

Grand canonical Peierls transition in In/Si(111)

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Starting from a Su-Schrieffer-Heeger-like model inferred from first-principles simulations, we show that the metal-insulator transition in In/Si(111) is a first-order grand canonical Peierls transition in which the substrate acts as an electron reservoir for the wires. This model explains naturally the existence of a metastable metallic phase over a wide temperature range below the critical temperature and the sensitivity of the transition to doping. Raman scattering experiments corroborate the softening of the two Peierls deformation modes close to the transition.

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A Peierls-like transition in indium wires on the Si(111) surface was first reported 16 years ago [1]. Since then this transition has been studied extensively [2–21], both experimentally and theoretically. The occurrence of both a metal-insulator transition around $T_c = 130$ K and a structural transition of the In wires from a 4×1 structure at room temperature to a 8×2 structure at low temperature are well established. Yet, the nature of the transition is still poorly understood and the relevance of the Peierls theory remains controversial [8,9,11,12,14,19,22].

The generic theory of Peierls systems is essentially based on effective models for the low-energy degrees of freedom in purely one-dimensional (1D) or strongly anisotropic three-dimensional (3D) crystals, such as the Ginzburg-Landau theory of 1D charge-density waves (CDW) [23] or the Su-Schrieffer-Heeger (SSH) model for conjugated polymers [24–28]. Hitherto it has been used without adaptation to discuss the relevance of the Peierls physics for experiments and first-principles simulations in In/Si(111). Thus a fundamental issue with previous interpretations based on these generic theories is that they do not consider how the 3D substrate affects the Peierls physics in a 1D atomic wire.

In this Rapid Communication, we investigate the phase transition in In/Si(111) theoretically using first-principles simulations and 1D model calculations, and experimentally with Raman spectroscopy. We show that it can be interpreted as a grand canonical Peierls transition, in which the substrate acts as a charge reservoir for the wire subsystem. The two Peierls distortion modes are essentially made of shear and rotary modes. The main difference with the usual (i.e., canonical) Peierls theory is that in the grand canonical theory the high-temperature phase can remain thermodynamically metastable below the critical temperature T_c and that the phase transition can become first order. This agrees with the interpretation of recent experiments and first-principles simulations in In/Si(111) [16–18,20,21].

First, we construct an effective 1D model for In/Si(111) in the spirit of the SSH model [24–27]. Our goal is a qualitative description of the phenomena with reasonable order

of magnitudes for physical quantities because we think that a quantitative description of this complex material can only be achieved with first-principles simulations [29]. For the same reason, we neglect correlation effects [27,28,30,31]. The accepted structural model for the uniform phase (i.e., the 4×1 phase) consists of parallel pairs of zigzag indium chains [32,33]. We consider a single wire made of four parallel chains of indium atoms arranged on a triangular lattice as shown in Fig. 1. One (Wannier) orbital per indium atom is taken into account, yielding four bands in the uniform phase. Density-functional theory (DFT) calculations actually show four bands corresponding to indium-related surface states [34]. Other electronic degrees of freedom, e.g., in the substrate, are not considered explicitly.

We use a tight-binding Hamiltonian model for the electronic degrees of freedom and assume that the only relevant hopping terms are between nearest-neighbor sites, i.e.,

$$H = \sum_{i,\sigma} \epsilon_i c_{i\sigma}^\dagger c_{i\sigma} - \sum_{\langle i,j \rangle, \sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}), \quad (1)$$

where the indices i, j number the indium atoms, $\sigma = \uparrow, \downarrow$ designs the electron spin, the second sum runs over every pair $\langle i, j \rangle$ of nearest-neighbor sites, and the operator $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) creates (annihilates) an electron with spin σ on site i . In the uniform phase the Hamiltonian is translationally invariant and the single-electron dispersions can be calculated analytically [29]. Thus we can determine parameters ϵ_i and t_{ij} to mimic the DFT band structure [17,34] shown in Fig. 2(a).

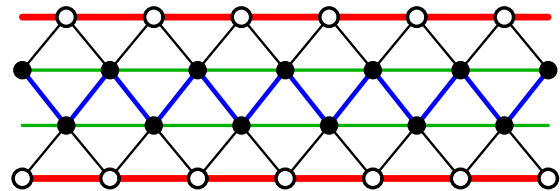


FIG. 1. 1D lattice model for an indium wire in the uniform configuration. Open and full circles represent outer and inner In atoms, respectively. The line widths are proportional to the hopping terms t_{ij} . The blue and red bonds define the central zigzag chain and the two outer linear chains, respectively.

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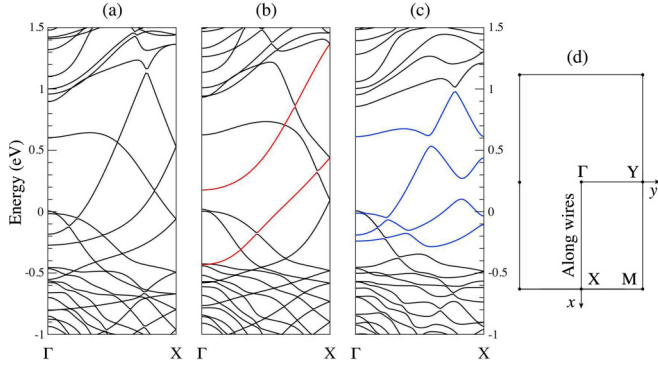


FIG. 2. DFT-LDA electronic band structure of In/Si(111) (a) in the 4×1 phase, (b) after a shear distortion, and (c) after a rotary distortion in the surface Brillouin zone of the 4×2 configuration shown in panel (d). Gaps (b) open at Γ between two red bands and (c) close to X between four blue bands.

We obtain three metallic bands and one full band if we assume that the 1D system is close to half filling (i.e., one electron per orbital on average).

The strength of the hopping terms t_{ij} is shown in Fig. 1. Clearly, the apparent structures are a central zigzag chain and two outer linear chains. The bond order (electronic density in the bonds between atoms) exhibits a similar structure [29]. This is quite different from the usual representation of the 4×1 configuration by two zigzag chains. Our effective 1D model focuses on the metallic bands and thus reveals the bonds responsible for the Peierls instability.

