Peierls instabilities in quasi-one-dimensional quantum double-well chains

Natalie I. Pavlenko*

Institute for Condensed Matter Physics, 1, I. Svientsitsky Str., UA-79011, Lviv, Ukraine

(Received 23 June 1999; revised manuscript received 19 August 1999)

Peierls-type instabilities in quarter-filled ($\overline{n}=1/2$) and half-filled ($\overline{n}=1$) quantum double-well hydrogen-bonded chain are investigated analytically in the framework of two-stage orientational-tunnelling model with additional inclusion of the interactions of protons with two different optical phonon branches. It is shown that when the energy of proton-phonon coupling becomes large, the system undergoes a transition to various types of insulator states. The influence of two different transport amplitudes on ground-state properties is studied. The results are compared with the pressure effect experimental investigations in superprotonic systems and hydrogen halides at low temperatures.

I. INTRODUCTION

It has long been known that the formation of hydrogen bonds between molecules or ionic groups is responsible for drastic changes in a wide variety of entire system properties such as structural phase transformations and proton ordering phenomena.[1,2] For example, proton transport phenomena and superionic properties discovered in some hydrogen-bonded crystals like $M_3\mathrm{H}(A\mathrm{O}_4)_2$ class (where $M=\mathrm{Rb,Cs,NH_4}$; $A=\mathrm{Se,S}$) are related closely to hydrogen-bonded network rearrangement. On heating these compounds transform into superionic conducting phase with dynamically disordered hydrogen-bonded network (Fig. 1). The protons can migrate through the two-dimensional conducting planes with low activation energy (~ 0.1 eV). In this case protonic conductivity increases significantly to the value about 0.1 $\Omega^{-1}\,\mathrm{cm}^{-1}$. It is generally accepted[3] that the two-stage conduction mechanism is required to sustain the proton transport. The intrabond proton tunnelling along the hydrogen bridge is connected with the transfer of ionic positive- and negative-charged defects, whereas the intermolecular proton transfer due to the reorientations of molecular group with proton leads to the breaking of the hydrogen bond and creation of one between another pair of molecular complexes. It is significant to remember that the interaction of proton subsystem with the displacements of ionic groups participating in hydrogen bonding can be of essential importance. The formation of the hydrogen bridge induces the distortion of groups involved in hydrogen bonding towards the proton that results in the shortening of this bond.[4] By this means the protonic polaron is localized between distorted ionic groups in the low-temperature ferroelastic phases, giving rise in this case to the dimerized structure. As has been shown in Ref. 5, the small polaron is formed due to the strong coupling of proton with the optical stretching vibration modes of the oxygen ions. It is evident that such the transformations from the superionic phase occurring in systems on cooling have the mixed (displacive and order-disorder) character. The hydrogen bond geometry is closely related to the reorientations of groups involved in H bond and undergoes a change at the structural phase transitions.[6] Moreover, it is shown in Ref. 7 that the latter effect is of primary importance for the description of the phase sequence occurring in several superionic crystals.

Theoretical investigations of both displacive and order-disorder ferroelectric-type orderings in hydrogen-bonded systems have been based generally on pseudospin Ising-type models with additional including the pseudospin-phonon interactions to describe the coupling of protons with lattice vibration modes.[1,2] In particular, the quantum double-well chain with quartic symmetric double-well potential has been used to model the transition from the symmetry-broken to the symmetry-restored ground state in hydrogen halides HX ($X=\mathrm{F,Br,Cl}$) (Ref. 8) which consist of hydrogen-bonded chains with weak interchain coupling. The dynamics of both ionic and orientational defects created by the rotations of molecular groups in hydrogen halides has been studied in the framework of classic approach based on soliton model.[9]

It must be emphasized that taking into account the two-stage transport mechanism renders the pseudospin formalism unsuitable for the proton subsystem description since the number of protons can differ from the number of possible (virtual) hydrogen bonds and the proton occupancy of each virtual bond can be smaller than unity due to reorientational hopping and consequent feasibility of proton migration along the chain. This situation, as an example, is observed in superionic materials of $M_3\mathrm{H}(A\mathrm{O}_4)_2$ type, which transform on cooling into dielectric state with dimerized structure.[10] It should be noted that such type of transitions to the dielectric

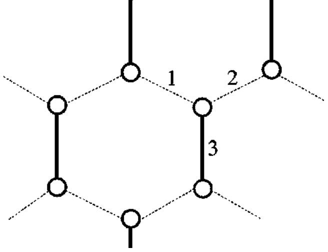

FIG. 1. Hydrogen-bonded network on the (001) plane of $M_3\mathrm{H}(A\mathrm{O}_4)_2$ crystal group; the solid lines indicate the possible type of dimerized structure which can appear with $(f=3)$th H-bonds frozen in. The circles denote the positions of the $A\mathrm{O}_4$ groups.

