Theoretical Study of of Antiferroelectrics and Dielectric Properties of SnCl₂·2H₂O Crystal†

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A two-sublattice pseudospin lattice coupled mode model along with third- and- fourth order phonon anharmonic interaction terms has been considered by using double-time thermal Green's function method for SnCl₂·2H₂O crystal, expressions for shift, width, renormalized soft mode frequency, Curie temperature, dielectric constant and loss tangent are obtained for tin chloride dihydrate crystal. By fitting model values of physical quantities temperature dependences of soft mode frequency, dielectric constant and loss tangent have been calculated for tin chloride dihydrate crystal. Theoretical results compare well with experimental results of Mognaschi *et al.*

Key Words: Ferroelectrics Green's function, Soft mode, Anharmonic interaction.

INTRODUCTION

Antiferroelectric and ferroelectric materials have got promising applications such as high permittivity capacitors, peizo-electric, transducers, modulators and deflectors, pyro-electric detectors, storage and laser devices and sensors.

Tin chloride dihydrate (SnCl₂·2H₂O) undergoes a peculiar isostructural and order-disorder type of phase transition at *ca.* -57 ºC (from space group P21/c to P21/c). This uncommon behaviour has drawn particular attention for the study of static and dynamic properties of phase transition in this crystal. The cell parameters at room temperature are a = 9.31 Å, b = 7.25 Å, c = 8.9Å and β = 114.9º.

Experimental investigations have been carried out by many workers on tin chloride dihydrate crystal. Kiriyama *et al.*[1] have carried out X-ray diffraction. Kiriyama *et al.*[2] and Youngblood *et al.*[3] have carried out neutron diffraction. Matsuo *et al.*[4,5] have carried out heat capacity measurements. Mognaschi *et al.*[6] have carried out dielectric and NMR experiments on tin chloride dihydrate crystal. Wang *et al.*[7] and Satija *et al.*[8] have carried out Raman and Brillouin spectra studies. These experiments showed the order- disorder transition in this crystal. This transition is associated with ordering of protonic positions in 2D layers of water molecule. Theoretical studies to understand mechanism of transition in tin chloride dihydrate crystal were initiated by Salinas and Nagle[9,10] and by Banerjee *et al.*[11]. Banerjee *et al.*[11] have considered two sub-

lattice pseudospin-lattice coupled mode model along with a fourth-order phonon anharmonic intraction term. They have not considered third-order phonon anharmonic interaction term. Moreover they decoupled the correlations at an early stage.

In the present study, third and fourth order phonon anharmonic terms[12,13] have been added in the two-sub-lattice pseudospin-lattice coupled mode model[11] for tin chloride dihydrate crystal. By applying double-time thermal Green's function method[13] expressions for shift, width, renormalized soft mode frequency, dielectric constant and loss tangent have been evaluated. By fitting model values in expressions, numerical values of soft mode frequency, dielectric constant and loss tangent have been calculated.. Theoretical results have been compared with experimental results of Mognaschi *et al.*[6].

THEORY

Model hamiltonian and Green's fuction: For tin chloride dihydrate crystal, the extended two-sublattice pseudospin lattice coupled mode model[11], along with third- and fourth-order phonon anharmonic interaction terms[12,13] is expressed as:

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

$$+ \frac{1}{4}\sum_{k}\omega_k\left(A_k A_k^+ + B_k B_k^+\right) + \sum_{k_1 k_2 k_3} V^{(3)}\left(k_1, k_2, k_3\right)A_{k_1} A_{k_2} A_{k_3}$$

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

where Ω is proton tunnelling frequency, S^z and S^x are components of pseudospin variable, S and J_{ij} is interaction between same lattice and K_{ij} is interaction between different lattices, V_{ik} is spin-lattice interaction and A_k and B_k are position and momentum operators, ω_k is harmonic phonon frequency $V^{(3)}$ and $V^{(4)}$ are third- and fourth-order atomic force constants defined by Semwal and Sharma[12].

