Three-Dimensional Structure and Intrinsic Defects in *trans*-Polyacetylene

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We report first-principles local-density-functional pseudopotential calculations of static and dynamic electronic structure properties of crystalline 3D *trans*-$(CH)_x$. We find a broken-symmetry ground state of $P2_1/a$ symmetry with in-phase dimerizations. Using a Green's-function technique, we show that the 3D character of the electronic band-edge states strongly suppresses self-trapping, destabilizing polarons, and possibly bipolarons as well in perfectly ordered 3D *trans*-$(CH)_x$.

Within strictly one-dimensional (1D) models of conducting polymers, such as *trans*-polyacetylene [$(CH)_x$], one expects a variety of localized, "self-trapped," nonlinear excitations—kink solitons, polarons, and bipolarons—with possible significant effects on optical and transport properties.[1] Present conducting polymers, on the other hand, are typically inherently three-dimensional (3D), partially crystalline films, in which interactions between polymer chains play an important role.[1] Indeed, "solid-state screening" effects, both intrachain and interchain, are frequently invoked to explain the apparent differences between the excited states observed in *trans*-$(CH)_x$ and those expected from extrapolations of both measurements and calculations on long but finite polyenes in the gas phase.

Although several studies[2,3] based on simplified theoretical models have suggested that 3D interchain coupling can have strong effects on the 1D excitations, previous *ab initio* theories[4-6] of the 3D structure of both *trans*- and *cis*-$(CH)_x$ have left for further investigation the critical question of whether the interchain couplings are sufficiently strong to destabilize the carrier self-trapping associated with intrinsic defects in 1D systems.

In this Letter we attempt to answer this and related questions by reporting the results of extensive first-principles studies of 3D crystalline *trans*-$(CH)_x$ and intrinsic defects in this material. For the electronic structure of crystalline 3D *trans*-$(CH)_x$, we employed parameter-free local-density-functional theory (LDA)[7] with *ab initio* norm-conserving pseudopotentials for carbon[8] and the Coulomb potential for hydrogen in a momentum-space representation.[9] The exchange-correlation energy is evaluated with the functional given by Painter.[10] The Kohn-Sham equations[9] are solved in a plane-waves basis with up to 1400 plane waves corresponding to a maximum kinetic energy of 30 Ry. All total energies are converged to 1 meV.

Since the crystal structure of 3D *trans*-$(CH)_x$ in its ground state is still not firmly established,[11,12] we have determined it from self-consistent minimizations of the total energy within LDA, augmented by a calculation of the Hellman-Feynman forces[9] on the ions. Experimen-

tally, two possible structures have been proposed,[11,12] namely the $P2_1/n$ symmetry with an antiphase arrangement of the dimerized backbone[11] and the $P2_1/a$ symmetry with an in-phase dimerization on neighboring chains.[12] It should be noted that the latter experiments used samples with significantly better aligned chains and could quantitatively identify the x-ray reflections characteristic for the $P2_1/a$ structure.[12]

In order to characterize fully either of the proposed monoclinic structures, ten structural constants need to be calculated.[12] With the exception of the dimerization amplitude $u_C = \pm 2u_0$ of the $C-C$ bonds in the chain direction, our total-energy and force calculations yield all structural parameters in excellent agreement with the experimental results.[12] They will be given in detail in a longer publication.[13] The calculation of the Hellman-Feynman forces proved crucial for an accurate assessment of u_C since they are an order of magnitude more sensitive to u_C than the total energy itself; because of this, previous total-energy studies[6] were not able to obtain an unambiguous result for u_C. Our calculations give $u_C = 0.01$ Å. Thus, we find the LDA to correctly predict a broken-symmetry ground state but—consistent with earlier studies[5,6]—to quantitatively underestimate the experimental value[12] which is $u_C = 0.05$ Å.

