Electrical conductivity in a crystal of polyacetylenelike chains

R. Al-Jishi, G. A. Worrell, and P. L. Taylor
*Department of Physics, Case Western Reserve University,
Cleveland, Ohio 44106*

M. Thakur and J. B. Lando
*Department of Macromolecular Science, Case Western Reserve
University, Cleveland, Ohio 44106*

Amitabha Das
550 Memorial Drive, No. 18C, Cambridge, Massachusetts 02139
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The temperature dependence of the conductivity of the crystalline polymerized dimer of 1,11-dodecadiyne has been measured, and indicates that the material is a semiconductor with an energy gap of about 0.36 eV. A band-structure calculation for the polyacetylenelike chains in this crystal supports this conclusion.

Much recent interest has been focused on the properties of electrically conducting polymers, and in particular of polyacetylene (PA). However, unavailability of single-crystal samples and uncertainties concerning the role of cross linking and other interchain interactions have placed some constraints on further progress in the study of this material. Thus, it was of great significance when the synthesis by solid-state polymerization of a material in which all *trans*-PA-like chains are separated by intervening chains of polydiacetylene (PDA) was announced. This orientable material, hereafter called PDD, is formed by polymerization of the dimer of 1,11-dodecadiyne. Of platelike morphology, it is stable in air, and exhibits a relatively high conductivity of about 1 S m^{-1} in its undoped state when not contaminated by trace impurities. It is the purpose of this paper to report the temperature dependence of the electrical conductivity of this material, and to demonstrate that this dependence can be accounted for in terms of the relative energies of the bonding and antibonding states calculated in a simple model.

The structure of PDD has recently been studied by Thakur and Lando.[1] The crystal is monoclinic, with lattice constants and angle γ between the a and b axes given by

$$a = 2.6779 \text{ nm}, \quad b = 0.821 \text{ nm}, \quad c = 0.493 \text{ nm},$$

$$\gamma = 119.558° \ .$$

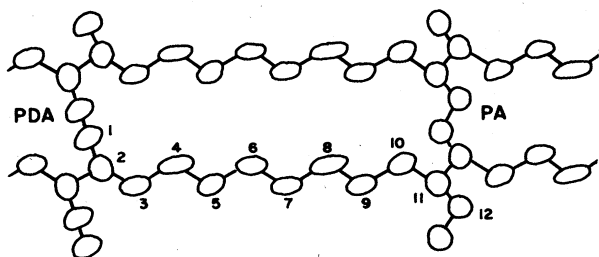X-ray structure analysis of this crystal reveals a unit cell in

which PA-like chains are surrounded by PDA-like chains. The chains are oriented parallel to the c axis and are interconnected in the ac plane by a chain of eight methylene (CH$_2$) units, as shown in Fig. 1. The bond lengths along the PA chains are about 0.146 nm for a carbon-carbon single bond (C–C), and about 0.136 nm for a carbon-carbon double bond (C=C), in agreement with reported values in PA. The C–C bond length along the methylene units is 0.154 nm, but C$_{10}$–C$_{11}$ is 0.151 nm, and the bond angles C$_9$C$_{10}$C$_{11}$ and C$_{10}$C$_{11}$C$_{12}$ are 112° and 167°, respectively. This asymmetry lifts the degeneracy of the ground state, and thus prevents the formation of soliton excitations.

The measured electrical conductivity of polycrystalline PDD is shown as as function of inverse temperature in Fig. 2. The slope of the straight line suggests the possibility that the crystal is a semiconductor in which the energy gap is about 0.36 eV. The occurrence of this high conductivity and simple temperature dependence in an undoped crystalline polymer is of great interest. In the ac plane, the PA and PDA chains are more than 1.3 nm apart and thus can be regarded as noninteracting, while in the b direction, they

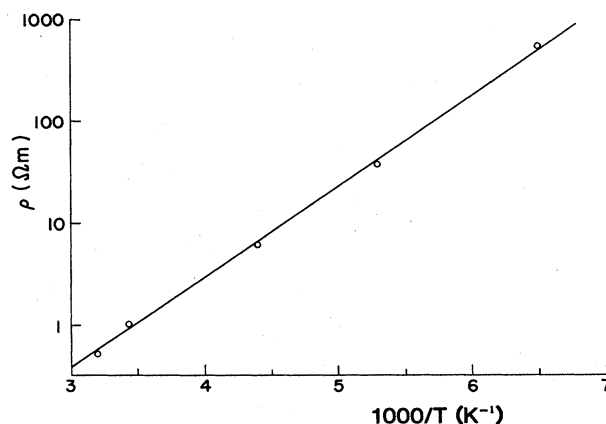FIG. 1. Arrangement of carbon atoms in the ac plane of PDD.