Following Zubarev[14], we consider the evaluation of Green's function (GF)

$$G_{ij}(t-t') = \left\langle\left\langle S_{i1}^z(t); S_{j1}^z(t')\right\rangle\right\rangle$$

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

Differentiating eqn. 2 with respect to time t and t' twice using eqn. 1, Fourier transforming and applying Dyson's equation approach one obtains

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

where

$$\hat{P}(\omega) = \frac{\pi i\left\langle[F, S_{1j}^y]\right\rangle}{\Omega\left\langle S_{1i}^x\right\rangle^2} + \frac{\pi^2}{\Omega^2\left\langle S_{1i}^x\right\rangle^2}\left\langle\left\langle F_i; F_j'\right\rangle\right\rangle, \quad (4)$$

The Green's function (GF) (3) becomes

$$G(\omega) = \frac{\Omega\left\langle S_{1i}^x\right\rangle}{\pi\left(\omega^2 - \tilde{\Omega}^2 - P(\omega)\right)} \quad (5)$$

where renormalized frequency $\tilde{\Omega}$, in the lowest approximation is given as:

$$\tilde{\Omega}^2 = 4\Omega^2 + \frac{i}{\left\langle S_{1i}^x\right\rangle}\left\langle[F, S_{1j}^y]\right\rangle \quad (6)$$

and polarization operator $P(\omega)$ (that is second terms of eqn. 4) is given as:

$$P(\omega) = \frac{\pi}{\Omega\left\langle S_i^x\right\rangle}\left\langle\left\langle F_i; F_j'\right\rangle\right\rangle \quad (7)$$

In order to evaluate correlation functions, it is assumed that

$$\frac{\left\langle Si^z\right\rangle}{a} = \frac{\left\langle Si^x\right\rangle}{b} = \frac{1}{2\tilde{\Omega}}\tanh\beta\frac{\tilde{\Omega}}{2} \quad (8)$$

so that

$$\tilde{\Omega}^2 = a^2 + b^2 - bc \quad (9)$$

where

$$a = 2J\left\langle S_1^z\right\rangle + K\left\langle S_2^z\right\rangle \quad (10)$$

$$b = 2\Omega ; \text{ and} \quad (11)$$

$$c = 2J\left\langle S_1^x\right\rangle + K\left\langle S_2^x\right\rangle \quad (12a)$$

$$\left\langle S_1^z\right\rangle = -\left\langle S_2^z\right\rangle = 0 \quad (12b)$$

The higher order Green's functions (GFs) in eqn. 7 are evaluated using symmetric decoupling scheme <abcd> = <ab><cd> + <ac> <bd> + <ad> <bc>. In this way $P(\omega)$ of eqn. 7 is evaluated.

Width, shift and soft mode frequency

For a vanishingly small quantity m, $P(\omega)$ can be expressed in terms of its real and imaginary parts using formula

$$\lim_{m\to 0}\frac{1}{x+im} = \left(\frac{1}{x}\right) \pm i\pi\delta(x).$$ The real part is known as shift $\Delta(\omega)$

and the imaginary part is called width, $\Gamma(\omega)$. From eqn. 7 one obtains shift and width as: Spin shift

$$\Delta_s(\omega) = \frac{a^4}{2\Omega\left(\omega^2 - \tilde{\Omega}^2\right)}$$

$$+ \frac{b^2 c^2}{2\Omega\left(\omega^2 - \tilde{\Omega}^2\right)}$$

$$+ \frac{V_k^2 N_k a^2}{2\Omega\left(\omega^2 - \tilde{\Omega}^2\right)} \quad (13)$$

spin-width

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

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

$$+ \frac{\pi V_{ik}^2 N_k a^2}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right] \quad (14)$$

spin-lattice coupled shift

$$\Delta_{s-p}(\omega) = \frac{2V_{ik}^2\left\langle S_{1i}^x\right\rangle\omega_k\delta_{kk'}\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)^2 + 4\omega_k^2\Gamma_k^2(\omega)\right]} \quad (15)$$

and spin lattice coupled width

$$\Gamma_{s-p}(\omega) = \frac{4V_{ik}^2\left\langle S_{1i}^x\right\rangle\omega_k\delta_{kk'}\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)^2 + 4\omega_k^2\Gamma_k^2(\omega)\right]} \quad (16)$$

