PHYSICAL REVIEW B **76**, 140101(R) (2007)

Adiabatic approximations of coupled dipole-proton model for hydrogen-bonded ferroelectrics

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(Received 29 June 2007; revised manuscript received 19 September 2007; published 16 October 2007)

In several hydrogen-bonded ferroelectrics, such as KH_2PO_4-type ferroelectrics, the protons are strongly coupled to the dipoles produced in the heavy-ion sublattice. It is not clear whether such a coupled dipole-proton system can be described by two traditional simple models, the model of interacting tunneling protons and the model of interacting dipoles, and which one is more appropriate. We show that both models follow from the coupled dipole-proton model under the opposite adiabatic approximations, and that the model of interacting dipoles seems to correspond better with the experiments.

DOI: 10.1103/PhysRevB.76.140101 PACS number(s): 77.84.Fa, 77.80.Bh

Hydrogen-bonded ferroelectrics show an isotope effect, i.e., a strong effect of proton-deuteron exchange on the critical temperature T_c of the phase transition.[1,2] The isotope effect and the phase transition mechanism in hydrogen-bonded ferroelectrics have not yet been completely explained.[3–6] There are two main types of theoretical model for the KH_2PO_4 (KDP) crystal as the representative of the hydrogen-bonded ferroelectrics: the proton-tunneling models[2,7,8] and the order-disorder models of PO_4 dipoles.[2,9,10] While the proton-tunneling models explain the isotope effect rather simply by deuteration-induced decrease in the tunneling frequency, the order-disorder models of PO_4 dipoles, which agree with some experimental results,[2] do not offer such a clear explanation of the isotope effect. It is generally accepted that the protons in KDP move in an anharmonic hydrogen-bond potential, which is probably of the double-well type, and that the protons are coupled with the dipoles produced in the heavy-ion sublattice (PO_4 dipoles).[2] In the ferroelectric (FE) phase below T_c, the PO_4 dipoles produce spontaneous electric polarization, and the protons localize at one of the two sites along the hydrogen bond, indicating a strong dipole-proton coupling. First-principles calculations[6] show that the KDP structure in the paraelectric (PE) phase above T_c is stable against lattice polarization, weakly unstable against displacements of protons, and strongly unstable if polarization and displacements of protons are simultaneously produced. This indicates that the dipole-proton interaction is the strongest interaction in the system. Also, these calculations indicate a single-well hydrogen-bond potential, as opposed to the proton tunneling models and the results of Compton scattering measurements in KDP.[4]

It is important to mention that quantum and thermal fluctuations of the protons and heavy-ion dipoles have to be taken into account to explain quantum effects such as the isotope effect. Although the self-consistent nonlinear model[6] qualitatively explained the isotope effect in KDP as resulting from hydrogen-bond lengthening upon deuteration (geometric isotope effect), a more complete model based on first-principles calculations, which would properly treat these fluctuations, is still missing. Since the precise form of the hydrogen-bond potential in KDP is still a matter of debate, and since we want to construct a simple and general model in which the quantum nature of protons and dipoles can be easily taken into account, we consider a model in which the dipoles, described as harmonic oscillators, are coupled with the protons that tunnel in a double-well potential. Because KDP-type ferroelectrics possibly belong to the group of hydrogen-bonded ferroelectrics whose quantum effects can be qualitatively explained by such a model, we use the dipole-proton system of KDP as the model system in the present study. As a result of the quantum treatment of protons and dipoles, the static properties of the system depend on their characteristic frequencies. Also, the proton and dipole degrees of freedom can be separated by adiabatic approximations that correspond to the case when the proton tunneling is faster than the oscillations of dipole, and vice versa. This separation is a key ingredient in this study, which leads to the two above-mentioned theoretical models. The differences in the static properties of the system within the two models are investigated.