In the hexamer structural model for the low-temperature phase, the deformation from the uniform to the dimerized (i.e., 8×2 or 4×2) phase corresponds essentially to the superposition of two rotary and one shear modes [8,9,11,15,17]. Therefore, we investigate the changes in the lattice structure, electronic band structure, and electronic density caused by each mode separately using first-principles frozen-phonon and deformation-potential calculations based on DFT within the local density approximation (LDA). The technical details correspond to earlier calculations by some of the present authors [14,17]. A very recent hybrid DFT calculation [22] largely agrees with the DFT-LDA results presented here. We use distortion amplitudes close to the ones necessary to transform the zigzag structure into the hexagon structure. The predicted vibration modes agree well with Raman spectroscopy measurements presented here and in previous works [4,12,15].

This study reveals, on the one hand, that the main effects of the shear distortion are to dimerize the central zigzag chain, as shown by the alternating density and bond lengths between inner In atoms in Fig. 3(a), and to open or enlarge a gap between two metallic bands close to the Γ point as seen in Fig. 2(b). On the other hand, the main effects of the rotary modes are to dimerize the outer chains, as shown by the alternating density and bond lengths between outer atoms in Fig. 3(b), and to open a gap between two metallic bands close to the X point, as seen in Fig. 2(c). These results confirm the central role of the structures seen in Fig. 1 (i.e., one inner zigzag chain and two outer linear chains) in the transition of In/Si(111). Moreover, the negligible length and density variation for the

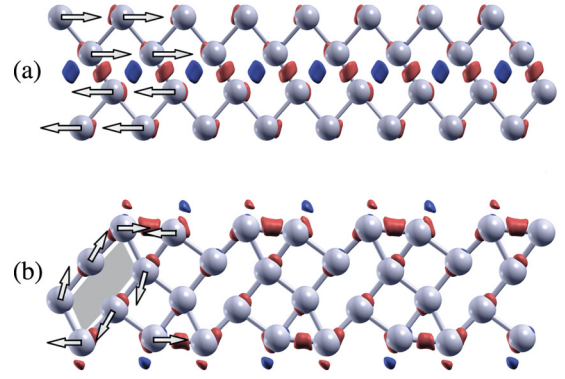


FIG. 3. Changes in the DFT-LDA electronic densities (red for an increase, blue for a reduction) with respect to the 4×1 phase caused by (a) a shear distortion and (b) a rotary distortion. The isosurfaces for density changes $\pm 0.02 \text{ e}\text{\AA}^{-3}$ are shown. Arrows show the atom displacements for both distortion modes.

bonds between inner and outer indium atoms in first-principles calculations, both for shear and rotation distortions, confirm that they are very strong covalent bonds and do not play any direct role in the transition.

The SSH model [24–27] is the standard model for the CDW on bonds caused by a Peierls distortion seen in Fig. 3. The bond length changes determined with first-principles methods can also be used to determine the hopping terms of the 1D model (1) for distorted lattice configurations. For this purpose, we assume that the hopping term between two orbitals i and j depends only on the distance d_{ij} between both atoms and choose the exponential form [35,36]

$$t_{ij}(d_{ij}) = t_{ij} \exp[-\alpha_{ij}(d_{ij} - d_{ij}^0)], \quad (2)$$

where t_{ij} and d_{ij}^0 are the hopping terms and bond lengths in the uniform configuration. Using reasonable values for the electron-lattice couplings $t_{ij}\alpha_{ij}$ (i.e., α_{ij}^{-1} is of the order of the covalent radius of an In atom), we find a qualitative agreement between first-principles and 1D model predictions for the changes in the band structure and density caused by shear and rotary modes [29].

The mechanism of the Peierls transition can be understood even better by focusing on the main features of the 1D model. Keeping only the most important hopping terms (thick lines in Fig. 1) and couplings to lattice distortions, the 1D model decouples into three independent chains with SSH-type Hamiltonians [24–27] and electron-lattice couplings (2): the inner zigzag chain, which couples only to the shear mode, and two identical outer linear chains, which couple only to one of the two rotary modes each. To complete the SSH-type Hamiltonians we add an elastic potential energy for the lattice deformation. The free energy of each chain ($l = 1, 2, 3$) is then given by

$$F_l(x_l) = F_l^e(x_l) + \frac{K_l}{2} x_l^2, \quad (3)$$

where F_l^e is the electronic free energy [23]. Within this mean-field and semiclassical approach, the stable configurations are given by the minima of the total free energy $F = \sum_l F_l$ of the 1D model with respect to the amplitudes x_l of the

three independent distortion modes. The bare elastic constants K_l can be estimated using the distortion amplitudes x_l necessary to form the hexamer structure in first-principles calculations [29].

This generalization of the SSH model includes more degrees of freedom than the generalized SSH model used very recently to investigate chiral solitons in indium wires [37]. Yet the model of Ref. [37] corresponds essentially to the restriction of our model to outer chains and rotary distortions. Furthermore, the model parameters found in Ref. [37] also agree quantitatively with our parameters for outer chains and rotary distortions [29]. In Ref. [22] Kim and Cho compare their DFT results to the two-chain SSH model of Ref. [37] and conclude that the transition in In/Si(111) is not a Peierls transition. However, their DFT results seem to agree largely with our three-chain SSH model and thus support the Peierls transition scenario presented here.

We can now analyze the 1D model in the mean-field approximation using known results for one-band-one-mode SSH-type models [24–27]. At half filling the outer chains have Fermi wave number $k_F = \pi/2$ and thus are unstable with respect to rotary distortions with the nesting wave number $Q = 2k_F = \pi$ [corresponding to the X point of the Brillouin zone in the 4×1 configuration of In/Si(111)]. As the zigzag chain has two orbitals per unit cell, its Fermi wave number is $k_F = \pi$ and thus it is unstable against a shear distortion with the nesting wave number $Q = 2k_F = 2\pi$ (corresponding to the Γ point). Therefore, if the system is exactly half filled, the twofold degenerate ground state of each chain is a band insulator with a dimerized lattice structure. The corresponding theoretical collective vibrational modes agree with the Raman spectroscopy results presented below.