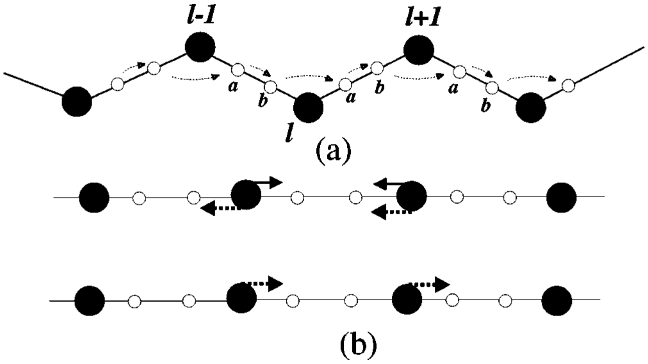

FIG. 2. (a) Zig-zag hydrogen-bonded chain in hydrogen halides, arrows indicate the possible path of proton migration along the chain. (b) Simplified model chains, the antiphase and in-phase displacements of ionic groups identified by the solid and dashed arrows, respectively.

states resembles that in electronic systems, in which the Peierls instabilities are observed. There have been many works to study the metal-insulator Peierls transitions in electron-phonon systems that are unstable against the electron-phonon interactions.[11–13] It is common knowledge that the Peierls instabilities occur with the formation of Peierls gap at $\boldsymbol{k}=\pm\boldsymbol{k}_F$ ($\boldsymbol{k}_F$ is the Fermi level) in the electronic energy band that connected with the electronic charge density waves condensation and structural lattice distortion modulations with $\boldsymbol{q}=2\boldsymbol{k}_F$. The appearance of insulator state together with the structural transformation can be modeled in the framework of the Holstein electron-phonon model without additional including the anharmonic terms in the lattice potential.

Recent investigations of Peierls transitions in electron-phonon systems have prompted us to study similar effects in several hydrogen-bonded solids. To analyze the influence of the proton-ionic group displacements coupling, we consider the simplified model, namely the quasi-one-dimensional quantum double-well chain along one of the proton pathways (for instance, the virtual hydrogen bond sequence $\cdots-1-3-1-3-\cdots$ in Fig. 1). As an initial step, we neglect the interproton repulsion and direct our attention to the analysis of the lattice effect on the proton subsystem thermodynamics. However, we take into account the possibility of proton exchange between our selected chain and surrounding. Besides the superionic compounds we also analyze in this work the influence of ionic group displacements on the proton subsystem behavior in quasi-one-dimensional solid hydrogen halides [see Fig. 2(a)]. We reveal possible symmetry-broken phases with proton charge disproportionalities coming from a Holstein coupling to the $A\mathrm{O}_4$ ionic groups or X atoms. We compare our conclusions with the results of the pressure effect theoretical studies in $M_3\mathrm{H}(A\mathrm{O}_4)_2$ (Ref. 14) and hydrogen halides.[8,15] Although the first step of our analysis consists in the quasi-one-dimensional chain study, we believe our results can also be relevant for other hydrogen-bonded materials.

II. DESCRIPTION OF THE MODEL

The object of our consideration is the chain shown in Fig. 2(a). However, to avoid the geometric complexities introduced by the kinks in such a zig-zag chain, we consider in our model linear chain [see Fig. 2(b) where two neighboring chains are shown]. The process of the proton transfer in the double-well H-bond potential is represented as the quantum tunnelling between two proton states with the intrabond transfer integral Ω_0

$$\Omega_0 \sum_l \left(c^+_{la} c_{lb} + c^+_{lb} c_{la}\right), \tag{1}$$

where $c^+_{l\nu}$, $c_{l\nu}$ denote proton creation and annihilation operators in the position $(l,\nu=a,b)$ of the chain. Besides that, we describe the interbond reorientational proton hopping in two-level approximation as the quantum tunnelling effect with the hopping amplitude Ω_R

$$\Omega_R \sum_l \left(c^+_{l+1,a} c_{lb} + c^+_{lb} c_{l+1,a}\right). \tag{2}$$

In this way, within the framework of orientational-tunnelling model proposed in Ref. 16 the two-stage proton migration mechanism can be considered as the sequential migration of the ionic and orientational defects.

As far as such a double-well chain is just a structural component of the system we also admit a possibility of proton exchange between the chain and surroundings by considering the system thermodynamics in the framework of the grand canonical ensemble with inclusion of the proton chemical potential

$$-\mu \sum_{l,\nu} n_{l\nu}, \tag{3}$$

which is to be determined at the given proton concentration in the chain from corresponding equation for the chemical potential.

