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RESEARCH ARTICLE

Effect of Electric Field on Ferroelectric and Dielectric Properties in Rochelle Salt Crystal

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Abstract: The model of two-sublattice pseudospin lattice coupled mode for Rochelle salt has been modified by adding third and fourth-order phonon anharmonic interaction terms and electric field term. By using double-time temperature dependent Green's function method, expressions for shift, width, soft mode frequency, dielectric constant and loss tangent were 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 agree with the experimental results of others.

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

Introduction

Potassium sodium tartrate ($NaKC_4H_4O_64H_2O$) or Rochelle salt (RS) is the material in which ferroelectricity was discovered earliest. 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 K to 297 K showing monoclinic structure in ferroelectric phase. On duteration, the transition temperatures shift to 251 K and 306 K respectively. The Theories of ferroelectric properties of Rochelle salt were initiated by Muller[1]. Mason[2] assumed that the displacement of the proton is the O-$(H_2O)_{10}$ hydrogen bond is the ferroelectric dipole and was able to obtain two curie points in agreement with observation. Chaudhuri *et al.,*[3] 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.*,[4] Shiozaki *et al.*,[5] Noda *et al.*,[6] Kikuta *et al.*,[7] have experimentally studied dielectric and other properties of Rochelle salt crystal. In the present work 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[8], 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.*,[3] temperature and field dependences of soft mode frequency, dielectric constant and loss tangent have been calculated. The theoretical results have been compared with experimental data of Sandy and Jones[9] for Rochelle salt.

Model Hamiltonian

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

$$H = -2\Omega\sum_i \left(S_{1i}^x + S_{2i}^x\right) - \sum_{ij} J_{ij}\left[\left(S_{1i}^z S_{1j}^z\right) + \left(S_{2i}^z S_{2j}^z\right)\right] - \sum_{ij} K_{ij}\left(S_{1i}^z S_{2j}^z\right) - \Delta\sum_i \left(S_{1i}^z + S_{2i}^z\right) - 2\mu E\sum_i \left(S_{1i}^z + S_{2i}^z\right)$$
$$- \sum_{ik} V_{ik} S_{1i}^z A_k - \sum_{ik} V_{ik} S_{2i}^z A_k^+$$
$$+ \frac{1}{4}\sum_k \omega_k \left(A_k A_k^+ + B_k B_k^+\right) + \sum_{k_1k_2k_3} V^{(3)}\left(k_1, k_2, k_3\right) A_{k_1} A_{k_2} A_{k_3}$$
$$+ \sum_{k_1k_2k_3k_4} V^{(4)}\left(k_1, k_2, k_3 k_4\right) A_{k_1} A_{k_2} A_{k_3} A_{k_4} \quad (1)$$

Where Ω is proton tunnelling frequency, S^z and S^x are components of pseudospin variables, J_{ij} is exchange interaction constant between spin of same lattices, K_{ij} is exchange interaction constant between spins of neighbouring lattices, V_{ik} is spin-lattice interaction constant, μ is dipole moment of O-H…O bond, 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[10,11].

Green's function

We consider the Green's function (GF)

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

Differentiating Eq. (2) with respect to time t and t' two times each using Hamiltonian (1), Fourier transforming it and writing into Dyson's equation form we obtain

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

$$\text{Where } \tilde{\Omega}^2 = a'^2 + b^2 + bc \quad (4)$$

$$a' = [J\langle S_1^x\rangle + K\langle S_2^z\rangle + 2\mu E + \Delta] \quad (5)$$

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

$$\text{and } c = \left[\left\lfloor j\left\langle s_1^x\right\rangle + k\left\langle s_2^x\right\rangle\right]\right. \quad (7)$$

Now $P(\omega)$ contains higher order Green's functions

$$\langle abcd \rangle = \langle ab \rangle\langle cd \rangle + \langle ac \rangle\langle bd \rangle + \langle ad \rangle\langle bc \rangle \tag{8}$$

The simpler Green's functions are solved in zeroth-order approximation, *i.e*. higher order Green's functions are neglected.

Shift, Width and Ferroelectric mode frequency

Then $P(\omega)$ is resolved into its real $\Delta(\omega)$ and imaginary parts $\Gamma(\omega)$. The Green's function given in Eq. 3 finally becomes

$$G_{ij}(\omega) = \frac{\Omega\langle S_{1i}^{x} \rangle\delta_{ij}}{\pi\left[\omega^2 - \Omega^2 - 2\Omega\ \{\Delta(\omega) + i\Gamma(\omega)\}\right]} \tag{9}$$

$$\text{with}\ \Delta(\omega) = \Delta_1(\omega) + \Delta_2(\omega) + \Delta_3(\omega) + \Delta_4(\omega) \tag{10}$$

$$\Delta_1(\omega) = \frac{a'^4}{2\Omega\left(\omega^2 - \tilde{\Omega}^2\right)} \tag{11}$$

