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Phonons in one-dimensional Peierls systems with internal degrees of freedom

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An extension of the frozen-phonon approach is presented that permits us to calculate phonon dispersion curves for a one-dimensional system subject to Peierls distortion in the whole Brillouin zone. A number of systems with monomers possessing both lattice and internal degrees of freedom and with various filling ratios are investigated. The nature of the soft mode common for all the systems studied is discussed putting emphasis on its difference from the soft mode in the well-studied Peierls systems with one degree of freedom per monomer. It is found that the presence of internal degrees of freedom has considerable impact on the soft modes and phonon dispersions. The behavior of the phonon dispersion curves and the force constants resulting from the electron-phonon interaction are studied as a function of electron-phonon coupling constants. A model system with two types of monomers, one of which possesses an internal degree of freedom and with a filling ratio of 3/4, is used to explain experimental results on a recently synthesized quasi-one-dimensional compound $Ca_{2-x}Sr_xCuO_3$.

I. INTRODUCTION

In recent years, distortions of one-dimensional chains due to the electron-phonon coupling, suggested by Peierls,[1] were intensively investigated. Starting with the pioneering work by Su, Schrieffer, and Heeger,[2] a detailed study of nonlinear excitations, such as solitons, polarons, etc. was performed,[3-7] especially the influence of electron-electron interaction on soliton formation was investigated.[6,8-10] The ground state of the Peierls-Hubbard Hamiltonian and the dependence of dimerization amplitude on the Hubbard parameter U were also a subject of intensive studies.[11-19] The last efforts are aimed at two-band Peierls-Hubbard models,[20-22] in which a variety of phases, including incommensurate ones, was found,[20] as well as at systems with internal (totally symmetric or Jahn-Teller-active) degrees of freedom, where an interesting interplay between lattice and internal dimerization takes place.[23-27]

One of the most intriguing problems, connected with Peierls-distorted systems, is electron-lattice interaction and phonon properties of these systems. Lattice vibrations in the vicinity of solitons have been studied in a number of papers.[28-32] Since 1978, phonon-dispersion curves were calculated for a number of model Hamiltonian describing Peierls systems without solitons.[33-36] These investigations revealed a number of general phonon properties, such as softening of the optical phonon in the vicinity of the wave vector $q=0$ and a positive quadratic dispersion of that phonon at small q. In the earlier papers, systems with filling ratio of $1/3$ and $1/4$,[33] as well as two-atomic systems,[34,35] were considered. In the recent work of Batistic and Bishop,[37] a two-band, $3/4$-filled Hamiltonian describing a halogen-bridged transition-metal chain was investigated, with a special emphasis on the phonon properties in the presence of polarons. A number of publications (see, e.g., A. Girlando, Painelli, and Soos[38] and references therein) have been devoted to the investigation of optical spectra of polyacetylene and its isotopic derivatives. Here, a modulation of the hopping integral resulting from interaction with several vibrational modes was considered. However, the phonon properties of systems with both internal vibrational degrees of freedom modulating on-site energies and lattice degrees of freedom modulating the hopping integral were not investigated so far.

As already mentioned, ground-state geometry and electronic structure of one-dimensional systems with internal degrees of freedom have been intensively studied in the last years. It was found that the competition between electron-lattice and electron-internal couplings may lead to an interesting phase diagram with a number of possible ground-state geometries. For a half-filled system with monomers possessing totally symmetric internal degrees of freedom (on-site electron energy depends linearly on the internal coordinate value), the ground state has either a lattice distortion, or an internal Peierls distortion, or a combination of both kinds of distortion, depending on the values of the coupling constants.[23,24] In other systems, such as quarter-filled alternating systems (i.e., systems with two types of monomers, one of which possesses and the other does not possess internal degrees of freedom), both types of distortions always coexist.[26] Such an interplay between lattice and internal degrees of freedom should obviously reflect itself in phonon properties of these systems. Of particular interest here is a behavior of the soft mode in systems with more than one Peierls-active coordinate. Thus, in the present work we are aiming at a comprehensive study of phonon-dispersion curves in systems where the Peierls distortion involves lattice as well as internal degrees of freedom. We give an extension of the frozen-phonon approach, which permits us to calculate phonon-dispersion curves in the whole Brillouin zone. This allows us to investigate phonon properties of a number of systems with various filling ratios and various types of distortions, as well as systems with alternating monomers. We show that the presence of internal degrees of freedom leads to unusual effects on

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phonon-dispersion curves, and analyze these effects in order to explain recent experimental results on a quasi-one-dimensional compound $Ca_{2-x}Sr_xCuO_3$.[39,40]

The paper is organized as follows. In Sec. II, the computational method is presented. The comparison with earlier results on systems with only lattice degrees of freedom and the new results for systems with both lattice and internal Peierls-active coordinates, including an analysis of $Ca_{2-x}Sr_xCuO_3$ experimental data, are collected in Sec. III. A discussion of the results is given in Sec. IV. Finally, Sec. V contains the concluding remarks and points out the line of possible further investigations.

II. THEORY

Vibrational frequencies and corresponding vibrational eigenvectors of a one-dimensional chain can be found from eigenvalues of the following linear system of equations:

$$\mathbf{D}(q)\mathbf{x}=\mathbf{M}\omega^2\mathbf{x} \ . \tag{1}$$

Here $\mathbf{D}(q)$ is the $N\times N$ dynamical matrix (N is the number of degrees of freedom in the unit cell), q is the wave vector, $\mathbf{x}$ the column vector representing the vibrational amplitudes, $\mathbf{M}$ is an $N\times N$ matrix whose diagonal elements M_{ii} are masses (or reduced masses) m_i of the ith degree of freedom; for $i\neq j$, $M_{ij}=0$. Thus, squares of the frequencies are given by the eigenvalues of the matrix $D_{ij}(q)/\sqrt{m_i m_j}$. The dynamical matrix can be expressed in the following form:

$$\begin{aligned} D_{ij}(q) &= \sum_{l=-\infty}^{\infty} \frac{\partial^2 E}{\partial x(0,i)\partial x(l,j)} e^{iql} \\ &\equiv \sum_{l=-\infty}^{\infty} F(0,i;l,j)e^{iql} \ . \end{aligned} \tag{2}$$

The summation is to be performed over all unit cells (they are numbered by the index l). The jth coordinate in the lth unit cell is denoted by $x(l,j)$, it can be either lattice or internal; E is the total energy of the system, its second derivatives with respect to the lattice coordinates (i.e., the force constants) are denoted by $F(0,i;l,j)$. It is supposed that the derivatives in (2) are taken at the ground-state geometry of the system (corresponding to the minimum of the total energy). In (2), as well as throughout the paper, we use a dimensionless representation of the wave vector. The first Brillouin zone corresponds to the values of q in the region $-\pi\leq q<\pi$. One can also use the wave vector q' with the dimension of inverse length ($q'\equiv q/a$), then the exponent in (2) will take the form $\exp(iq'la)$, with $-\pi/a\leq q'<\pi/a$, a being the size of the unit cell.

