Temperature and electric field dependence of soft mode frequency, dielectric constant and loss tangent in rochelle salt crystal

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A two-sublattice pseudospin lattice coupled mode model of Chaudhuri et al. [J Phys Soc Japan, 49 (1980) 609.] along with third-and fourth-order phonon anharmonic interaction terms and electric field term, has been considered. By using double-time temperature dependent Green's function method, expressions for shift, width, soft mode frequency, dielectric constant and loss tangent are obtained for rochelle salt crystal. By fitting model values of physical quantities, temperature dependence of soft mode frequency, dielectric constant and loss tangent have been calculated for different fields for rochelle salt. Theoretical results are seen to compare well with the experimental results of Sandy and Jones [Phys Rev, 168 (1968) 481].

Keywords: Ferroelectrics, Green's function, Soft mode, Anharmonic interaction

1 Introduction

Potassium sodium tartrate (NaKC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}4H\textsubscript{2}O) or rochelle salt is the material in which ferroelectricity was discovered. It is a colourless to blue-white salt crystallizing in orthorhombic system. It is slightly soluble in alcohol but more completely soluble in water. Its piezoelectric properties are more important. It is also used in phonograph pickups, sensing devices, in process of silvering mirrors. Large crystals of rochelle salt are easy to grow. Although, it is the earliest ferroelectric material but is still the subject of intensive study due to its two transitions. It is ferroelectric between 255 to 297 K showing monoclinic structure in ferroelectric phase. On deuteration, the transition temperatures shift to 251 K and 306 K, respectively.

The theories of ferroelectric properties of rochelle salt were initiated by Muller\textsuperscript{1} who proposed a phenomenological theory to describe susceptibility of rochelle salt based on atomic arrangements and Helmholtz free energy function. After that from microscopic view point, Mason\textsuperscript{2} assumed that the displacement of the proton in the O-(H\textsubscript{2}O)\textsubscript{10} hydrogen bond is the ferroelectric dipole and was able to obtain two Curie points in agreement with observation. He found it necessary, however, to assume that the dipole moment itself varies with temperature owing to the thermal expansion. Mitsui\textsuperscript{3} proposed a two-sublattice model based on the new information obtained from X-ray studies. Mitsui\textsuperscript{3} proposed that ferroelectric displacement arises from the ordering of protons in the O-(H\textsubscript{2}O)\textsubscript{10} hydrogen bond. Later on pseudospin model was used by Blinc et al.\textsuperscript{4} to explain the two transition temperatures in rochelle salt.

Chaudhuri et al.\textsuperscript{5} have used two-sublattice-pseudospin-lattice coupled mode model along with a fourth-order phonon anharmonic term. However, they decoupled the correlations at an early stage and neglected third-order anharmonic interaction term. They, therefore, could not obtain better and convincing results. Hlinka et al.\textsuperscript{6}, Shiozaki et al.\textsuperscript{7}, Noda et al.\textsuperscript{8}, Kikuta et al.\textsuperscript{9} have experimentally studied dielectric and other properties of rochelle salt crystal.

In the present study, an external electric field term, third-order phonon anharmonic interaction term and fourth-order phonon anharmonic interaction term, have been added in the two-sublattice pseudospin-lattice coupled mode model.

By applying double time thermal Green’s function method\textsuperscript{10}, expressions for shift, width, renormalized soft mode frequency, dielectric constant and loss tangent have been evaluated. By using model values of various physical quantities given by Chaudhuri et al.\textsuperscript{5} temperature dependence of soft mode frequency, dielectric constant and loss tangent have been calculated in the presence of external field for rochelle salt. The theoretical results have been compared with experimental data of Sandy and Jones\textsuperscript{11} for rochelle salt.
2 Theory

2.1 Model Hamiltonian and Green’s function

For rochelle salt, the extended two-sublattice pseudospin-lattice coupled mode model, along with third- and fourth-order phonon anharmonic interaction terms is expressed as:

\[ H = -2\Omega \sum_i (S_i^x + S_i^z) - \sum_j J_{ij} \left( \sum_i (S_i^y S_j^y + S_i^y S_j^y) \right) - \sum_i K_i (S_i^z)^2 - 2\mu E \sum_i \left( S_i^x + S_i^y \right) - \sum_{ik} V_{ik} S_i^z A_k \]

... (1)

where \( \Omega \) is proton tunnelling frequency, \( S^x \) and \( S^z \) are components of pseudospin variable, \( J_{ij} \) is exchange interaction constant between spine of same lattices, \( K_{ij} \) is exchange interaction constant between spins of neighbouring lattices, \( \Delta \) represents asymmetry in occupancies of the double positions, \( V_{ik} \) is spin-lattice interaction constant, \( \mu \) is dipole moment of O-H...O bond, \( A_k \) 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.

