One-dimensional model for cooperative hydrogen motion in ferroelectric crystals

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V.H. Schmidt, "One-dimensional model for cooperative hydrogen motion in ferroelectric crystals," Ferroelectrics 7, 199-200 (1974).
http://dx.doi.org/10.1080/00150197408237994

ONE-DIMENSIONAL MODEL FOR COOPERATIVE HYDROGEN MOTION IN FERROELECTRIC CRYSTALS †

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(Received September 10, 1973)

The static and dynamic behavior is examined for "Takagi groups" in double-minimum potential wells containing protons (or deuterons) coupled by harmonic forces. Predictions of this model are compared with observed isotope effects on domain wall mobility and dielectric relaxation in KH_2PO_4. The model predicts effects previously attributed to tunneling.

INTRODUCTION

Diffusion of Takagi DPO_4 and D_3PO_4 groups explains most dynamical properties of KD_2PO_4 (DKDP), while cooperative tunneling has been invoked to explain the much more rapid dynamical response of KH_2PO_4(KDP).[1] As an alternative to the tunneling mechanism a one-dimensional model for extended Takagi groups is developed, and used to predict certain dielectric phenomena in KDP and DKDP.

MODEL FOR EXTENDED TAKAGI GROUPS

The symmetric wells in Figure 1 indicate the effective potential per proton if all protons move in phase. The interproton forces are approximated by springs (not shown) of spring constant k' connecting neighboring protons. Given k' and an effective double well potential $U(x) = Bx^4 - Ax^2$, the hydrogen positions can be found for the even and odd Takagi group configurations shown in Figure 1, as well as the respective potential energies $\epsilon_1 - \epsilon_\mu$ and ϵ_1 for these configurations.

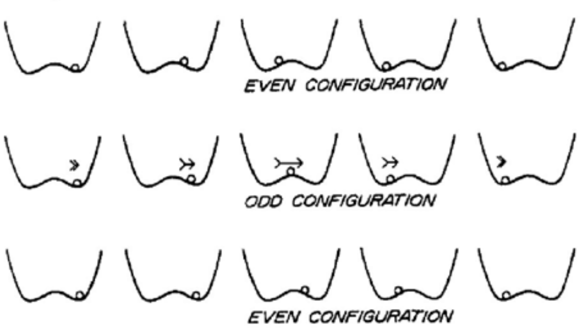

FIGURE 1 Takagi group transfer showing odd and even configurations. Arrows indicate proton displacements involved in moving the Takagi group one lattice space.

† This work supported by National Science Foundation.

The even configurations for six combinations of A, B, and k' are shown in Figure 2, together with the energies ϵ_1 and ϵ_μ. Each A, B combination gives minima at the measured[2] off-center displacements, taken as $x_0 = 0.200$ A° for DKDP and 0.164 A° for KDP. For the top two rows of Figure 2, it was further assumed

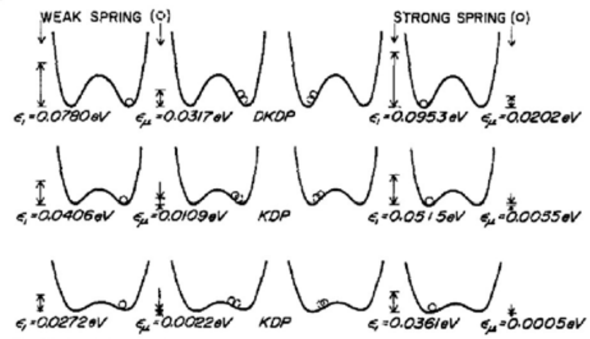

FIGURE 2 Takagi group energies and hydrogen positions for the even configuration for various well parameters and coupling strengths. Some dashed circles are omitted for clarity.

that both DKDP and KDP have the same actual potential $U_0(x) = B_0x^4 - A_0x^2$, and that

$$U(x) = \int_{-\infty}^{\infty} \exp\left[-(y-x)^2/2y_0{}^2\right] U_0(y)\, dy,$$

with y_{0D} and y_{0H} found from deuteron and proton wavefunctions for a harmonic potential having the same curvature as at the minima of $U_0(x)$. The effective potentials $U(x)$ have $B = B_0$ but have A_0 replaced by A_D for DKDP and by A_H for KDP. The wells on the bottom line of Figure 2 have $A = \frac{1}{2}A_H$ and $B = \frac{1}{2}B_0$.

The values for k' are based on deuteron spin-lattice relaxation results in DKDP, which yielded ϵ_1 of about 0.078 eV ($\epsilon_1/k = 900 \pm 200$ K).[1] The values of k' chosen are for "weak springs" giving $\epsilon_1/k = 900$ K and "strong springs" giving $\epsilon_1/k = 1100$ K.