This corresponds to an eightfold degenerate and insulating phase in the full 1D model. The neglected couplings between the three chains reduce the Peierls deformation modes to two linear combinations of the shear and rotary modes and the degeneracy to four states corresponding to the four hexamer structures of the 4×2 phase. The Peierls gap in the electronic band of the inner chain is at $k = 0$ while Peierls gaps for the outer chains are at $k = \pi/2$ (i.e., the X point of the 4×2 configuration). Typically, the electronic gap of the full 1D model is indirect and smaller than the Peierls gaps. Thus there is no obvious relation between critical temperature and electronic gap in this many-band Peierls system. The structural transition to the high-temperature uniform phase is continuous but may exhibit distinct critical temperatures for shear and rotary modes. The metal-insulator transition occurs at the lowest one.

This conventional Peierls scenario assumes a fixed band filling. The low-temperature insulating electronic structures found in DFT computations [8,17,34] correspond to half filling in the 1D model (1). However, for substrate-stabilized atomic chains, the electron chemical potential μ is determined by the substrate and may be modified by temperature and adatoms [38–40]. Therefore, we must investigate the 1D model in the grand canonical ensemble with μ set by an external electron reservoir, i.e., the rest of the In/Si(111) system. Focusing again on the decoupled 1D model, the free energies (3) are replaced by corresponding grand canonical potentials ϕ_l and ϕ .

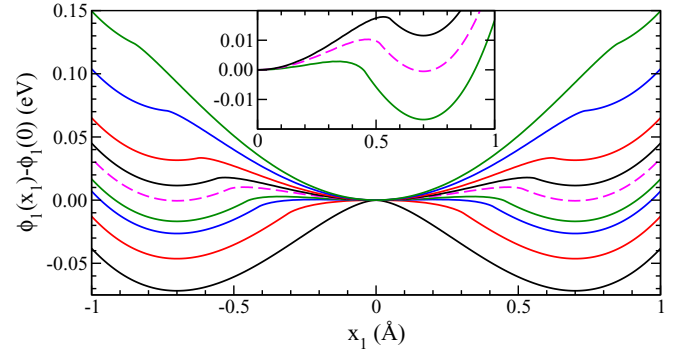


FIG. 4. Grand canonical potential ϕ_l of the inner zigzag chain as a function of the amplitude of the shear distortion x_1 at low temperature for several values of the chemical potential μ from the middle of the gap (bottom) to the band edge (top). The dashed line corresponds to the critical μ_c between dimerized and uniform phases. Inset: Enlarged view close to μ_c . The shift of μ between upper and lower bands corresponds to 7% of the Peierls gap.

We find that the grand canonical Peierls physics is much richer than the canonical one. Figure 4 shows the grand canonical potential of the inner chain at very low temperature as a function of the distortion amplitude for several values of μ . If μ lies at or close to the middle of the Peierls gap, we see the usual double well, indicating a stable and doubly degenerate dimerized state. When μ deviates slightly from the middle of the gap, a local minimum appears at $x = 0$ indicating that the uniform state is metastable. This case agrees qualitatively with the energetics of the phase transition in In/Si(111) calculated from first principles [18]. When μ moves even further toward the band edge, the uniform state becomes thermodynamically stable while two local minima for $x \neq 0$ show that the dimerized states are metastable. Finally, when μ approaches the band edge, we find a single-well potential, indicating that the Peierls instability is suppressed. The variation of the grand canonical potential with μ explains the sensitivity of the transition in indium wires to chemical doping [21,38–41] and to optical excitations [18,41]. In particular, the observation that the uniform phase is stabilized in n -doped samples [21,41] as well as by alkali-adsorption-induced charge transfer [38,39] is naturally explained by the occurrence of a metastable uniform state in the grand canonical potential in Fig. 4.

If the temperature is raised without varying μ , the grand canonical potential changes its shape progressively into a single well but the uniform and dimerized states never exchange their relative energy positions [29]. Therefore, if we assume that μ deviates slightly from the middle of the gap, the uniform state is metastable at low temperature but the structural transition remains continuous as in the canonical ensemble. Yet the actual electronic gap closes when one of the band edges reaches μ and thus the metal-insulator transition occurs discontinuously and at a lower temperature than the structural transition.

In the 1D model, however, μ represents the influence of the substrate and thus it is a function of temperature rather than an independent parameter. (Equivalently, the dependence of the electron number on μ could change with temperature [29].) Moreover, a small change in μ is sufficient to change the

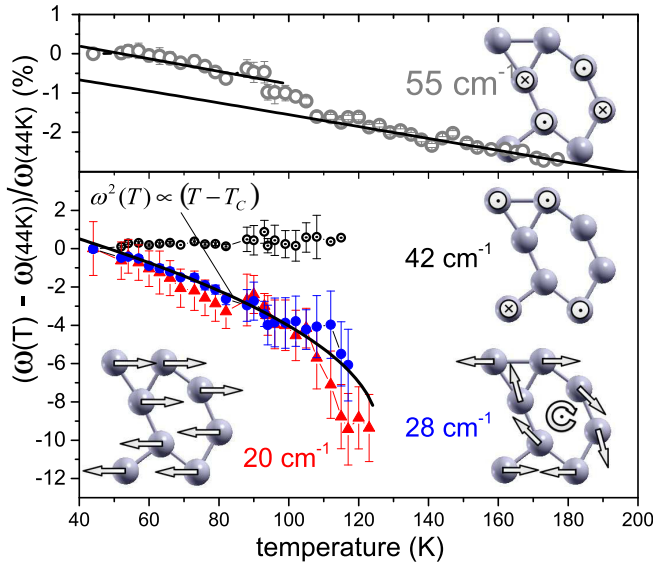


FIG. 5. Temperature dependence of the normalized frequencies of Raman modes and sketches of the assigned eigenmodes. The shear and rotary modes (red and blue symbols) at 20 and 28 cm^{-1} are Peierls amplitude modes and exhibit a significant softening, while the mode at 42 cm^{-1} (black symbols) remains at constant frequency and the one at 55 cm^{-1} (gray symbols) shows only a moderate decrease due to the lattice expansion.

shape of the grand canonical potential (see the inset of Fig. 4) and thus to cause a discontinuous transition [29]. This scenario is compatible with recent first-principles simulations and experiments [16–18,20,21]. Note that the dimerized configuration could be unstable toward the formation of domain walls (solitons) [37,42,43] but the study of spatial and thermal fluctuation effects is beyond the scope of this paper [26,27,30,31,44]. The finding of a first-order transition with a small reduction of the order parameter in the critical region (see Fig. 6 in Ref. [29]) justifies the neglect of fluctuations in first approximation.