Our main interest is to analyze the influence of the longitudinal optical ionic group vibration modes on the proton subsystem ground state. However, it was noted in Ref. 17 that the interactions between the protons of the neighboring chains can lead to the appearance of three-dimensional ordering. The more detailed analysis of the interchain proton interaction effect in this model together with the determination of stability conditions for the existence of the phases with different ordering type at finite temperatures will be presented elsewhere.[18] Here the interactions of protons with two different types of ionic group displacements are taken into account. Since our model allows to distinguish double-well structure of H-bond potential, the coupling to these displacements leads to the specific changes of the potential for each proton position (l,ν) within the bond. In particular, on the one hand we consider the antiphase stretching vibration mode that causes a change of H-bond length as indicated in Fig. 2(b) by solid arrows. The coupling to the first type of displacements leads to the equal change of the potential wells (l,a) and (l,b) depths within the H-bond

$$\sum_{l,q} \tau_l^{(1)}(q)\left(n_{la}+n_{lb}\right)\left(b_{q,1}+b^+_{-q,1}\right), \tag{4}$$

which is evident from the symmetry reasons. The term (4) follows from the well-known fact of the potential barrier decrease with the shortening of the distance between the H-bonded ions.[19] On the other hand, we also take into account the optical in-phase vibrations of ionic groups in the chain which induce their displacements with respect to the surrounding chains as identified in Fig. 2(b) by dashed arrows. The coupling to this vibration mode induces, for instance, the difference of the distances between the lth ion and the nearest proton positions (l,a) and $(l-1,b)$. It is easy to show that generally this interaction causes the difference of these potential minima depths

$$\sum_{l,q} \tau_l^{(2)}(q)(n_{la}-n_{l-1,b})(b_{q,2}+b^{+}_{-q,2}). \tag{5}$$

Here, $\tau_l^{(1)}(q)=-2ig_1\sqrt{\hbar/2MN\omega_1(q)}\sin(\frac{1}{2}qd)\exp[iq(l+1/2)d]$ and $\tau_l^{(2)}(q)=g_2\sqrt{\hbar/2MN\omega_2(q)}\exp[iqld]$ where g_1 and g_2 are corresponding coupling constants, M is the effective ionic group mass, N denotes the number of hydrogen bonds in chain and d is the lattice parameter. The jth optical phonon branch creation and annihilation operators $(j=1,2)$ are denoted by $b^{+}_{q,j}$ and $b_{q,j}$, respectively. Furthermore, we take a dispersionless approximation for the phonon frequencies: $\omega_1(q)=\omega_1$ and $\omega_2(q)=\omega_2$, and assume the harmonic approximation for the lattice vibration energies

$$\hbar\omega_1\sum_q b^{+}_{q,1}b_{q,1}+\hbar\omega_2\sum_q b^{+}_{q,2}b_{q,2}. \tag{6}$$

First of all, let us consider the case of the isolated chain without a coupling to the phonon bath. Since the Hamiltonian (1)–(3) can be exactly diagonalized, the proton energy spectrum

$$\varepsilon_\nu(k)=\pm|t_k|,\quad t_k=\Omega_0+\Omega_R e^{-ikd} \tag{7}$$

forms two energy bands with the bandwidth $\Delta\varepsilon=\Omega_0+\Omega_R-|\Omega_0-\Omega_R|$. The energy gap in this case is $\Delta_{ab}=2|\Omega_0-\Omega_R|$. Eliminating one of the elementary transport process by setting the hopping amplitude $\Omega_0=0$ or $\Omega_R=0$, we can see that both of the energy bands degenerate into the two energy levels and the quantum fluctuations between these two system states could be derived. It is clear that in the case when $\bar{n}=1/N\Sigma_{l\nu}\langle n_{l\nu}\rangle=1$ (one proton is averaged within the bond) the lower band is filled and the chemical potential μ is centered between bands–thus the material is in dielectric state. Such a situation can be observed in hydrogen halides. However, for $\bar{n}=\frac{1}{2}$ only half of the lower band is filled and this corresponds to the case of protonic conductor that occurs for example in superionic phases of superprotonic crystals.

We will discuss afterwards the consequences of the proton-phonon coupling effect focusing on the analysis of the two physically different cases $\bar{n}=\frac{1}{2}$ (1/4-filled two-band model) and $\bar{n}=1$ (half-filling case in two-band model).