Now, let us divide the dynamical matrix and the total energy into elastic and band (or, equivalently, into σ and π) parts:

$$\begin{aligned} E&=E_{\rm el}+E_{\rm band} \ , \\ D_{ij}&=D_{ij}^{\rm el}+D_{ij}^{\rm band} \ . \end{aligned} \tag{3}$$

The evaluation of $D_{ij}^{\rm el}$ usually does not represent a major problem, because in a good approximation the elastic interactions can be represented by (harmonic) force constants for bond stretches and angle bends; $D_{ij}^{\rm el}$ can then be easily found using standard lattice dynamics. The most important part for the systems with electron-phonon interaction is

$$\begin{aligned} D_{ij}^{\rm band}(q) &= \sum_{l=-\infty}^{\infty} \frac{\partial^2 E_{\rm band}}{\partial x(0,i)\partial x(l,j)} e^{iql} \\ &\equiv \sum_{l=-\infty}^{\infty} F_{\rm band}(0,i;l,j)e^{iql} \ . \end{aligned} \tag{4}$$

Note that it is more convenient to consider finite rather than infinite chains, because in the case of infinite chains the quantity $E_{\rm band}$ is also infinite [though the derivatives in (4) are still finite]. Thus, let our system be a finite chain consisting of L unit cells (numbered from 0 to $L-1$) with periodic boundary conditions. Let us first investigate the case $q=0$. Then,

$$D_{ij}^{\rm band}(q=0)=\sum_{l=0}^{L-1} \frac{\partial^2 E_{\rm band}}{\partial x(0,i)\partial x(l,j)} \ . \tag{5}$$

Due to translational invariance of the system,

$$\frac{\partial E_{\rm band}}{\partial x(0,i)}=\frac{\partial E_{\rm band}}{\partial x(m,i)}=\frac{1}{L}\sum_{m=0}^{L-1}\frac{\partial E_{\rm band}}{\partial x(m,i)} \tag{6}$$

and

$$D_{ij}^{\rm band}(q=0)=\frac{1}{L}\sum_{m=0}^{L-1}\sum_{l=0}^{L-1} \frac{\partial^2 E_{\rm band}}{\partial x(m,i)\partial x(l,j)} \ . \tag{7}$$

Now, let us introduce new collective coordinates

$$\begin{aligned} X_k(j)&=\frac{1}{L}\sum_{l=0}^{L-1} e^{ikl}x(l,j) \ , \\ x(l,j)&=\sum_{k=0}^{k_{\rm max}} e^{-ikl}X_k(j) \ , \end{aligned} \tag{8}$$

where k can take the following values: $k=2\pi(l/L)$, $l=0,1,\ldots,L-1$. Rewriting the above expressions in terms of the derivatives with respect to $X_k(j)$ one easily arrives at the following result:

$$D_{ij}^{\rm band}(q=0)=\frac{\partial^2 \varepsilon_{\rm band}}{\partial X_0(i)\partial X_0(j)} \ , \tag{9}$$

where $\varepsilon_{\rm band}=(1/L)E_{\rm band}$ is the band energy per unit cell. The derivatives in (9) are to be obtained numerically. It follows from (8) that $X_0(i)\neq 0$ with all other collective coordinates equal to zero corresponds to $X(l,i)=X_0(i)$ for all l, other lattice and internal coordinates being zero. Thus, one has to calculate the second derivative of $\varepsilon_{\rm band}$ with respect to distortions of ith and jth degrees of freedom which are *equal in all unit cells.* The chain remains translationally invariant, the size of the unit cell remains the same and it is only necessary to calculate the band energy for geometries slightly different from the ground-state geometry.

Turning now to the case $q\neq 0$, let us consider the system as consisting of L "large" unit cells, each "large" unit cell being a sequence of M usual unit cells. Then, the formula (4) can be rewritten as

$$D_{ij}^{\text{band}}(q)=\sum_{l=0}^{L-1}\sum_{m=0}^{M-1}e^{iq(lM+m)}\times\frac{\partial^2 E_{\text{band}}}{\partial x(0,i)\partial x(lM+m,j)} . \tag{10}$$

Now, note that for $q=2\pi(m/M)$, $m=0,1,\ldots,M-1$, $\exp(iqlM)=1$ and

$$D_{ij}^{\text{band}}(q)=\sum_{l=0}^{L-1}\sum_{m=0}^{M-1}e^{iqm}\frac{\partial^2 E_{\text{band}}}{\partial x(0,i)\partial x(lM+m,j)} . \tag{11}$$

In the following, one proceeds analogously to the case $q=0$, with the difference that now the "large" unit cell is considered as a usual unit cell. So, for the derivative with respect to $x(0,i)$ one obtains

$$\frac{\partial E_{\text{band}}}{\partial x(0,i)}=\frac{1}{L}\sum_{n=0}^{L-1}\frac{\partial E_{\text{band}}}{\partial x(nM,i)} . \tag{12}$$

The collective coordinates are introduced as follows:

$$\begin{aligned}X_k(m,j)&=\frac{1}{L}\sum_{l=0}^{L-1}e^{ikl}x(lM+m,j) ,\\ x(lM+m,j)&=\sum_{k=0}^{k_{\max}}e^{-ikl}X_k(m,j) ,\end{aligned}\tag{13}$$

with $0\le m\le M-1$, $k=2\pi(l/L)$, $l=0,\ldots,L-1$. The derivatives with respect to $x(nM,i)$ and $x(lM+m,j)$ are transformed into the derivatives with respect to collective coordinates and after some algebra one obtains

$$D_{ij}^{\text{band}}(q)=\sum_{m=0}^{M-1}e^{iqm}\frac{\partial^2 \varepsilon_{\text{band}}}{\partial X_0(0,i)\partial X_0(m,j)} . \tag{14}$$

Here, $\varepsilon_{\text{band}}=(1/L)E_{\text{band}}$ is the band energy per "large" unit cell. The derivatives in (14) are to be calculated numerically, the only difference from the case $q=0$ is that now the distortions are equal *in all "large" unit cells.* One now has to perform calculations for the translationally invariant system with the period of a large unit cell. The electronic Hamiltonian is an $Mp\times Mp$ square matrix, p being a number of electron levels in one usual unit cell. Proceeding in such a way, one can get the dynamical matrix and the vibrational frequencies for M values of the wave vector: $q=2\pi(m/M)$, $m=0,1,\ldots,M-1$; in fact, only the values of $q\le\pi$ are important, because $\omega(\pi+q)=\omega(\pi-q)$.