The Peierls/CDW theory predicts the existence of collective excitations (amplitude modes) which are Raman active [23,45–47]. For the Peierls wave number Q their frequency vanishes as $\omega(T) \propto \sqrt{|T - T_c|}$ when approaching T_c in a continuous transition (phonon softening) [23,47]. As the Peierls amplitude modes in In/Si(111) are essentially the shear and rotary modes, they should appear in the Raman spectrum at the Γ point below T_c and show significant (but incomplete) softening close to the first-order transition [29].

Figure 5 shows the temperature dependence of the normalized frequencies of some Raman spectra resonances measured for In/Si(111). The resonances observed experimentally were

assigned to specific vibrational modes by comparison to first-principles computations [4,12,15]. Here we discuss the low-frequency modes at 20, 28, 42 cm^{-1} in the (8×2) phase and the 55 cm^{-1} mode observed for both phases, which all involve displacements of In atoms. The resonances at 20 and 28 cm^{-1} (as measured at 44 K) are assigned to the shear and rotary modes. They exhibit a partial phonon softening when approaching the phase transition temperature and vanish above it. The mode at 42 cm^{-1} , in contrast, is at constant frequency with temperature while the mode at 55 cm^{-1} exhibits only moderate temperature shift. These observations agree qualitatively with our theoretical analysis but not with an order-disorder transition [9,13]. The rotary and shear modes are strongly coupled to the CDW by the lateral displacements of the In atoms and show the expected softening for Peierls amplitude modes; however, this softening remains only partial because the transition is discontinuous. The 42 and 55 cm^{-1} modes, in contrast, are related to vertical displacements of In atoms. Hence they are weakly coupled to the in-plane CDW and display a behavior related to the lattice expansion with temperature increase. Remarkably, the 42 cm^{-1} mode shows no frequency shift at all, i.e., the lattice expansion is compensated for by a stiffening of the involved In bonds. The 55 cm^{-1} mode displays a side-effect drop in eigenfrequency at the phase transition.

In summary, we have shown that the transition observed in In/Si(111) is a grand canonical Peierls transition. We think that the ongoing controversy about the nature of this transition can be solved by interpreting experiments and first-principles simulations [2,3,5–10,13–21] within a grand canonical Peierls theory. In particular, it explains the observation of a metastable metallic phase at low temperature and the sensitivity of the critical temperature to the substrate doping. Grand canonical theories could explain other charge-donation-related phenomena in atomic wires such as the reversible structural transitions in Au/Si(553) upon electron injection [48,49]. The present work suggests that variations of the substrate-induced chemical potential (e.g., with temperature or upon doping) is a key mechanism for understanding the realization of quasi-1D physics in atomic wires.

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Supplemental Material for
Grand canonical Peierls transition in In/Si(111)

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I. ELECTRONIC STRUCTURE OF THE UNIFORM 1D MODEL

The 1D tight-binding Hamiltonian, Eq. (1) in the paper, can be diagonalized exactly if it is translationally invariant (i.e., in the uniform phase). The only model parameters are the two local potentials ϵ_I and ϵ_O on the inner and outer sites, respectively, as well as the four nearest-neighbor hopping terms t_O between outer sites (red bonds in Fig. 1 in the paper), t_{I1} (blue diagonal bonds) and t_{I2} (horizontal green bonds) between inner sites, and t_{IO} between inner and outer sites (black bonds). The single-electron eigenenergies are given by

$$\epsilon_{n,m}(k) = \frac{1}{2} [\epsilon_O + \epsilon_I - 2(t_O + t_{I2}) \cos(k) - 2nt_{I1} \cos(k/2)] + m \sqrt{\frac{1}{4} [\epsilon_O - \epsilon_I - 2(t_O - t_{I2}) \cos(k) + 2nt_{I1} \cos(k/2)]^2 + 4t_{IO}^2 \cos^2(k/2)} \quad (1)$$

with quantum numbers $n, m = \pm 1$ labeling the four bands and wave numbers $k \in (-\pi, \pi]$. Note that the wave number interval $[0, \pi]$ corresponds to the ΓX line in the Brillouin zone of the 4×1 configuration of In/Si(111) and that we set the lattice constant $a = 1$ in the 1D model (corresponding to $a = 3.84 \text{ \AA}$ for the 4×1 unit cell in the indium wire direction [1]).

We find that for appropriate model parameters ϵ_i and t_{ij} , these dispersions can mimic the DFT band structure [2–4], shown in Fig. 2(a) in the paper. For instance, Fig. 1(a) shows the dispersions for

$$\epsilon_O = 0.056 \quad (2a)$$

$$t_O = -0.419 \quad (2b)$$

$$\epsilon_I = 0.089 \quad (2c)$$

$$t_{I1} = 0.284 \quad (2d)$$

$$t_{I2} = -0.204 \quad (2e)$$

$$t_{IO} = 0.147 \quad (2f)$$

(all values in eV). In particular, we obtain three metallic bands and one full band if we assume that the uniform system is half filled (i.e., one electron per site on average). Note that this choice of parameters is not unique and thus it is not clear whether they are appropriate for a quantitative description of In/Si(111). All parameter values given here are only exemplary.

