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Author's Review

The Soft Mode in H-Bonded Ferroelectrics Revisited

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The nature of the soft tunneling modes in KH_2PO_4 type ferroelectrics is discussed and a new model is described for the proton-lattice coupling in these systems.

I. INTRODUCTION

This paper is concerned with the present understanding of soft tunneling modes in H-bonded ferroelectrics — an idea which was pioneered by Hadži and co-workers[1] a long time ago.

According to the soft mode model[2] of structural phase transitions the frequency of the soft mode decreases on approaching the critical temperature T_c and the restoring force for the mode displacements tends to zero until the mode has condensed out at the stability limit. The static atomic displacements in the low temperature phase represent the frozen in displacements of the soft mode in the high temperature phase.

The traditional way[3-8] to describe the soft mode in KH_2PO_4 is to assume that the motion of the protons between the two off-centre sites in the H-bonds is accompanied with the displacements of the K and P lattice ions. As the two protons in the »upper« H-bonds of a PO_4 group move to sites »near« that group, the two protons in the »lower« bonds move away to the »far« sites, the P-ions move down along the 4-fold axis and the K-ions move up. This model — first proposed by Cochran[3] — is based on the changes in the crystal structure that occur on cooling through T_c: relative to the centre of mass, K moves up 0.04 Å, P moves down 0.08 Å and the protons order in the H-bonds. The direct determination[4] of the eigenvectors of the proposed soft mode by inelastic neutron scattering indeed confirmed that there is a soft excitation in which the atoms move very much so as they displace below T_c. Kobayashi[5] described this excitation as the result of the coupling of a pseudospin mode[6,7,8] — involving the motion of the hydrogens between two off-centre sites in an effective double minimum H-bond potential — with a polar optic lattice mode involving the K and P motion. Raman scattering data[9] have shown that this picture is at least qualitatively correct.

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II. THE MODEL HAMILTONIAN

The total Hamiltonian of the coupled proton-polar optic phonon system in a KH_2PO_4 type crystal

$$H = H_{\mathrm{p}} + H_{\mathrm{L}} + H_{\mathrm{I}} \tag{1}$$

can be in the local representation rewritten as

$$H = -\Omega \sum_{i\alpha} S_{i\alpha}^{z} - \sum_{\substack{i,j\\ \alpha,\beta}} J_{ij} S_{i\alpha}^{z} S_{j\beta}^{z} + \sum_{i} \left(\frac{1}{2} k_1 z_{1,i}^{2} + \frac{1}{2} k_2 z_{2,i}^{2} \right) - \\ - \sum_{ij\alpha} K_{ij}^{\alpha} z_{1,i} S_{j\alpha}^{z} - \sum_{ij\alpha} L_{ij}^{\alpha} z_{2,i} S_{j\alpha}^{z} \tag{2}$$

where the first two terms in eq. (2) represent the usual Ising model in a transverse tunneling field pseudo-spin 1/2 Hamiltonian[6-8] describing the motion of the four protons in the four O—H - - - O bonds surrounding a PO_4 group, the third term describes the potential energy for the P and K displacements along the polar (z) axis and the last two terms describe the proton-phosphorus and proton-potassium interactions. The term describing the direct coupling between the P and K ions has been omitted. We assumed that there are 4 protons and one K and one P atom per unit cell. The indices α, β thus run from 1 to 4 whereas i and j run over all unit cells. Ω stands for the tunneling integral in the symmetric double well single particle potential in the absence of interactions, i. e. when all other protons are assumed to be distributed among their two available sites with equal probability.

In the molecular field approximation (MFA) we obtain the familiar results

$$\langle z_1 \rangle = \frac{K_0}{K_1} \langle S^z \rangle \tag{3a}$$

$$\langle z_2 \rangle = \frac{L_0}{K_2} \langle S^z \rangle \tag{3b}$$

where

$$K_0 = \sum_{j\alpha} K_{ij}^{\alpha}, \quad L_0 = \sum_{j\alpha} L_{ij}^{\alpha} \tag{3c}$$

The model Hamiltonian (2) reduces in this approximation to

$$H_{\mathrm{S}}^{\mathrm{MFA}} = \Omega S^{x} - (J_0 + K_0 K_0^{\alpha}/k_1 + L_0 L_0^{\alpha}/k_2) \langle S_{\alpha}^{z} \rangle S_{\alpha}^{z} \tag{4a}$$

where

$$K_0^{\alpha} = \sum_{j} K_{ij}^{\alpha} = K_0/4, \quad L_0^{\alpha} = \sum_{j} L_{ij}^{\alpha} = L_0/4 \tag{4b}$$

and

$$J_0 = \sum_{i\alpha\beta} J_{ij}^{\alpha\beta} \tag{4c}$$

The transition temperature T_c is obtained from

$$2\Omega/\hat{J}_0 = \tanh\, (\Omega/2k_{\mathrm{B}}T_c) \tag{5a}$$

where

$$\hat{J}_0 = J_0 + K_0^{2}/4k_1 + L_0^{2}/4k_2 \tag{5b}$$

Eq. (5a) predicts an increase in T_c on deuteration when Ω is reduced.