The PO_4 dipole in KDP directed along the FE c axis is described by the coordinate μ_i and the momentum π_i ($i=1,\ldots,N$). It is represented as a harmonic oscillator with effective mass M and frequency ω_0, which is coupled to four neighboring protons with the dipole-proton interaction $-K\mu_i x_k$, where K is the dipole-proton coupling constant and x_k ($k=1,\ldots,2N$) is the displacement of the proton along the hydrogen bond from its center [Fig. 1(a)]. According to indications[6] that the dipole-proton interaction is the strongest interaction in KDP, the dipole-dipole and proton-proton interactions are neglected. It is assumed that the protons move in the double-well potential $V_{DW}(x_k)$ with moderately deep wells, for which only the two lowest-energy eigenstates $|\Phi_{0,1}\rangle$ with the tunneling energy splitting Δ can be taken into account.[1] Therefore, the protons are described by the pseudospin operators S_z and S_x that satisfy $S_z|\Phi_\pm\rangle=\pm(1/2)|\Phi_\pm\rangle$and $S_x|\Phi_\pm\rangle=(1/2)|\Phi_\mp\rangle$ for the states $|\Phi_\pm\rangle=(|\Phi_0\rangle\pm|\Phi_1\rangle)/2^{1/2}$, so that the dimensionless Hamiltonian of the coupled-proton system $h=H/\hbar\omega_0$ can be written in the form

$$h=\sum_{i}^{N}(P_i^2+Q_i^2)/2-\varepsilon\sum_{k}^{2N}S_x^k-\sqrt{\varepsilon\eta/2}\sum_{\langle ik\rangle}^{4N}Q_iS_z^k. \tag{1}$$

Here, $Q_i=\mu_i(M\omega_0/\hbar)^{1/2}$ and $P_i=\pi_i/(\hbar M\omega_0)^{1/2}$ are the dimensionless coordinate and momentum of the dipole, respectively. The adiabatic parameter of the proton is $\varepsilon=\Delta/\hbar\omega_0$

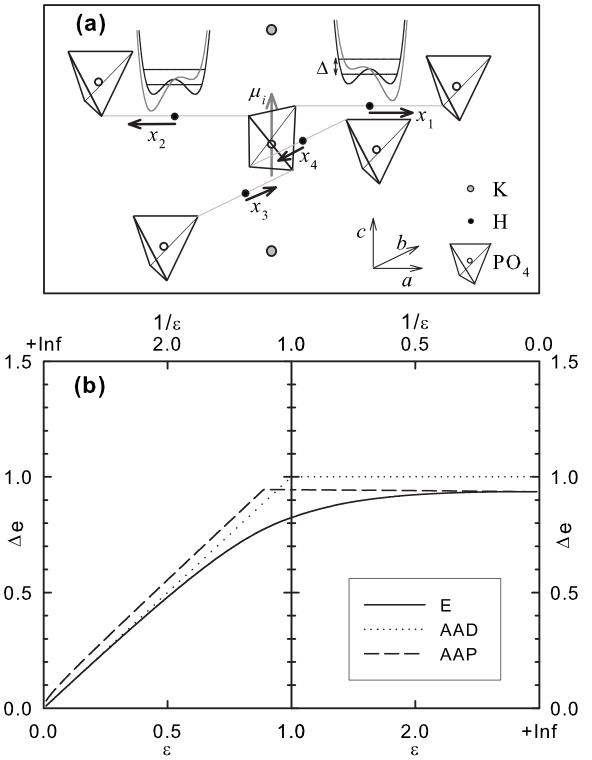

FIG. 1. (a) KDP structure and the coupled dipole-proton model. A proton in a double-well hydrogen-bond potential is a two-level system with the tunneling-splitting energy Δ. The PO$_4$ dipole μ_i induces the term $-K\mu_i x_k$ in the hydrogen-bond potential of four neighboring protons ($k=1,2,3,4$), where K is the dipole-proton coupling constant and x_k is the proton position along the hydrogen bond, relative to its center. (b) The calculated energy splitting between the two lowest-energy states of the coupled dipole-proton pair (E, exact Hamiltonian; AAD, adiabatic approximation for dipole; AAP, adiabatic approximation for proton).

and the relative interaction constant is $\eta=8I^2K^2/\Delta M\omega_0^2$, where $I=\langle\Phi_0|x|\Phi_1\rangle>0$.