The bond order is defined by

$$P_{ij} = \frac{1}{2} \sum_{\sigma} \langle c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma} \rangle \quad (3)$$

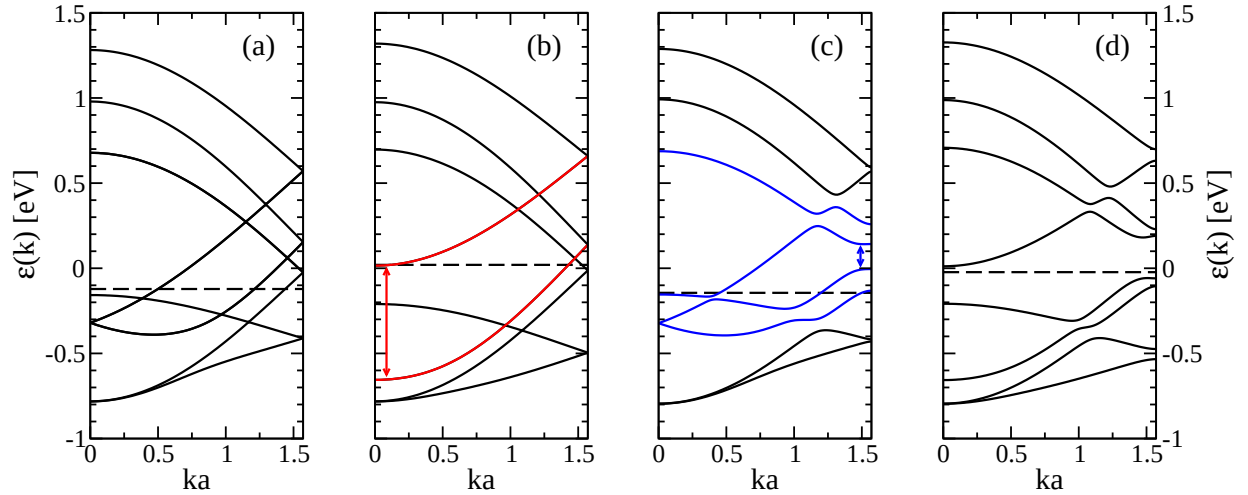


FIG. 1. Single-electron dispersions (a) in the uniform 1D model with the parameters (2), after (b) shear and (c) rotary distortions, and (d) in the dimerized configuration corresponding to the hexamer phase of In/Si(111). Peierls gaps are shown by arrows between the red bands at $k = 0$ in (b) and between the blue bands at $k \approx \pi/2$ in (c). We use the reduced Brillouin zone of the dimerized phase, $k \in [0, \pi/2]$, to facilitate the comparison with the DFT results in Fig. 2(a) in the paper. Horizontal lines show the Fermi energy at half filling.

where $\langle \dots \rangle$ represents the ground-state expectation value. This quantity is proportional to the electronic density in the bonds between atoms i and j . In Fig. 2 we show the nearest-neighbor bond orders obtained with the parameters (2). We see that they confirm the presence of three main electronic structures, a central zigzag chain and two outer linear chains, as observed for the hopping terms in Fig. 1 of the paper.

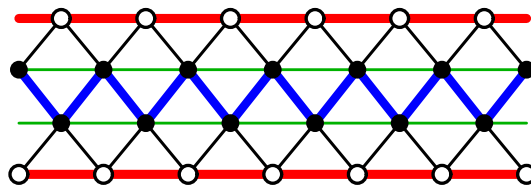


FIG. 2. Bond orders in the uniform 1D model with the parameters (2). The line widths are proportional to the bond orders and bond orders of the same color have the same value. Blue bonds define the inner zigzag chain while red bonds correspond to the two outer linear chains.

II. ELECTRONIC STRUCTURE OF THE DIMERIZED 1D MODEL

Assuming that the hopping terms t_{ij} depend on the bond lengths d_{ij} as in Eq. (2) of the paper and using the bond length changes $d_{ij} - d_{ij}^0$ determined from first principles, we can calculate the hopping terms for distorted lattice configurations. The single-electron dispersions can then be obtained by numerical diagonalization of the Hamiltonian matrix. This procedure allows us to examine changes in the band structure of the 1D model caused by the shear and rotary lattice distortions. We find an excellent qualitative agreement with the changes in the DFT band structures for reasonable parameters α_{ij} .

First, we notice that the shear distortion essentially induces alternating hopping terms t_{I1} in the central zigzag chain. For instance, we obtain $t_{I1} = 0.145$ eV and $t'_{I1} = 0.481$ eV with an electron-lattice coupling $\alpha_I = 1.4 \text{ \AA}^{-1}$ and the parameters (2). The electronic dispersions are shown in Fig. 1(b). We see that the main change is the opening of a gap between the two red bands at $k = 0$, which corresponds to the Γ point of the Brillouin zone in the 4×2 configuration of In/Si(111). This is similar to the changes observed in the DFT band structure in Fig. 2(b) of the paper. Similarly, the changes induced by the shear distortion in the bond orders of the 1D model in Fig. 3(a) agree well with the DFT density variations in Fig. 3(a) in the paper.

Second, we find that the rotary distortion essentially induces alternating hopping terms t_O between the outer sites. For instance, we obtain $t_O = -0.350$ eV and $t'_O = -0.501$ eV with $\alpha_O = 0.26 \text{ \AA}^{-1}$ and the parameters (2). The corresponding electronic bands are shown in Fig. 1(c). We see that the main change is the opening of gaps between the four blue bands close to $k = \pi/2$, which corresponds to the X point of the Brillouin zone in the 4×2

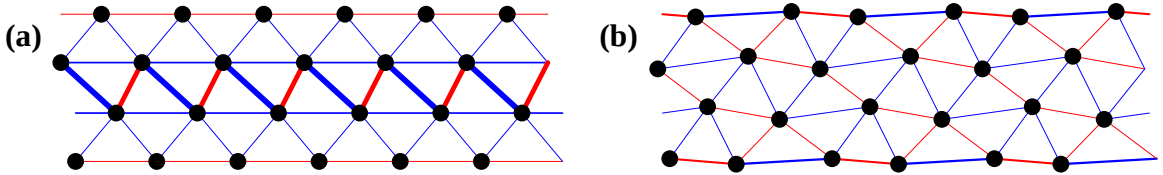


FIG. 3. Increase (red bonds) and decrease (blue bonds) of the bond orders in the 1D model caused by (a) a shear distortion and (b) both rotary distortions. The line widths are proportional to the bond order changes. The positions of the sites (circles) have been shifted according to the displacements calculated from first principles.

configuration of In/Si(111). Again, this is similar to the changes found in the DFT band structure in Fig. 2(c) of the paper. Likewise, the changes induced by the rotary modes in the bond orders of the 1D model in Fig. 3(b) agree well with the DFT density variations in Fig. 3(b) in the paper.