Irrespective of the precise value of u_C, our results show that the dimerized $P2_1/a$ structure is *lower* in total energy than the dimerized $P2_1/n$ structure. For the experimental value for u_C, the energy difference is 0.01 ± 0.003 eV per $(C_2H_2)_2$ unit.[14] This difference is consistent with the similarity of the two structures, and is of the order of optical phonon energies in solids. For the calculated force-free value of u_C and for zero bond alternation, the energy difference becomes 0.03 eV. We find this increasing stability of the $P2_1/a$ structure relative to the $P2_1/n$ structure to be caused by chemical bonding across the chains; for $u_C \to 0$ the overlapping carbon and hydrogen orbitals on adjacent chains are brought into closer alignment.

The $P2_1/n$ structure has been predicted to be favorable energetically assuming that the interchain interaction preserves the particle-hole symmetry for the carbon

p states.[15] We have analyzed the electronic valence charge density and find, as expected,[16] that the band states above and below the energy gap in crystalline $trans$-$(CH)_x$ consist primarily of molecular carbon p bands. In addition, however, we find a non-negligible admixture of hydrogen p-type states. This H admixture is larger for the top valence-band states than for the bottom conduction-band states, leading to a particle-hole asymmetry which shows up also in the band structure (see Fig. 1). Each H atom on one chain approximately points towards a π orbital of a C atom on one of the neighboring chains. The C-H distance across the chains is 2.9 Å in the $P2_1/a$ structure versus 3.1 Å in the $P2_1/n$ structure. This difference provides a crucial additional bonding energy that favors the $P2_1/a$ structure.

In Fig. 1, we present the band structure for the dimerized $P2_1/a$ phase of crystalline $trans$-$(CH)_x$ resulting from our self-consistent LDA calculations. In Fig. 1, the valence bands have energies less than zero.[17] Figure 1 reveals that the pair of the two lowest conduction and highest valence bands near the k point $B = (0,0,\frac{1}{2})$ are split by 0.53 and 0.46 eV, respectively. This splitting is caused by the interaction of electronic carbon and hydrogen states on adjacent chains. These interchain effects are sensitive to crystalline order; by increasing the distance between the two chains by 5%, the splittings in the band-edge states decrease by 31%. In the band structure of the $P2_1/n$ phase—which has been studied previously[4,5] as well as in our present work—the splittings occur near the k point $A = (-\frac{1}{2},0,\frac{1}{2})$ and are 0.23 eV for each of the band-edge states; these smaller splittings reflect the larger distance between the neighboring C and H atoms. Our results agree with those of the previous investigations[4,5] at the level consistent with their convergence criteria and with the k values they selected.

In a strictly 1D deformable chain and invoking adiabatic phonons, a charge carrier will always self-trap due to the electron-phonon interaction; this is in contrast to the behavior in 3D systems,[5] where self-trapping is not guaranteed and requires a strong electron-phonon cou-
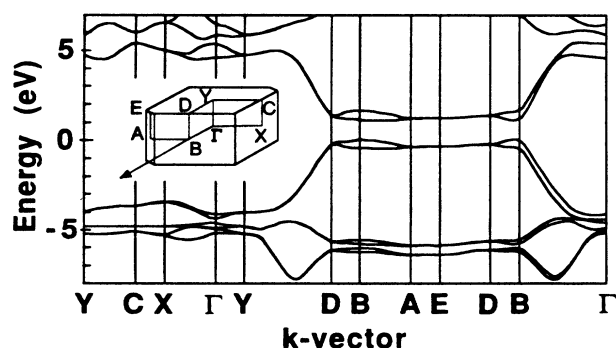
pling. The situation corresponds to a localized defect in an otherwise perfect host crystal and is analogous to a particle in an attractive well. In the 1D there is a bound state for any well depth, whereas in 3D a localized state occurs only when the potential strength exceeds a certain threshold value. Since our results show that the interchain interaction crucially alters the effective dimensionality (as well as the symmetry) of the electronic band states close to the minimum gap, it is clearly essential to study the influence of the interchain interaction on the intrinsic, nonlinear defects predicted by the 1D theories. To carry out this study, we have calculated the electronic structure of 3D crystalline $trans$-$(CH)_x$ containing frozen-in intrinsic defects and focused on the formation of bound states in the energy gap.