We have to evaluate the response function, whose poles give excitation frequency, which is directly related to dielectric susceptibility of crystals. We consider the Green’s function (GF):

\[ G_{ij}(t-t') = \left\langle \left\langle S_i^x(t); S_j^x(t') \right\rangle \right\rangle, \]

\[ = -i\theta(t-t') \left\langle \left\langle S_i^z(t); S_j^z(t') \right\rangle \right\rangle. \]

... (2)

Differentiating Eq. (2) with respect to times \( t \) and \( t' \) two times each using Hamiltonian given in Eq. (1), Fourier transforming it and writing into Dyson’s equation form:

\[ G_{(\omega)} = G^0(\omega) + G^0(\omega) P(\omega) G^0(\omega) \]

... (3)

one gets

\[ G^0(\omega) = \frac{\Omega \langle S_i^z \rangle \delta_{ij}}{\pi(\omega - \Omega)} \]

... (4)

and

\[ P(\omega) = \tilde{P}(\omega) + \tilde{P}(\omega) \]

... (5)

with

\[ \tilde{P}(\omega) = \frac{\pi}{\Omega \langle S_i^z \rangle^2} \left\langle \left\langle F_{ij}(t); F_{ij}(t') \right\rangle \right\rangle \]

... (6)

and

\[ \tilde{P}(\omega) = \frac{\pi}{\Omega \langle S_i^z \rangle^2} \left\langle \left\langle F_{ij}(t); F_{ij}(t') \right\rangle \right\rangle \]

... (7)

where

\[ F_{ij} = 2\Omega J_{ij} (S_i^x S_j^x + S_i^y S_j^y) - 2\Omega K_{ij} (S_i^z S_j^z) \]

... (8)

\[ F_{ij}' = 2\Omega J_{ij} (S_i^x S_j^x + S_i^y S_j^y) - 2\Omega K_{ij} (S_i^z S_j^z) \]

... (9)

Following Dyson’s Equation treatment, the Green’s function can now be written as:

\[ G_{ij}(\omega) = \frac{G^0(\omega)}{1 - G^0(\omega) P(\omega)} \]

i.e.

\[ G_{ij}(\omega) = \frac{\Omega \langle S_i^z \rangle}{\pi(\omega^2 - \Omega^2 - P(\omega))} \]

... (10)

Solving \( P(\omega) \), one gets:

\[ G_{ij}(\omega) = \frac{\Omega \langle S_i^z \rangle}{\pi(\omega^2 - \Omega^2 - P(\omega))} \]

... (11)

where \( \Omega^2 = a'^2 + b^2 + bc \)

... (12)

and \( a' = [J \langle S_i^x \rangle + K \langle S_i^z \rangle + 2\mu E + \Delta] \)

... (13)

\[ b = 2\Omega \]

... (14)

Now \( P(\omega) \) contains higher order Green’s functions, which are decoupled by using scheme

\[ \langle abcd \rangle = \langle ab \rangle \langle cd \rangle + \langle ac \rangle \langle bd \rangle + \langle ad \rangle \langle bc \rangle. \]

... (15)
The simpler Green’s functions are solved in zeroth-order approximation, i.e. higher order Green’s functions are neglected.

2.2 Shift, width and soft mode frequency

Now \( P(\omega) \) is resolved into its real \( \Delta(\omega) \) and imaginary parts \( \Gamma(\omega) \).