Both values for α_I and α_O appear to be realistic because they are of the order of the inverse of the covalent radius of an indium atom, 1.44 Å. In carbon-based Peierls systems, such as conjugated polymers, the electron-lattice coupling is known to be of the order of the inverse of the covalent radius of a C atom [5–7].

Additionally, Fig. 1(d) shows the band structure obtained in the 1D model for a dimerized lattice configuration combining both the shear and rotary modes and corresponding to the low-temperature hexamer phase of In/Si(111). Note that the electronic gap is indirect and substantially smaller than the actual Peierls gaps shown in Fig. 1 (b) and (c). Obviously, the relation $k_B T_P^{MF} \approx E_g/3.52$ [8] between the (mean-field) transition temperature T_P^{MF} and the gap E_g in a one-band/one-mode Peierls system does not apply to the indirect gap of In/Si(111). Finally, Fig. 4 shows the bond orders obtained in this dimerized configuration. The dimerization of central and outer chains is clearly visible. Although we can also recognize the so-called hexamers of the low-temperature phase of In/Si(111) [3, 9–11], they are not the most distinctive structure of the dimerized phase in the 1D model. As for the zigzag chains in the uniform phase, this apparent discrepancy occurs because the 1D model focuses on the bonds responsible for the Peierls instability.

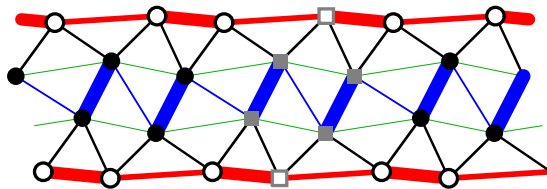


FIG. 4. Bond orders in the dimerized 1D model. The line widths are proportional to the bond orders. The blue and red bonds show the central zigzag and the two outer linear chains, respectively. The sites have been shifted according to the displacements calculated from first principles. Gray squares outline one hexamer.

III. PARAMETRIZATION OF SSH-TYPE MODELS

To specify complete SSH-type models [5–7, 12–14] for the three chains of the 1D model (one central zigzag chain and two outer linear chains seen in Fig. 2) within the approximation of uncoupled chains, we first define classical variables x_l representing the amplitudes of the shear and rotary distortions. We choose x_1 to be the displacement of the inner In atoms in the wire direction caused by the shear mode and $x_{2,3}$ to be the bond length changes between nearest-neighbor outer atoms caused by each rotary mode. The hopping terms are then given by

$$t_{I1}(x_1) = t_{I1} \exp(-0.613\alpha_I x_1) \quad (4)$$

for the zigzag chain (with a geometric factor of 0.613 due to the angle between these bonds and the wire direction) and

$$t_O(x_l) = t_O \exp(-\alpha_O x_l) \quad (5)$$

for the outer chains $l = 2, 3$.

In the canonical ensemble, the stable dimerized configurations are given by the conditions

$$\frac{dF_l}{dx_l} = \frac{dF_l^e}{dx_l} + K_l x_l = 0. \quad (6)$$

At zero temperature, the electronic energies F_l^e and their derivatives can be easily calculated numerically from the single-electron eigenenergies. The equilibrium distortion amplitudes obtained in first-principles simulations at very low temperature correspond to $x_l \approx 0.7 \text{ \AA}$ with our parametrization. Assuming half filling and using the parameters (2) and the electron-lattice couplings given above, we find bare elastic constants $K_1 = 0.768 \text{ eV\AA}^{-2}$ for the shear mode and $K_2 = K_3 = 0.101 \text{ eV\AA}^{-2}$ for each rotary mode. These values seem reasonable because they yield dimensionless SSH electron-phonon couplings [7, 14] $\lambda_1 = \frac{4(0.631\alpha_1)^2 |t_{I1}|}{\pi K_1} = 0.37$ (a factor 2 comes from the two sites per unit cell in the zigzag chain) and $\lambda_l = \frac{2\alpha_l^2 |t_O|}{\pi K_l} = 0.18$ for $l = 2, 3$. Therefore, the electron-lattice coupling in the zigzag chain appears to be stronger than in polyacetylene ($\lambda = 0.2$) while it is comparable in the outer chains [7, 14]. This difference between the coupling strengths is also illustrated by the stronger charge density waves in inner chains than in outer chains in Fig. 3 as well as in Fig. 3 in the paper. Note that the elastic constants calculated from first principles or determined experimentally (e.g., from the vibration spectrum) are the eigenvalues of the

force matrix

$$K_{ll'}^* = \frac{\partial^2 F}{\partial x_l \partial x_{l'}} \quad (7)$$

if one assumes an isotropic mass tensor. They coincide with the model parameters K_l in the high-temperature limit $T \rightarrow \infty$ only.

A SSH model for two coupled chains has recently been proposed to describe chiral solitons in In/Si(111) [15]. This generalization of the SSH model corresponds essentially to the restriction of our model to outer chains and rotary distortions only. Therefore, the model parameters should be comparable. Indeed, in the Supplementary Materials for Ref. [15], the hopping term between outer indium atoms is found to be $t_0 = 0.4$ eV, which agrees very well with our results $|t_O| = 0.419$ eV in Eq. (2). Although their spring constant $K = 0.55$ eV/Å² [16] and electron-phonon coupling $\alpha = 0.28$ eV/Å cannot be compared directly to our model parameters due to different definitions, the resulting dimensionless SSH electron-phonon coupling $\lambda = \frac{2\alpha^2}{\pi K t_0} = 0.23$ is independent of these conventions and we find that it also agrees very well with our value $\lambda_{2,3} = 0.18$. This excellent agreement supports the validity of our generalized SSH model.