It should be noted that the MFA is not capable of describing quantitatively the anomalies in the equilibrium thermodynamic properties at T_c and that a 4-particle cluster approximation[10–12] to the Hamiltonian (2) had to be used for a consistent description of the phase transition effects.

In the random phase approximation (RPA) the above model predicts two low lying pseudo-spin waves like normal modes:

i) a longitudinal excitation the frequency of which is zero both above and below T_c;

ii) a transverse soft excitation

$$\omega_{T-}^{2} = \Omega\left[\,[\Omega - \tilde{J}_q \langle S^x \rangle]\,\right] \approx (2\Omega)^2 \, \frac{T - T_c(q)}{T_c(q)}, \quad T > T_c \qquad (6)$$

the frequency of which vanishes at the transition temperature T_c. Here $\tilde{J}_q$ represents the spatial Fourier transform of $\tilde{J}_{ij}$, i. e.:

$$\tilde{J}_q = \Sigma\, \tilde{J}_{ij}\, e^{-i\vec{q}(\vec{r}_i - \vec{r}_j)} \qquad (7)$$

The point in the Brillouin zone where $\tilde{J}_q$ reaches its maximum value determines the nature of the low temperature phase:

a) If $\tilde{J}_q$ is a maximum at the Brillouin *zone centre* $(\tilde{J}_q)_{\max} = \tilde{J}_o$ the transition is a *ferrodistortive* one and the unit cell size does not change ($a' = a$) at T_c. This situation is realized in KH_2PO_4.

b) If $\tilde{J}_q$ is a maximum at the Brillouin *zone boundary* the transition is an *anti-ferrodistortive* one and the unit cell size increases below T_c ($a' = n \cdot a$ with $n = 2, 3, 4$, etc.). This situation is realized in $NH_4H_2PO_4$.

c) If $\tilde{J}_q$ is a maximum at a *general point* in the Brillouin zone, the periodicity of the frozen out soft mode displacements below T_c is incommensurate to the periodicity of the underlying high temperature lattice. ($\lambda/a \neq$ rational number). The translational periodicity of the lattice is lost and the new phase is an *incommensurate* one. This situation is realized in $(NH_4)_2BeF_4$ and $RbH_3(SeO_3)_2$.

The inclusion of higher order terms results in a damping of the soft modes without however changing the nature of the above conclusions. In case that the modes are overdamped we have for the critical relaxation time τ:

$$\frac{1}{\tau} \propto \frac{T - T_c(q)}{T_c(q)} \qquad (8)$$

III. SUBMILLIMETRE SPECTROSCOPY

The greatest progress in the last few years in the above field has been achieved recently[13,14] with the help of submillimetre dielectric spectroscopy.

The main results[13,14] in crystals of the KH_2PO_4 family can be summarized as follows:

a) In KH_2PO_4 (KDP), KH_2AsO_4 (KDA) and RbH_2PO_4 (RDP) a low frequency soft mode of B_2 symmetry is clearly seen for $\vec{E} \parallel \vec{c}$ (Figure 1). The temperature dependence is close to that predicted by eq. (8) with $q = 0$.

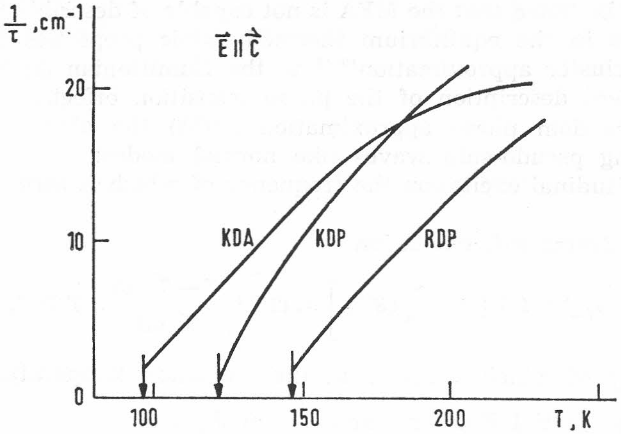

Figure 1. Temperature dependence of the frequencies of the soft modes of B_2 symmetry in KH_2AsO_4, KH_2PO_4 and RbH_2PO_4[13].