III. BROKEN-SYMMETRY SOLUTIONS

A. Case $\bar{n}=\frac{1}{2}$

Let us now focus on the case of quarter filling when the half of the lower proton band is filled (one proton is averaged per two bonds). Then the macroscopic condensed phonon state is predominantly stabilized at $q^{*}=2k_F=\pi/d$ (Ref. 11 and 12) and is characterized by the expectation values of the phonon creation and annihilation operators

$$\langle B_{q,1}\rangle=\langle b_{q,1}+b^{+}_{-q,1}\rangle=\frac{\Delta}{g_1}\sqrt{N}\delta_{q,q^{*}}, \tag{8}$$

where Δ denotes the introduced distortion order parameter which should be determined from the stationarity conditions of the free energy. Since the condensation of displacements (8) leads to the unit cell doubling, using the Fourier transformation $c_{l\nu(i)}=1/\sqrt{N/2}\Sigma_k c_{k\nu(i)}e^{ikld}$ where the index $i=\{+,-\}$ denotes $(l=2m)$ or $(l=2m+1)$th unit cell, the Hamiltonian in condensed state with static periodic distortions (8) (we assume that the adiabatic treatment is applicable for these systems, which is justified by the small ratio between the proton mass and the mass of H-bonded ionic group[20]) is given by

$$\begin{aligned}H={}&(-\mu+\tilde{\Delta})\sum_{k\nu} n_{k\nu(+)}-(\mu+\tilde{\Delta})\sum_{k\nu} n_{k\nu(-)}+\frac{1}{8}N\frac{\tilde{\Delta}^2}{E_0}\\&+\Omega_0\sum_{k,i}(c^{+}_{ka(i)}c_{kb(i)}+c^{+}_{kb(i)}c_{ka(i)})\\&+\Omega_R\sum_k\sum_{i\neq i'}(c^{+}_{ka(i)}c_{kb(i')}e^{-ikd}+c^{+}_{kb(i')}c_{ka(i)}e^{ikd}),\end{aligned} \tag{9}$$

where $E_0=(\hbar g_1)^2/2M(\hbar\omega_1)^2$ is well known from polaron theory[21] the protonic polaron binding energy, which appears in the expression for the elastic energy per H-bond $1/8\tilde{\Delta}^2/E_0$ and $\tilde{\Delta}=4\Delta\sqrt{\hbar/2M\omega_1}=4\Delta\sqrt{E_0\hbar\omega_1}/g_1$. The similar result can be obtained when we consider the second type of the ionic group displacements, in this case $\langle B_{q,2}\rangle=\langle b_{q,2}+b^{+}_{-q,2}\rangle=\Delta'/g_2\sqrt{N}\delta_{q,q^{*}}$, and the Hamiltonian in condensed state has the form similar to (9) with $\tilde{\Delta}\to\tilde{\Delta}'=2\sqrt{\hbar/2M\omega_2}$ and $E_0\to E_0'=(\hbar g_2)^2/2M(\hbar\omega_2)^2$. Since the inclusion of the coupling to the second phonon mode leads merely to renormalization of the binding energy E_0 in the Hamiltonian, further we focus on the analysis of Eq. (9) with only one type of displacements taken into account. Introducing the double-time one-fermion diagonal Green functions, one can get rigorously the density of proton states

$$\begin{aligned}\rho(\varepsilon)={}&\frac{2}{\pi}\frac{|\varepsilon|\cdot|t_1-\varepsilon^2|}{B_1B_2}\{\Theta[\varepsilon\cdot\mathrm{sgn}(\varepsilon)-\sqrt{t_1-t_2^0}]\\&-\Theta[\varepsilon\cdot\mathrm{sgn}(\varepsilon)-\sqrt{(\Omega_0-\tilde{\Delta})^2+\Omega_R^2}]+\Theta[\varepsilon\cdot\mathrm{sgn}(\varepsilon)\\&-\sqrt{t_1+t_2^0}]-\Theta[\varepsilon\cdot\mathrm{sgn}(\varepsilon)-\sqrt{(\Omega_0+\tilde{\Delta})^2+\Omega_R^2}]\},\end{aligned} \tag{10}$$

where

$$\begin{aligned}B_1&=\sqrt{(t_1-\varepsilon^2)^2-4\Omega_0^2\tilde{\Delta}^2},\\B_2&=\sqrt{4\Omega_0^2(\tilde{\Delta}^2+\Omega_R^2)-(t_1-\varepsilon^2)^2}\end{aligned} \tag{11}$$