In eqns. 14 and 15 $\Gamma_k(\omega)$ is the phonon width due to third and fourth-order phonon anharmonic, interactions and using last three terms of Hamiltonian (1) which is obtained as

$$G_{kk'}(\omega) = \omega_k\delta_{kk'}\Pi^{-1}\left[\omega^2 - \tilde{\omega}^2_k - 2i\omega_k\Gamma_k(\omega)\right].$$ In this GF phonon width $\Gamma_k(\omega)$ and corresponding shift are obtained now

$$\tilde{\tilde{\omega}}^2 = \tilde{\omega}^2 + 2\omega_k\Delta_k(\omega); \ \overline{\omega^2} = \omega_k + A_k.$$

$\tilde{\omega}_k$ is modified phonon frequency.

Phonon shift is given as:

$$\Delta_k(\omega) = \text{Re}\, P_k(\omega)$$

$$= 18P\sum_{k_1 k_2}\left|V^{(3)}\left(k_1, k_2, -k\right)\right|^2$$

$$\frac{\omega_{k1}\omega_{k2}}{\widetilde{\omega}_{k1}\widetilde{\omega}_{k2}}\left\{\left(n_{k1}+n_{k2}\right)\frac{\widetilde{\omega}_{k1}+\widetilde{\omega}_{k2}}{\omega^2-\left(\widetilde{\omega}_{k1}+\widetilde{\omega}_{k2}\right)^2}\right.$$

$$\left.+\left(n_{k_2}-n_{k_1}\right)\frac{\widetilde{\omega}_{k1}+\widetilde{\omega}_{k2}}{\omega^2-\left(\widetilde{\omega}_{k1}+\widetilde{\omega}_{k2}\right)^2}\right\}$$

$$+48P\sum_{k1_1k_2k_3}\left|V^{(4)}\left(k_1k_2,k_3,-k\right)\right|^2\frac{\omega_{k_1}\omega_{k2}\omega_{k3}}{\widetilde{\omega}_{k_1}\widetilde{\omega}_{k_2}\widetilde{\omega}_{k_3}}$$

$$\left\{\left(1+n_{k_1}n_{k_2}+n_{k_2}n_{k_3}+n_{k_3}n_{k_1}\right)\frac{\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k2}+\widetilde{\omega}_{k3}}{\omega^2-\left(\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_2}+\widetilde{\omega}_{k_3}\right)^2}\right.$$

$$+3\left(1-n_{k_2}n_{k_1}+n_{k_2}n_{k_3}-n_{k_3}n_{k_1}\right)$$

$$\left.\frac{\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k2}+\widetilde{\omega}_{k3}}{\omega^2-\left(\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_2}+\widetilde{\omega}_{k_3}\right)^2}\right\} \tag{17}$$

and phonon width is given as:

$$\Gamma_k(\omega)=\mathrm{Im}\,P_k(\omega)$$

$$=9\pi\sum_{k_1k_2}\left|V^{(3)}(k_1,k_2,-k)\right|^2\frac{\omega_{k_1}\omega_{k_2}}{\widetilde{\omega}_{k_1}\widetilde{\omega}_{k_2}}$$

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

$$-\delta\left(\omega-\widetilde{\omega}_{k_1}-\widetilde{\omega}_{k_1}\right)+\text{(higher terms)}$$