Finally, let us make two general remarks. First, if one takes the number M of usual unit cells in the large one to be very large, the comparison of (4) and (14) shows that the value

$$\Phi(0,i;m,j)\equiv\frac{\partial^2 \varepsilon_{\text{band}}}{\partial X_0(0,i)\partial X_0(m,j)}$$

tends to the band force constant $F_{\text{band}}(0,i;m,j)$. Thus, the force constant resulting from the electron-phonon interaction can be obtained as a limit of $\Phi(0,i;m,j)$ when the size M of the large unit cell tends to infinity. Second, the results presented in this section can be used even if the Hamiltonian of the system includes, in addition to usual Peierls terms, the terms which take into account the electron-electron interaction. All the formulas (1)–(14) remain valid with the only difference that the quantity E_{band} is no more the band energy of the system but the lowest eigenvalue of the total electronic Hamiltonian. The only approximation used in derivation of (1)–(14) is the adiabatic approximation which permits us to divide the total energy and the dynamical matrix into elastic and electronic parts. With this approximation the results presented are a complete scheme of phonon calculations in the whole Brillouin zone for systems with electron-phonon interaction.

III. NUMERICAL RESULTS

The following computational procedure was used for all the systems studied in this section. The second derivatives of the band energy were computed by the finite differences method. The step was about 10^{-4} times the size of the unit cell; the results obtained were precise enough everywhere except the cases when the dimerization amplitude in the ground-state geometry was comparable with this step. In the latter situation an appropriately reduced step size has to be used. Usually, the phonon frequencies were calculated in 5 or 10 points in the Brillouin zone to obtain the full dispersion curves; it was found to be a sufficient number, because the dispersion curves are flat enough.

A. Systems without internal degrees of freedom

As a check of the theory proposed, a comparison with earlier results of Schulz[33] and Rice and Mele[35,36] was performed. Firstly, vibrational frequencies of half- and quarter-filled systems described by the usual Peierls Hamiltonian

$$\begin{aligned}H&=\frac{M}{2}\sum_n\dot{u}_n^2+H_{\text{el}}+H_{\text{band}}\\&=\frac{M}{2}\sum_n\dot{u}_n^2+\frac{K}{2}\sum_n(u_{n+1}-u_n)^2\\&\quad-\sum_{n\sigma}t_n(a_{n\sigma}^\dagger a_{n+1\sigma}+\text{H.c.}) ,\end{aligned}\tag{15}$$

$$t_n=t_0-\tilde{\gamma}(u_{n+1}-u_n) \tag{16}$$

were calculated. The phonon-dispersion curves of these systems have been studied by Schulz[33] using a Green's-functions method. In our calculations, we used the following parameter values: $K=7.57$ eV/Å^2, $t_0=1.67$ eV, $M=16$ a.m.u. For the comparison with Ref. 33, the values of $\tilde{\gamma}$ were chosen so as to give $\Delta=0.1W$, Δ being a Peierls gap and $W=4t_0$ the bandwidth in the absence of the Peierls distortion: $\tilde{\gamma}=1.712$ eV/Å for the half-filled and $\tilde{\gamma}=2.147$ eV/Å for the quarter-filled system. The results are given in Fig. 1. They are in a very good qualitative and quantitative agreement with corresponding results of Ref. 33. The most important peculiarities of both systems are soft optical modes at $q=0$. In the half-filled system, there is only one (amplitude) soft mode; in the quarter-filled system, both amplitude and phase soft modes are present, the last one has the smaller frequency. Summarizing, we can conclude that for systems without internal degrees of freedom our method provides equally good results as the method used in Ref. 33. However, we believe that our method is more convenient to apply to more complicated systems with internal degrees of freedom.

In a review article of Mele,[36] results of calculations of phonon frequencies in the whole Brillouin zone are presented for Hamiltonian (15) with parameters representative for $(\mathrm{CH})_x$: $K=68.6$ eV/Å^2, $t_0=3$ eV, $\tilde{\gamma}=8$ eV/Å. To obtain the dependence of the band energy on atomic displacements for a given phonon wave vector q, a second-order perturbation theory was used. The frequency of the $q=0$ optical phonon is 1492 cm^{-1}, which is very close to our calculations $\omega(q=0)=1479$ cm^{-1}. However, at the end of the Brillouin zone there is no splitting between the two phonon branches in strong disagreement with the results of Schulz[33] and with our results. Our calculations predict for $q=\pi$ vibrational frequencies of 1539 and 1673 cm^{-1}. The vibration with the lowest frequency corresponds to in-phase movement of doubly bonded neighboring monomers, while in the high-frequency vibration there is an out-of-phase movement of such monomers. It is obvious that the frequencies of these vibrations must be different for any nonzero value of the dimerization amplitude and the absence of the corresponding gap in the phonon spectrum given in Ref. 36 is a consequence of the approximations used there.

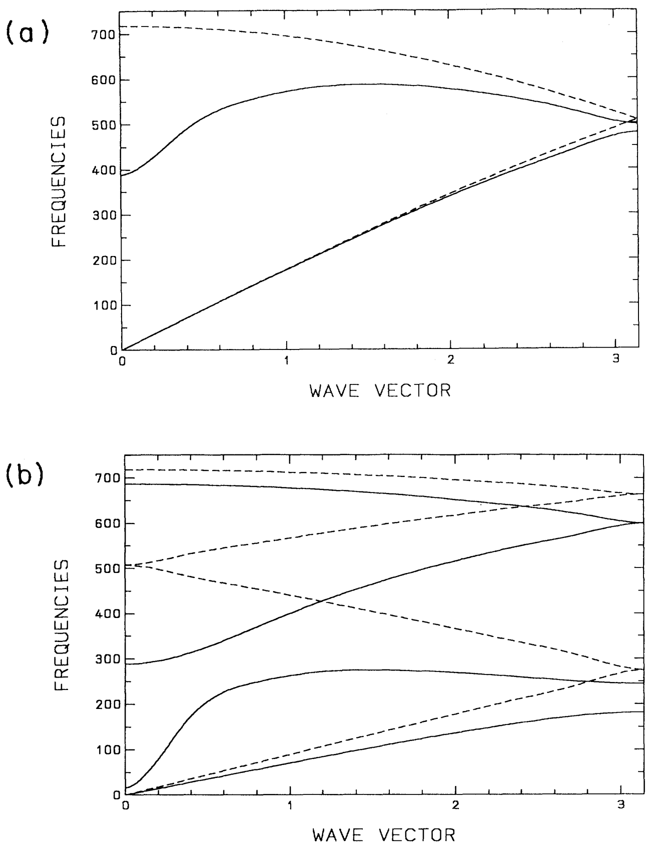

FIG. 1. Phonon-dispersion curves of half- (a) and quarter- (b) filled Peierls-distorted systems (full lines). For comparison, phonon-dispersion curves without electron-lattice interaction are also shown (dashed lines). The frequencies are in cm^{-1}. The parameters of the Hamiltonian (15) and (16) used are given in the text.