The Green’s function given in Eq.(11) finally becomes:

\[
G_{ij}(\omega) = \frac{\Omega(S_{ij}^{\dagger})\delta_{ij}}{\pi[\omega^2 - \Omega^2 - 2\Omega(\Delta(\omega) + i\Gamma(\omega))]} \tag{18}
\]

with \( \Delta(\omega) = \Delta_{1}(\omega) + \Delta_{2}(\omega) + \Delta_{3}(\omega) + \Delta_{4}(\omega) \) \tag{19}

where

\[
\Delta_{1}(\omega) = \frac{a^4 r}{2\Omega(\omega^2 - \Omega^2)} \tag{20}
\]

\[
\Delta_{2}(\omega) = \frac{V_{ik}^2 N a^4 r}{2\Omega(\omega^2 - \Omega^2)} \tag{21}
\]

\[
\Delta_{3}(\omega) = \frac{2V_{ik}^2 \langle S_{ij}^{\dagger} \rangle \omega_{k} \left( \omega^2 - \tilde{\omega}_{k}^2 \right)}{\left( \omega^2 - \tilde{\omega}_{k}^2 \right)^2 + 4\omega^2 \Gamma_k(\omega)} \tag{22}
\]

\[
\Delta_{4}(\omega) = \frac{4\mu^2 E^2 a^6 r}{2\Omega(\omega^2 - \Omega^2)} \tag{23}
\]

and \( \Gamma(\omega) = \Gamma_{1}(\omega) + \Gamma_{2}(\omega) + \Gamma_{3}(\omega) + \Gamma_{4}(\omega) \) \tag{24}

\[
\Gamma_{1}(\omega) = \frac{\pi a^4 r}{4\Omega \omega} \left[ \delta(\omega - \tilde{\omega}) - \delta(\omega + \tilde{\omega}) \right] \tag{25}
\]

\[
\Gamma_{2}(\omega) = \frac{V_{ik}^2 N a^4 r}{4\Omega \omega} \left[ \delta(\omega - \tilde{\omega}) - \delta(\omega + \tilde{\omega}) \right] \tag{26}
\]

\[
\Gamma_{3}(\omega) = \frac{4V_{ik}^2 \langle S_{ij}^{\dagger} \rangle \left( \omega^2 - \tilde{\omega}_{k}^2 \right)}{\left( \omega^2 - \tilde{\omega}_{k}^2 \right)^2 + 4\omega^2 \Gamma_k(\omega)} \tag{27}
\]

\[
\Gamma_{4}(\omega) = \frac{4\mu^2 E^2 a^6 r}{4\Omega \tilde{\omega}} \left[ \delta(\omega - \tilde{\omega}) - \delta(\omega + \tilde{\omega}) \right] \tag{28}
\]

In Eq. (26), \( N_k \) is phonon occupation number \( N_k = \cot \hbar \tilde{\omega}_k \).

In Eqs (22) and (27), \( \tilde{\omega}_k \) is renormalized phonon frequency and \( \Gamma_k(\omega) \) is phonon width. These are obtained by solving phonon Green’s function \( G_{kk}(\tau - \tau') = \left\langle A_k(\tau); A_k^{\dagger}(\tau') \right\rangle \). In this way, one obtains:

\[
G_{ik}(\omega) = \frac{\omega_k \delta_{ik}}{\pi[\omega^2 - \omega_k^2 - 2\omega_k(\Delta_k(\omega) + i\Gamma_k(\omega))]} \tag{29}
\]

where

\[
\Delta_k(\omega) = 18P \sum_{k,k'} \left| V^{(3)}(k_1,k_2,k_3-k) \right|^2 \frac{\omega_{k_1} \omega_{k_2}}{\omega_{k_1} \omega_{k_2}} \left( n_{k_1} + n_{k_2} \right) \left( \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} \right)^2 + \left( n_{k_1} - n_{k_2} \right) \left( \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} \right)^2 \right)
\]

\[
\times \left( 1 + n_{k_1} n_{k_2} + n_{k_3} n_{k_4} + n_{k_1} n_{k_3} \frac{\omega_{k_1} + \omega_{k_2} + \omega_{k_3}}{\omega_{k_1}^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3})^2} + 3 \left( 1 - n_{k_1} n_{k_2} + n_{k_3} n_{k_4} - n_{k_1} n_{k_3} \right) \right)
\]

\[
\times \left( \frac{\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}}{\omega^2 - (\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3})^2} \right) + \text{... (higher terms)} \tag{30}
\]

and

\[
\Gamma_k(\omega) = 9\pi \sum_{k_1,k_2} \left| V^{(3)}(k_1,k_2,k_3-k) \right|^2 \frac{\omega_{k_1} \omega_{k_2}}{\omega_{k_1} \omega_{k_2}} \left( n_{k_1} + n_{k_2} \right) \left[ \delta(\omega - \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta(\omega - \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}) \right]
\]