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

$$+48\pi\sum_{k_1k_2k_3}\left|V^{(4)}\left(k_1,k_2,k_3,-k_4\right)\right|^2\frac{\omega_{k_1}\omega_{k_2}\omega_{k_3}}{\widetilde{\omega}_{k_1}\widetilde{\omega}_{k_2}\widetilde{\omega}_{k_3}}$$

$$X\left\{\left(1+n_{k_1}n_{k_2}+n_{k_2}n_{k_3}+n_{k_3}n_{k_4}\right)\right.$$

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

$$+3\left(n_{k_1}n_{k_2}+n_{k_2}n_{k_3}-n_{k_3}n_{k_4}\right)+3\left(n_{k_1}n_{k_2}+n_{k_2}n_{k_3}-n_{k_3}n_{k_4}\right)$$

$$X\left.\left[\delta\left(\omega+\widetilde{\omega}_{k_1}-\widetilde{\omega}_{k_2}-\widetilde{\omega}_{k_3}\right)-\delta\left(\omega-\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_2}+\widetilde{\omega}_{k_3}\right)\right]\right\} \tag{18}$$

In eqns. 17 and 18 Re and Im stand for real and imaginary parts respectively. $n_{ki}=\cot h\beta\,\widetilde{\omega}_{ki}$ and p stands for principal part.

The value of Green's function, (GF) (5) by putting value of P(ω) in eqn. 7, is finally obtained as:

$$G(\omega+ix)=\pi^{-1}\Omega\langle S_i^x\rangle\delta_{ij}\left[\left(\omega^2-\hat{\Omega}^2\right)+2i\Omega\Gamma(\omega)\right]^{-1} \tag{19}$$

where

$$\hat{\Omega}^2=\widetilde{\widetilde{\Omega}}^2+2\Omega\Delta_{s-p}(\omega) \tag{20a}$$

with

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

Solving eqn. 20a self consistently, one obtains renormalized frequency $\hat{\Omega}_-$ as

$$\hat{\Omega}_-^2=\frac{1}{2}\left\{\left(\widetilde{\widetilde{\omega}}_k^2+\widetilde{\widetilde{\Omega}}^2\right)\pm\left[\left(\widetilde{\widetilde{\omega}}_k^2-\widetilde{\widetilde{\Omega}}^2\right)^2+16V_{ik}\langle S_1^x\rangle\Omega\right]^{1/2}\right\} \tag{21}$$

Transition temperature: The frequency $\hat{\Omega}_-$ is the antiferroelectric mode frequency which critically depends on temperature and is responsible for phase transition.

The Curie temperature, T$_c$, can easily be obtained by applying the stability condition of paraelectric phase *i.e.* $\hat{\Omega}_-\to0$, as $T\to T_c$, which gives at once

$$T_c=\frac{\eta}{2k_B\tanh^{-1}\left(\dfrac{\eta^3}{4\Omega^2 J^*}\right)} \tag{22}$$

with $\eta^2=\left(2J-K\right)^2\sigma^2+4\Omega^2$,
and

$$J^*=\left(2J+K\right)+\frac{2V_{ik}^2\widetilde{\widetilde{\omega}}_k^2}{\left[\widetilde{\widetilde{\omega}}_k^4+4\omega_k\Gamma_k^2\right]} \tag{23}$$

J* is renormalized exchange interaction constant.