FIG. 2. Resistivity of PDD is shown as a function of $1000/T$, with T the temperature in degrees kelvin. The linear relation is indicative of an energy gap 0.36 eV.

are separated by 0.41 nm. This allows us to justify the neglect of interchain matrix elements in the calculation. Let us assume, for the sake of argument, that some of the p_z orbitals in these chains are oriented towards each other. A comparison may then be made with the case of graphite, in which the electronic p_z orbitals on the carbon atoms are oriented normally to the graphite planes. The coupling between them is a weak van der Waals coupling,[2] and band-structure calculations suggest[3,4] a value of 0.39 eV for the Hamiltonian matrix element between those p_z orbitals, in adjacent planes, that are pointing towards each other. The corresponding matrix element in PDD is expected to be considerably less than 0.39 eV, as the separation between graphite layers is 0.335 nm, whereas that between successive PA and PDA chains is 0.41 nm. Consequently, to a very good approximation, the PA- and PDA-like chains in PDD can be considered isolated. The conductivity of un-doped PA is normally very low ($< 10^{-4}$ S m^{-1}) at room temperature, and that of PDA is even lower because of its larger energy gap. At this point we remark that the coupling betwen the PA and PDA chains reduces the energy gap in PA. However, we believe that the main reduction in the energy gap is due to the reason we present below, and that the coupling between the PA and PDA chains acts to help further reduce this energy gap.

In PA itself, which has the formula $(CH)_x$, the bonding σ bands are much lower in energy than the bonding π bands, whereas the antibonding σ bands are higher than the antibonding π bands, thus justifying a model in which only the π bands are considered in calculating electrical properties. This, however, is not the case for the PA-like chains in PDD, where we find that an antibonding σ band exists which is lower in energy than the antibonding π bands.

In Fig. 3 we illustrate a section of the PA chain along with the electronic orbitals, numbered 1 through 16, in the plane of the chain. Orbitals 4 and 9 are sp_3 hybrids; 12 and 13 are $1s$ hydrogen orbitals, while the rest are sp_2 hybrid orbitals. Since the p_z electrons do not overlap the s, p_x, and p_y orbits, the π and σ bands can be separately calculated. To calculate the σ bands we use the linear combination of atomic orbitals (LCAO) approach.[5] In this method, the Hamiltonian matrix elements between different electronic oribtals are needed. We treat interactions only between nearest-neighbor atoms, and the required matrix elements are calculated according to the method described by Harrison,[6] in which the matrix element between electronic orbitals l and l' on atoms separated by a distance d is given by

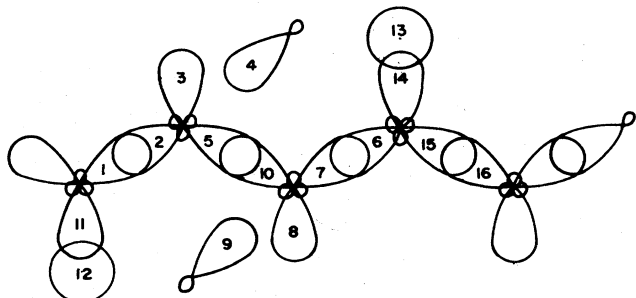$$V_{ll'm} = \langle lm|H|l'm\rangle \eta_{ll'm} \hbar^2/m_0 d^2 \quad ,$$

where m_0 is the electron mass, and $\eta_{ss\sigma} \simeq 1.4$, $\eta_{sp\sigma} \simeq 1.84$, $\eta_{pp\sigma} \simeq 3.24$, and $\eta_{pp\pi} \simeq 0.9$. In the band-structure calculation of graphite,[7] however, it was found[6] that the σ bonding matrix element $V_{pp\sigma}$ between p states is approximately half that predicted by use of the above expression. We thus take $\eta_{pp\sigma} \simeq 1.62$. Because the values of the $V_{pp\pi}$'s in PA have been estimated[8] by more direct methods to be 2.1 and 2.8 eV for the longer and shorter bonds, respectively, the quantities $\eta_{pp\pi}$ are not needed.

To determine the Hamiltonian matrix elements we still need the energies, $\epsilon(2s)$, $\epsilon(2p_x)$, $\epsilon(2p_y)$, and $\epsilon(2p_z)$, of the atomic states. For an isolated carbon atom, Herman and Skillman[9] give

$$\epsilon(2s) = -19.44 \text{ eV} \quad ;$$

$$\epsilon(2p_x) = \epsilon(2p_y) = \epsilon(2p_z) = -11.40 \text{ eV} \quad .$$

For systems with axial symmetry or a reflection plane, the threefold degeneracy of the $2p$ state is lifted by the different crystal-field screening in different directions. For systems having their σ manifold in the xy plane, penetration effects of an atomic orbital on a given carbon atom of the screened field of nearby atoms have been shown[10] to lower the energy of the $2p_x$ and $2p_y$ states relative to the $2p_z$ state. The values usually assigned[11,12] are

$$\epsilon(2p_x) = \epsilon(2p_y) \simeq -13.11 \text{ eV}; \quad \epsilon(2p_z) \simeq -9.69 \text{ eV} \quad .$$

As a test of the validity of our band-structure calculation method, we compare, in Fig. 4, our calculated band structure of isolated PA chains with those of Grant and Batra[13] and Young.[14] The π bands and antibonding σ bands in our calculation compare very well with those of Ref. 13, whereas the σ bands in our calculation, but not the π bands, compare well with those of Ref. 14.

