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Dependence of dielectric constant and loss tangent on electric field in antiferroelectric squaric acid crystal

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Abstract : The double-time thermal Green function method with the symmetric and antisymmetric decoupling scheme and modified pseudospin model proposed by Li and Qin for squaric acid have been used in present study to discuss the effect of electric field on some dielectric properties. Expressions for shift, width, soft mode frequency, dielectric constant, loss and transition temperature have been evaluated. By fitting model values of physical quantities in the theoretical expressions thermal dependence of antiferroelectric mode frequency, dielectric constant and loss have been calculated in presence of electric field in the vicinity of transition temperature. Theoretical results are similar to other antiferroelectric crystals.

Keywords : Dielectric constant, Pseudospin phonon interaction, Antiferroelectric, Electric field, Squaric acid.

INTRODUCTION

Squaric acid (SQA), $C_4O_4H_2$ is a strong organic acid and belongs to the group of hydrogen bonded ferroelectrics. SQA is an antiferroelectric substance and used in the area of medical, electronics, optics[1,2]. SQA has layered structure. Each molecule is a square with oxygen ions at its four vertices linked by hydrogen bonds on equal footing[3]. At about 371 K, the crystal undergoes a first order phase transition to paraelectric phase[4-7]. Because of the planar H-bonds, the interaction between molecules in the same layers is stronger than in the interlayers. Below transition temperature, protons are arranged in ordered pattern. The direction of lattice spontaneous polarization are the same for one molecular plane and opposite for neighbouring ones. The antiferroelectric phase is monoclinic with space group $P2_1/m$ and the lattice dimensions are a=6.13Å, b=5.23Å, c=6.14Å while the paraelectric phase is tetragonal with space group I4/m with new lattice dimensions a= 6.26Å, b=5.36Å , c=6.30Å .

The hydrogen bonded geometry of crystal structure of SQA and its other forms has been observed by CSD[8], thermogravimetric method[9] and finite field procedure[10]. The geometry of crystal is responsible for non-linear electrical properties. There is an order-disorder transition in SQA[11].This phase transition has been investigated by various methods such as C-NMR study[12],optical birefringence[13], neutron scattering[14]. Due to its first order phase transition there is no thermal hysteresis can be detected[15]. There is a measurable increase in imaginary part of dielectric constant which denotes loss in microwave range[16]. An intermediate liquid like state has been identified between ferroelectrically-ordered state and completely disordered paraelectric state by unbiased QMC simulations[17]. Theoretically SQA has been studied by microscopic model[18], simulation technique[11], pseudo spin model[19-21], cluster approximation and tunneling of protons[22]. Li and Qin[19] have considered pseudospin model to 1 and 2 kinds of layers stacked alternatively along the b-axis. By using Green's function method, they evaluated soft mode frequency and the conditions of para and antiferroelectric phases, order parameter, dispersion relation, internal energy and transition entropy. External electric field has pronounced effects on temperature dependence of dielectric properties and

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transition temperature of KH_2PO_4, $PbHPO_4$ and $C_4H_4O_2$ crystals. However, no theoretical study has been made to study the effect of external electric field on transition and dielectric properties of squaric crystals.

In the present study the pseudospin model for layers 1 and 2 of Li and Qin[19] has been modified by adding pseudospin-lattice interaction term, third and fourth-order phonon anharmonic interaction terms as well as an external electric field term. By using modified model and the method of double time thermal Green's function, expressions for width, shift, normal mode frequency, dielectric constant and loss tangent have been derived. By fitting model values in these expressions thermal dependence of normal mode frequency, dielectric constant and tangent loss have been calculated. Theoretical results in absence of electric field have been compared with experimental results of Maier et.al.[23], Muser[24] and Samara and Semmingsen[25] in absence of electric field while for different electric field strength their thermal behaviour have been compared with experimental variations obtained by others[26,27] for antiferroelectric ADP crystal and copper formate terahydrate crystals.

