

Temperature dependence of antiferroelectric mode frequency, dielectric constant and loss tangent in deuterated squaric acid crystal

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By fitting model values of physical quantities for deuterated SQA crystal in theoretically derived expression for AFE mode frequency, dielectric constant and loss tangent in my earlier paper [*Indian J Pure & Appl Phys*, 47 (2009) 119] temperature dependence of these quantities have been calculated and compared with experimental data of Maier *et al.*, *Phys Status Solidi (b)*, 89 (1978) 578 and Semmingsen, D, *Acta Chem Scand*, 27 (1977) 3961, which show a good agreement.

Keywords: Antiferroelectrics, Anharmonic, Dielectric constant, Loss tangent, Phase transition

1 Introduction

Squaric acid ($C_4H_2O_4$) crystal (SQA) undergoes antiferroelectric transition at 373 K. On deuteration, ($C_4D_2O_4$) the transition temperature shifts to 516 K showing large isotope effects. This fact suggests that the hydrogen bonds play an important role in the phase transition mechanism. Squaric acid has layered structure. Each molecule is a square with oxygen ions at its four vertices linked by hydrogen bonds on equal footing. At room temperature, the layers are ferroelectrically ordered and antiferroelectrically stacked. Because of the planar H-bonds, the interactions between molecules in the same layers are stronger than in the interlayers. Below transition temperature, protons are arranged in ordered pattern. The directions of lattice spontaneous polarization are the same for one molecular plane and opposite for neighbouring ones. The antiferroelectric structure is monoclinic with space group $P2_1/m$ and the lattice dimensions are $a=6.13\text{\AA}$, $b=5.23\text{\AA}$, $c=6.14\text{\AA}$ (at 500 K). This is low temperature phase. The paraelectric high temperature phase is tetragonal with space group $I4/m$ with new lattice dimensions $a=6.26\text{\AA}$, $b=5.36\text{\AA}$ and $c=6.30\text{\AA}$ (at 540 K). The low and high temperature structures are shown in Figs 1 and 2.

Extensive experimental studies on SQA and its deuterated form (DSQA) have been carried out by many experimentalists. Semmingsen and Feder¹ have done birefringence study. Semmingsen² has carried out X-ray diffraction to determine crystal structures of SQA and DSQA. Neutron scattering experiment has been done by Stucky *et al.*³. Dielectric measurements were carried out on SQA and DSQA by Maier *et al.*⁴.

Raman scattering experiments were done by Morimoto⁵ in SQA and DSQA crystals.

Theoretical studies on SQA were initiated by Deininghaus and Mehring⁶ who used three dimensionally coupled Ising chains, Muser⁷ used this model and applied simulation technique to determine temperature dependence of order parameter of transition. Zinenko⁸ used cluster approximation and tunneling of protons. Li and Qin⁹ have considered two-sub lattice pseudo spin model. They have used Greens function method and obtained soft mode frequency, conditions of antiferroelectric and paraelectric phases, order parameter, dispersion relation, internal energy and transition entropy. Matsushita *et al.*¹⁰ have extensively studied transition in SQA by using pseudo spin model with coupling of lattice distortion with proton system. They have used mean field approximation to discuss elastic constants, electric susceptibility and isotope effect in SQA. Earlier researchers have not considered spin-lattice interactions and third-and fourth-order phonon anharmonic interactions. They have decoupled the correlations at an early stage. So that they could not produce better and convincing results. In our earlier paper¹¹, we have considered spin-lattice interactions and phonon anharmonic contraction terms.

In the present study, we shall fit model values of physical quantities in the expressions obtained in my earlier paper¹¹ for deuterated squaric acid crystal. Temperature dependence of antiferroelectric mode frequency, dielectric constant and loss tangent will be calculated for DSQA crystal. Theoretical results will be compared with experimental results of Muser,⁷ Maier⁴ and Samara and Semmingsen¹².

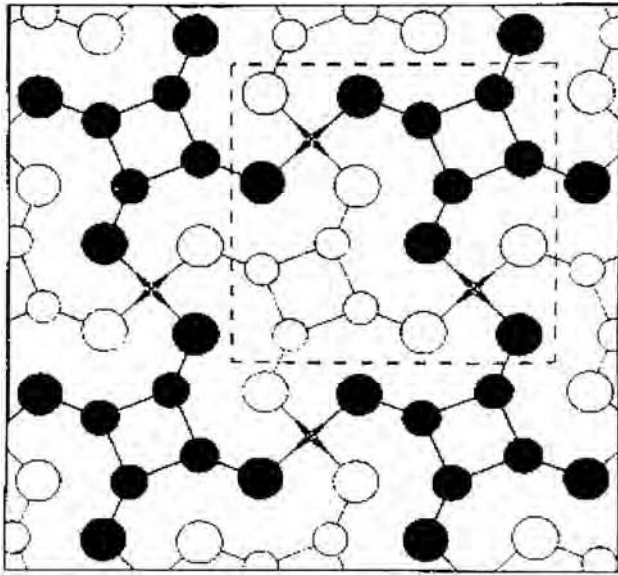


Fig. 1 — (a) Squaric acid crystal in the high temperature phase. Big circles show O-atoms, small circles C-atoms, double arrows show the positions of the hydrogen bonds. Dotted lines show a- and c-axes (Pettersson and Maier) Full and open circles belong to different layers

