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Note

Temperature dependence of soft mode frequency, dielectric constant and loss tangent of deuterated Rochelle salt crystal

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By fitting model values for physical quantities for deuterated Rochelle salt crystal in theoretical expressions for soft mode frequency, dielectric constant and loss tangent derived for Rochelle salt in our earlier studies temperature dependences of these quantities have been calculated. Theoretical results have been compared with experimental results reported in literature, which shows a good agreement. Isotope effects on both transition temperatures have been explained successfully.

Keywords: Ferroelectrics, Green's function, Isotope effect, Soft mode

1 Introduction

Rochelle salt ($NaKC_4H_4O_6.4H_2O$) crystal is extensively studied firstly due to its wide use in photographic pickups and secondly, its being first crystal in which ferroelectricity was earliest discovered. It is ferroelectric between 255 K and 297 K. On deuteration of Rochelle salt (RS) crystal both transition temperatures shift to 251 K and 306 K, respectively. This shows important role played by hydrogen bonds in phase transition mechanism. Deuterated Rochelle salt (DRS) crystal is orthorhombic in non-polar and monoclinic in polar phase. The crystals are easily grown by slow evaporation method. A very large number of investigations have been made on Rochelle salt and deuterated Rochelle salt crystals, ever since Valashek's discovery[1]. Apih *et al.*[2] have carried out ^{23}NaNMR experimental studies on DRS. Kobayashi *et al.*[3] have measured optical properties of deuterated Rochelle salt crystals. Deyet *et al.*[4] have measured heat capacity of deuterated Rochelle salt crystal. Kalisz *et al.*[5] have measured dielectric relaxation and capacity of Rochelle salt crystal. Kamba *et al.*[6] have carried out soft mode frequency measurements in deuterated Rochelle salt crystal. Suzuki[7] have done the X-ray diffraction measurements in deuterated Rochelle salt. Araujo *et al.*[8] have done measurements of dielectric constant of Rochelle salt at different frequencies. Noda *et al.*[9] have measured specific heat in Rochelle salt. Hlinka *et al.*[10] have done inelastic neutron scattering measurements on Rochelle salt crystal. Kikuta *et al.*[11] have measured dielectric constant of deuterated Rochelle salt. Yaldovker and Berger[12] have measured the size and orientation of domains in deuterated Rochelle salt crystal.

Theoretical studies were initiated by Muller[13], Mason[14] and Devonshire[15] in Rochelle salt. These authors tried to explain physical properties in terms of atomic rearrangements. Mitsui[16] proposed a two sublattice model for Rochelle salt crystal. Blincet *et al.*[17] have used two sublattice pseudo-spin model for Rochelle salt crystal. Chaudhuri *et al.*[18] have modified Blinc's model by adding spin-lattice interaction and fourth-order an harmonic term. Earlier authors[13,14] have used over-simplified model which could not explain experimental facts. Others[18] have decoupled correlations at an early stage and not considered third order term due to which some important interactions were disappeared from their results.

In our previous work[19], we have modified two-sublattice pseudo-spin lattice coupled mode model by adding third- and fourth-order phonon an harmomic interaction terms[20] for Rochelle salt crystal. With the help of double-time thermal Green's function method[21], we had derived expressions for soft mode frequency, dielectric constant and loss tangent for Rochelle salt crystal[22]. By fitting model values[18] of physical quantities for DRS crystal in the expressions obtained in our earlier paper, for Rochelle salt crystal, temperature dependence of soft mode frequency, dielectric constant and loss tangent will be calculated for DRS crystal. Theoretical results will be compared with experimental results of Kamba *et al.*[6]and Sandy and Jones[22].

2 Calculation and Results

In our earlier paper, a two sub-lattice coupled mode model was modified by adding third-and fourth-order phonon an harmonic interactions for Rochelle salt crystal. The Green's function $G_{ij}(t-t') = \langle\langle S^z_{1i}(t); S^z_{1j}(t')\rangle\rangle$ was evaluated with the help of modified Hamiltonian[16]. The evaluated Green's function was:

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$$G(\omega) = \pi^{-1}\Omega\langle S^x_{i1}\rangle\delta_{ij}\left[\left(\omega^2 - \hat{\Omega}\right) + 2i\Omega\Gamma(\omega)\right]^{-1}, \quad \ldots (1)$$

where

$$\hat{\Omega}^2 = \tilde{\Omega}^2 + \Delta(\omega), \quad \ldots (2)$$

$$\tilde{\Omega}^2 = a^2 + b^2 - bc, \quad \ldots (3)$$

where

$$a = 2J_0\langle S_1^z\rangle + K_0\langle S_2^z\rangle, \quad \ldots (4)$$

$$b = 2\Omega \text{ and} \quad \ldots (5)$$

$$c = 2J_0\langle S_1^x\rangle + K_0\langle S_2^x\rangle, \quad \ldots (6)$$

$$\langle S_1^z\rangle = -\langle S_2^z\rangle \neq 0, \; T < T_c. \quad \ldots (7)$$

In Eqs (1) and (2) $\Gamma(\omega)$ and $\Delta(\omega)$ are width and shift of response function. Their values have been given in our earlier paper[18] on Rochelle salt.