TAKAGI GROUP CONCENTRATION AND MEAN FREE PATH

The fractional Takagi group concentration obtained by minimizing the free energy is $N_T N = [1 + e^{(\epsilon_1 - \epsilon_\mu)/kT}]^{-1}$, so the average separation between Takagi groups is $d = N/N_T \geqslant 2$. For Takagi group length $n > 2$ the Takagi groups would merge at high temperature, but no experimental evidence for such merging has been found in KDP-type crystals. Here n is defined by $n = 1 + \sum_i |(x_0 - x_i)/x_0|$ over the hydrogen positions in the even configurations.

The mean free path cannot exceed the mean Takagi group spatial separation da, where $a = 5.27$ Å is the interbond spacing. Scattering by phonons which see the Takagi group as a region with slightly higher (or lower) density has been calculated to have no significant effect. A third path-limiting process is thermalization by interactions with neighboring heavy atoms. The standard assumption is a probability $\nu_0 e^{-u}$ per unit time for hops to adjacent sites, where $u = \epsilon_\mu/kT$. If immediately after hopping the Takagi group has probability e^{-u} of making another hop in the same direction instead of stopping, its mean free path is $\lambda = a/(1 - e^{-u})$.

DOMAIN WALL MOBILITY

A domain wall is an unpolarized layer in which the preceding expression for N_T/N is approximately correct.[1] With a field present, the barrier heights become $\epsilon_\mu \pm \frac{1}{2}pE$ which substituted in the hopping-limited expression for λ yields Takagi group drift velocity $v_d = a\nu_0(pE/kT)\, e^{-u}/(1 - e^{-u})^2$, where p has values 2.44×10^{-28} and 3.03×10^{-28} coul-cm for KDP and DKDP respectively. For $\nu_0 = kT/h$ and $\mu_w = v_d N_T/NE$ the mobilities μ_w shown in Table I for temperatures of 100 K in KDP and 200 K in DKDP are obtained. The half-strength potential yields a strong isotope effect, but not as great as the measured[3] ratio of about 10^6. The DKDP values agree quite well with previously reported results.[1]

The dielectric relaxation is assumed to be governed by a single relaxation time $\tau = P_\infty/(dP/dt)_0$, where $P_\infty = \epsilon_0 \epsilon_h E$ (MKS units) and $(dP/dt)_0$ is evaluated when the small field E is first applied. For λ limited by annihilation with neighboring Takagi groups $\tau_a = h\epsilon_0 \epsilon_h/Np^2\ e^{-u}$, while for hopping-limited λ, $\tau_h = \tau_a(1 - e^{-u})^2 N/N_T$. Assuming $\tau = \tau_a + \tau_h$ and using 28 and 40 for the H-bond-dependent part ϵ_h of the dielectric constants for KDP and DKDP respectively at 300 K, the values for τ given in Table I are obtained. Deuteration increases τ by roughly a factor of 10. The DKDP values are in general agreement with previous calculated and measured results.[1]

DISCUSSION

By introducing the concept of an extended Takagi group and decomposing the energies of such groups into creation and mobility components, it is possible to predict quite strong isotope effects in KDP without invoking cooperative tunneling. An isotope effect on Takagi group energies was obtained by taking account of quantum-mechanical effects of the isotope mass differences in a qualitatively reasonable way. Isotope effects on the Slater group energies could be found in a similar manner for a two- or three-dimensional model.

The above-described cooperative motion involves only the hydrogens in an extended Takagi group. Coupling of such motion with a heavy-ion TO mode to obtain a coupled "soft mode" is now being studied.

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TABLE I

Takagi group length n, domain wall mobility μ_W, and dielectric relaxation time τ for various well parameters and coupling strengths.

Xtal	Coupling	A	B	n	μ_W, cm^2/V-sec (T_C − 22 K)	τ, sec (300 K)
DKDP	weak	A_D	B_0	1.26	3.54×10^{-4}	19.1×10^{-12}
KDP	weak	A_H	B_0	1.39	3.26×10^{-4}	3.1×10^{-12}
KDP	weak	$\frac{1}{2}A_H$	$\frac{1}{2}B_0$	1.79	1.54×10^{-2}	1.5×10^{-12}
DKDP	strong	A_D	B_0	1.47	1.98×10^{-4}	18.2×10^{-12}
KDP	strong	A_H	B_0	1.70	2.16×10^{-4}	2.1×10^{-12}
KDP	strong	$\frac{1}{2}A_H$	$\frac{1}{2}B_0$	2.32	9.00×10^{-2}	1.4×10^{-12}