Theory

For SQA crystal, one of the molecular planes of squaric acid each hydrogen bond is shared between two C_4O_4 radicals, one can assign two of the four neighbouring hydrogen bonds as belonging to the central C_4O_4 radical. It is sufficient to consider one of these two neighbouring hydrogen bonds only. As for layer-layer interactions only the interaction of neighbouring layers is taken into account. We add Hsp, Hanh and HE terms to Li and Qin model[19] Hs, so that the total model for SQA is now expressed as

$$H = H_s + H_{sp} + H_{anh} + H_E \qquad ...(1)$$

With

$$H_s = -2\Omega\sum_i (S_{1i}^x + S_{2i}^x) - \sum_{ij}[J_{ij}(S_{1i}^z S_{1j}^z + S_{2i}^z S_{2j}^z) + K_{ij} S_{1i}^z S_{2j}^z] \qquad ...(2)$$

$$H_{sp} = -\sum_k V_{ik}(S_{1i}^z A_k + S_{2j}^z A_k^\dagger) + \frac{1}{4}\sum_k \omega_k (A_k^\dagger A_k + B_k^\dagger B_k) \qquad ...(3)$$

$$H_{anh} = +\sum_{k_1 k_2 k_3} V^{(3)}(k_1, k_2, k_3) A_{k_1} A_{k_2} A_{k_3} + \qquad ...(4)$$

$$\sum_{k_1 k_2 k_3 k_4} V^{(4)}(k_1, k_2, k_3, k_4) A_{k_1} A_{k_2} A_{k_3} A_{k_4}$$

$$H_E = -2\mu E \sum_{ij}(S_{i1}^Z + S_{j2}^Z) \qquad ...(5)$$

where Ω is tunneling frequency of proton, S^x_1 and S^z_1 are the x- and z components of pseudospin variable S respectively. The indices 1 and 2 refer to the two layers, J_{ij} is spin-spin exchange interaction constant within a given chain and K_{ij} is the effective interaction constant between neighbouring chains, V_{ik} is pseudospin-lattice interaction constant, ω_k is phonon frequency, Ak and Bk are operators corresponding to position and momenta, $V^{(3)}$ (k_1, k_2, k_3) and are Fourier transforms of the third and fourth order atomic force constants.

Green's Function and field dependent shift and width

We consider the evaluation of Green's function

$$G_{ij}(t-t') = \left\langle\left\langle S_{1i}^z(t); S_{1j}^z(t')\right\rangle\right\rangle = -i\theta(t-t')\left\langle[S_{1i}^z(t); S_{1j}^z(t')]\right\rangle \qquad ...(6)$$

Differentiating Green's function Eq (6) with respect to times t and t′ respectively twice with the help of modified Hamiltonian given in eq(1), then Fourier transforming and writing in Dyson's equation form one obtains

$$G_{ij}^{z}(\omega)=\frac{\Omega\langle S_i^x\rangle}{\pi[\omega^2-\widetilde{\Omega}^2-P(\omega)]}, \qquad ...(7)$$

where

$$\widetilde{\Omega}^2=4\Omega^2+\frac{i\langle[F_i,S_{1j}^y\rangle}{\langle S_{1j}^x\rangle} \qquad ...(8)$$

and

$$P(\omega)=\frac{\pi}{\Omega\langle S_{1i}^x\rangle}\langle\langle F_i(t);F_j'(t')\rangle\rangle \qquad ...(9)$$

with

$$\begin{aligned}\langle\langle F(t);F(t')\rangle\rangle=[\langle\langle\{&-2\Omega J_{ij}(S_{1i}^xS_{1i}^z+S_{1i}^zS_{1i}^x)+2\mu E(S_{1i}^x+S_{2i}^x)-2\Omega K_{ij}S_{1j}^xS_{1j}^z\};\\ &\{-2\Omega J_{ij}(S_{1j}^xS_{1j}^z+S_{1j}^zS_{1j}^x)+2\mu E(S_{1i}^x+S_{2i}^x)-2\Omega K_{ij}S_{1j}^xS_{2j}^z\}\rangle\rangle\\ &+4\Omega^2V_{ik}^2\langle A_kA_k^\dagger\rangle\langle\langle S_{1j}^x;S_{1j}^x\rangle\rangle+4\Omega^2V_{ik}^2\langle S_{1i}^x;S_{1i}^x\rangle\langle\langle A_kA_k^\dagger\rangle\rangle\end{aligned} \qquad ...(10)$$

In $\langle\langle F(t);F(t')\rangle\rangle$ there are higher order Green's functions, which are evaluated by decoupling them using scheme $\langle abcd\rangle=\langle ab\rangle\langle cd\rangle+\langle ac\rangle\langle bd\rangle+\langle ad\rangle\langle bc\rangle$. The simpler Green's functions are then evaluated in Zeroth-order approximation.