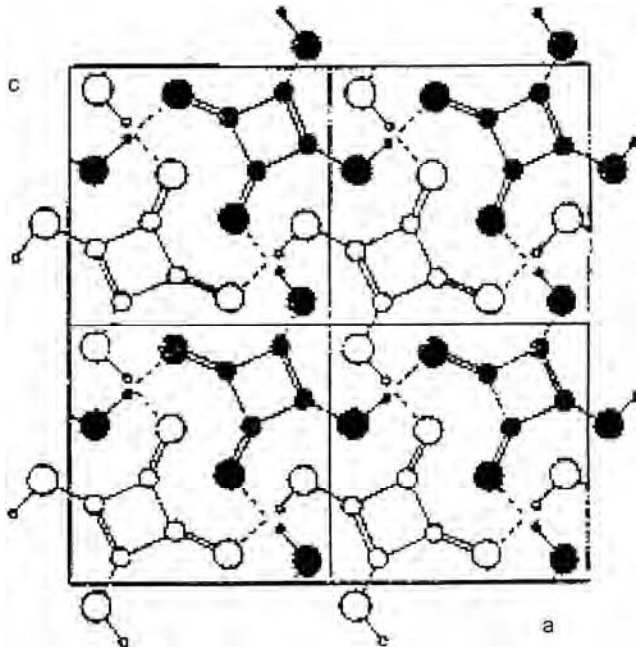


Fig. 2 — Two layers of squaric acid crystal in the low temperature phase. Big circles show O-atoms, small circles C-atoms, and small H atoms. Full and open circles belong to different layers. (Fischer and Genzal)

2 Calculations and Results

In my earlier paper¹¹, a two-sub lattice pseudo spin⁹ lattice coupled mode¹⁴ model along with third- and fourth-order phonon anharmonic interaction¹⁵ terms¹⁶ have been considered for SQA crystal. The Green's

function.¹⁷ is differentiated twice with respect to time t and t' With the help of modified Hamiltonian which is then set into Dyson's equation form. As a result Green's function, was obtained as :

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

$$\text{where } \tilde{\Omega}^2 = \tilde{\Omega}^2 + \Delta(\omega), \quad \dots(2)$$

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

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

$$b = 2\Omega; \quad \dots(5)$$

$$c = 2J_0 \langle S_1^x \rangle + K \langle S_2^x \rangle \quad \dots(6)$$

$\Delta(\omega)$ and $\Gamma(\omega)$ are shift and width of response function of Green's function $G(\omega)$. Values of $\Delta(\omega)$ and $\Gamma(\omega)$ have been given in earlier paper¹¹. By solving Eq. (2), the AFE mode frequency was obtained as:

$$\hat{\Omega}_\pm^2 = \frac{1}{2} \left\{ \left(\tilde{\omega}_k^2 + \tilde{\Omega}^2 \right) \pm \left[\left(\tilde{\omega}_k^2 - \tilde{\Omega}^2 \right)^2 + 16V_{ik} \langle S_i^x \rangle \Omega \right]^{1/2} \right\}. \quad \dots(7)$$

The dielectric constant ϵ is related to susceptibility χ as $\epsilon = 4\pi\chi$ which in turn is related¹⁸ to retarded Green's function given in Eq. (2) as $\chi = -2N\mu^2 G(\omega + iX)$. Therefore, putting the value of Green's function in Eq. (1), the value of dielectric constant ϵ is obtained as:

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

The dissipation of power when crystal is exposed to electromagnetic field is expressed as loss tangent. The loss tangent is the ratio of imaginary to real parts of dielectric constant:

$$\tan \delta = \frac{2\Omega\Gamma(\omega)}{\hat{\Omega}^2} \quad \dots(9)$$

By using model values of physical quantities for deuterated squaric acid crystal presented in Table 1, temperature dependence of antiferroelectric mode frequency, dielectric constant and loss tangent have been calculated and shown in Figs 1-3.