Dielectric constant and loss tangent: The response of crystal to electric field is expressed by electrical susceptibility χ which using Zubarev's[14] formalism is expressed as;

$$\chi=-\underset{x\to0}{\lim}2\pi N\mu^2 G_{ij}\left(\omega+ix\right) \tag{24}$$

where N is number of dipoles having dipole moment μ in the unit volume. Using relation $\in=1+4\pi\chi$, the expression for dielectric constant $\in$ with the help of eqns. 19 and 24 can be expressed as:

$$\in(\omega)=\left(-8\pi N\mu^2\right)\langle S^x\rangle\left(\omega^2-\hat{\Omega}^2\right)\left[\left(\omega^2-\hat{\Omega}^2\right)^2+4\Omega^2\Gamma^2\right]^{-1} \tag{25}$$

The dissipation of power can conveniently be expressed in dielectrics as tangent loss (tan δ) as:

$$\tan\delta=\frac{\in''}{\in'} \tag{26a}$$

Using eqns. 25 and 26a one obtains

$$\tan\delta=\frac{-2\Omega\Gamma(\omega)}{\left(\omega^2-\hat{\Omega}^2\right)} \tag{26b}$$

At microwave frequencies, $\omega\langle\langle\hat{\Omega}$, eqn. 26b reduces to

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

In eqn. (27) $\Gamma(\omega)=\Gamma_s(\omega)+\Gamma_{s-p}(\omega)$

Numerical calculations and results: By using model values of various quantities in expressions from literature (Table-1) temperature dependence of <S$^x_1$>, <S$^x_2$>, <S$^x_1$>, <S$^z_2$> width, shift antiferroelectric mode frequency, dielectric constant and loss tangent for tinchloride dihydrate crystal have been calculated. Calculated variation tenperature of antiferroelectric mode frequency and loss tangent are compared with experimental temperature variation of these are shown in Figs. 1-3.

RESULTS AND DISCUSSION

The two sublattice model along with phonon anharmonic interaction terms explains the features of phase transition and dielectric properties of tinchloride dihydrate crystals. Earlier

TABLE-1
MODEL VALUE OF PHYSICAL PARAMETER FOR SnCl$_2$·2H$_2$O CRYSTAL GIVEN BY Banrjee *et al.*[11]

ω_k^2 (cm^{-2})	Ω (cm^{-1})	J (cm^{-1})	K (cm^{-1})	V$_k$ (cm$^{-3/2}$)	T$_c$ (K)	C (K)	μ (10^{18} esu)	J* (cm^{-3})
1024	5	3785.61	1261.87	24.44	219.5	126.7	2.66	8369
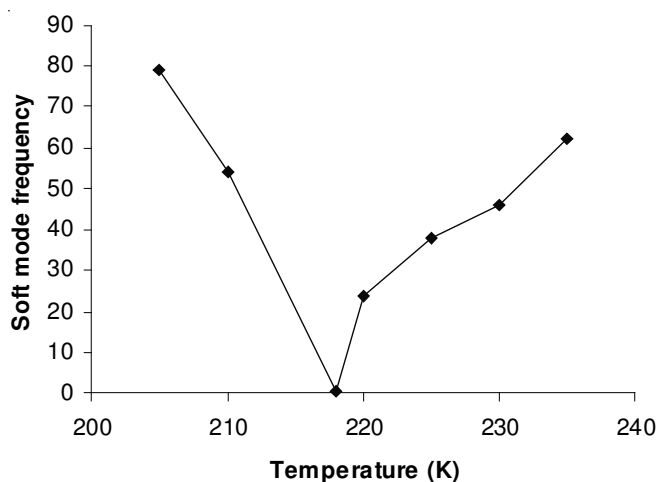
Fig. 1. Calculated temperature dependence of soft mode frequency in SnCl$_2$·2H$_2$O crystal -; Experimental data[6]
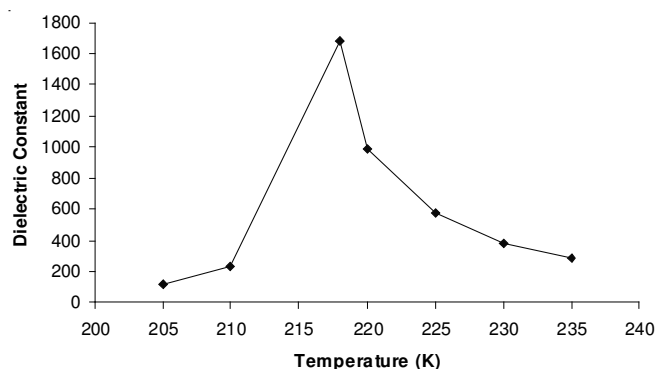
Fig. 2. Calculated temperature dependence of inverse dielectric constant in SnCl$_2$·2H$_2$O crystal -; Experimental data[6]