We have mapped our first-principles calculations for the perfect $trans$-$(CH)_x$ crystal onto an accurate, multiorbital, three-dimensional tight-binding model.[13] The intersite Hamiltonian matrix elements have been fitted with explicit functions of the distance between the atomic sites. The model reproduces both the energy bands, the atomic character of the bands as obtained from integrated charge densities in each valence band, and the electron–acoustic-phonon deformation potentials for the band-edge states; further, if all interchain couplings are set to zero, the fit reproduces the standard (Su-Schrieffer-Heeger) values of Ref. 16 for t_0 and a. Details will be given elsewhere[13] Because of the theoretical uncertainty of u_C, we have performed these calculations for several values of u_C.

The full consequences of a spatially localized defect with potential V in an otherwise perfect crystal with a translationally invariant Hamiltonian H_0 can be explored using the scattering-theoretic Green's-function

FIG. 1. Calculated electronic band structure of $trans$-$(CH)_x$ in the $P2_1/a$ structure.
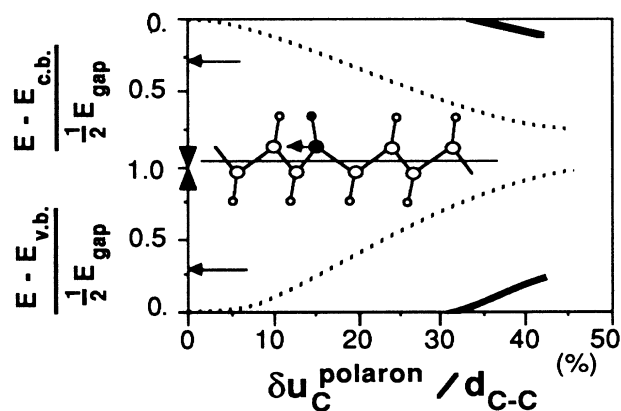

FIG. 2. The intragap electronic levels as a function of distortion for a "single-site" polaron. The solid curve is with interchain coupling; the dashed curve is the purely 1D result. Inset: Schematic atomic displacement pattern for the single-site polaron. The distorted chain is embedded in the 3D crystal.

technique.[18] The bound states E_T in the energy gap of H_0 follow from the determinantal equation $\det[1 - G_0(E_T)V] = 0$, where $G_0(E) = (E - H_0)^{-1}$. The size of the determinant is determined by the range of V. For any given lattice distortion on a single C-H chain, the defect matrix (which contains nonzero interchain matrix elements) and, consequently, the bound states in the energy gap can then be computed.

We have calculated the electronic structure of 3D trans-$(CH)_x$ in the $P2_1/a$ structure with a localized polaron defect[19] in an otherwise perfectly 3D dimerized crystal. In Fig. 2, we show the bound-state energies E relative to the valence- and conduction-band edges, respectively, corresponding to a single-site polaron as a function of the distortion as indicated in the inset of this figure. By increasing the distortion $\delta u_C^{polaron}$, we can simulate the effect of a spatially more extended lattice relaxation.[20]

Significantly, we find that the 3D character of the band-edge states prevents the formation of self-trapping intragap states; this destabilizes the one-dimensional polaron excitation[3] in crystalline trans-polyacetylene. In principle, bound states in the energy gap can be formed, but these require unrealistically large lattice distortions of more than 30% of the C-C distance in the localized defect. When we artificially set all interchain matrix elements equal to zero, the polaron bound states appear in the gap for any lattice distortion, in complete agreement with known 1D results.[19,20]