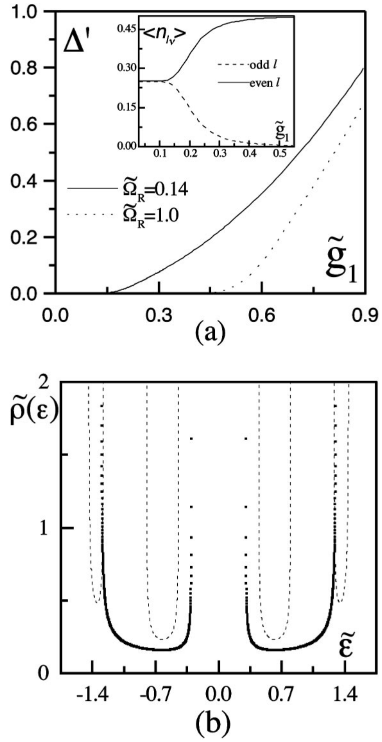

FIG. 3. (a) Distortion parameter $\Delta'=|\tilde\Delta|/\hbar\omega_1$ as a function of proton-phonon coupling $\tilde g_1=g_1/\hbar\omega_1$ for $\tilde\Omega_0=\Omega_0/\hbar\omega_1=0.5$; inset: dependence of the average proton occupancies on $\tilde g_1$ for $\tilde\Omega_R=\Omega_R/\hbar\omega_1=0.14$. (b) Proton density of states $\tilde\rho(\varepsilon)=\rho(\varepsilon)/\hbar\omega_1(\tilde\varepsilon=\varepsilon/\hbar\omega_1)$, the dashed and dotted curves indicate the cases of $\Delta'=0.5$ and $\Delta'=0.0$, respectively.

and the following notations are introduced: $t_1=\Omega_0^2+\Omega_R^2+\tilde\Delta^2$, $t_2^0=2\Omega_0\sqrt{\Omega_R^2+\tilde\Delta^2}$ and $\Theta(x)$ is the Heaviside step function. The expression for the ground state energy can be obtained easily from (9) and (10):

$$E=\frac{N}{8}\frac{\tilde\Delta^2}{E_0}-\sum_k\sqrt{t_1+2\Omega_0\sqrt{\tilde\Delta^2+\Omega_R^2\cos^2 kd}}. \tag{12}$$

To determine the stable phase the equation $\partial E/\partial\tilde\Delta=0$ should be solved. It appears that this equation has besides $\tilde\Delta=0$, a nonzero additional solution $\tilde\Delta\neq0$ for $g_1>g_P$ where g_P is the crossover proton-phonon coupling strength. The solution $\tilde\Delta\neq0$ corresponds to the global minimum of E and, as a result, implies the structural distortion stabilization with the amplitude $u_l=\sqrt{\hbar/2MN\omega_1}\langle B_{q*}\rangle=\tilde\Delta/2g_1(-1)^l$ [see Fig. 3(a)]. Let us discuss the proton position average occupancies on the bonds and the band structure. At $g_1=g_P$ each proton band splits into two subbands

$$\begin{aligned}\varepsilon_{a(+/-)}(k)&=\mp\sqrt{t_1+2\Omega_0\sqrt{\tilde\Delta^2+\Omega_R^2\cos^2 kd}},\\ \varepsilon_{b(+/-)}(k)&=\pm\sqrt{t_1-2\Omega_0\sqrt{\tilde\Delta^2+\Omega_R^2\cos^2 kd}}\end{aligned} \tag{13}$$

as shown in Fig. 3(b) where the proton density of states in the disordered and dimerized phases is represented. The Peierls energy gap between either of the two (lower and upper) subbands $\Delta_1=\sqrt{t_1+2\Omega_0\tilde\Delta}-\sqrt{t_1-2\Omega_0\tilde\Delta}\approx2\Omega_0\tilde\Delta/\sqrt{\Omega_0^2+\Omega_R^2}$ tends to zero for $\Omega_0\to0$. In this case, $\tilde\Delta=\pm\sqrt{4E_0^2-\Omega_R^2}$ and the phase transition (change in the nature of the ground state) occurs when the localization energy $E_0\sim(g_1^*)^2=\frac{1}{2}\Omega_R$. The energy gap between the second and third subbands increases for $g_1>g_P$

$$\Delta_{ab}=2\sqrt{t_1-2\Omega_0\sqrt{\tilde\Delta^2+\Omega_R^2}}.$$

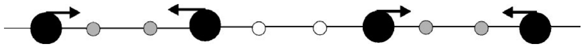

FIG. 4. Dimerized structure which appears in the case of quarter-filled chain.