In the mean-field approximation (MFA) of the Hamiltonian (1), the replacements $Q_i=\langle Q\rangle$ and $S_z^k=\langle S_z\rangle$ are made for two neighboring dipoles of one proton (spin) and for four neighboring spins of one dipole, respectively. The effective field acting on the spin $\mathbf{S}=(S_x,S_z)$ is then $\mathbf{h}_e=(\varepsilon,4\varepsilon\eta\langle S_z\rangle)$, which gives the self-consistency equation $|\mathbf{h}_e|/2\varepsilon\eta=\tanh(|\mathbf{h}_e|/2t)$ for the dependence of $\langle S_z\rangle$ on $t=k_\mathrm{B}T/\hbar\omega_0$. This equation gives the relation $t_c=\varepsilon/2\tanh^{-1}(1/2\eta)$ for the relative critical temperature $t_c=k_\mathrm{B}T_c/\hbar\omega_0$ of the second-order phase transition (where $\langle S_z\rangle\to 0$), which is the same relation as in the proton-tunneling model.[1,2,7,8] Also, this relation is in agreement with the concept of quantum temperature,[11,12] according to which the critical temperature of the FE system decreases from the classical critical temperature T_0 to

$$T_c=T_s/\tanh^{-1}(T_s/T_0), \tag{2}$$

when quantum fluctuations of atoms are taken into account through the saturation temperature T_s. As follows from (2), the system exhibits a FE phase transition ($T_c>0$) for $T_0>T_s$ and does not exhibit it for $T_0<T_s$. For $T_0>T_s$, the system is either in the classical ferroelectric (CFE) region $T_c>3T_s/2$, where T_c slightly deviates from T_0 ($T_0>T_c>0.87T_0$), or in the quantum ferroelectric (QFE) region $3T_s/2>T_c>0$, where it is strongly affected by quantum fluctuations ($0.87T_0>T_c>0$). For $T_0<T_s$, the system is either in the quantum paraelectric (QPE) region $0<T_0<T_s$, where the phase transition is suppressed by the quantum fluctuations, or in the classical paraelectric (CPE) region $T_0<0$. The relations $t_c=\varepsilon/2\tanh^{-1}(1/2\eta)$ and (2) coincide if $t_s=k_\mathrm{B}T_s/\hbar\omega_0=\varepsilon/2$ ($T_s=\Delta/2k_\mathrm{B}$) and $t_0=k_\mathrm{B}T_0/\hbar\omega_0=\varepsilon\eta(T_0=8I^2K^2/k_\mathrm{B}M\omega_0^2)$. The boundary between the QFE and CFE regions $3T_s/2=T_c$ (QFE-CFE boundary) corresponds to $\eta=1/[2\tanh(2/3)]\approx 0.86$ and the boundary between the QPE and QFE regions $T_0=T_s$ (QPE-QFE boundary), where $T_c=0$, corresponds to $\eta=1/2$. Thus, different regions in the parametric ε, η space for the coupled dipole-proton system (1) are determined only by the parameter η in the MFA.

In the adiabatic approximation for dipoles (AAD), which is expected to work well when the proton tunneling is slower than the oscillations of the dipole ($\varepsilon=\Delta/\hbar\omega_0<1$), the dipole occupies an adiabatic state that is an eigenstate of the displaced harmonic-oscillator Hamiltonian $h_S=(P^2+Q^2)/2-S(\varepsilon\eta/2)^{1/2}Q$, with $S=\Sigma_{k=1}^4 S_k^z$. Since the eigenstate energies are $e_n=E_n/\hbar\omega_0=n+1/2-S^2\varepsilon\eta/4$ ($n=0,1,\ldots$), the Hamiltonian (1) in the AAD reads

$$h_\mathrm{AAD}=-\varepsilon\sum_k^{2N}S_x^k-\varepsilon\eta/2\sum_{\langle kl\rangle}^{6N}S_z^kS_z^l, \tag{3}$$

when we neglect constant terms. This is a proton-tunneling Hamiltonian in which the effective proton-proton interaction responsible for the FE phase transition is caused by the adiabatic-state energies of dipoles.

In the adiabatic approximation for protons (AAP), which is expected to work well in the opposite case $\varepsilon>1$, the spin occupies an adiabatic state that is an eigenstate of the Hamiltonian $-\mathbf{h}_{ij}\mathbf{S}$, where $\mathbf{h}_{ij}$ is the instantaneous field produced by two neighboring dipoles i,j.[13] The Hamiltonian (1) in the AAP has the form

$$h_\mathrm{AAP}=\sum_i^N(P_i^2+Q_i^2)/2-\sum_{\langle ij\rangle}^{2N}(-1)^{m_{ij}}h_{ij}/2, \tag{4}$$

where $h_{ij}=\varepsilon[1+\eta(Q_i+Q_j)^2/2\varepsilon]^{1/2}$ is the absolute value of instantaneous field. The proton occupies the ground adiabatic state (GAS) when $m_{ij}=0$ and the excited adiabatic state (EAS) when $m_{ij}=1$. The contributions of EAS energies in (4) can be neglected at low temperatures $t\ll\varepsilon$, where the GAS Hamiltonian

$$h_\mathrm{GAS}=\sum_i^N(P_i^2+Q_i^2)/2-\sum_{\langle ij\rangle}^{2N}h_{ij}/2 \tag{5}$$

describes the whole system well. The GAS energy terms change the local potential of the dipole and introduce the effective dipole-dipole interaction responsible for the FE phase transition.