The numerical results in Fig. 2 were obtained with a value of $u_C = 0.05$ Å and the $P2_1/a$ structure. We find that smaller dimerizations do not visibly deepen the bound states, because a shallow bound state consists of electronic states very close to the band edge. Conse-
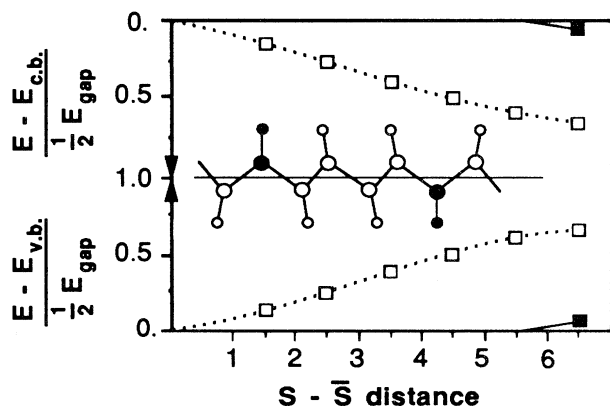
quently, its formation is insensitive to the gap itself, and therefore, to the dimerization. In the $P2_1/n$ structure, on the other hand, we find a bound state to appear in the gap for a polaron distortion of 15% of the bond length.

In Fig. 3, the bound states due to a bipolaronic displacement pattern—corresponding to a separated kink (S) and antikink ($\bar{S}$) soliton—are shown. Again, the interchain coupling strongly impedes the formation of bound states in the energy gap of three-dimensional trans-$(CH)_x$. Only for separations exceeding 6 lattice constants (14 carbon sites in the chain direction) between the kind and antikink solitons (S-$\bar{S}$) does a pair of shallow bound states appear in the energy gap.

If we simply extrapolate the numerical results to larger S-$\bar{S}$ distances, the binding energies barely exceed room-temperature thermal energies for distances (S-$\bar{S}$) smaller than 8–10 lattice constants. There are two additional factors which limit the stability of a bipolaron. First, as has long been recognized, the formation of a separated kink-antikink pair costs interchain bonding energy due to misalignment of the dimerized phases on adjacent chains in the region between the S-$\bar{S}$ pair. We estimate from our total-energy calculations that the maximum kink separation attainable in a perfectly ordered crystal is of the order of 50 lattice constants in the chain direction. Since the electronic wave function in a kink-bound state is expected to extend over 5–10 lattice constants,[16] this interchain confinement to 50 lattice constants strongly limits the formation of a bipolaron. Second, if two electrons are captured in the (S-$\bar{S}$) bound state, the Coulomb repulsion will further reduce the total effective binding energy. These qualitative arguments, being backed by our Green's-function calculations, make it plausible that bipolarons are also destabilized in perfectly ordered crystalline trans-$(CH)_x$.

To conclude, we discuss the limitations, both theoretical and in application to presently existing conducting polymers, of our results and mention some important open issues. First, the LDA calculations capture only part of the correlation energy due to electron-electron many-body interactions.[7] For the ground states of many semiconductors, insulators, as well as van der Waals crystals,[21] however, the LDA methods are known to be accurate, providing correct energies, pressure dependences, phonons, and phase transition information.[9] Second, the calculated gap in the LDA effective single-particle spectrum is not the optical gap but differs from it by a (weakly k dependent) self-energy, Σ_{el}.[17] Third, even though the force-free value of the dimerization in our study is too small, the critical band-edge splittings are unaffected both by the self-energy correction and —as our calculations show—by the precise value of the dimerization. Fourth, previous studies[1] suggest that for localized intrinsic defects Coulomb effects typically drive the intragap levels towards the band edges, further reducing their depth. We therefore expect that none of

FIG. 3. The intragap electronic levels as a function of separation for a bipolaron composed of an S-$\bar{S}$ pair. The solid squares are with interchain coupling; the open squares are the purely 1D result. The connecting lines only guide the eye. Inset: Schematic atomic displacement pattern for the bipolaron. The distorted chain is embedded in the 3D crystal.

these theoretical limitations will invalidate our ground-state calculations of the interchain coupling strengths and their effects on the localized intrinsic defects.