The proton chemical potential μ is centered between two lowest subbands with further increasing of $g_1>g_P$ that points on the insulator state appearance. We see from inset in Fig. 3(a) that the distortion stability is accompanied by the formation of the proton charge-density-wave state in which $\langle n_{la}\rangle=\langle n_{lb}\rangle=\frac{1}{4}[1+(-1)^l]$ that means the forming of dimerized structure as shown in Fig. 4. Consider further the ground-state phase diagrams $(\tilde g_1=g_1/\hbar\omega_1,\tilde\Omega_0=\Omega_0/\hbar\omega_1)$ and $(\tilde g_1,\tilde\Omega_R=\Omega_R/\hbar\omega_1)$ shown in Fig. 5. We see the strong influence of the amplitude Ω_R on the dimerized state stability. The increasing of Ω_R suppresses dimerization. At $\Omega_R\to0$ (without reorientational hopping) the system is brought

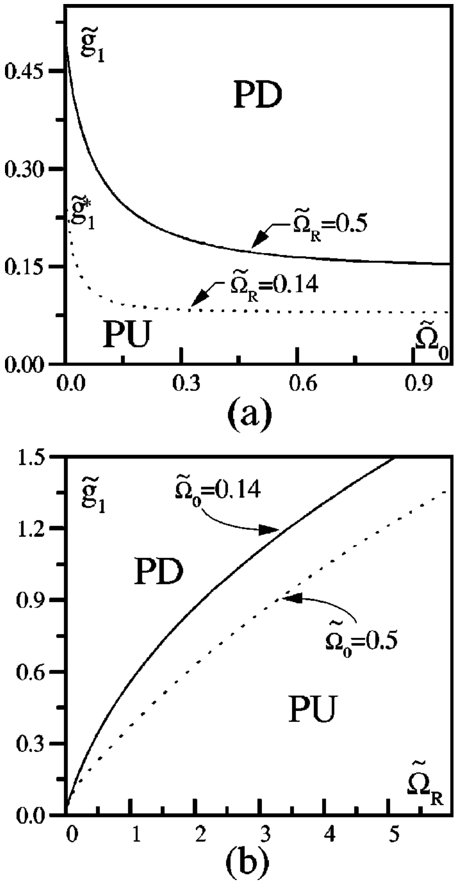

FIG. 5. Ground-state phase diagrams (a) $(\tilde g_1,\tilde\Omega_0)$ and (b) $(\tilde g_1,\tilde\Omega_R)$. The notations PD and PU denote the dimerized and uniform phases, respectively.

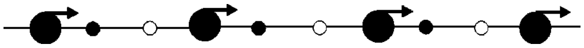

FIG. 6. Broken-symmetry structure that appears in the case of half-filled chain.

immediately into the dimerized state. Only for the finite values of Ω_R the uniform disordered phase begins to appear and the ''metal''-insulator transition occurs.

It is necessary to mention that the hopping amplitudes Ω_0 and Ω_R depend strongly on external pressure. In particular, the Ω_0 value decreases with pressure that deduced from the quantum mechanical calculations.[19] This is associated with the shortening of the distance between two potential minima (l,ν) on the bond. Thus, we can make a conclusion about the pressure effect on the system state from the diagrams shown in Fig. 5. Using the obtained in Ref. 5 values for parameters Ω_R, g_1 and ω_1 [$\Omega_R/\hbar\omega_1\approx 0.14$ and $\hbar^2 g_1^2/2M(\hbar\omega_1)^3\approx 3.8$] we reveal that the dimerized state is always stable at $T=0$ under pressure for this set of parameters. It is interesting that the similar picture has been observed in $M_3\mathrm{H}(A\mathrm{O}_4)_2$ materials from experimentally measured baric dependencies at low temperatures.[14] Nevertheless, we notice that as g_1 decreases and approaches the critical value $g_1^*=\sqrt{\Omega_R/2}$, the transition from the dimerized to the uniform state occurs with pressure. This effect appears due to the more weak proton-phonon coupling and, as a result, to the tendency of the proton disorder in the chain, when the overlapping integral between the proton states within the H-bond decreases.

B. Case $\bar{n}=1$

Let us discuss another case when one proton in average is placed in the bond. According to Peierls theory[11] such a system is very susceptible towards the lattice modulation at $q^*=0$. It should be noted that in this case only the second type of optical vibrations (interchain mode $j=2$) contributes to the lattice distortions condensation. The Hamiltonian in condensed phase has the form

$$H=\sum_k [(-\mu+\tilde{\Delta})n_{ka}-(\mu+\tilde{\Delta})n_{kb}]+\frac{1}{8}N\frac{\tilde{\Delta}^2}{E_0}+\sum_k (t_k c^+_{ka}c_{kb}+t^*_k c^+_{kb}c_{ka}). \tag{14}$$