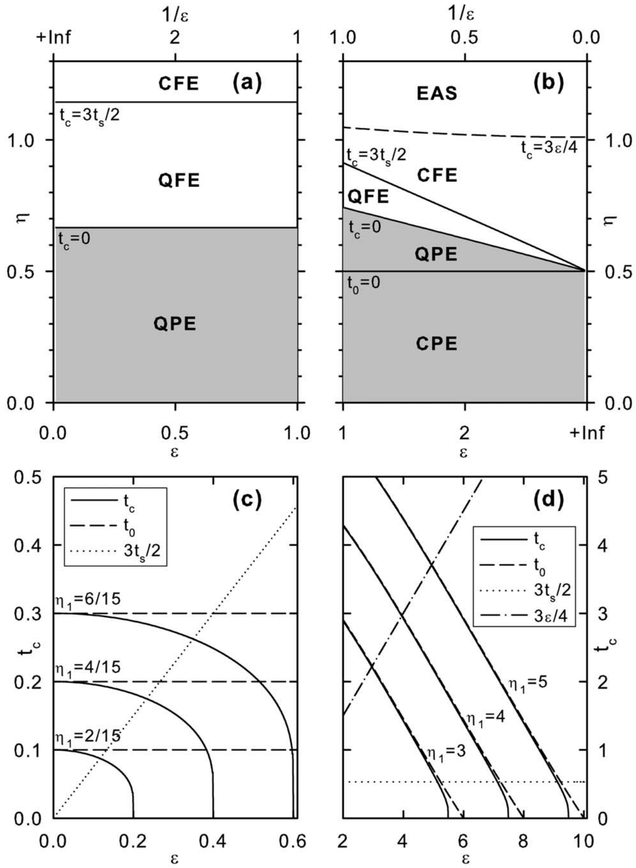

FIG. 2. MFA results for the regions in the ε, η space (a), (b) and the dependencies of t_c, t_0, and $1.5t_s$ on ε along the $\eta=\eta_1/\varepsilon$ curves (c), (d) of the coupled dipole-proton system in the AAD region $\varepsilon<1$ (a), (c) and in the AAP region $\varepsilon>1$ (b), (d).

To check the applicability of the adiabatic approximations, the energy difference between the first excited state and the ground state $\Delta e=(E_1-E_0)/\hbar\omega_0$ of one coupled dipole-proton pair in the system (1) is numerically calculated for the exact, AAD, and AAP Hamiltonians of the pair, which are obtained from Hamiltonians (1), (3), and (4), respectively. The Δe calculated as a function of ε for $\eta=1/2$ [Fig. 1(b)] shows that the AAD is exact in the limit $\varepsilon\rightarrow 0$ and gives good results for $\varepsilon<0.5$, whereas the AAP is exact in the limit $\varepsilon\rightarrow\infty$ and gives good results for $\varepsilon>2$. As expected, the AAD works better than the AAP for $\varepsilon<1$, whereas the AAP works better than the AAD for $\varepsilon>1$. These results lead to the idea of applying the AAD for $\varepsilon<1$ and the AAP for $\varepsilon>1$ on the Hamiltonian (1) before using the MFA.

In the MFA of the AAD Hamiltonian (3), the effective field acting on the spin $\mathbf{h}_e=(\varepsilon,3\varepsilon\eta\langle S_z\rangle)$ gives the self-consistency equation $2|\mathbf{h}_e|/3\varepsilon\eta=\tanh(|\mathbf{h}_e|/2t)$ and $t_c=\varepsilon/2\tanh^{-1}[2/(3\eta)]$. Comparison with (2) gives the same saturation temperature $t_s=\varepsilon/2$ as in the MFA of the Hamiltonian (1), and the smaller classical critical temperature $t_0=3\varepsilon\eta/4$. Different regions in the ε, η space [Fig. 2(a)] are determined again by η, but the QPE-QFE boundary $t_0=t_s$ and the QFE-CFE boundary $t_c=3t_s/2$ are now given by $\eta=2/3$ and $\eta=2/[3\tanh(2/3)]\approx 1.14$, respectively.