A slightly more complicated system is a diatomic polymer $(AB)_x$ studied in Ref. 35, which is described by the following Hamiltonian:

$$H=\frac{1}{2}M_A\sum_i \dot{u}_i^2+\frac{1}{2}M_B\sum_j \dot{y}_j^2+H_{\mathrm{el}}+H_{\mathrm{band}} , \tag{17}$$

$$H_{\mathrm{el}}=\frac{K}{2}\sum_i (y_{i+1}-u_i)^2+\frac{K}{2}\sum_j (u_{j+1}-y_j)^2 , \tag{18}$$

$$\begin{aligned}H_{\mathrm{band}}=&\frac{1}{2}\Delta\varepsilon\left[\sum_{i\sigma} a_{i\sigma}^{\dagger}a_{i\sigma}-\sum_{j\sigma} b_{j\sigma}^{\dagger}b_{j\sigma}\right]\\&-\sum_{i\sigma} t_i(a_{i\sigma}^{\dagger}b_{i+1\sigma}+\mathrm{H.c.})\\&-\sum_{j\sigma} t_j(b_{j\sigma}^{\dagger}a_{j+1\sigma}+\mathrm{H.c.}) ,\end{aligned} \tag{19}$$

where M_A, M_B are masses of atomic constituents $A,B,\Delta\varepsilon=\varepsilon_A-\varepsilon_B$ is a difference of on-site energies. Displacements of atoms A and B along the chain are denoted by u_i and y_j, respectively; $a_{i\sigma}^{\dagger}$ and $b_{j\sigma}^{\dagger}$ are the corresponding electron creation operators. The authors of Ref. 35 used parameters representative for $(\mathrm{CH})_x$ (see above) in their model of $(\mathrm{CH{=}N})_x$. The results for various values of $\Delta\varepsilon$ are given in Fig. 2 of Ref. 35. The common feature is the lowering of frequency of the optical vibration at $q=0$ with respect to the case of elastic interaction only, and the appearance of a gap between acoustical and optical vibrations at the end of the Brillouin zone. With increasing $\Delta\varepsilon$, the dimerization decreases and becomes 0 for $\Delta\varepsilon=\Delta_0$, Δ_0 being the gap in the electronic spectrum for $\Delta\varepsilon=0$. The frequency of the optical vibration also decreases with increasing $\Delta\varepsilon$ and tends to 0 when the dimerization disappears. At the same time, the optical vibrational frequency at the end of the Brillouin zone does not depend on $\Delta\varepsilon$, according to Ref. 35, as is also the case for the whole acoustical branch. The magnitude of the gap between optical and acoustical vibrational frequencies at the end of the Brillouin zone does not depend on $\Delta\varepsilon$ and is about 300 cm^{-1}. Our calculations confirm the softening of the optical vibration at $q=0$ and the decrease of $\omega_{\mathrm{opt}}(q=0)$ with increasing $\Delta\varepsilon$, as well as the existence of the gap at $q=\pi$. However, the actual values of frequencies are different from those in Ref. 35. For example, for $\Delta\varepsilon=0$ we obtained $\omega_{\mathrm{opt}}(q=0)=1453$ cm^{-1}, the result of Rice and Mele being 1412 cm^{-1}. In the whole Brillouin zone, both optical and acoustical branches have higher frequencies in our calculations than in Ref. 35. The value of the gap at $q=\pi$ is about 144 cm^{-1} in our calculations, compared with about 300 cm^{-1} obtained by Rice and Mele. The strongest disagreement between our results and that of Ref. 35 is the decrease of the gap at $q=\pi$ with increasing $\Delta\varepsilon$ and decreasing dimerization. When the dimerization approaches 0, the gap in our calculation is about 58 cm^{-1} and the ratio $\omega_{\mathrm{opt}}(q=\pi)/\omega_{\mathrm{acoust}}(q=\pi)$ becomes equal to $(M_{\mathrm{N}}/M_{\mathrm{CH}})^{1/2}=1.038$. It is obvious that in the absence of dimerization the vibrations at $q=\pi$ are either movement of N atoms only or that of CH species only and that both vibrations cause equal change of the band energy. Consequently, the ratio of their frequencies must indeed be equal to $(M_{\mathrm{N}}/M_{\mathrm{CH}})^{1/2}$. The fact that the results for the phonon-dispersion curves presented in Refs. 35 and 36 are particularly poor at the end of the Brillouin zone shows that the second-order perturbation theory approach cannot give qualitatively good results for the whole phonon spectrum unless the system is in a weak-coupling limit ($\gamma \equiv \tilde{\gamma}^2/Kt_0 \ll 1$; for the parameters used in Refs. 35 and 36, $\gamma=0.31$ and the electron-phonon coupling cannot be treated as weak). We can conclude that our approach provides better qualitative and quantitative values than the perturbation theory used in Refs. 35 and 36.

B. Half-filled homogeneous system with internal degrees of freedom

The ground-state geometry and the band structure of this system have been investigated by Fischer, Köppel, and Cederbaum.[23–25] Each monomer possesses two degrees of freedom: a monomer distortion coordinate along the chain u_n and an internal, totally symmetric coordinate U_n. The Hamiltonian of the system looks as follows:

$$\begin{aligned} H=&\frac{M}{2}\sum_n \dot{u}_n^2+\frac{K}{2}\sum_n (u_n-u_{n+1})^2 \\ &-\sum_{n\sigma} t_n (c_{n\sigma}^{\dagger}c_{n+1\sigma}+\mathrm{H.c.}) \\ &+\frac{\mu}{2}\sum_n \dot{U}_n^2+\frac{F}{2}\sum_n U_n^2+\sum_{n\sigma}\varepsilon_n c_{n\sigma}^{\dagger}c_{n\sigma} . \end{aligned} \tag{20}$$

Here, the first three terms describe a usual Peierls system; the last three terms are responsible for the internal coordinate U of the monomer. The reduced mass of the internal degree of freedom is denoted μ, the corresponding force constant is F. The last term is an on-site energy of the monomers, which, analogously to the hopping term of the Hamiltonian is supposed to depend linearly on the internal coordinate:

$$\varepsilon_n=\varepsilon_0+\tilde{\kappa}U_n . \tag{21}$$

It was found[5,23–25] that the ground-state geometry of the system is determined by two dimensionless electron-phonon coupling constants:

$$\begin{aligned} \gamma&=\tilde{\gamma}^2/Kt_0 , \\ \kappa&=\tilde{\kappa}^2/Ft_0 . \end{aligned} \tag{22}$$

At large κ, the doubling of the unit cell takes place due to internal distortions of the monomers; at large γ, only lattice distortions take place; in a small region of (κ,γ)-parameter space, both types of distortions coexist. In order to study the behavior of the phonon modes in the vicinity of transitions between these regions, we have calculated phonon-dispersion curves for three close-lying sets of coupling constants corresponding to these three regions (Fig. 2). The following parameters were used:

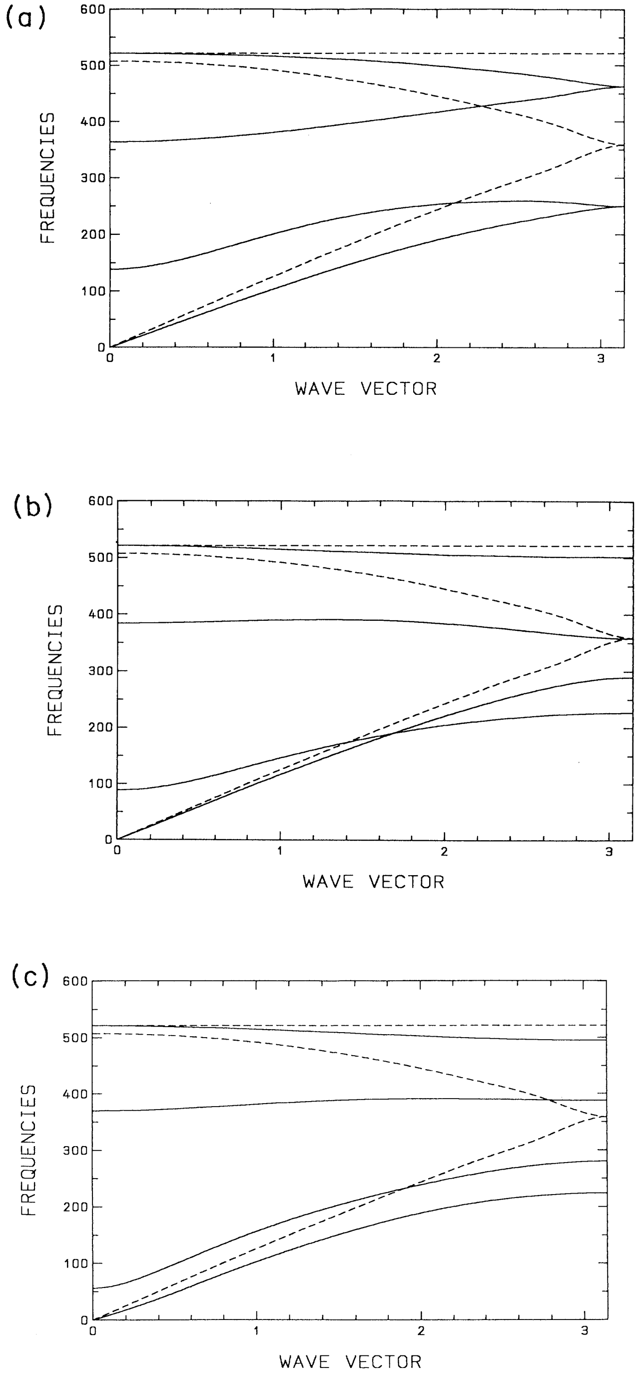

FIG. 2. Phonon-dispersion curves of half-filled homogeneous system with internal degrees of freedom. The frequencies are in cm^{-1}. The ground-state geometries of the system are the following: internal distortions only (a), $\kappa=1.45$, $\gamma=0.55$; lattice distortions only (b), $\kappa=1.30$, $\gamma=0.55$; coexistence of lattice and internal distortions (c), $\kappa=1.35$, $\gamma=0.55$. For other parameters of the Hamiltonian, see text. Dashed lines show the phonon dispersions without electron-phonon interaction taken into account. Note that in the ground states with purely internal or lattice distortions, vibrational modes are also purely internal or lattice. It makes the crossing of two low-lying phonon branches at (b) possible.

$t_0=1.67$ eV, $K=7.57$ eV/Å, $F=7.99$ eV/Å, $M=32$ a.m.u., $\mu=8$ a.m.u. Dashed lines are the phonon dispersions without electron-phonon interaction taken into account. The upper dashed line corresponds to internal vibration and is doubly degenerate (due to the folding of the Brillouin zone), the two low-lying dashed lines are the lattice optical and acoustical phonons. The common feature of all the three figures is the presence of a low-lying optical mode showing a positive curvature at $q=0$ (i.e., $\partial^2\omega/\partial q^2\geq 0$). At the values of parameters, at which a transition from one ground-state geometry to another takes place, the frequency of this mode becomes equal to 0. This is illustrated by Fig. 3, where three $q=0$ optical vibrational frequencies of the system are shown as functions of the internal coupling constant κ. While the frequencies in the region 300–600 cm^{-1} only slightly depend on κ, the soft mode goes to 0 when the transitions lattice dimerization–lattice and internal dimerization ($\kappa=1.338$) and lattice and internal dimerization–internal dimerization ($\kappa=1.368$) take place. The existence of a soft mode is a general situation for all Peierls-distorted systems and an indication of the fact that the system is in the vicinity of a phase transition. However, in the present case, unlike in Peierls systems with only lattice degrees of freedom, the low-frequency vibration mainly consists of those degrees of freedom which are not dimerized for the given (κ,γ) values. In Fig. 2(a), the low-frequency optical branch is an out-of-phase lattice vibration, while in Fig. 2(b) it is an out-of-phase internal vibration. The soft mode in Fig. 2(c) is a superposition of internal and lattice vibrations.

One can easily anticipate which vibration should be the soft mode. As the electron-lattice coupling constant γ increases and the system transforms from the ground state with only internal distortions to the ground state with both types of distortions, the ground-state value of the lattice distortion changes from 0 to a finite value. In this parameter region the dependence of the ground-state energy of the system on the lattice Peierls coordinate has a usual form characteristic for a system undergoing the phase transition, i.e., it should be a lattice distortion coordinate which takes part in the soft-mode vibration. Analogously, in the (κ,γ) region in the vicinity of the transition from the ground state with only lattice distortions to the ground state with a combined lattice-internal distortion, the soft mode is an out-of-phase vibration of the internal coordinate. For values of (κ,γ) parameters, for which both lattice and internal degrees of freedom are dimerized, the situation is slightly more complicated. If the lattice dimerization is very small (the system is in the vicinity of the transition into the phase with pure internal dimerization), the corresponding soft mode consists mainly of lattice vibration with small admixture of the internal one. The opposite case takes place if the lattice dimerization dominates over the internal one. Thus, in both cases the soft-mode vibration is orthogonal to the actual Peierls distortion. One can conclude that if the system is in the vicinity of transition between two ground-state geometries, the soft-mode vibration indicates the minimal energy path between them. Obviously, the soft mode does not coincide with the actual Peierls distortion.

