Soft modes and proton tunneling in PbHPO4, squaric acid and KH_2PO_4, type ferroelectrics

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SOFT MODES AND PROTON TUNNELING IN $PbHPO_4$, SQUARIC ACID AND KH_2PO_4 TYPE FERROELECTRICS†

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It is pointed out that the huge observed differences in the soft mode frequencies of KH_2PO_4, $PbHPO_4$, CsH_2PO_4 and squaric acid do not necessarily reflect a large difference in the proton O—H———O tunneling frequencies but rather result from a difference in the short range correlations renormalizing the single proton O——H—O tunneling frequency.

I. INTRODUCTION

Order—disorder type hydrogen bonded ferroelectrics — where the proton moves between two equilibrium sites in an O—H———O bond — are generally well described by the pseudo—spin 1/2 Ising model in a transverse field Hamiltonian [1] :

$$\mathcal{H} = -\tilde{\Omega}\sum_i S_i^x - \frac{1}{2}\sum_{i,j}\tilde{J}_{ij}S_i^z S_j^z \quad . \tag{1}$$

Here $\tilde{\Omega}$ is the effective tunneling integral and $\tilde{J}$ the effective pseudo—spin — pseudo—spin coupling constant [2] . The above Hamiltonian has been successfully used to explain:

i) The significant increase in the ferroelectric transition temperature T_c on deuteration [3] .

ii) The large decrease in the soft mode frequency ω_0 (or the inverse soft mode relaxation time τ^{-1}) on deuteration [3] .

iii)The fact that the slightly overdamped soft mode in KH_2PO_4 becomes

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underdamped[4] above 6 kbars as expected for a tunneling mode where $\tilde{\Omega}$ increases with increasing pressure and decreasing O—H———O bond length.

iv) The observation that the ferroelectric transition temperature in KH_2PO_4 is reduced to zero, $T_c \to 0$ K, at $p_c \geqslant 17$ kbar while the corresponding critical pressure for KD_2PO_4 exceeds 70 kbars[5] .

There are however still several open problems:

i) The soft mode frequencies in $PbHPO_4$[6] , CsH_2PO_4[7] and squaric acid[8] are much lower than in KH_2PO_4 though the O—H———O bond lengths and the isotope effects in T_c on deuteration are close to the ones in KH_2PO_4 type ferroelectrics.

ii) The tunneling frequencies needed to explain the equilibrium thermodynamic properties are generally several times larger than the ones deduced from dynamic experiments.

It is the purpose of this note to try to explain the above discrepancies in terms of a renormalization of the single particle O—H———O tunneling integrals due to short range correlations.

II. SOFT MODE DYNAMICS

The soft mode dynamics of systems described by expression (1) is usually treated[3] in the random phase approximation (RPA). Here one finds the square of the soft mode frequency ω_o as

$$\omega_o^2 = \tilde{\Omega}[\tilde{\Omega} - \tilde{J}\langle S^x\rangle] \, , \quad T \geqslant T_c \; . \tag{2}$$

In the vicinity of T_c this becomes

$$\omega_o^2 = \lambda \, \frac{T - T_c}{T_c} \, , \qquad T \geqslant T_c \tag{3a}$$

with

$$\lambda = \frac{\tilde{\Omega}^2}{4} \, \frac{\tilde{J}}{(kT_c)^2} \, \frac{1}{\cosh^2(\beta\tilde{\Omega}/2)} \, , \quad \beta = \frac{1}{kT} \tag{3b}$$

whereas

$$\omega_o^2 = \tilde{\Omega}^2 \, , \quad T \to \infty \; . \tag{4}$$

The soft mode frequency above T_c is thus proportional to the effective tunneling frequency $\tilde{\Omega}$ and reaches $\tilde{\Omega}$ at high enough temperatures.

If one now identifies $\tilde{\Omega}$ with the proton tunneling frequency in a single O—H——O bond, one reaches the conclusion that pseudo—spin systems with a comparable O—H——O bond potential should have a comparable soft mode frequency. This is true within the KH_2PO_4 family of crystals but is far from being fulfilled when one compares KH_2PO_4 with $PbHPO_4$, CsH_2PO_4 or squaric acid.

The above conclusion is not changed when the damping of the soft mode is taken into account. This is achieved by considering non—linear terms in the equations of motion [3] which are neglected in the RPA though they may even lead to a chaotic response [9] of the pseudo—spin system to a periodic external field. In case of overdamping the response of the system becomes relaxational

$$\tau^{-1} \approx \omega_o^2/\Gamma = \tilde{\tau}_o^{-1} \frac{T - T_c}{T_c} , \quad T \geqslant T_c \tag{5}$$

where $\tilde{\tau}_o^{-1} = \lambda/\Gamma$ and Γ is a damping coefficient [3] .