Table 1 — Model values of physical quantities for deuterated Squaric acid crystal

$T_c(k)$	Ω (cm^{-1})	(2 J-K)	Vik	$N \times 10^{-36}$	$\mu 10^{18}$	C(k)	ω_k (cm^{-1})	$A_k 10^{17}(\text{erg K}^{-1})$
516	0.8	632	72	35.59	5.8	18000	100	35

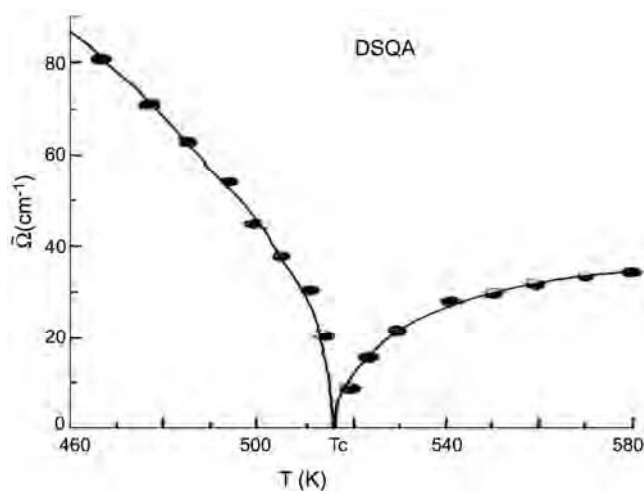


Fig. 3 — Calculated temperature dependence of soft mode frequency in DSQA.Exp. •

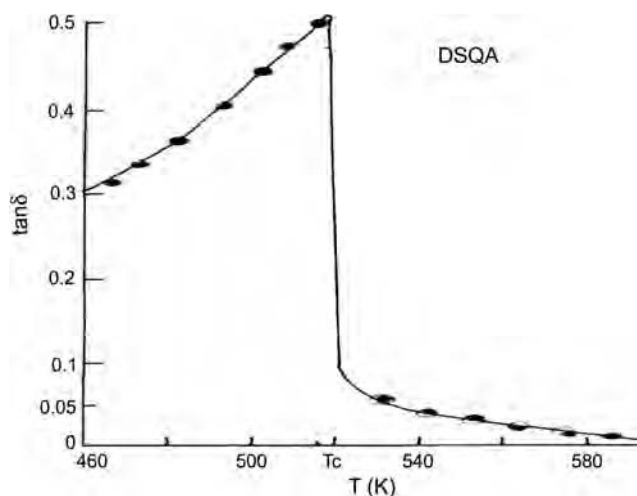
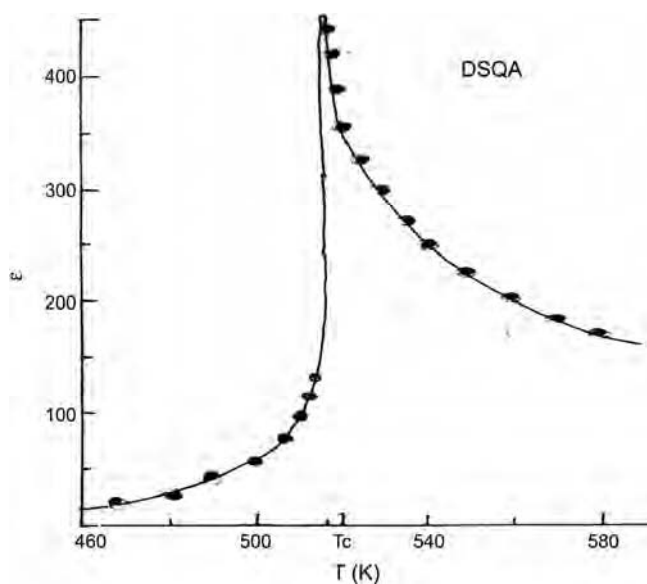


Fig. 5 — Calculated temperature dependence of loss tangent in DSQA-Exp. •

Fig. 4 — Calculated temperature dependence of ϵ in DSQA.Exp. •

Calculated temperature dependences have been compared with experimental values of Maier *et al.*⁴ and Semmingsen².

3 Discussion

In the present work, by fitting model values for deuterated squaric acid crystal in the expressions obtained for squaric acid crystal in my earlier paper¹¹, the temperature dependence of antiferroelectric mode

frequency, dielectric constant and loss tangent has been calculated. Theoretically calculated results compare well with experimentally reported results of Maier *et al.*⁴ and Semmingsen² for deuterated squaric acid crystal.

The main aim of the present work is to explain isotope effect in DSQA. On deuteration, the transition temperature shifts from 371 to 516 K, and both dielectric constant and loss tangent versus temperatures curves shift to quite new values. Our expression for transition temperature T_c with values for DSQA explains fairly isotope effect on T_c . Our expressions given in Eqs (8-10) explain temperature dependence of antiferroelectric frequency, dielectric constant and loss tangent for DSQA. The change in tunneling frequency is mainly responsible for isotope effects in DSQA crystal. Hence, with the expressions obtained for SQA crystals and different values of physical quantities for DSQA crystal, one can explain antiferroelectric, dielectric and isotope effects in deuterated squaric acid crystal.

4 Conclusions

Present study reveals that the modified model i. e. two sub lattice pseudo spin-lattice coupled mode model with addition of third and fourth order phonon anharmonic interaction terms explain quantitatively well the antiferroelectric and dielectric behaviour of

pure as well as deuterated squaric acid crystal. Theoretical results agree with experimental results of Maser *et al*⁴. and Semmingsen², which show the applicability of the present modified model for both SQA and DSQA crystals.

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