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

\[
+ 48\pi \sum_{k_1,k_2} \left| V^{(4)}(k_1,k_2,k_3,k_4) \right|^2 \left[ \delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}) - \delta(\omega - \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}) \right]
\]

\[
\times \left( 1 + n_{k_1} n_{k_2} + n_{k_3} n_{k_4} + n_{k_1} n_{k_3} \frac{\omega_{k_1} + \omega_{k_2} + \omega_{k_3}}{\omega_{k_1}^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3})^2} + \text{... (higher terms)} \right) \tag{31}
\]

and

\[
\tilde{\omega}_k^2 = \tilde{\omega}_k^2 + A_k(T) \tag{32}
\]

In Eq. (30), \( P \) stands for principal part.
Now Green’s function (18) becomes:

\( G_i(\omega) = \frac{\Omega \langle S^i \rangle \delta_i}{\pi \omega^2 - \hat{\omega}^2 - 2\Omega \Gamma(\omega)} \) ... (33)

with \( \hat{\omega}^2 = \hat{\Omega}^2 + 2\Omega \Delta(\omega) \) ... (34)

Solving Eq (34) self consistently one gets

\[
\hat{\Omega}_\pm^2 = \frac{1}{2} \left( \hat{\Omega}_x^2 + \hat{\Omega}_y^2 \right) \pm \frac{1}{2} \left[ \left( \hat{\Omega}_x^2 - \hat{\Omega}_y^2 \right)^2 + 8V_{ik} \langle S^i \rangle \Omega\omega \right]^{1/2} \]

... (35)

2.3 Transition temperatures

The frequency \( \hat{\Omega}_- \) is the soft mode frequency which approaches to zero as the transition temperature is approached. This frequency depends upon tunneling frequency, inter-and intrachain interactions, spin-lattice interaction as well as on electric field term. If the condition of stability is applied, \( \hat{\Omega}_- \rightarrow 0 \) as \( T \rightarrow T_c \) expressions for Curie temperatures are obtained at once.

\[
T_{c1} = \frac{\eta}{\left( 2k_B \tanh^{-1} \eta / 4\Omega^4 J^* \right)} \]

and

\[
T_{c2} = \frac{\eta}{\left( 2k_B \tanh^{-1} \eta / 4\Omega^4 \left( J + K \right)^* \right)} \]

Where

\[
J^* = (J + K) \]

and

\[
(J + K)^* = (J + K) + \frac{V_{ik}^2 \hat{\Omega}_x^2}{\hat{\Omega}_x^4 + 4\omega_\Omega \Gamma_x^2} \]

... (39)

with

\[
\eta^2 = \left( 2J + K + 4\Omega^2 + \Delta^2 + 2\mu E \right) \]

... (40)

2.4 Dielectric constant and loss tangent

The response of a crystal to electromagnetic field is expressed by electrical susceptibility given by:

\[
\chi = \frac{\lim_{\epsilon \rightarrow 0} \pi N \mu^2 G_i(\omega + i\varepsilon)}{2} \]

... (41)

where \( N \) is number of dipoles having dipole moment \( \mu \) in the sample.

The dielectric constant \( \varepsilon(\omega) \) is related to susceptibility as:

\[
\varepsilon(\omega) = 1 + 4\pi \chi \]

... (42)

We have from Eqs (33), (41) and (42):

\[
\varepsilon(\omega) = \frac{-8\pi N \mu^2 \langle S^i \rangle \Omega \delta_i}{\left( \Omega^2 - \hat{\Omega}^2 + 2\Omega \Gamma(\omega) \right)} \]

... (43)

Since \([\varepsilon(\omega)\rangle_{1}] \), in ferroelectrics i.e. \( \varepsilon = 4\pi \chi \).

Eq. (43) shows that dielectric constant explicitly depends upon electric field through \( \hat{\Omega}_- \).

The dissipation of power in dielectrics is expressed as tangent loss given by:

\[
\tan \delta = \frac{\text{Imaginary } \varepsilon}{\text{Real } \varepsilon} = -\frac{2\Omega \Gamma(\omega)}{\left( \Omega^2 - \hat{\Omega}^2 \right)} \]

... (44)

Eq. (44) shows that loss tangent explicitly depends upon electric field since both \( \hat{\Omega}_- \) and \( \Gamma(\omega) \) contain electric field terms.