(b) The frequency of the solft mode in KH_2PO_4 is very sensitive to the replacement of hydrogen by deuterium (Figure 2) demonstrating that the soft mode is connected with an excitation of the proton sub-system.

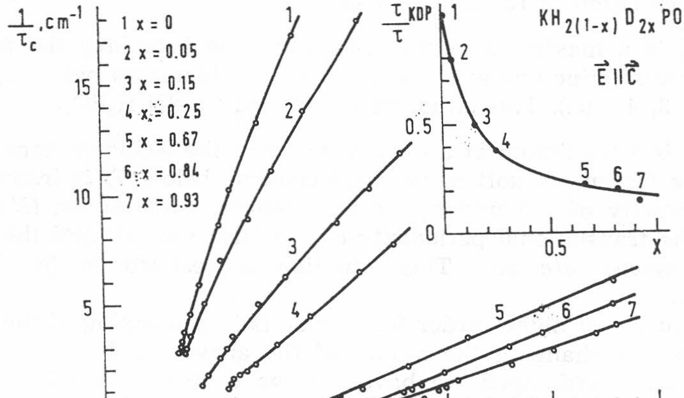

Figure 2. Dependence[13] of the soft mode frequency in $KH_{2(1-x)}D_{2x}PO_4$ on deuterium concentration for $\vec{E} \parallel \vec{c}$.

c) In the $NH_4H_2PO_4$ (ADP) family, on the other hand, the modes stay hard at $\vec{E} \parallel \vec{c}$ but tend to become soft at $\vec{E} \perp \vec{c}$ as predicted. In view of the fact that the transition occurs at $q \neq 0$ and is of first order $1/\tau$ never vanishes.

d) In DADP the characteristic frequencies decrease by nearly an order of magnitude as compared to ADP demonstrating that here too the soft mode is connected with an excitation of the proton sub-system.

e) The fact that in KH_2PO_4, RbH_2PO_4 KH_2AsO_4 and $NH_4H_2PO_4$ the dielectric dispersion is of resonant character demonstrates the influence of proton tunneling (i. e. $\Omega \neq 0$).

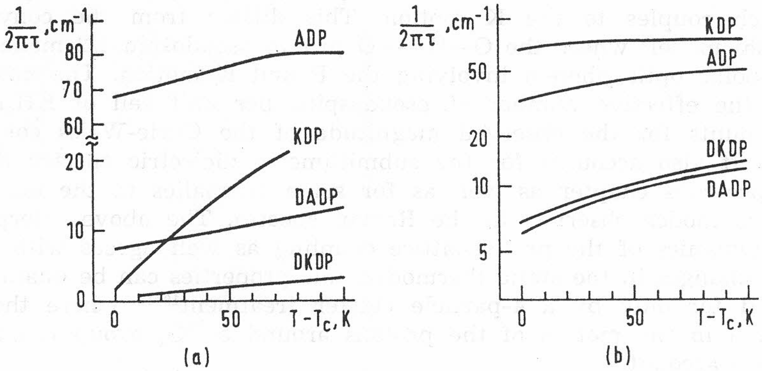

Figure 3. Characteristic frequencies[14] of proton modes of KDP type crystals; a) $\vec{E} \parallel \vec{c}$, b) $\vec{E} \perp \vec{c}$.

f) Tunneling effects are strongly decreased in KD_2PO_4 and $ND_4D_2PO_4$ resulting in a lower frequency of the soft mode which becomes overdamped.

g) The fact that isomorphic substitution of P by As results in a more significant change than isomorphic substitution of K by Rb means that the proton subsystem is more strongly coupled to the PO_4 tetrahedron than to the K^+ ion.

IV. NMR AND EPR

Deuteron NMR and proton-^{17}O double resonance measurements of KH_2PO_4 type crystals have clearly shown[15] that the protons respectively deuterons move between two equilibrium sites in the O—H - - - O bonds above T_c and order into one of the two sites below T_c. The possibility of a symmetric H-bond and a displacive transition is definitely excluded by these data.