$$\Delta_2(\omega) = \frac{V_{ik}^2 N_k a^2}{2\Omega\left(\omega^2 - \tilde{\Omega}^2\right)} \tag{12}$$

$$\Delta_3(\omega) = \frac{2V_{ik}^2\langle S_1^x\rangle\omega_k\ \left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)^2 + 4\omega_k^2\Gamma_k^2(\omega)\right]} \tag{13}$$

$$\Delta_4(\omega) = \frac{4\mu^2 E^2 a'^2}{2\Omega\left(\omega^2 - \tilde{\Omega}^2\right)} \tag{14}$$

$$\text{and}\ \Gamma(\omega) = \Gamma_1(\omega) + \Gamma_2(\omega) + \Gamma_3(\omega) + \Gamma_4(\omega) \tag{15}$$

$$\Gamma_1(\omega) = \frac{\pi a'^4}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right] \tag{16}$$

$$\Gamma_2(\omega) = \frac{V_{ik}^2 N_k a'^2}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right] \tag{17}$$

$$\Gamma_3(\omega) = \frac{4V_{ik}^2\langle S_1^x\rangle\ \left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)^2 + 4\omega_k^2\Gamma_k^2(\omega)\right]} \tag{18}$$

$$\Gamma_4(\omega) = \frac{4\pi\mu^2 E^2 a'^2}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right] \tag{19}$$

In Eqs 13 and 18, $\tilde{\tilde{\omega}}_k$ is renormalized phonon frequency and $\Gamma_k(\omega)$ is phonon width. These are obtained by solving phonon Green's function

$G_{kk'}(t-t') = \langle\langle A_k(t); A_k^{+}(t')\rangle\rangle$.

$$\Delta_k(\omega) = \mathrm{Re}\,P(\omega)$$
$$= 18P\sum_{k_1k_2} \left|V^{(3)}(k_1,k_2-k)\right|^2$$
$$\frac{\omega_{k_1}\omega_{k_2}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}}\left\{(n_{k_1}+n_{k2})\frac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})^2}\right.$$
$$\left.+(n_{k_2}+n_{k_1})\frac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})^2}\right\}$$
$$+48P\sum_{k1_1k_{2}k_3}\left|V^{(4)}(k_1,k_2,k_{3,}-k)\right|^2\frac{\omega_{k_1}\omega_{k_2}\omega_{k_3}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}\tilde{\omega}_{k_3}}$$
$$\{(1+n_{k_1}n_{k_2}+n_{k_2}n_{k_3}+n_{k_3}n_{k_1})\frac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3}}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2}$$
$$+3(1-n_{k_2}n_{k_1}+n_{k2}n_{k_3}-n_{k_3}n_{k_1})$$
$$\frac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3}}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k3})^2}+\text{(higher terms)} \tag{20}$$

and

$$\Gamma_k(\omega) = 9\pi\sum_{k_1k_2}\left|V^{(3)}(k_1,k_2,-k)\right|^2\frac{\omega_{k_1}\omega_{k_2}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}}$$
$$\{(n_{k_1}+n_{k_2})[\delta(\omega+\tilde{\omega}_{k_1}+\tilde{\omega}_{k_1})$$
$$-(\omega-\tilde{\omega}_{k_1}-\tilde{\omega}_{k_1})$$
$$+(n_{k_2}-n_{k_1})[\delta(\omega+\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})-\delta(\omega+\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})]\} \tag{21}$$
$$+48\pi\sum_{k_1k_2k_3}\left|V^{(4)}(k_1,k_2,k_3,k_4)\right|^2$$
$$X\{(1+n_{k_1}n_{k_2}+n_{k_2}n_{k_3}+n_{k_3}n_{k_4})$$
$$X[\delta(\omega+\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})-(\omega-\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}-\tilde{\omega}_{k_3})]$$
$$+3(n_{k_1}n_{k_2}+n_{k_2}n_{k_3}-n_{k_3}n_{k_4})$$

and

$$\tilde{\tilde{\omega}}_k{}^2 = \tilde{\omega}_k{}^2 + A_k(T) \tag{22}$$

Now Green's function (9) becomes

$$G_{ij}(\omega) = \frac{\Omega\langle S_{1i}^x\rangle\delta_{ij}}{\pi\left[\omega^2 - \tilde{\Omega}^2 - 2\Omega i\Gamma(\omega)\right]} \tag{23}$$

$$\text{With } \tilde{\Omega}^2 = \tilde{\Omega}^2 + 2\Omega\Delta(\omega) \tag{24}$$

Solving Eq 24 self consistently one gets

$$\tilde{\Omega}_{-}^2 = \frac{1}{2}\left[(\tilde{\tilde{\omega}}_k{}^2 + \tilde{\tilde{\Omega}}^2) \pm (\tilde{\tilde{\omega}}_k{}^2 - \tilde{\tilde{\Omega}}^2)^2 + 8V_{ik}\langle S_{1i}{}^x\rangle\Omega\,\omega_k\right]^{\frac{1}{2}} \tag{25}$$

Dielectric constant and loss tangent

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

$$\chi = -\lim_{\in\to 0} 2\pi N\mu^2 G_{ij}(\omega + i\in) \tag{26}$$

Where N is number of dipoles having dipole moment μ in the sample. The dielectric constant $\in(\omega)$ is related to susceptibility as

$$\in = 1 + 4\pi\chi \tag{27}$$

We have from Eqs 26, 27 and 23

$$\in(\omega) = \frac{(-8\pi N\mu^2)\langle S_{1j}^x\rangle\Omega\delta_{ij}}{\left[\omega^2 - \tilde{\Omega}^2 - 2\Omega i\Gamma(\omega)\right]} \tag{28}$$

since $[\in(\omega)\rangle\rangle 1]$, in ferroelectrics .