Since we are primarily interested in the region around $t_c\rightarrow 0$, where $t\ll\varepsilon$, the MFA is applied on the GAS Hamiltonian (5). The local potential of the ith dipole (when $Q_j=0$) is $v_0=Q_i^2/2-2\varepsilon(1+\eta Q_i^2/2\varepsilon)^{1/2}$, as follows from (5). This is a double-well potential for $\eta>1$ (order-disorder region) and a single-well potential for $\eta<1$ (displacive region). The homogeneous FE state of classical dipoles ($Q_i=Q$) has the potential energy per dipole $e_{\text{pot}}=Q^2/2-\varepsilon(1+2\eta Q^2/\varepsilon)^{1/2}$, as follows from (5). The energy has minima at $Q_m\neq 0$ for $\eta>1/2$, so that the CPE region is $\eta<1/2$ [Fig. 2(b)]. The GAS Hamiltonian (4) is approximated in the MFA by the trial Hamiltonian of independent harmonic oscillators[14,15]

$$h_0=\sum_i^N (P_i^2+s^2y_i^2)/2, \qquad (6)$$

where $y_i=Q_i-Q_0$. The dimensionless frequency $s=\omega/\omega_0$ and the mean position Q_0 of the oscillator are variational parameters in minimization of the dimensionless free energy per dipole,

$$f=F/N\hbar\omega_0=f_0+\langle h_{\text{GAS}}-h_0\rangle_0/N, \qquad (7)$$

where $f_0=t\ln[2\sinh(s/2t)]$ is the free energy of one oscillator and the expectation value is calculated by integrating $h_{\text{GAS}}-h_0$ over the distribution functions of the oscillators $\rho_i=(\gamma/\pi)^{1/2}\exp(-\gamma y_i^2)$, where $\gamma=s\tanh(s/2t)$. The obtained critical temperature t_c satisfies (2), with the saturation temperature $t_s=2^{-3/2}$ ($T_s=\hbar\omega_0/2^{3/2}k_{\text{B}}$) and the classical critical temperature $t_0=\varepsilon/4\eta u_1^{-1}(1/4\eta)$, where $u_1(z)=z^{1/2}U(1/2,0,z)/2$ (U is the confluent hypergeometric function). Since $u_1^{-1}(\eta\rightarrow 1/2)\rightarrow\infty$, it is confirmed that the boundary between the CPE and QPE regions, $t_0=0$, is the line $\eta=1/2$. The QPE-QFE boundary $t_0=t_s$ and the QFE-CFE boundary $t_c=3t_s/2$ lie in the displacive region $\eta<1$ [Fig. 2(b)], making the results consistent with the assumption that the system (5) can be well approximated by the harmonic-oscillator system (6). The EAS region $t_c>3t_s^{AAD}/2=3\varepsilon/4$, where the EAS energies contribute substantially to the energy of the system at t_c, lies in the order-disorder region $\eta>1$ [Fig. 2(b)].

To account for the isotope and pressure effects on the coupled dipole-proton system, it is assumed that both deuteration and pressure affect tunneling energy Δ much more than the other parameters, because Δ in general sensitively depends on the mass of the tunneling particle as well as on the height and width of the energy barrier in the double-well potential, as strong pressure-dependent quantities. The decrease in Δ with deuteration is assumed to be a combined effect of the mass increase and hydrogen-bond lengthening (geometric isotope effect). In other words, we calculate how changes in Δ affect the system, while the other parameters remain constant. Since $\varepsilon\propto\Delta$ and $\eta\propto 1/\Delta$, changing Δ moves the system along the curves $\eta=\eta_1/\varepsilon$ in the ε, η space, where η_1 is a constant. Six $\eta=\eta_1/\varepsilon$ curves are chosen: three ($\eta_1=2/15$, $4/15$, $6/15$) in the AAD region $\varepsilon<1$ and three ($\eta_1=3$, 4, 5) in the AAP region $\varepsilon>1$. The temperatures t_c, t_0, and $3t_s/2$ calculated along these curves according to the corresponding approximation depend differently on ε in the AAD region [Fig. 2(c)] and the AAP region [Fig. 2(d)]. The temperature $3t_s/2$ linearly increases with ε in the AAD region, while it is constant in the AAP region. The temperature t_0 is constant in the AAD region, while it decreases nearly linearly with ε in the AAP region. As expected, t_c strongly deviates from t_0 in the QFE region $t_c < 3t_s/2$, while $t_c \approx t_0$ in the CFE region $t_c > 3t_s/2$. The decrease in t_c and t_0 with ε in the AAP region [Fig. 2(d)] is expected to deviate from linearity in the EAS region $t_c > 3\varepsilon/4$.