The RPA used to derive Eq. (2) is just the dynamic equivalent of the molecular field approximation (MFA). It is known [10,11,12] that the equilibrium properties of KH_2PO_4 ferroelectrics cannot be quantitatively described by the MFA in view of the importance of the short range Slater—Takagi interactions between the four protons surrounding a given PO_4 group. There is no reason to assume that the situation should be different in the dynamic case and that the RPA should be better than the MFA. The proper way to treat the dynamic properties of the Hamiltonian (1) for KH_2PO_4 is to use a dynamic four particle cluster approximation [13] , i.e. a dynamic analogue to the cluster approximations used to treat the static properties [11,12,14] . The reason that this is not usually done is the prohibitive complexity of such a treatment which is rather inconvenient for an analysis of the experimental data.

To retain the simplicity of the analytical expressions (2 — 4) for the soft mode frequency and at the same time to take into account the correlations of the four protons around a given PO_4 group it was recently suggested [2,15] that one should take as the basic reorientable dipole in KH_2PO_4 type crystals not the O—H——O bond but the whole H_2PO_4 group. This argument can be easily extended to $PbHPO_4$, CsH_2PO_4 and squaric acid. The renormalized effective "cluster" tunneling integral $\tilde{\Omega}$ is now determined by the requirement that the RPA analysis of expression (1) should yield the same ground state splitting as the appropriate cluster approximation to the Hamiltonian

$$\mathcal{H} = -\Omega \sum_i S_i^x - \frac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z \; . \qquad (6)$$

Here Ω is now the unrenormalized O–H–––O tunneling integral which described the ground state splitting of an isolated O–H–––O bond and J_{ij} the unrenormalized pseudo–spin – pseudo–spin coupling constant. In KH_2PO_4 this procedure corresponds to a projection of the 16–dimensional "Slater–Takagi" space to a two–dimensional "Ising" space and leads to a dependence of $\tilde{\Omega}$ on the single particle tunneling integral Ω and the Slater–Takagi energy parameters ϵ, w and w_1 (Table I). Let us now analyze the form of this renormalization for KH_2PO_4, squaric acid and $PbHPO_4$.

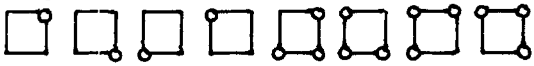
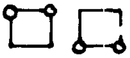
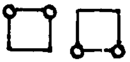
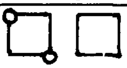
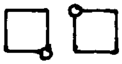
i) <u>KH_2PO_4</u>: Here $T_{c,H}$ = 121 K and $T_{c,D}$ = 220 K. The O–H–––O bond length is [16] R_{O--O} = 2.494 + 6.5 x 10^{-5} (T – 295 K) Å at atmospheric pressure and the distance between the two proton equilibrium sites is $2\ell \approx \approx 0.4$ Å. For an OH stretching frequency of $\hbar\omega$ = 2200 cm^{-1} and a double harmonic oscillator type potential one finds the proton tunneling integral as Ω = 299 cm^{-1}. This is significantly higher than the value $\tilde{\Omega}$ = 86 cm^{-1} deduced by Peercy [4] from the soft mode Raman scattering data but only slightly higher than the value of Ω used to explain the equilibrium properties in the four particle cluster approximation [12].

The H_2PO_4 energy matrix for KH_2PO_4 has been derived by Blinc and Svetina [11]. It can be written as the direct product

$$A^{(6)} \otimes A^{(3)} \otimes A^{(3)} \otimes B^{(3)} \otimes A^{(1)}$$

where $A^{(n)}$ and $B^{(n)}$ are matrices of order n. It should be noted that in reference (11) where the explicit form of these matrices is given the Hamiltonian was expressed in terms of Pauli spin matrices. Above T_c the eigenvalue problem reduces to solving an equation of fourth degree and quadratic and linear equations. The splitting between the two lowest eigenstates in the four particle cluster approximation is presented as a function of Ω/w in Fig. 1.