The results of the one-dimensional band-structure calculations of the PA-like chains in PDD are shown in Fig. 5. The four π bands are similar in form to those obtained by a zone folding of the two π bands of ordinary PA chains, since the Brillouin zone of the PA-like chain in PDD is half that of an ordinary PA chain. The striking feature of PDD
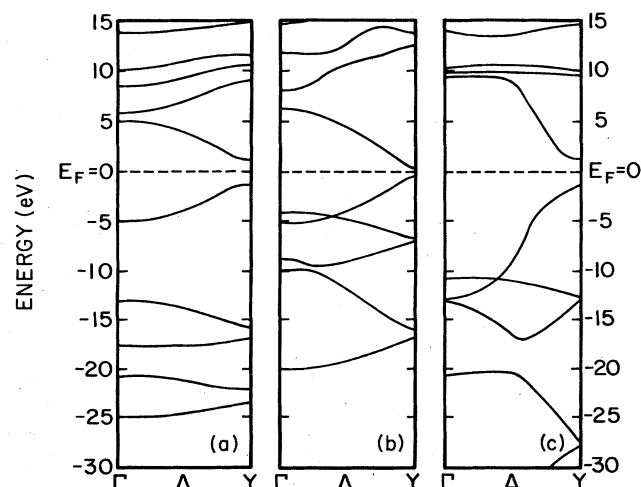

FIG. 3. Section of the PA-like chain with associated electronic orbitals, numbered 1–16, in the plane of the chain.

FIG. 4. Calculated energy bands of $trans$-$(CH)_x$ according to (a) present method, (b) Grant and Batra (Ref. 13), (c) Young (Ref. 14).
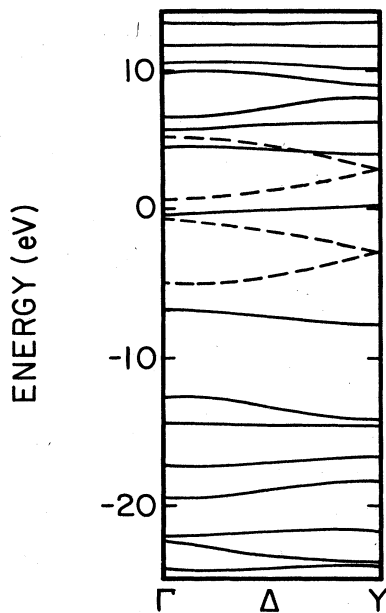
FIG. 5. Energy bands associated with the PA-like chain in PDD. Solid lines are σ bands and dashed lines are π bands.

is the lowering of the lowest antibonding σ band to lie below the π antibonding band. The reason for this σ band having a low enegy is the fact that in Fig. 3 neither orbitals 3 and 4, nor 8 and 9 are oriented towards each other; this reduces the overlap that would otherwise exist between them and increases that between orbitals 4 and 5, and between 9 and 10. We thus propose that in PDD the lowest antibonding σ band is the band to which electrons from the valence π band are promoted by thermal excitations. The energy gap between the π valence band and the lowest anti-

bonding σ band is about 0.45 eV, in good agreement with the value of the experimental gap deduced from the temperature dependence of the conductivity. Our preliminary optical-absorption measurements in PDD show a very strong peak at ~ 0.4 eV and a weak one at ~ 2 eV. According to our calculation, the strong peak at ~ 0.4 eV should be assigned to π-σ^* transitions in PA-like chains whereas the weak one at 2 eV should be due to π-π^* transitions in PDA-like chains.

Thermal excitation will thus give rise to σ electrons and π holes. The effective mass of the holes at the top of the valence band is found to be about $m_0/7$, where m_0 is the free-electron mass. On the other hand, the σ-electron mass is found to be about $10m_0$. We, therefore, deduce that the electrical conduction is due mainly to the holes. Thermoelectric or Hall-effect measurement might serve as a test for such a prediction.

In summary, we have carried out a band-structure calculation of the PA-like chains in the polymerized crystalline dimer of 1,11-dodecadiyne. The calculated energy gap is in good agreement with that obtained from our measurement of the temperature dependence of the electrical conductivity. We note that, according to our calculation, this system presents a rare situation in which a σ band acts as a conduction band, whereas a π band acts as a valence band. Thermal excitation creates electron-hole pairs of heavy σ electrons and light π holes.

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