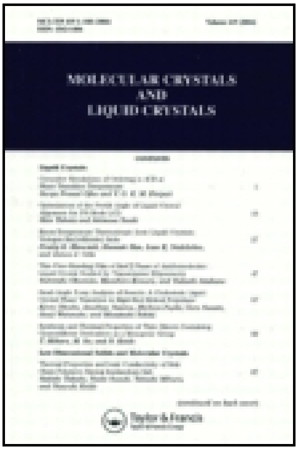

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First Principles Three-Dimensional Band-Structure of Trans-Polyacetylene

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FIRST PRINCIPLES THREE-DIMENSIONAL BAND-STRUCTURE OF TRANS-POLYACETYLENE

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Abstract The three-dimensional (3-D) band-structure of ideally crystalline trans-$(CH)_x$ is calculated self-consistently, with no adjustable parameter, using the LMTO-ASA method. The results are in good agreement with experiment. It is found that the quasi one-dimensional (1-D) behavior of the system is sensitive to the 3-D symmetry.

Most models on trans-$(CH)_x$ assume isolated 1-D chains. Actually, these chains are arranged in 3-D micro-crystals of the $P2_1/n$ space group[1] (see Figure 1) and thus a 3-D band-structure calculation is essential to test such models.

The calculation is carried out using the LMTO-ASA method[2], which is a fast method based on energy linearization and development in spherical basis functions around centers of approximate spherical symmetry. These centers are taken at the C and H atomic sites, and

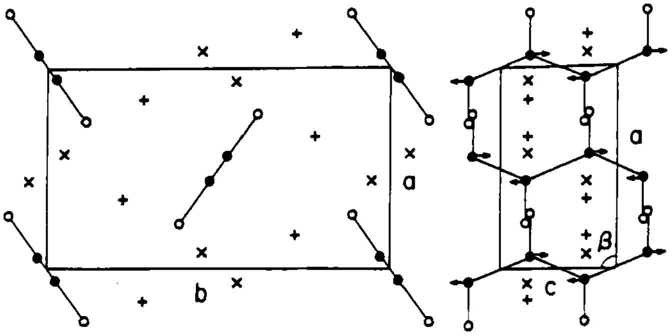

FIGURE 1 Crystal structure of trans-$(CH)_x$ (see ref.1). C atoms are denoted by black circles, H atoms by empty circles, I interstitial sites by +, and J interstitial sites by ×. The small arrows distinguish the (shorter) "double bonds" from the (longer) "single bonds".

also at interstitial sites of two types, denoted here by I and J (see Figure 1). The muffin-tin spheres cover 61% of the crystal volume. They are increased to atomic spheres of radii 2.74, 1.76, 1.56 and 0.98 a.u. around the I, J, C and H sites respectively. The results are insensitive to small variations in the radii.

The crystal potential is constructed self-consistently, using the local density approximation (LDA)[3] for the exchange-correlation potential. We use spherical functions of $\ell = 0, 1, 2$ in the I spheres, and of $\ell = 0, 1$ in the J, C and H spheres. This yields 84 basis functions per unit cell. Due to the smallness of the monoclinic distortion, it is sufficient to sample on the 1/8 Brillouin zone (BZ) shown in Figure 2. Density of states (DOS) results converge for linear interpolation in a mesh of 252 points (4×3×21 points along the k_x, k_y, k_z axes, respectively).

The band-structure and DOS results are shown in Figure 2. Below the Fermi level E_F one finds quasi-1-D behaviour close to the 1-D results of Mintmire and White[4], and the DOS results fit the XPS and UPS spectra shown in ref.4. Above E_F free-electron like 3-D bands are found. There is general agreement between our results and the 3-D pseudopotential results of Grant and Batra[5], but their energy gap is considerably smaller.

In Figure 3 we show the joint DOS (JDOS) results. They show a quasi 1-D peak centered at 1.8 eV, dropping steeply to an absorption edge at 0.75 eV. These results agree with optical

