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THEORY OF 3-D STRUCTURE AND INTRINSIC DEFECTS OF TRANS-POLYACETYLENE

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ABSTRACT

First-principles local-density functional pseudopotential calculations of static and dynamic electronic structure properties of crystalline 3-D *trans*-(CH)_x are reported. The P2₁/a structure is predicted to have a lower energy than the P2₁/n structure. A Green function calculation reveals that the 3-D character of the electronic band edge states destabilizes polarons and bipolarons and prevents self-trapping in perfectly ordered 3-D *trans*-(CH)_x.

INTRODUCTION

Strictly one-dimensional theories in quasi-one-dimensional solids predict a variety of localized, nonlinear excitations [1, 2]. Relatively little attention has been paid to the effects that arise because the real films of *trans*-(CH)_x are inherently three-dimensional [3]. Theoretical studies [4, 5] have indicated that the interchain coupling can affect strongly the nature of the one-dimensional (1-D) excitations.

Ab-initio theories [6, 7,8] of the 3-D structure of polyacetylene in both the *cis*- and *trans*-isomers have left for further investigation a number of critical questions, including: (1) In *trans*-(CH)_x is the 3-D ground state expected to have P2₁/n symmetry with an anti-phase arrangement of the dimerized backbone (as deduced from experiments in [9,10]) or P2₁/a symmetry with an in-phase dimerization on neighboring chains (as deduced from experiments in [11]) and (2) Are the interchain couplings sufficiently strong to destabilize the carrier self-trapping associated with intrinsic dynamic defects in 1-D systems?

Accordingly, in this article we report extensive parameter-free first-principles studies of the three-dimensional structure of 3-D crystalline *trans*-(CH)_x and intrinsic

defects in this material.

THEORY

We have employed parameter-free local-density-functional theory (LDA) [12] with *ab-initio* norm-conserving pseudopotentials for carbon [13] in a momentum-space representation [14]. The exchange-correlation energy is evaluated with the functional given by Painter [15]. The Kohn-Sham equations [14] are solved in a 1400 plane-waves basis (corresponding to a maximum kinetic energy of 30 Rydbergs). All total energies are converged to 1 meV.

In order to characterize fully any of the proposed monoclinic structures, the following structural constants need to be known: the lattice constants a , b , c , the monoclinic angle β between a and c , two setting angles ϕ_C and ϕ_H between the C-C and C-H plane in a chain, respectively, and the b -axis, the projection p of the C-C distance in a chain onto the a - b plane, the nearest neighbor distance l_{C-H} between the carbon and hydrogen atoms, the dimerization amplitude $u_C = \pm 2u_0$ of the C-C bonds in the c -direction, and the displacement u_H in the c -direction of a hydrogen atom relative to its adjacent carbon atom [11,16]. Table 1 lists the parameters used in the present work.

TABLE 1

Structural data for crystalline *trans*-polyacetylene used in present calculation.

a (Å) ^a	b (Å) ^a	c (Å) ^a	β ^a	ϕ_C ^a	ϕ_H ^b	p (Å) ^a	u_C (Å) ^a	l_{C-H} (Å) ^b	u_H (Å) ^b
4.18	7.34	2.455	90.5°	55.1	57.0	0.64	0.05	1.12	0.04

^a Reference 11

^b This work (optimized by Hellman-Feynman force and self-consistent total energy calculations [14])

RESULTS: STRUCTURE

Relative stability of $P2_1/a$ and $P2_1/n$ structure

The present calculations show that the $P2_1/a$ structure is lower in total energy by an amount of 0.01 eV per cell (for comparison, cubic diamond is more stable than hexagonal diamond by 0.06 eV per cell [17]). When the bond alternation is set equal to zero, the relative stability of the $P2_1/a$ structure relative to the $P2_1/n$ structure increases and the energy difference becomes 0.03 eV.

The $P2_1/n$ structure has been predicted to be energetically favorable assuming that the interchain-interaction preserves the particle-hole symmetry for the carbon π -states [18]. We have analyzed the electronic valence charge density and find the top valence band states in crystalline *trans*-(CH)_x to consist primarily of molecular carbon- π -bands (as expected [19]) but to contain additionally a non-negligible admixture of hydrogen states, whereas the bottom conduction band states are pure carbon states. This asymmetry shows up also in the band structure (see below). Each H-atom on one chain approxi-

mately 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, and 3.1 Å in the $P2_1/n$ structure. This difference provides a crucial additional bonding energy that favors the $P2_1/a$ structure.

Band structure

Figures 1,2 show the band structures for the dimerized $P2_1/a$ and $P2_1/n$ phases of crystalline *trans*-(CH)_x, respectively, resulting from our self-consistent LDA calculations.

The zero of energy has been chosen in such a way that the valence bands have energies less than zero. The quasi-particle eigenvalues in an insulator or semiconductor have been shown to differ from the LDA band structure to an excellent level of approximation by a wave-vector independent self energy Σ_{el} which rigidly shifts the conduction bands upwards [20]. We have estimated this self energy by calculating the combined density of states of *trans*-(CH)_x in the $P2_1/a$ structure and comparing it with experimental optical absorption data from Graz/Durham material [21] and find $\Sigma_{el} = 0.74$ eV. This self energy is already included in Figures 1,2.

The band structure of 3-D *trans*-(CH)_x in the $P2_1/a$ phase (Fig. 1) reveals 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 across the chains. These interchain effects are very sensitive to crystalline order; by increasing the distance between the two chains by 5%, the splittings in the band edge states decrease by 31%. The band splittings are also weaker in the $P2_1/n$ structure (see Fig. 2; the band edge states are split by 0.23 eV), since the distance between the neighboring C and H atoms is larger in this case.