With regard to applications of results to presently existing conducting polymers, we stress that our calculations have been made for perfectly ordered crystalline 3D $trans$-$(CH)_x$. Any extrinsic defect is likely to produce gap states. At present, the chain lengths even in highly oriented, crystalline Durham-Graz $trans$-$(CH)_x$ are believed to be smaller than 40 C-H units,[12,22] and there is a high density of broken bonds. In the morphologically complex Shirakawa material, many chains are in a disordered environment near the fibril surface;[23] it is thus conceivable that optical excitations in particular in this material exhibit properties which are more characteristic of single chains of $trans$-$(CH)_x$ than of the 3D crystal. Our results strongly suggest that a number of experimental issues, including the interpretation of optical absorption spectra, require extensive further study. In this regard, recent discussions[24] of the nonsolitonic and extrinsic nature of the picosecond photoconductivity in $trans$-$(CH)_x$ may prove illuminating.

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[1]Excellent review articles may be found in *Handbook of Conducting Polymers,* edited by T. A. Skotheim (Dekker, New York, 1986).

[2]Yu. N. Gartstein and A. A. Zakhidov, Solid State Commun. **60**, 105 (1986).

[3]D. Emin, Phys. Rev. B **33**, 3973 (1986).

[4]P. M. Grant and I. P. Batra, J. Phys. (Paris), Colloq. **44**, C3-437 (1983); Synth. Met. **1**, 193 (1979).

[5]J. Ashkenazi, E. Ehrenfreund, Z. Vardeny, and O. Brafman, Mol. Cryst. Liq. Cryst. **117**, 193 (1985).

[6]J. Ashkenzai, W. E. Pickett, B. M. Klein, H. Krakauer, and C. S. Wang, Synth. Met. **21**, 301 (1987).

[7]For a review, see J. Callaway and N. H. March, Solid State Phys. **38**, 136 (1984).

[8]R. W. Jansen and O. F. Sankey, Phys. Rev. B **36**, 6520 (1987).

[9]J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[10]G. S. Painter, Phys. Rev. B **24**, 4264 (1981).

[11]Y. B. Moon, M. Winokur, A. J. Heeger, J. Barker, and D. C. Bott, Macromolecules **20**, 2457 (1987).

[12]H. Kahlert, O. Leitner, and G. Leising, Synth. Met. **17**, 467 (1987).

[13]P. Vogl and D. K. Campbell (to be published).

[14]We note that the optimization procedure yields the same structural parameters for both monoclinic structures.

[15]B. Horovitz, Phys. Rev. B **12**, 3174 (1975); D. Baeriswyl and K. Maki, Phys. Rev. B **28**, 2068 (1983).

[16]W.-P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980); **29**, 2309 (1984).

[17]To account for the difference in the quasiparticle eigenvalues and the LDA band structure, the conduction bands include a wave-vector–independent self-energy $\Sigma_{el} = 0.74$ eV (the "scissors operator") [R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B **37**, 10159 (1988); M. S. Hybertsen and S. G Louie, Phys. Rev. B **34**, 5390 (1986)]. Rather than calculating this shift from first principles, we have obtained this value from a comparison of the experimental and calculated optical-absorption spectra (Ref. 13). This self-energy does not enter the ground-state calculations of intrinsic defects in this work, however; for a discussion of these subtleties, see Godby, Schlüter, and Sham, and Hybertsen and Louie (in this footnote).

[18]G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954); **96**, 1208 (1954).

[19]D. K. Campbell and A. R. Bishop, Phys. Rev. B **24**, 4859 (1981).

[20]S. Phillpot, D. Baeriswyl, A. R. Bishop, and P. Lomdahl, Phys. Rev. B **35**, 7533 (1987).

[21]S. B. Trickey, F. R. Green, Jr., and F. W. Averill, Phys. Rev. B **8**, 4822 (1973).

[22]B. Ankele, G. Leising, and H. Kahlert, Solid State Commun. **62**, 245 (1987).

[23]T. Ito, H. Shirakawa, and S. Ikeda, J. Polymer Sci. Polym. Ed. **12**, 11 (1974).

[24]H. Bleier, K. Donovan, R. H. Friend, S. Roth, L. Rothberg, R. Tubino, Z. Vardeny, and G. Wilson, Synth. Met. **28**, D189 (1989).