In this case, the density of proton states

$$\rho(\varepsilon)=\frac{2}{\pi}\frac{|\varepsilon|}{\sqrt{4\Omega_0^2\Omega_R^2-(\varepsilon^2-t_1)^2}}\{\Theta[\varepsilon\cdot\mathrm{sgn}(\varepsilon)-\sqrt{\tilde{\Delta}^2+(\Omega_0-\Omega_R)^2}]-\Theta[\varepsilon\cdot\mathrm{sgn}(\varepsilon)-\sqrt{\tilde{\Delta}^2+(\Omega_0+\Omega_R)^2}]\} \tag{15}$$

points on the two-band structure

$$\varepsilon_\nu(k)=\pm\sqrt{\tilde{\Delta}^2+|t_k|^2} \tag{16}$$

with the Peierls energy gap $\Delta_{ab}=2\sqrt{\tilde{\Delta}^2+(\Omega_0-\Omega_R)^2}$. The chemical potential always is centered between two bands, i.e., $\mu=0$. We present the equation for determination of $\tilde{\Delta}\neq 0$ which follows from the stationary condition of E

$$\frac{1}{4E_0}=\frac{1}{N}\sum_k\frac{1}{\sqrt{\tilde{\Delta}^2+|t_k|^2}}. \tag{17}$$

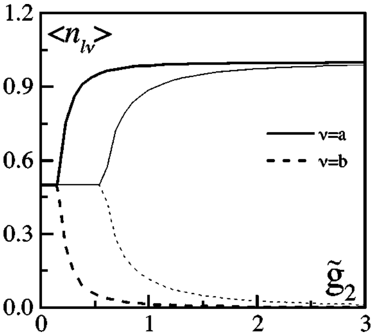

FIG. 7. The average proton occupancies as a function of $\tilde{g}_2$ for $\tilde{\Omega}_0=0.8$; the bold and thin curves indicate the cases when $\tilde{\Omega}_R=0.5$ and $\tilde{\Omega}_R=2.5$.

The nonzero solution, which appears for $g_2>g_P$, corresponds to the formation of a proton charge density wave in chain together with the distortions $u_l=\tilde{\Delta}/2g_2$ stabilization (see Fig. 6). The typical dependencies of the proton position average occupancies $\langle n_{l\nu}\rangle$ are represented in Fig. 7. It is interesting that the system now is invariable with respect to the interchanging $\Omega_0\leftrightarrow\Omega_R$. Thus, it is sufficiently to analyze the system behavior as a function of Ω_0 for instance, with the given fixed value of Ω_R. The ground-state phase diagram $(\tilde{g}_2=g_2/\hbar\omega_2,\tilde{\Omega}_0=\Omega_0/\hbar\omega_2)$ (see Fig. 8) differs essentially from the case of $\bar{n}=\frac{1}{2}$. The phase equilibrium curve has the specific salient point at $\Omega_0=\Omega_R$. The drastically decrease of g_P in the vicinity of $\Omega_0=\Omega_R$ is connected with the fact that the transfer anisotropy $|\Omega_0-\Omega_R|$ forms the additional transverse field, which competes with the ordering stabilization process. This anisotropy is vanished at $\Omega_0=\Omega_R$ that leads to the lowering of the crossover proton-phonon coupling energy g_P required for the ordering stabilization. The interpretation of the diagram $(\tilde{g}_2,\tilde{\Omega}_0)$ with re-

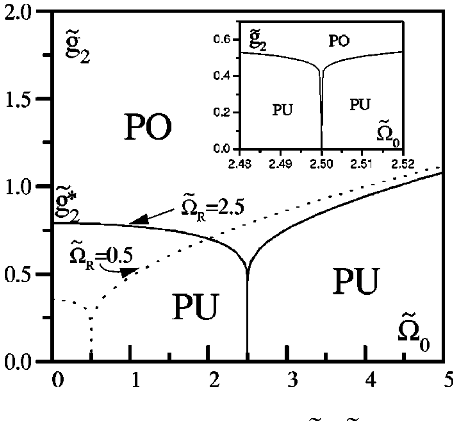

FIG. 8. Ground-state phase diagrams $(\tilde{g}_2,\tilde{\Omega}_0)$. The notation PO indicates the symmetry-broken phase with proton ordering on the hydrogen bonds; inset: the region $\Omega_0\sim\Omega_R$ for $\tilde{\Omega}_R=2.5$ in more detail.

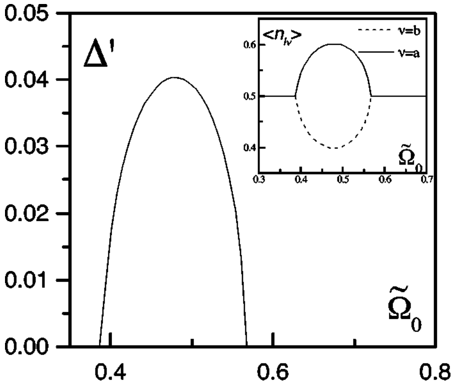

FIG. 9. Distortion parameter as a function of $\tilde{\Omega}_0$ for $\tilde{g}_2 = 0.32$ and $\tilde{\Omega}_R = 0.5$; inset: the corresponding dependencies of the average proton occupancies.