Substituting values of various Green's functions in Eq(10) and then resolving P(ω) into its real and imaginary parts, one obtains shift Δ(ω) and width Γ(ω) respectively. Green's function given in Eq.(7) finally becomes:

$$G_{ij}(\omega+i\varepsilon)=\frac{\Omega\langle S_{1i}^x\rangle}{\pi[\omega^2-\hat{\Omega}^2-2i\Omega\Gamma(\omega)]} \qquad ...(11)$$

with

$$\hat{\Omega}^2=\widetilde{\widetilde{\Omega}}^2+\Delta_{sp}(\omega) \qquad ...(12)$$

$$\widetilde{\widetilde{\Omega}}^2=\widetilde{\Omega}^2+\Delta_s(\omega) \qquad ...(13)$$

$$\widetilde{\Omega}^2=a^2+b^2-bc \qquad ...(14)$$

$$a=(2J-K)\langle S_1^z\rangle+2\mu E \qquad ...(15)$$

$$b=2\Omega \qquad ...(16)$$

$$c=(2J-K)\langle S_i^x\rangle \qquad ...(17)$$

$\langle S_1^z\rangle=-\langle S_2^z\rangle$ for $T<T_c$

$\langle S_1^z\rangle=\langle S_2^z\rangle=0$ for $T>T_c$

Shift and width are obtained as

$$\Delta_s(\omega) = \frac{a'^4}{2\Omega(\omega^2 - \widetilde{\Omega}^2)} + \frac{V_{ik}{}^2 N_k a'^2}{2\Omega(\omega^2 - \widetilde{\Omega}^2)} + \frac{4\mu^2 E^2 a'^2}{2\Omega(\omega^2 - \widetilde{\Omega}^2)} \qquad ...(18)$$

$$\Gamma_s(\omega) = \frac{\pi a'^4}{4\Omega\widetilde{\Omega}}\{\delta(\omega - \widetilde{\Omega}) - \delta(\omega + \widetilde{\Omega})\} + \frac{\pi V_{ik}{}^2 N_k a'^2}{4\Omega\widetilde{\Omega}}\{\delta(\omega - \widetilde{\Omega}) - \delta(\omega + \widetilde{\Omega})\}$$

$$+ \frac{4\mu^2 E^2 a'^2}{4\Omega\widetilde{\Omega}}\{\delta(\omega - \widetilde{\Omega}) - \delta(\omega + \widetilde{\Omega})\} \qquad ...(19)$$

$$\Delta_{sp}(\omega) = \frac{2V_{ik}^2 \langle S_{1i}^z \rangle \omega_k \delta_{kk'}(\omega^2 - \widetilde{\widetilde{\omega}}_k^2)}{[(\omega^2 - \widetilde{\widetilde{\omega}}_k^2) + 4\omega_k^2 \Gamma_k^2(\omega)]} \qquad ...(20)$$

$$\Gamma_{sp}(\omega) = \frac{4V_{ik}^2 \langle S_{1i}^z \rangle \omega_k \delta_{kk'}(\omega^2 - \widetilde{\widetilde{\omega}}_k^2)}{[(\omega^2 - \widetilde{\widetilde{\omega}}_k^2) + 4\omega_k^2 \Gamma_k^2(\omega)]} \qquad ...(21)$$

In Eqs (20) and (21) $\widetilde{\widetilde{\omega}}_k$ and $\Gamma_k(\omega)$ are renormalized phonon frequency and phonon width, respectively obtained in the evaluation of phonon Green's function $\langle\langle A_k ; A_k^\dagger \rangle\rangle$. The phonon Green's function is obtained as

$$\langle\langle A_k ; A_k^\dagger \rangle\rangle = \frac{\omega_k \delta_{kk'}}{[\omega^2 - \widetilde{\widetilde{\omega}}_k^2 - 2i\omega_k \Gamma_k(\omega)]} \qquad ...(22)$$