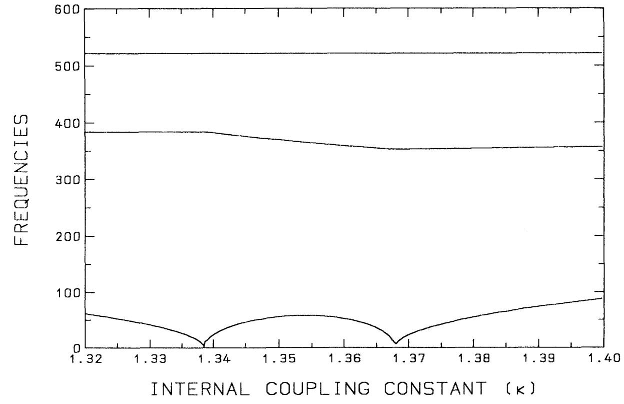

FIG. 3. Frequencies (in cm^{-1}) of optical vibrations of half-filled homogeneous system with internal degrees of freedom at $q=0$ as functions of the internal coupling constant κ. The parameters of the Hamiltonian are given in the text, $\gamma=0.55$.

Now, let us mention that at very small γ or κ the system should be very close to a usual Peierls system with one degree of freedom, and hence the softening of the distorted mode must also take place. Indeed, we can see from Fig. 2(a) that one of internal vibrations is also slightly softened (third phonon branch) although we are in the parameter region where only internal distortions take place. An analogous finding holds for one of the lattice vibrations in Fig. 2(b), which describes a system which has only lattice distortions in its ground state. The situation in this system is, in some respect, similar to the case of quarter-filled system without internal degrees of freedom, where, as we mentioned above, there are amplitude and phase soft modes, the last one having the lower frequency. The amplitude mode is a vibration of the amplitude of the Peierls distortion, while the phase mode represents a vibration, which tends to shift the distortion to the neighboring monomers. In Figs. 2(a) and 2(b) there is also a slightly softened amplitude mode and a much stronger softened "ground-state" vibration, which tends to move the system to a new ground-state geometry with another Peierls-distortion structure. Such an interesting similarity between the half-filled homogeneous system and the quarter-filled system without internal degrees of freedom deserves more attention and may be a subject for further investigations.

C. Quarter (3/4)-filled alternating system with internal degrees of freedom

This system represents an example of a system with internal degrees of freedom, in which the coexistence of internal and lattice distortions takes place at any values of coupling constants. The system now is an alternating chain: . . .-A-M-A-M-. . ., where A denotes an "atomlike" monomer (without those internal degrees of freedom, which could influence the electronic structure), and M is a "moleculelike" monomer with internal degrees of freedom. The Hamiltonian has the following form:[26]

$$H=\frac{1}{2}\sum_n m_n\dot{u}_n^2+\frac{1}{2}\sum_n \mu\dot{U}_n^2+H_{\mathrm{el}}+H_{\mathrm{band}}\ ,$$
$$H_{\mathrm{el}}=\frac{K}{2}\sum_n (u_n-u_{n+1})^2+\frac{F}{2}\sum_n U_n^2\ , \qquad (23)$$
$$H_{\mathrm{band}}=\sum_{n\sigma}\varepsilon_n c_{n\sigma}^{\dagger}c_{n\sigma}-\sum_{n\sigma}t_n(c_{n\sigma}^{\dagger}c_{n+1\sigma}+\mathrm{H.c.})\ .$$

The on-site energy ε_n depends on the internal coordinate now only for each second monomer:

$$\varepsilon_n=\frac{\Delta\varepsilon}{2}+\tilde{\kappa}U_n,\quad n\in M\ ,$$
$$\varepsilon_n=-\frac{\Delta\varepsilon}{2},\quad n\in A\ , \qquad (24)$$

here $\Delta\varepsilon$ takes into account the difference of on-site energies between A and M moieties. Analogously, the terms in H_{el}, which are responsible for the internal motion, are present only for $n\in M$; $m_n=m_A$ or m_M for $n\in A$ or $n\in M$, respectively.

It was shown in Ref. 26 that the system with filling ratio of 3/4 can be mapped onto the quarter-filled system by the substitution $\Delta\varepsilon\rightarrow-\Delta\varepsilon$. In the same paper, the ground state of the system was determined and it was found that the internal and lattice distortions are always coupled, independently of the values of $\tilde{\kappa}$ and $\tilde{\gamma}$. The internal distortions lead to different equilibrium values of U on neighboring M monomers, while the lattice distortions cause a shift of A monomers. The atoms move towards the molecule with large or small value of U, depending on the sign of $\tilde{\kappa}$. Note that the M monomers are not subject to lattice distortions; thus, internal and lattice distortions are taking place on different types of monomers.[26]

In the distorted system, the unit cell consists of four monomers, two of which possess both lattice and internal degrees of freedom. Accordingly, there are now six branches in the phonon spectrum. In the undistorted system, two of them (those which correspond to internal vibrations of M) are degenerate and their frequencies do not depend on the value of q. The other four branches are usual phonon-dispersion curves of a two-atom linear chain (doubled due to the folding of the unit cell). The electron-phonon interaction removes the degeneracy of internal vibrations and causes a softening of *all* phonon frequencies.

Recently, Raman experiments on the Cu-O chain compound $\mathrm{Ca}_{2-x}\mathrm{Sr}_x\mathrm{CuO}_3$ were performed,[39,40] in which, in addition to two allowed peaks at 306 and 530 cm^{-1}, at least three Raman-forbidden peaks at 440, 500, and 690 cm^{-1} were found. In Refs. 41 and 42, a simple one-dimensional model was proposed, which explains the appearance of the forbidden peaks as a consequence of a superstructure resulting from electron-phonon coupling. The Hamiltonian (23) was used as a model Hamiltonian describing CuO_3 chains. Within a simple tight-binding approach the chains were modeled by a two-band Hamiltonian using the antibonding orbitals of the CuO_2 "molecules" (M monomers) and the p_y orbital of the bridging oxygen (A monomers). The strong interaction (hybridization) between CuO_2 molecules and chain oxygens is fully taken into account diagonalizing the electronic part of the Hamiltonian. The Raman-active totally symmetric bond-stretching vibration of the CuO_2 unit can be regarded as an internal mode strongly coupled to the chain electrons. Using suitable values of spring constants and couplings, a good quantitative description of Raman- and infrared-active vibrations was obtained.[41,42] In particular, the existence of forbidden vibrational modes was explained as a consequence of the doubling of the unit cell due to the Peierls distortion. The parameters used are as follows: $\Delta\varepsilon=1.23$ eV, $t_0=1.4$ eV, $\gamma\equiv\tilde{\gamma}^2/Kt_0=0.8$, $\kappa\equiv\tilde{\kappa}^2/Ft_0=0.4, K=18$ eV/Å^2, $F=8.5$ eV/Å^2. With these parameters, one obtains the amplitude of internal distortion $U_0=0.15$ Å and that of the lattice distortion of bridging oxygens $u_0=0.14$ Å. The dispersion curves of this system calculated in the present work are shown in Fig. 4. Here, as usual, the dashed lines are the bare dispersions (i.e., the dispersions in the absence of the electron-phonon coupling). The doubly degenerate internal vibration has a frequency of 538 cm^{-1} and is placed in a gap between high- and low-frequency translational branches (corresponding to vibrations of light O atoms and heavy CuO_2 molecules, respectively). The change of the ground-state geometry due to the electron-phonon coupling results in a mixing of internal and lattice vibrational modes. The degeneracies of the phonon modes at the end of the Brillouin zone are removed. All the phonon frequencies are now softened, with the most pronounced effect for the $q=0$ lattice vibration of CuO_2 units, whose frequency decreases from 319 to 135 cm^{-1} (see Fig. 4). We suppose that this vibration is, as for the system studied in Sec. III B, an analog of the phase mode in systems without internal degrees of freedom. Strong softening of this mode indicates an existence of another ground-state geometry, which becomes the true energy minimum for a system with a slightly changed Hamiltonian (see the Discussion).