TABLE I. *Proton configurations and Slater–Takagi group energy levels in KH_2PO_4, $C_4O_4H_2$ and $PbHPO_4$. The energy levels for $C_4O_4H_2$ represent just one possible assignment.*

Crystal	Energy	Proton Configuration
KH_2PO_4 (3 D)	$E = w_1$	
	$E = w$	
	$E = \epsilon$	
	$E = 0$	
$C_4O_4H_2$ (2 D crossings of 1 D chains)	$E = w_1$	
	$E = w$	
	$E = \epsilon$	
	$E = 0$	
$PbHPO_4$ (1 D chains)	$E = w$	
	$E = 0$	

For $w_1 \gg w$ and $\Omega/w \ll 1$ this splitting[11,15] becomes $\Delta E_o = \tilde{\Omega} = \Omega^4/(w^2\epsilon/2)$ yielding

$$\frac{\tilde{\Omega}}{\Omega} \approx \frac{\Omega^3}{w^2\epsilon/2} \quad , \qquad \Omega \ll w \tag{7}$$

for the ratio between the tunneling integral of the H_2PO_4 group and the tunneling integral of a proton in an isolated O–H–––O bond.

The H_2PO_4 tunneling integral $\tilde{\Omega}$ is thus generally significantly smaller[15] than the single O–H–––O proton tunneling integral Ω (Fig. 2). $\tilde{\Omega} \to 0$ for $w \to \infty$. Only for $\Omega/w > 1$ one finds

$$\tilde{\Omega}/\Omega \approx 1 \ , \quad \Omega/w > 1 \ . \tag{8}$$

In this limit – which does not correspond to the situation in KH_2PO_4 – there would be no ferroelectric transition at all ($T_c = 0$) and the system

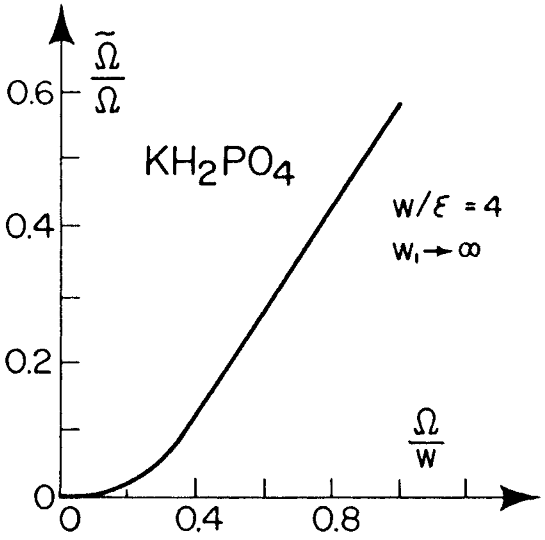


FIGURE 1 Splitting of the H_2PO_4 group ground state in KH_2PO_4 as a function of Ω/w for $w_1 \to \infty$ and $w/\epsilon = 4$.

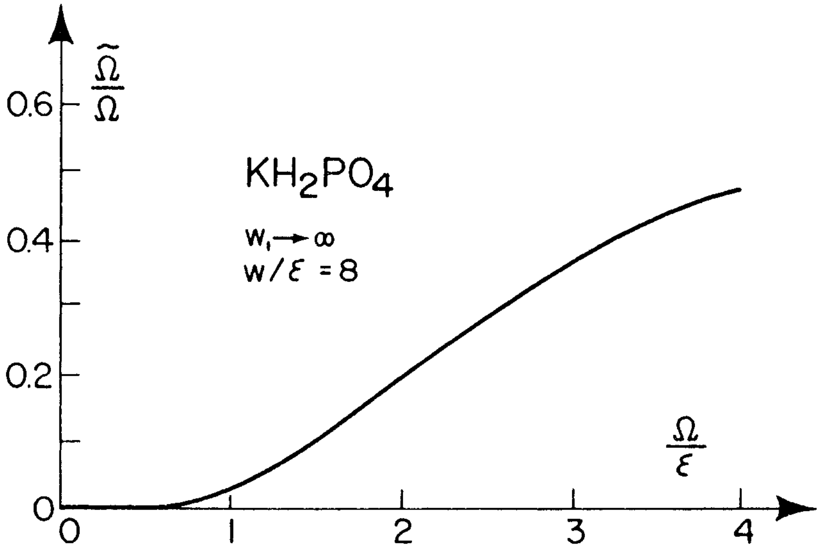


FIGURE 2 Ratio between the tunneling integral of a H_2PO_4 group $\tilde{\Omega}$ in KH_2PO_4 and the single proton O–H–––O tunneling integral Ω as a function of Ω/ϵ for $w/\epsilon = 8$, $w_1 \to \infty$.

would be disordered at all non–zero temperatures.