Phonon frequency is obtained as

$$\widetilde{\widetilde{\omega}}^2 = \widetilde{\omega}_k^2 + 2\omega_k \Gamma_k(\omega) \qquad ...(23)$$

Phonon width is obtained as:

$$\Gamma_k(\omega) = 9\pi \sum_{k_1 k_2} \left|V^{(3)}(k_1, k_2 - k)\right|^2 \frac{\omega_{k_1}\omega_{k_2}}{\widetilde{\omega}_{k_1}\widetilde{\omega}_{k_2}} \left\{ \begin{matrix} (n_{k_1} + n_{k_1})[\delta(\omega + \widetilde{\omega}_{k_1} + \widetilde{\omega}_{k_2}) - \delta(\omega - \widetilde{\omega}_{k_1} - \widetilde{\omega}_{k_2})] \\ + (n_{k_2} - n_{k_1})[\delta(\omega + \widetilde{\omega}_{k_1} - \widetilde{\omega}_{k_2}) - \delta(\omega - \widetilde{\omega}_{k_1} + \widetilde{\omega}_{k_2})] \end{matrix} \right\}$$

$$+ 48\pi \sum_{k_1 k_2 k_3} \left|V^{(4)}(k_1, k_2, k_3, -k)\right|^2 \left\{ (1 + n_{k_1} n_{k_2} + n_{k_2} n_{k_3} + n_{k_3} n_{k_1}) \frac{\omega_{k_1}\omega_{k_2}\omega_{k_3}}{\widetilde{\omega}_{k_1}\widetilde{\omega}_{k_2}\widetilde{\omega}_{k_3}} \right\}$$

$$\times [\delta(\omega + \widetilde{\omega}_{k_1} + \widetilde{\omega}_{k_2} + \widetilde{\omega}_{k_3}) - \delta(\omega - \widetilde{\omega}_{k_1} - \widetilde{\omega}_{k_2} - \widetilde{\omega}_{k_3})]$$

$$+ \ldots\ldots\ldots\ldots\ldots\ldots \text{(higher terms)} \qquad ...(24)$$

Phonon shift is obtained as:

$$\Delta_k(\omega) = 18P \sum_{k_1 k_2} \left|V^{(3)}(k_1, k_2 - k)\right|^2 \frac{\omega_{k_1}\omega_{k_2}}{\widetilde{\omega}_{k_1}\widetilde{\omega}_{k_2}} \left\{ \begin{matrix} (n_{k_1} + n_{k_2}) \dfrac{\widetilde{\omega}_{k_1} + \widetilde{\omega}_{k_2}}{\omega^2 - (\widetilde{\omega}_{k_1} + \widetilde{\omega}_{k_2})^2} + \\ (n_{k_2} + n_{k_1}) \dfrac{\widetilde{\omega}_{k_1} + \widetilde{\omega}_{k_2}}{\omega^2 - (\widetilde{\omega}_{k_1} + \widetilde{\omega}_{k_2})^2} \end{matrix} \right\}$$

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

$$\left\{ \begin{matrix} (1 + n_{k_1} n_{k_2} + n_{k_2} n_{k_3} + n_{k_3} n_{k_1}) \dfrac{\omega_{k_1} + \omega_{k_2} + \omega_{k_3}}{\omega^2 - (\widetilde{\omega}_{k_1} + \widetilde{\omega}_{k_2} + \widetilde{\omega}_{k_3})^2} \\ + 3(1 - n_{k_2} n_{k_1} + n_{k_2} n_{k_3} - n_{k_3} n_{k_1}) \dfrac{\widetilde{\omega}_{k_1} - \widetilde{\omega}_{k_2} - \widetilde{\omega}_{k_3}}{\omega^2 - (\widetilde{\omega}_{k_1} - \widetilde{\omega}_{k_2} - \widetilde{\omega}_{k_3})^2} \end{matrix} \right\}$$