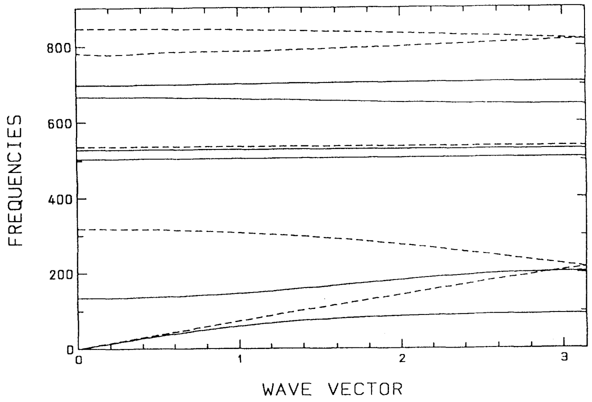

FIG. 4. Phonon-dispersion curves of quarter-filled alternating system with internal degrees of freedom. The frequencies are in cm^{-1}. Values of force constants and couplings are chosen so as to fit experimental data on Raman and infrared scattering in $\mathrm{Ca}_2\mathrm{CuO}_3$ (see text). Dashed lines show the phonon dispersions without electron-phonon interaction taken into account.

IV. DISCUSSION

Phonon frequencies are a suitable tool for studying Peierls systems, because the onset of instability manifests itself in that one of the optical-phonon frequencies goes to 0. For systems with only one degree of freedom, such an instability takes place at a finite temperature T_P, leading to the appearance of the Peierls superstructure and reduction of the first Brillouin zone (see, e.g., Ref. 33). For $T<T_P$, the optical frequencies remain finite at any values of the coupling constant and the Peierls instability results in a softening of the corresponding vibrational mode and in a positive sign of its second derivative with respect to the wave vector: $\partial^2\omega/\partial q^2 \geq 0$. This effect increases with decreasing electron-phonon coupling constant, and in the limit $\gamma \rightarrow 0$, the frequency of the $q=0$ optical phonon also goes to 0.[33,36] For systems with both internal and lattice degrees of freedom the situation is quite different, however. There the Peierls transition can take place at finite values of the coupling constants and at $T=0$, being thus a transition between various possible ways of dimerization. An example of such a system is the half-filled homogeneous system (Sec. III B). We have seen that when the system continuously changes from one region in the (κ,γ)-phase diagram to another, one of its phonon frequencies goes to 0. If the phonon frequencies were calculated for a wrong ground-state geometry, at least one of the vibrations would have an imaginary frequency, pointing out at instability of the system. Thus, the method presented in the paper can be used for a search of a true ground-state geometry of a Peierls system with many degrees of freedom.

Another point to be noticed is the fact that in systems with both internal and lattice degrees of freedom those vibrational modes are mostly softened which are not involved in the Peierls distortion. Examples are the systems presented in Secs. III B and III C. As already pointed out in Sec. III B, the softening of the phonon mode which is not dimerized shows that this mode can be dimerized by a relatively small change of the coupling constants. An analogous situation is encountered, in fact, for the alternating system of Sec. III C. To check this, let us turn for a moment to a slightly more complicated system consisting of two different monomers, each of which possesses internal degrees of freedom (moleculelike monomers). Denoting the monomers M_1 and M_2, their on-site energies are now given by

$$\begin{aligned} \varepsilon_n &= \frac{\Delta\varepsilon}{2} + \tilde{\kappa}_1 U_n, \quad n \in M_1 , \\ \varepsilon_n &= -\frac{\Delta\varepsilon}{2} + \tilde{\kappa}_2 U_n, \quad n \in M_2 , \end{aligned} \tag{25}$$

instead of (24). It is easily seen that if $\tilde{\kappa}_2 \rightarrow 0$, the present system transforms itself into the alternating system studied in Sec. III C, i.e., only the M_1 monomers are subject to the internal distortion. Now, starting from the point in the $(\tilde{\kappa}_1,\tilde{\kappa}_2)$ space where $\tilde{\kappa}_1 \gg \tilde{\kappa}_2$ and moving our system toward the point with $\tilde{\kappa}_1 \ll \tilde{\kappa}_2$, we will finally arrive at the situation where only the M_2 monomers will be distorted. In the limit $\tilde{\kappa}_1 \rightarrow 0$, we will again arrive at the system studied in III C, with atom- and moleculelike monomers changing their places. Thus, somewhere in the $(\tilde{\kappa}_1,\tilde{\kappa}_2)$-parameter space there is a phase transition between two ground-state geometries in which either M_1 or M_2 monomers are distorted. The lattice distortions in these ground-state geometries are taking place either at M_2 or at M_1 monomers, respectively. Under these circumstances, one should await that in the phase where the M_1 monomers are internally distorted and the M_2 monomers are subject to the lattice distortions, the vibrational mode consisting of lattice vibrations of M_1 monomers and internal vibrations of M_2 monomers would be strongly softened, indicating a possibility of the phase transition. In the system studied in III C, we have exactly this case, with the only difference that the M_2 monomers do not possess internal degrees of freedom ($\tilde{\kappa}_2=0$), so that the soft mode is the lattice vibration of M_1 monomers (CuO_2 units) only. Like in the case of half-filled homogeneous system, relatively small softening of phonon modes involved in the actual Peierls distortion also takes place.