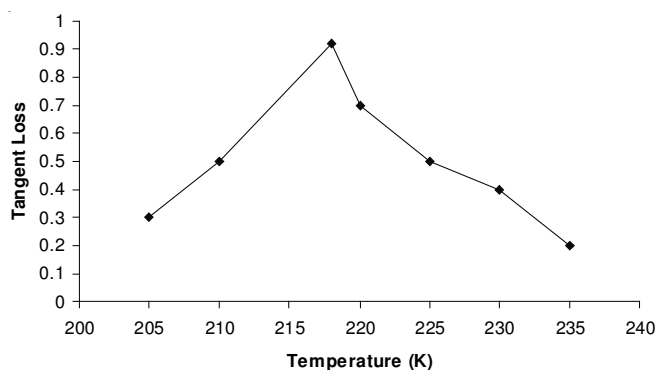1Fig. 3. Calculated temperature dependence of tangent loss in SnCl$_2$·2H$_2$O crystal; Experimental data[6]

authors[11] have decoupled the correlation functions at an early stage. Therefore, some important interactions disappeared from their results. The soft mode frequency $\hat{\Omega}_-$ of Banerjee *et al.*[11] contains terms like $\Delta_{s-p}(\omega)$ (given in eqn. 15). But our soft mode frequency $\hat{\Omega}_-$ contains extra tems in $\tilde{\tilde{\omega}}_k$ and $\Gamma_k(\omega)$

(appearing in eqn. 18a). These extra terms are $\left|V^3(k_1, k_2, -k)\right|^2$ given in $\Delta_k(\omega)$ and $\Gamma_k(\omega)$. Our $\tilde{\tilde{\Omega}}$ is different from corresponding value of $\tilde{\tilde{\Omega}}$ in Banerjee *et al.*[10] results. These terms differentiate our expressions with those of Banerjee *et al.*[11]. The inclusion of third-order phonon anharmonic interaction is quite important to predict correct temperature dependences of ferroelectric and dielectric properties of tinchloride dihydrate crystal. Fig. 3 shows that loss of tangent first increases with temperature upto T$_c$ and then sharply decreases showing Curie-Weiss law. Loss tangent increases linearly with frequency *i.e.* it does not give relaxational behaviour. If width, shift and third order interaction, from the expressions are neglected, the results reduce to the results of Banerjee *et al.*[11]. The theoretically obtained temperature dependences of soft mode frequency, dielectric constant and loss tangent (Figs. 1-3) compare well with the experimental data of Mognaschi *et al.*[6]. Our data are in better agreement with experiment[6] as compared to the calculated data of Banerjee *et al.*[11]. Dielectric loss first increases with temperature below T$_c$. Above T$_c$ it decreases. A transverse radiation field derives the low-lying transverse mode of the material in a forced vibration. Energy is transferred from the electromagnetic field to this lattice mode and is them degraded into other vibrational modes of the material. Due to an harmonic 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 for fourth order interactions.

Conclusion

Present study reveals that the two-sublattice pseudospin lattice coupled mode model along with third and fourth-order phonon anharmonic interaction terms explains well the temperature dependences of soft mode frequency, dielectric constant and loss tangent in tinchloride dihydrate crystal. Present theoretical results fairly agree with experimental results of Mognaschi *et al.*[6]. Present results with some little or no changes may also be applicable to other similar crystals such as Rochelle salt, triglycine sulphate and squaric acid crystals. Calculations on these compounds are in progress in our laboratory.

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