$$+ \ldots\ldots\ldots\ldots\ldots\ldots \text{(higher terms)} \qquad ...(25)$$

Field dependent renormalized soft mode frequency

Solving Eq (11) self consistently one obtains antiferroelectric soft mode frequency as

$$\hat{\Omega}^2 = \frac{1}{2}[(\tilde{\tilde{\omega}}_k^2 + \tilde{\tilde{\Omega}}^2) \pm \{(\tilde{\tilde{\omega}}_k^2 - \tilde{\tilde{\Omega}}^2)^2 + 8V_{ik}^2\langle S_{1i}^x\rangle\Omega\}^{1/2}] \quad ...(26)$$

Soft mode frequency $\hat{\Omega}$ explicitly depends upon modified pseudospin frequency, $\tilde{\tilde{\Omega}}$ as well as renormalized phonon frequency $\tilde{\tilde{\omega}}_k$.

By applying Condition, $\hat{\Omega} \to 0$ as $T \to T_c$ givev

$$T_c = \frac{\Omega}{2k_B \tanh^{-1}\left(\frac{4\Omega}{\tilde{J}}\right)} \quad ...(27)$$

Where

$$\tilde{J} = (2J - K) + 2\mu E + \frac{2V_{ik}^2\omega_k^2}{\tilde{\tilde{\omega}}_k^2} \quad ...(28)$$

Antiferroelectric transition temperature T_c is explicit function of tunneling frequency, Ω inter layer and intra-layer interactions, spin-lattice interaction constant, phonon anharmonic interactions as well as electric field.

Electric field dependent dielectric constant and loss tangent

The susceptibility χ is related to Green's function

$$\chi = -\lim_{x\to 0} 2\pi N\mu^2 G_{ij}(\omega + ix) \quad ...(29)$$

N is number of dipoles per unit volume and μ is dipole moment associated with O—H....O bond. The dielectric constant ε is related to susceptibility χ as

$$\varepsilon = 1 + 4\pi\chi \quad ...(30)$$

We may write $\varepsilon = 4\pi\chi$, as $\varepsilon >> 1$ for ferroelectrics.

From Equations (11), (29) and (30) we obtain dielectric constant ε as

$$\varepsilon = -\frac{8\pi N\mu^2\Omega\langle S_1^x\rangle}{(\omega^2 - \hat{\Omega}^2)} \quad ...(31)$$

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.

$$\tan\delta = \frac{\text{Im}\, aginary \quad \varepsilon}{\text{Re}\, al \quad \varepsilon} = -\frac{2\Omega\Gamma(\omega)}{(\omega^2 - \hat{\Omega}^2)} \quad ...(32)$$

Above Eq (32) shows that loss tangent is function of proton tunneling frequency, width function. It is also inversely proportional to square of normal mode frequency.

NUMERICAL CALCULATION AND DISCUSSION

By using model values of physical parameters appearing in expressions derived for SQA crystal, i.e. Ω=107 cm^{-1}, T_c=371K, $\tilde{J}$ =1086 cm^{-1}, K= 160 cm-1, V_{ik}=64 cm^{-1}, N=35.59 cm^{-1}, $\mu\times10^{18}$(cgs)=4.86, ω_k=100 cm^{-1}, C= 18000K. The thermal variations for normal mode frequency, dielectric constant and loss tangent using Eqs (26), (31) and (32) have been

calculated and shown in figures 1, 2 and 3. Theoretical results for soft mode frequency, dielectric constant and tangent loss. Our theoretical results agree with experimental results, in absence of electric field. For different electric field strengths the results are similar to experimental variations obtained by others[26,27] for antiferroelectric ADP crystal and copper formate tetrahydrate crystals. The experimental data for SQA crystal for different electric field strengths are not available in the literature.