Eq. 28 shows that dielectric constant explicitly depends upon electric field through $\tilde{\Omega}$ .The dissipation of power in dielectrics is expressed as tangent losss given by

$$\tan\delta = \frac{\operatorname{Im}aginary\in}{\operatorname{Re}al\in} = -\frac{2\Omega\Gamma(\omega)}{(\omega^2 - \tilde{\Omega}^2)} \tag{29}$$

Eq. 29 shows that loss tangent explicitly depends upon electric field since both $\tilde{\Omega}$ and $\Gamma(\omega)$ contain electric field terms.

Numerical calculations

By using model values given in Table 1 the temperature and field dependences of shift, width, soft mode frequency and dielectric constant and loss have been calculated (Figure 1, 2 & 3) and compared with experimental results of Sandy and Jones[9].

Table 1. Model values of physics parameters for Rochelle salt crystal

J, cm^{-1}	K, cm^{-1}	T_{c1}, K	T_{c2}, K	Ω, cm^{-1}	Δ, cm^{-1}	η, cm^{-1}	V_{ik}, cm^{-1}	ω_k, cm^{-1}	A_{kg}x10^{17} erg/K
354	351	255	2.96	1.82	0.678	5.51	11.5	27.20	5.73

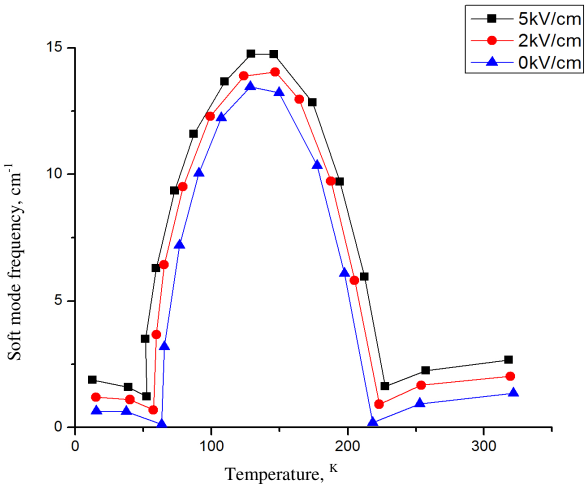

Figure 1. Calculated temperature dependence of soft mode frequency of RS with comparision of experimental data

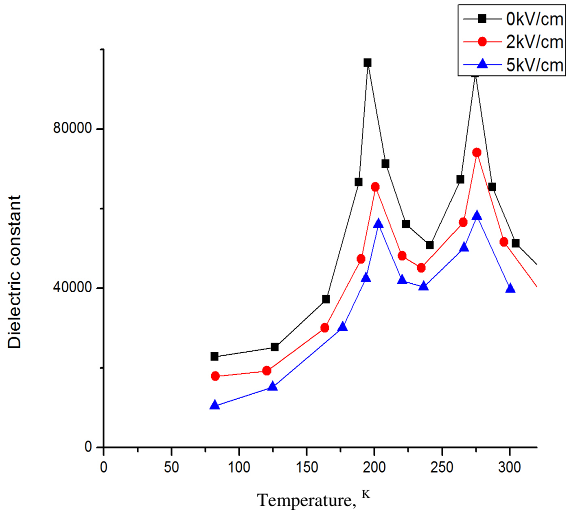

Figure 2. Calculated temperature dependence of dielectric constant of RS with comparision of experimental data

Results and Discussion

Earlier researchers[3] 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*[3]. However, our soft mode frequency $\hat{\Omega}_{-}$ contains extra terms $\Delta(\omega)$. The soft mode frequency of Chaudhuri *et al.,*[3] contains terms like $\Delta(\omega)$. But our soft mode frequency $\hat{\Omega}_{-}$ contains extra term in $\tilde{\tilde{\omega}}_k$ and

$\Gamma_k(\omega)$. These extra terms are $\left|V^3(k_1,k_2,-k)\right|^2$ term given in $\Delta_k(\omega)$ in $\Gamma_k(\omega)$. These terms differentiate our expressions with the expressions given in the work of Chaudhuri *et al*[3]. 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.

Conclusion

The two sublattice-pseudospin-latttice 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 in the presence of electric field. Theoretical results agree well with experimental results of Sandy and Jones[9].

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