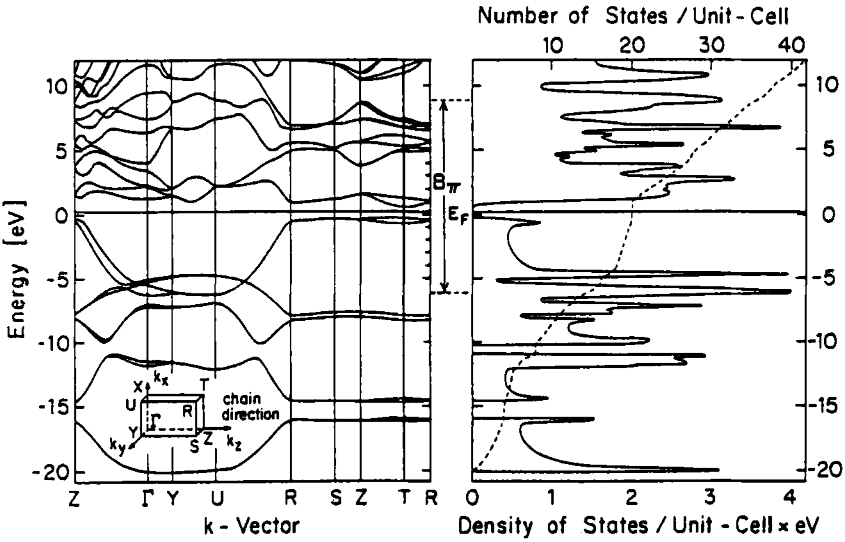

FIGURE 2 Band-structure, density of states, number of states (dashed line), and 1/8 the Brillouin zone of trans-$(CH)_x$.

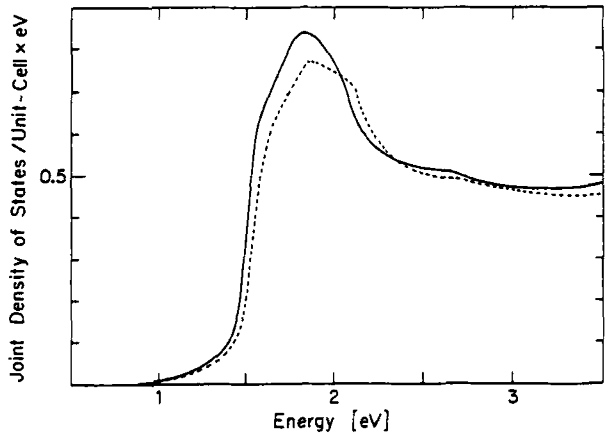

FIGURE 3 Joint density of states of trans-(CH)$_x$: regular - solid line; 2% compression in the linear dimensions - dashed line.

absorption data[6]; the absorption peak is centered at an energy higher by 0.2 eV, which is consistent with the observation that the LDA underestimates minimal band-gaps by about 30%[7]. The band edge tail below the peak fits recent PDS absorption results on compensated films[8]. We also show in Figure 3 JDOS results under homogenous compression of 2% in the linear dimensions. The height of the peak is then decreased by about 9%, which is in agreement with the effect of pressure of 13.1 kbar[6]. (Note that the experimental compression is not homogenous, resulting in a different shift of the peak.)

In order to study the possibility of existence of mobile solitons we repeated the calculation for a hypothetic crystal where in every second chain (namely in the chains at the centers of the a-b rectangles in Figure 1) the single and the double C-C bonds have been exchanged. The band-structure results of this configuration are shown in Figure 4. The main effect is that degenerate levels are split due to the reduction of the 3-D symmetry, the quasi 1-D peak is considerably smeared and the minimal gap almost disappears. This shows the importance of 3-D effects on the band-gap of trans-(CH)$_x$, and that one has to be careful when single chain models are applied to the system.

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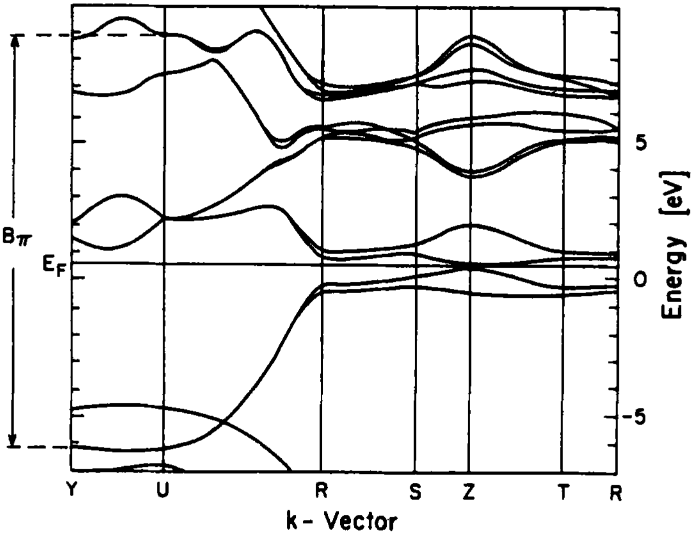

FIGURE 4 Band-structure of hypothetic trans-(CH)$_x$ where single and double bonds have been exchanged in every second chain.

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