V_{ik}^2 J_{ij}^2 N_k \langle S_1^x \rangle^2}{(\omega^2 - \tilde{\Omega}^2)} \\ &+ \frac{a^2 V_{ik}^2 K_{ij}^2 N_k \langle S_1^z \rangle^2}{2b\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{V_{ik}^2 K_{ij}^2 N_k \langle S_1^x \rangle^2}{(\omega^2 - \tilde{\Omega}^2)} + \frac{a^2 V_{ik}^4 N_k}{\Omega b (\omega^2 - \tilde{\Omega}^2)} + \frac{4\Omega V_{ik}^2 \langle S_1^x \rangle \omega_k \delta_{kk'}}{[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} \\ &+ \frac{8\Omega a V_{ik}^2 \langle S_1^z \rangle \omega_k \delta_{kk'} (\omega^2 - \tilde{\omega}_k^2)}{b[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \frac{2V_{ik}^2 J_{ij}^2 \langle S_1^x \rangle \langle S_1^z \rangle^2 \omega_k \delta_{kk'} (\omega^2 - \tilde{\omega}_k^2)}{\Omega[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \frac{V_{ik}^2 K_{ij}^2 \langle S_1^x \rangle \langle S_1^z \rangle^2 \omega_k \delta_{kk'} (\omega^2 - \tilde{\omega}_k^2)}{\Omega[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \\ &\frac{2V_{ik}^4 \langle S_1^x \rangle N_k \omega_k \delta_{kk'} (\omega^2 - \tilde{\omega}_k^2)}{\Omega[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \frac{2a V_{ik}^4 \langle S_1^z \rangle N_k \omega_k \delta_{kk'} (\omega^2 - \tilde{\omega}_k^2)}{\Omega b [(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} \end{aligned} \quad (8)$$

$$\Gamma(\omega) = \frac{a^4}{2\tilde{\Omega}} \{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \} + \frac{b^2 c^2}{2\tilde{\Omega}} \{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \} + \frac{V_{ik}^2 N_k a^2}{2\tilde{\Omega}} \{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \}$$

$$\begin{aligned}
 & + \frac{8\Omega^2 V_{ik}^2 N_k}{2\tilde{\Omega}} \{\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\} + \frac{a^2 V_{ik}^2 J_{ij}^2 N_k \langle S_1^z \rangle^2}{2\Omega b \tilde{\Omega}} \{\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\} + \frac{2V_{ik}^2 J_{ij}^2 N_k \langle S_1^x \rangle^2}{2\tilde{\Omega}} \{\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\} \\
 & + \frac{a^2 V_{ik}^2 K_{ij}^2 N_k \langle S_1^z \rangle^2}{4b\Omega\tilde{\Omega}} \{\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\} + \frac{V_{ik}^2 K_{ij}^2 N_k \langle S_1^x \rangle^2}{2\tilde{\Omega}} \{\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\} + \frac{a^2 V_{ik}^4 N_k}{2b\Omega\tilde{\Omega}} \{\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\} \\
 & + \frac{4\Omega V_{ik}^2 \langle S_1^x \rangle \omega_k (2\omega_k \Gamma_k(\omega))}{[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \frac{8\Omega a V_{ik}^2 \langle S_1^z \rangle \omega_k (2\omega_k \Gamma_k(\omega))}{b[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \frac{2V_{ik}^2 J_{ij}^2 \langle S_1^x \rangle \langle S_1^z \rangle^2 \omega_k (2\omega_k \Gamma_k(\omega))}{\Omega[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} \\
 & + \frac{V_{ik}^2 K_{ij}^2 \langle S_1^x \rangle \langle S_1^z \rangle^2 \omega_k (2\omega_k \Gamma_k(\omega))}{\Omega[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \frac{2V_{ik}^4 \langle S_1^x \rangle N_k \omega_k (2\omega_k \Gamma_k(\omega))}{\Omega[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} + \frac{2a V_{ik}^4 \langle S_1^z \rangle N_k \omega_k (2\omega_k \Gamma_k(\omega))}{b\Omega[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega)]} \quad (9)
 \end{aligned}$$

Solving Eq(6) self consistently we obtain

$$\begin{aligned}
 \hat{\Omega}^2 = & \frac{1}{2}(\tilde{\omega}_k^2 + \tilde{\Omega}^2) \pm \frac{1}{2} [(\tilde{\omega}_k^2 - \tilde{\Omega}^2)^2 + 4\{4\Omega^2 V_{ik}^2 \langle S_1^x \rangle \omega_k + \frac{8\Omega a V_{ik}^2 \langle S_1^z \rangle \omega_k}{b} \\
 & + \frac{2V_{ik}^2 J_{ij}^2 \langle S_1^x \rangle \langle S_1^z \rangle^2 \omega_k + V_{ik}^2 J_{ij}^2 \langle S_1^x \rangle \langle S_1^z \rangle^2 \omega_k + 2V_{ik}^4 \langle S_1^x \rangle N_k \omega_k + \frac{2a V_{ik}^4 \langle S_1^z \rangle N_k \omega_k}{b\Omega}\}]^{1/2} \quad (10)
 \end{aligned}$$

Above Equation shows that frequency corresponding to negative sign is vibrational frequency. Eq(10) shows that soft mode frequency depends explicitly on phonon frequency as well as spin lattice interaction terms.