IV. GRAND CANONICAL TRANSITION

For a non-interacting electron model like our 1D model, the grand canonical potential can be easily calculated from the single-electron eigenenergies. Figure 4 in the paper shows the grand canonical potential ϕ_1 of the SSH-type model for the uncoupled zigzag chain as a function of the shear distortion amplitude x_1 for several values of the chemical potential μ . We use the model parameters presented above and a very low temperature $T = 1$ K. The Peierls gap for zero temperature and half filling is $E_g \approx 0.67$ eV. The chemical potential varies from the middle of the gap ($\mu = \epsilon_I$) to slightly inside the conduction band ($\mu = \epsilon_I + 0.4$ eV.). There is a first-order transition from the dimerized to the uniform phase at the critical chemical potential $\mu_c \approx \epsilon_I + 0.25$ eV.

Figure 5 shows the grand canonical potential ϕ_1 of the same system for several temperatures but a fixed chemical potential $\mu = \epsilon_I + 0.22$ eV, which yields a metastable uniform configuration at low temperature. If the temperature is raised and μ is kept constant, we find that this metastable configuration first vanishes around 800 K but that a continuous structural transition from the dimerized configuration to the uniform configuration occurs around

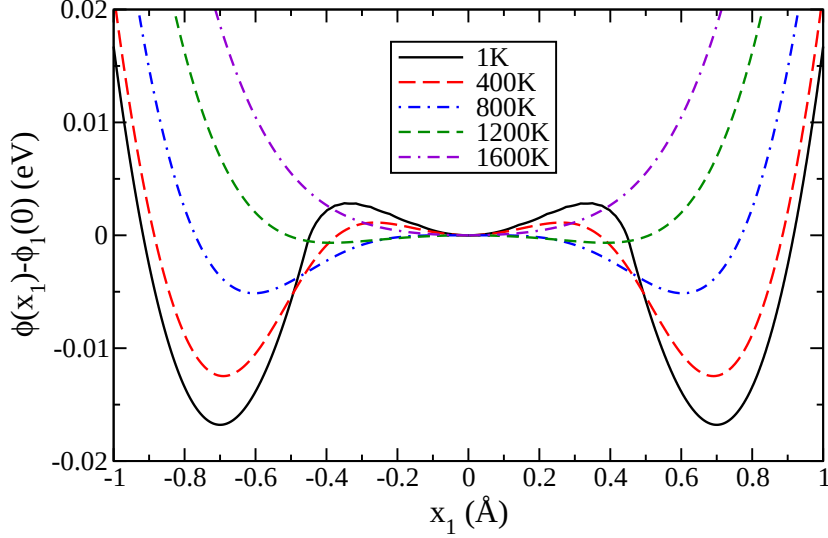


FIG. 5. Grand potential of the SSH-type model as a function of the lattice distortion amplitude for several temperatures. The model parameters correspond to the central zigzag chain coupled to the shear mode. The chemical potential $\mu = \epsilon_I + 0.22$ eV is chosen so that the uniform state is metastable at low temperature.

1400K. However, a first-order metal-insulator transition takes place at a lower temperature $T \approx 1100$ K. Indeed, as the Peierls band gap diminishes with increasing temperature, the lower edge of the conduction band drops down until it reaches μ , causing a sudden vanishing of the electronic gap. It should be kept in mind that all temperatures given here are calculated within a mean-field approximation and that in quasi-1D systems thermal fluctuations and inter-chain interactions can modify the temperature scales significantly [8, 17–19].

To obtain a first-order transition from a low-temperature dimerized configuration to a high-temperature uniform configuration, we can assume that the chemical potential induced by the substrate changes slightly with temperature. For instance, we find a first-order transition at $T = 273$ K for a linear increase $\mu(T) = CT + \epsilon_I + 0.22$ eV with $C = 10^{-4} K^{-1}$. The resulting grand canonical potentials for $\mu(T = 0) = \epsilon_I + 0.22$ eV and $\mu(T = 500\text{K}) = \epsilon_I + 0.27$ eV are shown as the lower and upper curves in the inset of Fig. 4 in the paper. In Fig. 6 we see that the gapped dimerized phase remains metastable over a wide range of temperature above T_c while the gapless uniform phase is metastable from $T = 0$ to the critical temperature. Electronic gap, distortion amplitude x_1 , and lattice stiffness K_1^* are clearly discontinuous at T_c . Note that changing the chemical potential of the reservoir is not

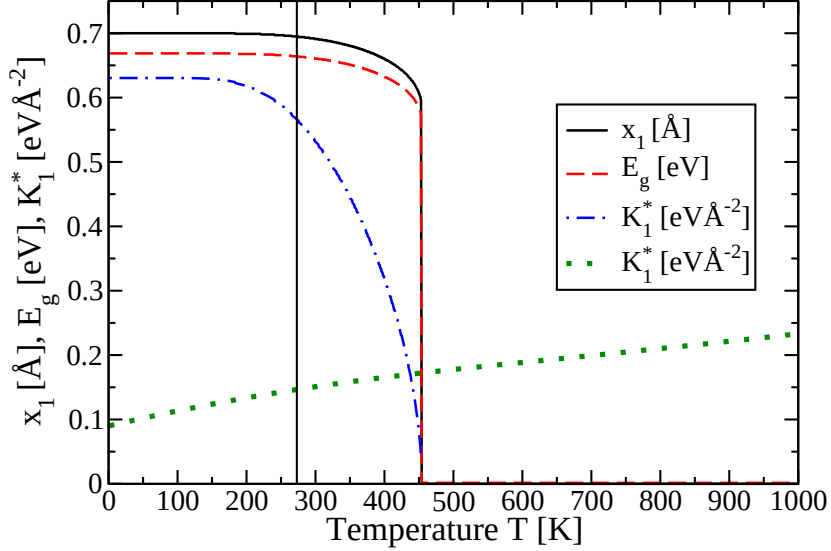


FIG. 6. First-order phase transition in the SSH-type model for the central zigzag chain coupled to the shear mode with a temperature-dependent chemical potential. The curves show the lattice distortion amplitude x_1 and Peierls band gap E_g of the dimerized configuration as well as the effective lattice stiffness K_1^* of both uniform and dimerized configurations as a function of temperature. The vertical line indicates the first-order transition at $T_c \approx 273\text{K}$. The blue dot-dashed line is the lattice stiffness of the dimerized configuration, which is stable below T_c , while the green dotted line indicates the lattice stiffness of the uniform configuration, which is stable above T_c .