Using the values of Vaks, Zein and Strukov[12] $w/\epsilon = 9$, $\Omega/\epsilon = 2.5$ one finds $\tilde{\Omega}/\Omega \cong 0.3$ thus removing the apparent discrepancy between the values of the tunneling integral determined from static and dynamic data[4,12].

ii) Squaric acid, $C_4H_4O_2$: Here $T_{c,H} = 371$ K and $T_{c,D} = 516$ K. Each C_4O_4 group is linked by O–H–O bonds to four neighbouring molecules within the same layer[17]. The protons are – similarly as in KH_2PO_4 – disordered above T_c and ordered below T_c. According to neutron scattering data[18] the O–––O bond distance is 2.55 Å and the distance between the two proton equilibrium sites $2\ell = 0.52$ Å. Recent ^{17}O magnetic resonance data[19] seem to show a somewhat shorter O–––O distance and a somewhat smaller interproton separation: $R_{O--O} = 2.47 \pm 0.05$ Å and $2\ell = 0.41$ Å. Ω was estimated from static data as 105 K [20]. At T_c the soft mode condenses at the Z (1/2, 1/2, 1/2) point of the body centered tetragonal lattice inducing an antiferroelectric stacking of ferroelectrically ordered layers. Raman scattering measurements below T_c failed to detect the soft mode whereas dielectric relaxation measurements[8] above T_c yielded a characteristic relaxation frequency of about 60 GHz. This shows that the soft mode frequency is definitely lower than in KH_2PO_4. The energies of the 16 possible proton configurations around a C_4O_4 group are – in contrast to KH_2PO_4 – not yet definitely established. A possible energy level scheme[20] is presented in Table I. The $H_2C_4O_4$ energy matrix in the four particle cluster approximation for this level scheme is similar to the one in KH_2PO_4

$$\mathcal{H}_4 = A^{(6)} \otimes B^{(3)} \otimes B^{(3)} \otimes B^{(3)} \otimes A^{(1)} \tag{9a}$$

where again the Pauli spin matrix basis is used and where for $T > T_c$

$$A^{(6)} = \begin{vmatrix} 0 & 0 & 0 & 2x & 0 & 0 \\ 0 & 0 & 0 & 0 & 2x & 0 \\ 0 & 0 & 1 & 2x & 2x & 0 \\ 2x & 0 & 2x & y & 0 & x\sqrt{2} \\ 0 & 0 & 0 & x\sqrt{2} & x\sqrt{2} & z \end{vmatrix} , \quad B^{(3)} = \begin{vmatrix} y & 0 & x\sqrt{2} \\ 0 & y & x\sqrt{2} \\ x\sqrt{2} & x\sqrt{2} & z \end{vmatrix} , \quad A^{(1)} = [x] \tag{9b}$$

with $\Omega/\epsilon = x$, $w/\epsilon = y$ and $w_1/\epsilon = z$. The ground state splitting $\tilde{\Omega}$, i.e. the difference between the two smallest eigenvalues of $A^{(6)}$ exhibits here a similar Ω dependence as in KH_2PO_4. The effective tunneling frequency $\tilde{\Omega}$ of the $H_2C_4O_4$ group is thus here renormalized in an analogous manner as in

KH_2PO_4. Since the single proton tunneling integral should be comparable to the one in KH_2PO_4, w has to be relatively large ($\Omega/w = 1/16$, $\tilde{\Omega}/\Omega = 10^{-2}$) to account for the rather low soft mode frequency.

It should be mentioned that a model of interacting one dimensional Ising spin chains has been recently proposed[17] for squaric acid. If this model holds the 4–particle cluster is a rather poor approximation. We shall return to this case later in connection with $PbHPO_4$.

iii) $\underline{PbHPO_4}$: Here $T_{c,H} = 310$ K and $T_{c,D} = 452$ K. The PO_4 groups are linked by O—H———O bonds to form isolated one–dimensional chains which are coupled to each other by long range dipolar forces only. The length of the O—H———O bonds is about 2.5 Å and the protons are disordered above $T_c = 310$ K and ordered below[21]. In the isomorphous compound $PbHAsO_4$ Ω was estimated as 87 cm^{-1} [22]. In spite of the fact that the O—H———O bond length in $PbHPO_4$ and $PbHAsO_4$ is close to the one in KH_2PO_4 the soft mode is of much lower frequency[6] than in KH_2PO_4 and purely relaxational. For $PbHPO_4$ one has[6,22]: $1/(2\pi\tau) \approx 0.7\,(T - T_c)\ cm^{-1}$ for $T > T_c$. $\tilde{\Omega}$ was estimated to be less than 2 cm^{-1} whereas Ω was obtained[6] from dT_c/dp measurement as $\approx 87\ cm^{-1}$.

In the absence of tunneling and long range interactions the four possible arrangements of the two protons around a given PO_4 group give rise to two two–fold degenerate energy states with $E_{1,2} = 0$ and $E_{3,4} = w$ (Table I). The Slater model with long range coupling $J_\perp$ between the chains is here equivalent to the exact solution of a one–dimensional Ising chain in a molecular field.