The difference in the thermal behaviour of the K, Rb and Cs ions on one side and the P and As ions on the other side[16] is as well seen in nuclear magnetic resonance[15] and electron paramagnetic resonance experiments[17]. The ^{75}As quadrupole coupling in KH_2AsO_4, RbH_2AsO_4 and CsH_4AsO_2 sharply increases on approaching T_c from above, whereas no such critical increase is seen in the temperature dependence of the ^{87}Rb and ^{133}Cs quadrupole coupling in RbH_2PO_4 and CsH_2AsO_4. The electron paramagnetic resonance spectra[17] of KH_2PO_4 type crystals doped at the PO_4 sites — i. e. with AsO_4^{3-}, SeO_4^{3-}, CrO_4^{3-} centres — all show a spontaneous dynamic breaking of the symmetry of the high temperature phase far above T_c whereas no such symmetry breaking is seen in the EPR spectra of those paramagnetic centres — Tl^{2+}, Cu^{2+}, Fe^{3+} etc. — which substitute the K ions. The Kobayashi model as well runs into difficulties when attempting to explain some finer details of the Raman scattering data. It is furthermore rather difficult to account quantitatively for the magnitude of the Curie-Weiss constant of KH_2PO_4 within this model.

The difference in the temperature dependence of the nuclear quadrupole coupling and the nuclear quadrupole spin-lattice relaxation of the K, Rb and Cs nuclei on one side and the As nuclei on the other side can be understood within a model where the whole H_2PO_4 group repsrents the pseudospin 1/2 which couples to the K motion. This differs from the conventional Kobayashi model[5] where the O—H - - - O proton pseudospin 1/2 mode couples with a polar optic phonon involving the P and K motion. The new model reduces the effective number of pseudospins per unit cell of KH_2PO_4 and thus accounts for the observed magnitude of the Curie-Weiss constant in KH_2PO_4. It also accounts for the submillimetre dielectric spectra discussed in the previous chapter as well as for some anomalies in the ω_- and ω_+ Kobayashi modes observed in the Raman spectra. The above interpretation of the dynamics of the proton-lattice coupling as well agrees with the fact that the changes in the static thermodynamic properties can be quantitatively accounted for only by a 4-particle cluster treatment[10–12] where the strong correlation in the motion of the protons around a PO_4 group is explicitely taken into account.

The increased effective mass of the tunneling »pseudospin« as well accounts for the fact that the observed value of Ω lies in the 10—10^2 cm^{-1} region and not in the 10^3 cm^{-1} region[18] as expected for an isolated proton tunneling through a low barrier between two sites in the O—H - - - O bond 0.34 Å apart.

V. CONCLUSIONS

Though the excitation spectrum of H-bonded systems is extremely rich and far from being completely understood it is clear that:

i) The presence of more than one equilibrium site per proton per hydrogen bond results in a collective behaviour which is completely different from the one observed in systems with one proton equilibrium site per H-bond (e. g. KHF_2).

ii) The soft pseudo-spin mode description of the dynamics of order-disorder transitions in H-bonded solids is basically correct and the predicted soft tunneling modes have been observed. The strong correlation of the motion of the protons around a PO_4 group leads to a cluster description and a new interpretation of the proton-lattice coupling in these systems.

iii) The existence of incommensurate H-bonded systems opens a completely new field of research which is intermediate between translationally periodic classical crystals and aperiodic biological and other systems.

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IZVLEČEK

Mehki načini nihanja v feroelektrikih z vodikovimi vezmi

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V članku je podan pregled sedanjega razumevanja nestabilnih mrežnih nihanj v feroelektrikih z vodikovimi vezmi in predlagan nov model sklopitve med gibanjem protonov v vezeh O—H---O in gibanjem težkih mrežnih ionov v kristalih vrste KH_2PO_4.

Strukturni fazni prehodi v feroelektrikih so posledica nestabilnosti nizkofrekvenčnega polarnega normalnega načina nihanja. Nestabilno nihanje zamrzne pri T_c in struktura nizko-temperaturne faze predstavlja superpozicijo zamrznjenih atomskih pomikov tega načina nihanja mreže in strukture visokotemperaturne faze. V kristalih z vodikovimi vezmi, kjer ima proton več kot eno ravnovesno lego, predstavlja vodikova vez reorientabilni dipol, katerega reorientacija je eden izmed osnovnih elementov nestabilnosti kristalne mreže.

V klasičnem modelu nestabilnega mrežnega nihanja v KH_2PO_4 je gibanje protonov med dvema ravnovesnima legama v vezeh O—H---O sklopljeno s pomiki K in P atomov v nasprotnih smereh vzdolž feroelektrične osi. Z ozirom na to, da je sklopitev protonov s P ionom mnogo močnejša kot s K ionom, je v članku predlagan nov model, kjer predstavlja H_2PO_4 skupina osnovni feroelektrični dipol z dvema ravnovesnima legama. Gibanje tega dipola med obema ravnovesnima legama lahko popišemo s pseudo-spinom 1/2, ki je sklopljen z gibanjem K^+ iona. Novi model zadovoljivo razloži nekaj anomalij v NMR in EPR spektrih kristalov vrste KH_2PO_4, ki jih nismo mogli razložiti v okviru klasičnega modela.