The results for the $P2_1/n$ band structure generally agree with prior first-principles band structure calculations of Grant and Batra [6] and of Ashkenazi *et al.* [7]. Differences in the conduction bands are likely to originate in differences in the method and atomic positions. The present results are more accurate than those in [6] in the sense of numerical convergence and number of basis states and contain no approximations to the shape of the crystal potential such as used in [7].

It should be noted that Grant and Batra [6] did not include the wave vectors close to the k -point A = (-1/2 0 1/2) (see Fig. 2) in their published $P2_1/n$ band structure; since the interchain interaction shows up significantly only for this k -vector, the three-dimensional interchain coupling appeared to be much smaller. Our results are consistent with those of Ashkenazi *et al.* [7,8].

RESULTS: INTRINSIC DEFECTS

We find that interchain interaction crucially alters the symmetry and dimensionality of the band states close to the minimum gap.

A charge carrier in strictly 1-D systems will always self-trap due to the electron-

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

Fig. 2. Calculated electronic band structure of $trans-(CH)_x$ in the $P2_1/n$ structure.

phonon interaction, in contrast to the behavior in 3-D systems [22]. The situation is analogous to a particle in an attractive well. In 1-D, there is a bound state for any well-depth, whereas in 3-D, a localized state occurs only when the potential strength exceeds a certain threshold value.

In order to study the influence of the interchain interaction on intrinsic defects, we have carried out electronic structure calculations of 3-D crystalline *trans*-(CH)_x containing frozen-in intrinsic defects and focused on the formation of bound states in the energy gap.

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 function technique [23]. 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 .

We have mapped the first-principles calculations for the perfect *trans*-(CH)_x crystal onto an accurate, multi-orbital, three dimensional tight-binding model [24]. 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 and the electron-acoustic phonon deformation potentials for the band edge states. Details will be given elsewhere [24]. For any given lattice distortion on a single C-H chain, the defect matrix (which contains non-zero interchain matrix elements) and, consequently, the bound states in the energy gap can then be computed. The size of the defect matrix is of the order of 100 by 100 for the defects we have studied.

We have calculated the electronic structure of 3-D *trans*-(CH)_x in the P2₁/a structure with a localized polaron defect in an otherwise perfectly 3-D dimerized crystal [19,25] (see Fig. 3(b)). By increasing the distortion shown in Fig. 3(b), a spatially extended lattice relaxation can be simulated [25,26].

Significantly, we find that the 3-D character of the band edge states prevents the formation of self-trapping gap states which completely destabilizes the one-dimensional polaron excitation [5] in crystalline *trans*-polyacetylene. In principle, bound states in the energy gap can be formed but require unrealistically large lattice distortions of more than 35 percent of the C-C distance in the localized kink-antikink pair depicted in Fig. 3(b). When all interchain matrix elements are set equal to zero, the polaron bound states appear in the gap for any lattice distortion in complete agreement with known 1-D results [25,26].

In Fig. 3(c), a bipolaronic displacement pattern corresponding to a separated kink and anti-kink soliton is depicted. Our 3-D Green function calculations show that bipolarons do not produce bound states in the energy gap of three-dimensional *trans*-(CH)_x up to a separation of 6.5 lattice constants (14 carbon sites in chain direction) between the kink- and antikink-soliton. For larger separations, two bound states appear in the gap, which eventually coincide and lie close to the center of the gap for infinite

Fig. 3. Schematic atomic displacement patterns in *trans*-(CH)_x. The distortions are grossly exaggerated. (a) Unperturbed, dimerized chain. (b) Distortion corresponding to a localized polaron, modelled by moving a single C-H pair of atoms (black circles). (c) Distortion corresponding to a bipolaron, i.e. a pair of confined kink anti-kink solitons. The distorted chains are embedded in the 3-D crystal.

separation. For distances smaller than 10 lattice constants, we estimate that the binding energies are only of the order of kT at room temperature.

The formation of a separated kink-antikink pair costs interchain bonding energy due to the anti-phase dimerized backbone. This energy is of the same order of magnitude as the energy difference between the $P2_1/a$ and the $P2_1/n$ structure, namely 0.01 eV per unit cell. Since the theoretical binding energy of an unconfined kink-antikink pair is approximately 0.5 eV according to single-chain calculations [19,1], the maximum kink separation attainable in a perfectly ordered crystal is of the order of 50 lattice constants in chain direction. In the $P2_1/a$ structure, it is probably less than that due to the stronger interchain coupling.

In view of thermal and disorder fluctuations, we obtain the striking result: that neither polarons nor bipolarons can be generated by optical excitation or doping in perfect crystalline *trans*-(CH)_x. As a consequence, extra electrons which are placed into the conduction band will remain free carriers with an effective mass $m^*/m \leq 1$.

Our results apply only to perfectly ordered crystalline three-dimensional material. At present, the chain lengths even in highly oriented, crystalline Graz/Durham *trans*-(CH)_x are smaller than 40 C-H units [11,27] and there is a high density of broken bonds. It is therefore not clear how relevant our findings are for this real material. In the

morphologically complex Shirakawa material many chains are in a disordered environment near the fibril surface [28,29]; it seems conceivable that optical excitations in this material exhibit properties which are more characteristic of single-chains of *trans*-(CH)_x than of a three-dimensionally ordered crystal. This will be discussed in greater detail elsewhere.

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