For the transition temperature T_c and Curie–Weiss constant C one finds

$$e^{-\beta_c w} = 2J_\perp \beta_c\,,\quad \beta_c = 1/(kT_c) \qquad (10a)$$

$$C = \frac{V_o\, P_s^2\, e^{w/kT_c}}{\epsilon_o\,(1 + w/kT_c)} \qquad (10b)$$

where V_o is the unit cell volume and $\epsilon_o = 8.8 \times 10^{-12}$ As/Vm. A comparison with the experimental data now yields $w = 2J_\parallel = 1392$ K and $J_\perp = 1.74$ K thus confirming the extreme anisotropy of the interactions.

In the two particle cluster approximation the introduction of tunneling again results in a splitting of the HPO_4 energy levels (Table I): $\lambda_1 = 0$, $\lambda_2 = w$, $\lambda_{3,4} = \frac{w}{2} \pm \sqrt{(\frac{w}{2})^2 + \Omega^2}$. For $\Omega \ll w/2$ we find from the ground state splitting the renormalization of the effective HPO_4 tunneling frequency $\tilde{\Omega}$ as

$$\tilde{\Omega}/\Omega = \Omega/w/2\,,\qquad \Omega \ll w/2 \qquad (11a)$$

whereas

$$\tilde{\Omega} = \Omega \quad , \qquad \Omega \gg w/2 \quad . \tag{11b}$$

The reduction of the effective HPO_4 tunneling frequency due to short range correlations (Fig. 3) is significant but probably not large enough to account for the difference between $\tilde{\Omega}$ and Ω deduced from the experimental data. This is probably due to the fact that a two particle cluster is not a very good approximation for a system of coupled one–dimensional Ising chains. For a classical system of one–dimensional pseudo–spin chains where the intra–chain interactions are taken into account exactly whereas the inter-chain interactions are approximated by a molecular fields one finds[23] the renormalization factor for the inverse single dipole reorientation time τ_o^{-1} – expression (5) – as:

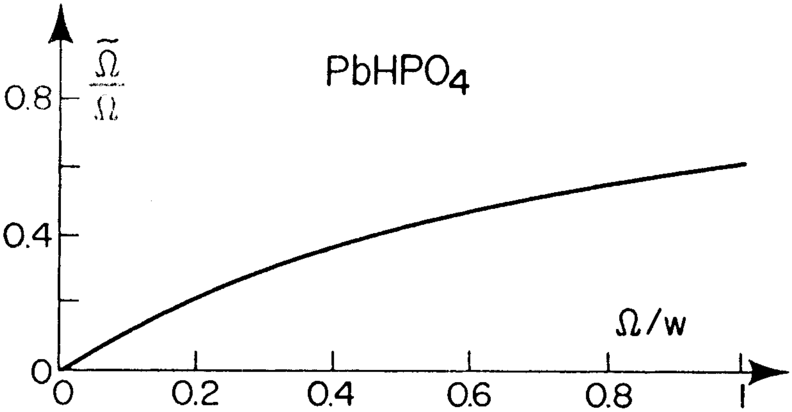


FIGURE 3 Ratio between the tunneling integral of a HPO_4 group $\tilde{\Omega}$ and the single proton O—H——O tunneling integral Ω in $PbHPO_4$ as a function of Ω/w obtained in a two particle cluster approximation.

$$\frac{\tilde{\tau}_o^{-1}}{\tau_o^{-1}} = \left(\frac{d_{\parallel}}{\xi_{1D}}\right)^2 \frac{J_{\parallel}}{kT} \tag{12}$$

where $d_{\parallel}$ is the distance between two neighbouring pseudo–spins along a chain and ξ_{1D} is the one–dimensional correlation length for intra–chain short range order. Close to T_c this amounts to

$$\frac{\tilde{\tau}_0^{-1}}{\tau_0^{-1}} \approx 2e^{-2J_\parallel/kT_c} = 2e^{-w/kT_c}, \qquad w \gg kT_c \tag{13}$$

thus resulting in a huge additional slowing down ($\sim 10^{-3}$) of the pseudo–spin fluctuations due to the anisotropy of the interactions and the resulting short range order along the chains. This effect may be also responsible for the slow soft mode dynamics in pseudo–onedimensional CsH_2PO_4 and squaric acid and for the discrepancies between the single particle deuteron intra–bond jump times in pseudo–onedimensional CsD_2PO_4 [7c] and threedimensional KD_2PO_4 [3].

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