3 Numerical Calculations and Results

By using model values\(^4\) presented in Table 1, the temperature and electric field dependence of shift, width, soft mode frequency, dielectric constant and loss have been calculated and compared with experimental results of Sandy and Jones\(^1\), are shown in Figs 1-3.

4 Discussion

In the present work, by considering two-sublattice pseudospin lattice coupled mode model along with third-and fourth-order phonon anharmonic interaction terms, as well as external electric field term, theoretically, expressions have been derived for soft mode frequency, transition temperature, dielectric

| Table 1 — Model values\(^5\) of physical parameters for rochelle salt crystal |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( J \) (cm\(^{-1}\)) | \( K \) (cm\(^{-1}\)) | \( T_{c1} \) (K) | \( T_{c2} \) (K) | \( \Omega \) (cm\(^{-1}\)) | \( \Delta \) (cm\(^{-1}\)) | \( \eta \) (cm\(^{-1}\)) | \( V_{ik} \) (cm\(^{-1}\)) | \( \omega_\hbar \) (cm\(^{-1}\)) | \( A_{ik} \times 10^{17} \) erg/K |
| 354             | 351             | 255             | 296             | 1.82            | 0.678           | 5.51            | 11.5            | 27.20           | 5.73            |
constant and loss tangent for rochelle salt crystal (Table 2). For the derivation, double-time thermal Green's function method\(^1\) has been used. By fitting model values from literature\(^5\) in the expressions, temperature dependence of soft mode frequency, dielectric constant and loss tangent have been calculated in the presence of external electric field. Theoretical results have been compared with experimental results of Sandy and Jones\(^11\). The two sublattice pseudospin model which was originally proposed and found to be suitable for ferroelectric crystals such as rochelle salt lead monohydrogen phosphate and of course antiferroelectric squaric acid crystal. In these crystals, some salient features have been observed such as very low values of tunnelling frequency, on dimensional chain of O-H---O bonding and perpendicular direction of polarization with hydrogen ion displacements. Earlier researchers\(^5\) have not considered third order phonon anharmonic interaction term. They decoupled the correlation at an early stage, due to which some important interactions disappeared from their expressions. It can be seen from our expressions that our frequency \(\tilde{\Omega}\) is the same as the initial frequency of Chaudhuri et al.\(^5\) [see Eq. (13)]. However, our soft mode frequency \(\tilde{\Omega}_\omega\) contains extra terms \(\Delta(\omega)\) [given by Eq. (19)]. The soft mode frequency of Chaudhuri et al.\(^5\) contains terms like \(\Delta(\omega)\) [given by Eq. (22)]. But our soft mode frequency \(\tilde{\Omega}_\omega\) contains extra term in \(\tilde{\omega}_0\) and \(\Gamma_\omega(\omega)\) [appearing in Eq. (30)]. These extra terms are \(|V^3(k_1,k_2-k)|^2\) term given in \(\Delta_\omega(\omega)\) in \(\Gamma_\omega(\omega)\) [Eq. (30)]. These terms differentiate our expressions with the expressions given in the work of Chaudhuri et al.\(^5\). The inclusion of third-order phonon anharmonic interaction terms is quite important since its inclusion gives correct experimental temperature dependence of ferroelectric and dielectric properties of rochelle salt crystal. The phonon anharmonic interactions modify the soft mode frequency through spin-lattice interaction. The soft mode frequency increases while both dielectric constant and loss tangent decrease with the increase in the electric field strength. This finding is found to be in agreement with the experimental observations.

5 Conclusions

Hence, the two-sublattice-pseudospin-lattice coupled mode model along with third and fourth order phonon anharmonic interaction terms explains well the temperature dependence of soft mode frequency dielectric constant and loss tangent in rochelle salt crystal.
Theoretical results agree fairly well with experimental results of Sandy and Jones\textsuperscript{11}. The present model may also be applicable to other crystals such as PbHPO\textsubscript{4}, C\textsubscript{4}O\textsubscript{4}H\textsubscript{2}, TGS etc. The calculations on these crystals are in progress in our laboratory.

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