spect to the pressure effect is very interesting. The second-order transition from the uniform to the ordered state occurs under pressure (with Ω_0 decrease) for $g_2 > g_2^* = \sqrt{\Omega_R}/2$. However, in the region $g_2 < g_2^*$ the additional reentrant transition from the symmetry-broken to the uniform state appears (see Fig. 9). In this case the region of symmetry-broken phase equilibrium narrows with g_2 decrease. We notice that the first-principle calculations[15,17,22] and the results of Monte Carlo simulations[8] in quasi-one-dimensional hydrogen halides show a transition from the symmetry-broken phase shown in Fig. 6 to the uniform symmetric phase under pressure at low temperatures. Thus, our results in the vicinity of $\Omega_0 \approx \Omega_R$ and for considerably weak proton-phonon coupling $g_2 < g_2^*$ are in qualitative agreement with the conclusions of Refs. 8 and 15 confirming a proper treatment of the quantum effects in these hydrogen-bonded materials.

IV. CONCLUSIONS

In the present work, the lattice effect on the ground-state properties of the quantum quasi-one-dimensional hydrogen-bonded chain is analyzed in the framework of the two-stage orientational-tunneling model. The interaction of protons with two different types of the surrounding ionic group optical displacements is considered. We show that when the proton-phonon coupling energy becomes large, the system undergoes a transition from disordered to broken-symmetry phases. The different cases of proton concentration have been analyzed: $\overline{n} = 1/2$ and $\overline{n} = 1$. It is shown that in the first case the Peierls transition to the dimerized phase occurs, whereas in the second one we obtain a transformation into the proton-ordered state. The influence of two different transport amplitudes on ground-state properties is also studied. We compare our ground-state phase diagrams with the pressure effect experimental investigations in superprotonic systems and hydrogen halides at low temperatures.

ACKNOWLEDGMENT

This work was partially supported by INTAS Grant No. 95-0133.

---

*Electronic address: natalie@icmp.lviv.ua

[1] R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974).
[2] V.L. Aksenov, N.M. Plakida, and S. Stamenković, *Neutron Scattering by Ferroelectrics* (World Scientific, Singapore, 1989).
[3] A.V. Belushkin, C.J. Carlile, and L.A. Shuvalov, Ferroelectrics **167**, 21 (1995).
[4] A. Pietraszko, B. Hilczer, and A. Pawlowski, Solid State Ionics **119**, 281 (1999).
[5] N. Pavlenko, J. Phys.: Condens. Matter **11**, 5099 (1999).
[6] A. Katrusiak, Phys. Rev. B **48**, 2992 (1993).
[7] I.V. Stasyuk and N. Pavlenko, J. Phys.: Condens. Matter **10**, 7079 (1998).
[8] X. Wang, D.K. Campbell, and J.E. Gubernatis, Phys. Rev. B **49**, 15 485 (1994).
[9] A.V. Savin and A.V. Zolotaryuk, Solid State Ionics **77**, 15 (1995).
[10] A. Pietraszko, K. Łukaszewicz, and M.A. Augustyniak, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **48**, 2069 (1992); K. Łukaszewicz, A. Pietraszko, and M.A. Augustyniak, *ibid.* **49**, 430 (1993); A. Pietraszkos and K. Łukaszewicz, Bull. Polish Acad. Sci. **41**, 157 (1993).
[11] R.E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, 1955).
[12] M.J. Rise and S. Strässler, Solid State Commun. **13**, 125 (1973).
[13] E. Jeckelmann and S.R. White, Phys. Rev. B **57**, 6376 (1998); E. Jeckelmann, C. Zhang, and S.R. White, cond-mat/9903149 (unpublished).
[14] V.V. Sinitsyn, A.I. Baranov, E.G. Ponyatovsky, and L.A. Shuvalov, Solid State Ionics **77**, 118 (1995).
[15] R.W. Jansen, R. Bertocini, D.A. Pinnick, A.I. Katz, R.C. Hanson, O.F. Sankey, and M. O'Keeffe, Phys. Rev. B **35**, 9830 (1987).
[16] I.V. Stasyuk, O.L. Ivankiv, and N. Pavlenko J. Phys. Stud. **1**, 418 (1997).
[17] M. Springborg, Phys. Rev. B **40**, 5774 (1989).
[18] N. Pavlenko (unpublished).
[19] S. Scheiner, in *Proton Transfer in Hydrogen-Bonded Systems* (Plenum Press, New York, 1992).
[20] Y. Yamada, Ferroelectrics **170**, 23 (1995).
[21] Yu. A. Firsov, *Polarons* (Nauka, Moscow, 1975) (in Russian).
[22] M. Springborg, Phys. Rev. B **38**, 1483 (1988).