Now from

$$\varepsilon = 1 + 4\pi \left\{ -\lim_{x \rightarrow 0} 2\pi N \mu^2 G_{ij}(\omega + ix) \right\} \quad (11)$$

Dielectric constant is obtained as

$$\varepsilon = - \frac{8\pi N \mu^2 \Omega \langle S_1^x \rangle}{(\omega^2 - \hat{\Omega}^2)} \quad (12)$$

The dissipation of power when any ferroelectric or dielectric is exposed to electric field is given by ratio of imaginary to real parts of dielectric constant, i.e.

$$\tan \delta = \frac{\text{Imaginary } \varepsilon}{\text{Real } \varepsilon} = - \frac{2\Omega \Gamma(\omega)}{(\omega^2 - \hat{\Omega}^2)} \quad (13)$$

Above Eq (13) shows that loss tangent is function of proton tunneling frequency, width function. It is also inversely proportional to square of vibrational frequency.

RESULTS AND DISCUSSION

By using model values of physical parameters $\Omega=0.2(\text{cm}^{-1})$, $V_{ik} \times 10^2=1(\text{cm}^{-1})$, $J=320(\text{cm}^{-1})$, $K=160(\text{cm}^{-1})$, $\omega_k =5.9933(\text{cm}^{-1})$, $N \times 10^{-21} =3.92(\text{cm}^{-3})$, $\mu \times 10^{18}=3.39$ (esu×cm),

thermal variations for vibrational frequency and dielectric constant using Eqs(10) and (12) have been calculated and shown in figures 1 and 2.

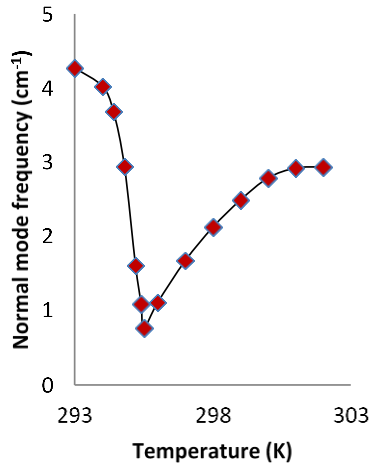


Fig.1 Thermal dependence of vibrational frequency of TGSe crystal(—our results, experimentally correlated values for dielectric data¹⁵)

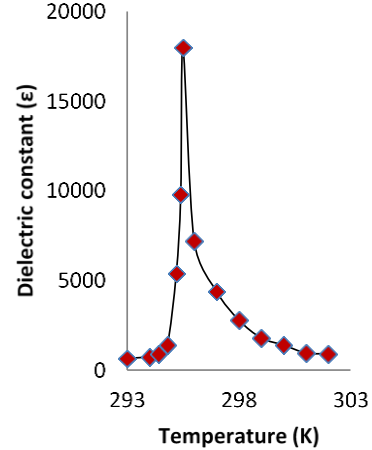


Fig.2 Thermal dependence of dielectric constant of TGSe crystal(—our results, experimentally values for dielectric data¹⁵)

In this paper, by modifying two sublattice pseudospin lattice coupled mode model for TGSe ferroelectric crystal by adding third and fourth order phonon anharmonic interaction terms and extra spin-lattice coupling terms theoretically expressions for shift, width, loss tangent, dielectric constant and vibrational frequency have been derived. With the help of model values and by using Eq (8),(9),(10),(12) and (13) thermal dependence of width, shift, vibrational frequency, dielectric constant and loss tangent have been obtained. A double time thermal Green's function method has been used for derivation. Earlier researchers have not considered phonon anharmonic interactions and also some spin-lattice interactions. They have decoupled the correlations at an early stage. As a result some important interactions disappeared from their calculations. The width and shift are the results of present calculations. If these are neglected the results of present calculations reduce to the results of chaudhuri *et al.*,¹⁴.

The temperature variations of vibrational frequency and dielectric constant have been shown in figures 1 and 2 respectively. Theoretical results for dielectric constant have been compared with experimental results of Polandov *et al.*,¹⁵ and correlated values of vibrational frequency obtained from dielectric data of Polandov for TGSe crystal. Our theoretical results agree with experimental results of Polandov *et al.*,¹⁵.

From figure 1 and Eq (10), it is observed that vibrational frequency decreases as we approach from low temperature side towards Curie temperature. At Curie temperature vibrational frequency becomes infinitesimally small and increases above it.

From figure 2 and Eq (12) it is shown that dielectric constant first increases as we increase temperature from low temperature side becoming anomalously large at transition

temperature. Above T_c dielectric constant decreases with increasing temperature. Our findings agree with experimental results of Polandov *et al.*,¹⁵.

CONCLUSION

From present study it can be concluded that the two sub-lattice pseudospin coupled mode model modified with third and fourth order phonon anharmonic interactions and extra spin-lattice coupling terms explains the ferroelectric and dielectric behaviour of triglycine selenate crystal. Our theoretical results are in agreement with experimental results which show the applicability of the present modified model for TGSe crystal. The expressions of this study can also be used to explain the dielectric and ferroelectric behaviour of other similar crystals such as triglycine sulphate, triglycine fluoberyllate, diglycine nitrate etc.

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