Since for several hydrogen-bonded crystals the ratio of the critical temperatures in deuterated and nondeuterated crystals $T_c^{\mathrm{D}}/T_c^{\mathrm{H}}$ is between 1.5 and 2,[16] it is obvious that such a strong isotope effect in the AAD region [Fig. 2(c)] is possible only if at least nondeuterated crystal, with higher values of Δ and ε than the deuterated one, is in the QFE region. However, a strong deviation of the susceptibility in the PE phase from the Curie-Weiss law is expected for the system in the QFE region, which is contrary to the experiment.[2] In the AAP region, on the other hand, both crystals can be in the CFE region with the ratio $t_c^{\mathrm{D}}/t_c^{\mathrm{H}}$ as high as two [Fig. 2(d)].

Since it is reasonable to assume that the height and width of the energy barrier in the hydrogen-bond potential decrease with pressure p, resulting in an increase in both Δ and ε, the disappearance of ferroelectricity in the system with increasing ε [Figs. 2(c) and 2(d)] corresponds to the experimental fact that T_c in hydrogen-bonded ferroelectrics decreases with p and vanishes at the critical pressure p_c.[17,18] The experimental T_c-p dependence in KDP-type ferroelectrics is linear at low pressures, with a downward deviation at higher pressures near p_c, which is attributed to the quantum fluctuations of atoms.[17,18] This experimental dependence corresponds well with the t_c-ε dependence in the AAP region [Fig. 2(d)] if we assume that ε increases almost linearly with p. More precisely, t_c in the AAP region shows an almost linear decrease with ε in the CFE region and deviates downward in the QFE region due to quantum fluctuations of dipoles. In the AAD region, where t_c deviates downward from t_0 in the QFE region due to tunneling of protons, an additional strong linear decrease of t_0 with p is required to reproduce such T_c-p dependence [Fig. 2(c)]. Dielectric measurements[19] on KDP show that T_0 strongly decreases and T_s weakly increases with pressure from the value $T_s = T_0 \approx 50$ K at p_c, which is in qualitative agreement with Fig. 2(d). Also, the high value of tunneling energy $\Delta/k_{\mathrm{B}} \approx 1000$ K estimated from the neutron measurements on KDP at ambient pressure[4] indicates that T_s corresponds to the dipole frequency and not to the tunneling frequency. Assuming $\Delta/k_{\mathrm{B}} \approx 1000$ K, $T_s \approx 50$ K, and $T_c = 122$ K for KDP at ambient pressure and using Eq. (2) with $T_s = \hbar\omega_0/2^{3/2}k_{\mathrm{B}}$, it follows that $T_0 \approx 130$ K and $\hbar\omega_0/k_{\mathrm{B}} \approx 140$ K, which implies that the system is near the line $\eta_1 = 4$ at $\varepsilon \approx 7$ [Fig. 2(d)]. This indicates that KDP at ambient pressure is in the CFE subregion of the AAP region with a weak effect of EAS energies at T_c, which is exactly what is assumed in the recent models of interacting PO_4 dipoles.[9,10] Since they are more realistic models for KDP than this simple model, it is expected that a more quantitative comparison with experiment will be provided by these models.

In conclusion, we may say that the experimental results for hydrogen-bonded ferroelectrics with predominating dipole-proton interaction have to be reexamined according to the above theory, which suggests that the isotope effect can be explained by the change in tunneling energy Δ, but that the model of interacting tunneling protons can be applied only if $\Delta < \hbar\omega_0$, while in the opposite case the model of interacting dipoles is more appropriate. Also, similar results are expected in the case of a single-well anharmonic hydrogen-bond potential, for which the isotope-dependent energy Δ corresponds to the energy splitting between the first excited and ground states of proton. The theory for this case is in progress.

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