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TITLE 3-D STRUCTURES AND INTRINSIC DEFECTS IN TRANS-POLYACETYLENE

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3-D Structures and Intrinsic Defects in *trans*-polyacetylene

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Abstract. We report first-principles local-density functional pseudopotential calculations of static and dynamic electronic structure properties of crystalline 3-D *trans*-(CH)_x. We find a broken symmetry ground state of P2₁/a symmetry with in-phase dimerizations. Using a Green's function technique, we show that the 3-D character of the electronic band edge states strongly suppresses self-trapping, destabilizing polarons and possibly bipolarons as well in perfectly ordered 3-D *trans*-(CH)_x.

1. Introduction

Within strictly one-dimensional (1-D) 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 (3-D), partially crystalline films, in which interactions between polymer chains play an important role [1]. Indeed, "solid state screening" effects, both intra- and inter-chain, 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 3-D interchain coupling can have strong effects on the 1-D excitations, previous *ab-initio* theories [4,5,6] of the 3-D structure of both *trans*- and *cis*-(CH)_x have left for further investigation the crucial question of whether the interchain couplings are sufficiently strong to destabilize the carrier self-trapping associated with intrinsic defects in 1-D systems.

In this paper we report the results of extensive first-principles studies of 3-D crystalline *trans*-(CH)_x and intrinsic defects in this material. For the electronic

structure of crystalline 3-D *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 Rydbergs. All total energies are converged to 1 meV.

2. Crystal and electronic structure

Since the crystal structure of 3-D *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.

In order to characterize fully either of the proposed monoclinic structures, 10 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 elsewhere [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 unambiguous results for u_C . Our calculations give $u_C = 0.01 \text{ \AA}$. 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 $u_C = 0.05 \text{ \AA}$.

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 $0.01 \pm 0.003 \text{ eV}$ per (C₂H₂)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.

We have analyzed the electronic valence charge density of both monoclinic structures and find, as expected [15], that the band states above and below the energy gap in crystalline *trans*-(CH)_x consist primarily of molecular carbon- π -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 [16] which shows up also in the band structure. Each H-atom on one chain approximately points towards a p-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 the band structure for the dimerized $P2_1/a$ phase of crystalline $trans-(CH)_x$ we find that the pair of the two lowest conduction and highest valence bands near the k -point $B = (0, 0, 1/2)$ are split by 0.53 eV and 0.46 eV, respectively. This splitting is caused by the interaction of electronic carbon and hydrogen states on adjacent chains. 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 $A = (-1/2, 0, 1/2)$ 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.

3. Intrinsic Defects

In a strictly 1-D 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 3-D systems, [5] where self-trapping is not guaranteed and requires a strong electron-phonon coupling. 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 1-D theories. To carry out this study, we have calculated the electronic structure of 3-D 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, multi-orbital, three dimensional tight-binding model [13]. The inter-site Hamiltonian matrix elements have been fitted to 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. Details will be given elsewhere [13]. Due to the theoretical uncertainty of u_C we have performed these calculations for several values of u_C .

Employing a multi-orbital Koster-Slater Green function method [17], we have calculated the electronic structure of 3-D $trans-(CH)_x$ in the $P2_1/a$ structure with a localized polaron defect [18] in an otherwise perfectly 3-D dimerized crystal.

Significantly, we find that the 3-D character of the band edge states prevents the formation of self-trapping in-gap states; this destabilizes the one-dimensional polaron excitation [3] in crystalline $trans$ -polyacetylene. 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 1-D results [18,19].

We have also computed the bound states due to a bipolaronic displacement pattern – corresponding to a separated kink (S) and anti-kink (\bar{S}) soliton. 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 chain direction) between the kink- and antikink-soliton (S – \bar{S}), a pair of shallow bound states appears 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 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 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]. We are presently applying the so-called self-interaction corrected LDA [20] to single chains of (CH)_x; we find that this method tends to give a substantially larger dimerization than LDA. That 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 self-energy, Σ_{01} [22,23]. 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 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 3-D

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, [12,24] 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 [25]; 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 3-D 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 [26] of the non-solitonic and extrinsic nature of the picosecond photoconductivity in *trans*-(CH)_x may prove illuminating.

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