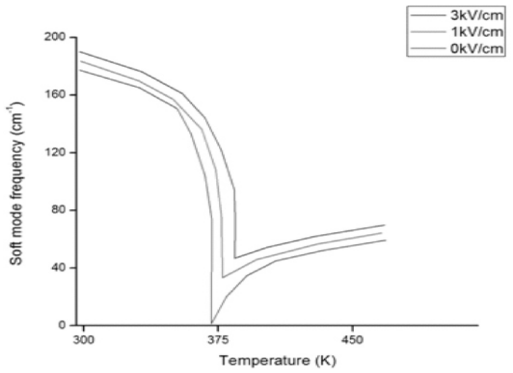

Fig. 1 : Temperature and field dependence of soft mode frequency $\hat{\Omega}$ (cm^{-1}) of SQA crystal (- our results)

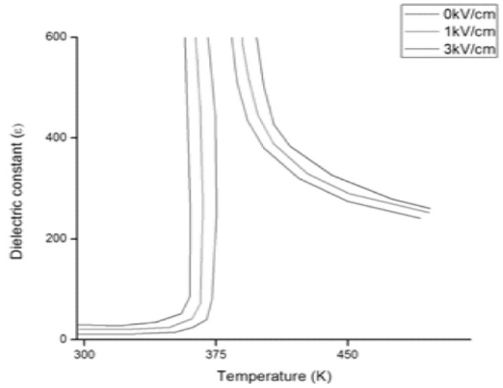

Fig. 2 : Temperature and field dependence of Dielectric constant (ε) of SQA crystal (- our results)

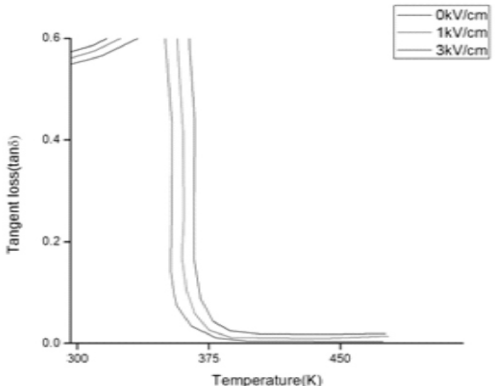

Fig. 3 : Temperature and field dependence of tangent Loss (tan δ) of SQA crystal (— our results)

It emerges from present study that the modified pseudospin model for layer 1 and 2 coupled with phonon along with third and fourth order phonon anharmonic interaction terms explains well the temperature dependences of dielectric properties and phase transition in SQA crystal. The phonon anharmonic terms renormalize the soft mode frequency. The renormalized soft mode frequency explains the nature of transition at 371K in SQA crystal. If shift, width, pdeudospin- phonon interaction term and phonon anharmonic terms are neglected from our calculatiuons, our results at once reduce to the results of Li and Qin[19]. These authors have decoupled the correlations in the early stage and have not considered spin-phonon interaction and anharmonic interaction terms. Therefore, they could not obtain better and convincing results to explain antiferroelectric transition in SQA crystal. In the present work, the correlations have been solved by decoupling them at proper stage. Hence all the important interactions could be contained in the expressions. Therefore, present results arte much better and convincing, our expressions (31),(27), (32) and (26) show that the dielectric constant, curie temperature, dielectric loss and renormalized frequency respectively are all explicitly electric field dependent. The dielectric constant decreases with increase in electric field strength. Loss also decreases with increase in electric field. The effect of electric field is to shift the peak of dielectric constant to higher temperatures. Our theoretical results for the change in values of dielectric constant, transition temperature and tangent loss agree with experimental results, in absence of electric field. Experimental data for SQA crystal are not available in literature.

A transverse radiation field derives the low-lying transverse mode of this lattice mode and is then degraded into other vibrational modes of the material. Due to anharmonic phonon interactions, decay processes take place. For example, third-order interaction leads to the decay of a virtual phonon into two real phonons or the virtual phonon may be destroyed by scattering a thermally excited phonon. Similar processes occur may be destroyed by scattering a thermally excited phonon. Similar processes occur for fourth and higher order interactions.

CONCLUSION

From present study it can be concluded that the two sub-lattice pseudospin lattice coupled mode model modified with third and fourth order phonon anharmonic interactions and extra spin-lattice interaction terms explains the ferroelectric and dielectric behaviour of squaric acid crystal. Our theoretical results are in agreement with experimental results in absence of electric field which show the applicability of the present modified model for SQA crystal.

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