Finally, let us turn to the problem of approximation of the phonon frequencies by force-constant models. In such models, one usually supposes a rapidly decreasing dependence of the force constants on the intermonomer distance, so that one takes into account an interaction between nearest and next-nearest neighbors only, neglecting the force constants for more than two intermonomer distances. Besides, a monotonous dependence of the force constants on distance is supposed. It is easy to check that it is not the case for Peierls-distorted systems. Already in Ref. 36 it was mentioned that there is an oscillating behavior of the force constants between the monomers as a function of distance. We have shown in Sec. II that the force constants resulting from the electron-phonon interaction (band force constants) can be obtained in a calculation with large enough unit cell. In order to investigate the dependence of the force constants on the distance between monomers and on the electron-lattice coupling constant, we performed the corresponding calculations for the half-filled system without internal degrees of freedom (15) and (16). The parameters of the Hamiltonian were those used by Su, Schrieffer, and Heeger in their model of $(CH)_x$:[2] $t_0=2.5$ eV, $K=21$ eV/Å^2. For the coupling constant $\tilde{\gamma}=4.1$ eV/Å, the equilibrium distortion is 0.08 Å. In Fig. 5, the calculated values of the band force constants for a number of coupling constants $\tilde{\gamma}$ are presented. Note that the total force constants are a sum of band and elastic force constants, so that the band force constants alone do not provide stability of the chain. The constants with negative values are those between the first monomer in the 0th unit cell and the first monomer in the lth unit cell: $F_{\text{band}}(0,1;l,1)$, the number l is given at the abscissa. The force constants $F_{\text{band}}(0,1;l,2)$, i.e., the constants between the monomers distorted in opposite directions, have positive values. One can note the oscillating behavior of the force constants, in agreement with Ref. 36. Though the absolute value of $F_{\text{band}}(0,1;l,i)$ decreases with increasing l, it is clear that only with the force constants between the nearest neighbors one cannot satisfactorily describe the

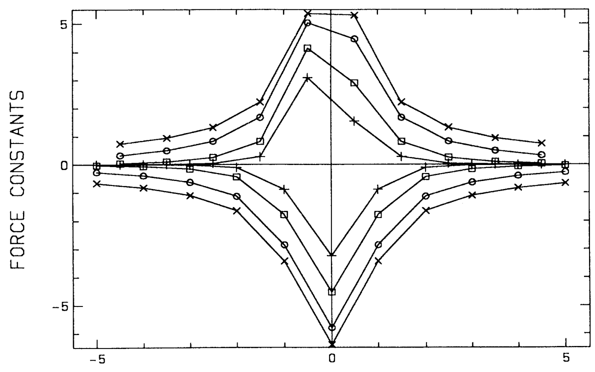

FIG. 5. Band force constants $F_{\text{band}}(0,1;l,j)$ (arbitrary units) for the half-filled system without internal degrees of freedom. At the abscissa, the number l of the unit cell is given. The constants with negative and positive values are those for $j=1$ and $j=2$, respectively. The values of the electron-lattice coupling constants are as follows: $\tilde{\gamma}=4.92$ eV/Å (+), 4.1 eV/Å (□), 3.28 eV/Å (○), 2.46 eV/Å (×). Other parameters of the Hamiltonian are given in the text.

phonon spectrum except for large values of $\tilde{\gamma}$. With decreasing $\tilde{\gamma}$, the band force constants decrease with distance more and more slowly, until in the limit $\tilde{\gamma}\rightarrow 0$, which corresponds, for the system under consideration, to a point of Peierls transition, the force constants do not depend on the distance between the monomers. In order to check how realistic is the force-constant model for the present system, we calculated vibrational frequencies in the $q=0$ and $q=\pi$ points, using only the elastic and band force constants between the nearest neighbors. The results are compared with the exact results in Table I. At $q=\pi$, where the electron-phonon interaction only slightly influences the phonon frequencies [see Fig. 1(a)], the difference is small and almost does not depend on $\tilde{\gamma}$. However, for the soft mode at $q=0$ the difference increases drastically with decreasing $\tilde{\gamma}$ and dimerization amplitude. Thus, we can conclude that the force-constant models can be applied to the systems with electron-phonon interaction only if these systems are far enough from the Peierls transition.

TABLE I. Vibrational frequencies (in cm^{-1}) of the half-filled system without internal degrees of freedom: a comparison of exact results (1) and results obtained when only elastic and band force constants between the nearest neighbors are taken into account (2). For each value of the electron-lattice coupling constant $\tilde{\gamma}$, an equilibrium dimerization amplitude d is given.

$\tilde{\gamma}$, eV/Å	d, Å	ω_{opt}, $q=0$ 1	2	ω_{acoust}, $q=\pi$ 1	2	ω_{opt}, $q=\pi$ 1	2
2.46	0.0016	508	1188	920	865	921	866
3.28	0.0243	676	1099	895	806	918	831
4.10	0.0793	829	1052	848	745	926	833
4.92	0.1489	951	1059	789	701	934	861

V. CONCLUSIONS

The approach to the phonon properties of Peierls-distorted systems with internal degrees of freedom developed in the present paper is based on a calculation of the total energy of a system for a number of distorted geometries. Then, one obtains the second derivatives of energy with respect to distortions and the dynamical matrix. Such an approach may be considered as an extension of the frozen-phonon method. The latter was already used for investigation of a number of materials, including high-temperature superconductors (see, e.g., the review[43]). However, only selected vibrational modes were studied, as a rule, for the wave vector $q=0$. We have presented a complete scheme for calculation of dynamical matrix, force constants, phonon eigenfrequencies, and eigenvectors in the whole Brillouin zone for systems with arbitrarily strong electron-phonon interaction. The method may be also used for Hamiltonians with electron-electron interaction taken into account; besides, the method is not restricted to model Hamiltonians and may be applied to realistic systems if their total energy can be calculated with sufficient precision. In the present paper, we restricted ourselves to a comprehensive treatment of a number of systems with pure Peierls Hamiltonian, in which both internal and lattice distortions interact with the electrons. It was shown that an interplay between internal and lattice coupling constants which results for the half-filled homogeneous system in a number of ground-state geometries reflects itself also in the phonon properties of the system. The soft mode is a lattice or internal vibration, or a mixing of both types, depending on the values of the coupling constants. The frequency of the soft mode becomes 0 at the point where the transition between different ground-state geometries takes place. This is in contrast to well studied Peierls systems with only one degree of freedom, in which the soft mode goes to 0 only in the limit of infinitely small coupling constant.

For both homogeneous and alternating systems it was found that the most strongly softened mode is that one which is not involved in the Peierls transition. The existence of such a mode indicates a possible change in the ground-state geometry of the system if the coupling constants are changed (see the Discussion). For all the systems and all the values of coupling constants studied, the softening of the actually distorted mode was substantially lower than that of the nondistorted mode. Certainly, the interrelation between the softenings should be an object of further investigations.

The method presented, being a general one, can be applied to systems with various numbers of monomers in the unit cell and various types of monomers, various filling ratios, etc. Of particular interest here is a possibility to investigate nonlinear excitations in one-dimensional systems, such as solitons and polarons. As mentioned in Sec. IV, the phonon frequencies can be used for a search of the true ground state of a system. Then, vibrations in the vicinity of an excitation can be investigated. For example, a polaron can be simulated as an extra charge, i.e., as a system with a filling ratio slightly more (or less) than

1/2. Obviously, the size of the unit cell must be taken large enough to make the interaction between neighboring defects as small as possible.

Finally, let us note that further investigations should be directed not only towards new systems or new types of elementary excitations, but also towards a deeper understanding of relatively simple systems and an improvement of the method. In that way, it is necessary to take into account in the Hamiltonian terms describing electron-electron interactions as well as possible nonadiabatic effects.

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