the only way to realize a first order transition. Equivalent results are found if one modifies the dependence of the subsystem chemical potential $\mu'(N, T) = \left(\frac{\partial F}{\partial N}\right)_T$ on the temperature T and the number N of electrons in the four bands because chemical equilibrium requires $\mu'(N, T) = \mu$. For instance, this can be easily realized if one keep μ constant but vary the on-site potentials with temperature, i.e., replace $\epsilon_{I,O}$ by $\epsilon_{I,O}(T) = \epsilon_{I,O} - CT$. Moreover, comparing the chemical potentials μ' at half filling for the uniform [Fig. 1(a)] and dimerized [Fig. 1(d)] 1D models, we see that μ' can be different for high and low temperatures even without varying ϵ_I and ϵ_O .

V. TEMPERATURE DEPENDENCE OF PEIERLS MODES

The theory of Peierls systems predicts the existence of amplitude modes which are collective excitations involving both electronic CDW and phonons, are Raman active, and

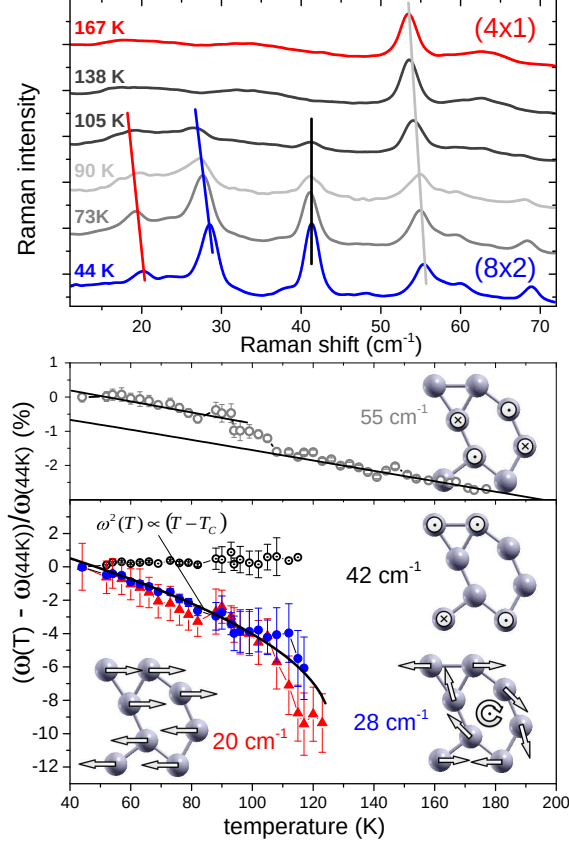


FIG. 7. Upper panel: Selected Raman spectra of In/Si(111) at different temperatures around the phase transition. Some modes appear in the (8×2) phase only. Frequency shifts with temperature are marked by vertical lines. Lower panel: Temperature dependence of the normalized frequencies of Raman modes and sketches of the assigned eigenmodes. The shear and rotary modes (red and blue symbols) at 20 and 28 cm⁻¹ are Peierls amplitude modes and exhibit a significant softening, while the mode at 42 cm⁻¹ (black symbols) remains at constant frequency and the one at 55 cm⁻¹ (grey symbols) shows only a moderate decrease due to the lattice expansion.

show strong anomalies around the wave number Q of the Peierls distortion (phonon softening) [8, 17, 20, 21]. They have been observed experimentally in quasi-one-dimensional bulk materials [8] such as the blue bronze [22] and polyacetylene [23]. For a fixed band filling the Peierls transition is continuous and the frequency of amplitude modes vanishes as

$$\omega_Q(T) = \begin{cases} \omega_Q \sqrt{\frac{T-T_c}{T_c}} & \text{if } T > T_c \\ \sqrt{2}\omega_Q \sqrt{\frac{T_c-T}{T_c}} & \text{if } T < T_c \end{cases} \quad (8)$$

where $Q = 2k_F$ above T_c while $Q = 0$ below T_c [8, 17]. As discussed in the paper, the Peierls amplitude modes in In/Si(111) are essentially made of the shear and rotary modes. Both modes should appear at the Γ point below T_c . Above T_c , however, the shear mode could still be visible at the Γ point while the rotary modes should be at a finite wave vector in the Brillouin zone. Moreover, for a first-order transition, the continuous vanishing of $\omega_Q(T)$ should be replaced by a jump at T_c . This frequency is proportional to $\sqrt{K_1^*}$ in the SSH model for the inner chain. Thus Fig. 6 indicates that in this grand canonical Peierls transition the frequency of the amplitude mode decreases sharply with increasing temperature in the dimerized phase close to T_c , then changes discontinuously at T_c , and finally does not exhibit any distinctive temperature dependence in the uniform phase above T_c .

Figure 7 shows Raman spectra measured for In/Si(111) at various temperatures. The resonances observed experimentally at 44 K were assigned to specific vibrational modes by comparison to first-principles computations at zero temperature [11, 24, 25]. The peaks at 20 and 28 cm^{-1} are assigned to the shear and rotary modes while the peaks at 42 cm^{-1} and 55 cm^{-1} are related to vertical displacements of In atoms. The temperature dependence of these resonance frequencies is discussed in the paper (see Figure 5) and is shown again in the lower panel of Fig. 7. As explained in the paper, the observed temperature dependence agrees qualitatively with our theoretical analysis.

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