Solving Eq. (2) self-consistently we obtained soft mode frequency as:

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

The dielectric constant was obtained as:

$$\in(\omega) = \left(-8\pi N\mu^2\right)\langle S^x\rangle\left(\omega^2 - \hat{\Omega}^2\right)\left[\left(\omega^2 - \hat{\Omega}^2\right)^2 + 4\Omega^2\Gamma(\omega)^2\right]^{-1} \quad \ldots (9)$$

where N is numbers of dipoles in unit cell each with dipole moment μ. The loss tangent was obtained as:

$$\tan\delta = \frac{2\Omega\Gamma(\omega)}{\hat{\Omega}^2} \quad \ldots (10)$$

By putting model values of various physical quantities in Eqs (8), (9) and (10) temperature dependences of soft mode frequency, dielectric constant and loss tangent for DRS crystal have been calculated. These are shown in Figs 1-3. Theoretical results have been compared with experimental results of Sandy and Jones[22].

3 Results and Discussion

In the present work, by fitting model values for deuterated Rochelle salt crystal in the expressions obtained for Rochelle salt crystal in our earlier paper[19], the temperature dependence of soft mode

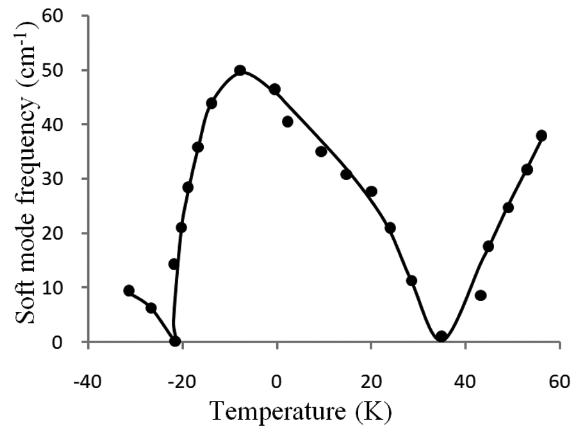

Fig. 1 — Temperature dependence of soft mode frequency in deuterated Rochelle salt (— present calculation, ● Correlated values with experimental values of Sandy and Jones[22] for dielectric constant).

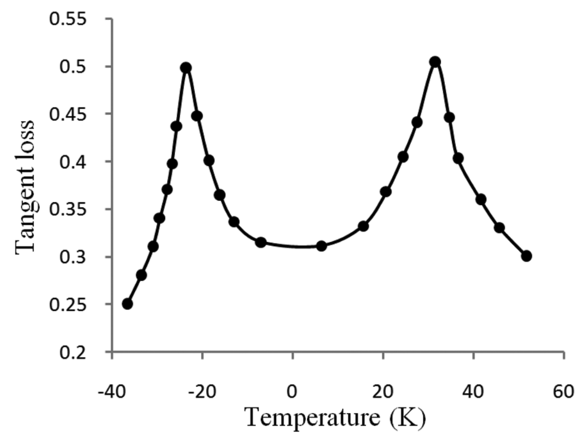

Fig. 2 — Temperature dependence of tangent loss in deuterated Rochelle salt (— present calculation, ● experimental values of Sandy and Jones[22]).

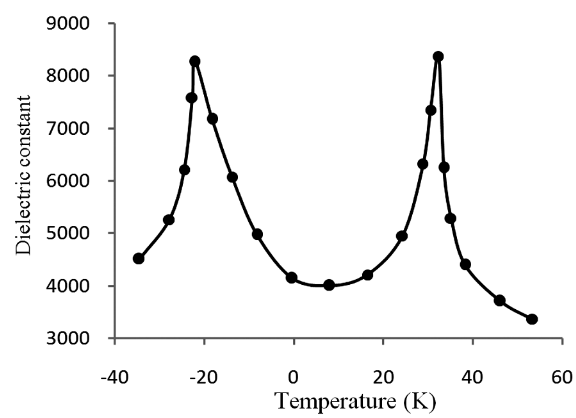

Fig. 3 — Temperature dependence of dielectric constant in deuterated Rochelle salt (— present calculation, ● experimental values of Sandy and Jones[22]).

Table 1 — Model values of physical quantities for deuterated Rochelle salt crystal.

Ω	J	K	V_{ik}	T_{c1}	T_{c2}	C_1	C_2	$\omega_k^{1/2}$	μ
(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(K)	(K)	(K)	(K)	($cm^{-1/2}$)	(esu)
1.710	399.15	395.96	14.16	251.3	306.6	1935	2865	9.5	5.16×10^{-18}

frequency, dielectric constant and loss tangent have been calculated. Theoretically calculated results compare well with the experimentally reported results of Kamba *et al.*[6] and Sandy and Jones[22] for deuterated Rochelle salt crystal.

The main purpose of the present work is to explain isotope effect in DRS. On deuteration, the transition temperatures shift from 255 K and 297 K to 251 K and 306 K, respectively, and both dielectric constant and loss tangent versus temperature curves shift to quite new values. Our expressions for T_{c1} and T_{c2} with values for DRS explain fairly isotope effect on both transition temperatures. Our expressions given in Eqs (8-10) explain temperature dependence of ferroelectric soft mode frequency, dielectric constant and loss tangent for DRS. The change in tunneling frequency of proton in double well potential is responsible for observed effects and also explain a small isotope effect in Curie-Weiss constant in DRS. Value of Curie-Weiss constant changes from 1830 K to 1935 K on deuteration.

4 Conclusions

Present study shows that the modified model, *i.e.*, two-sublattice pseudo-spin lattice coupled mode model with addition of third- and fourth-order phonon an harmonic interactions explains quantitatively the ferroelectric and dielectric behaviors of RS as well as DRS crystals. Theoretical results agree with experimental results of Kamba *et al.*[6] and Sandy and Jones[22]. Present study shows the applicability of present modified model for both RS and DRS crystals.

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