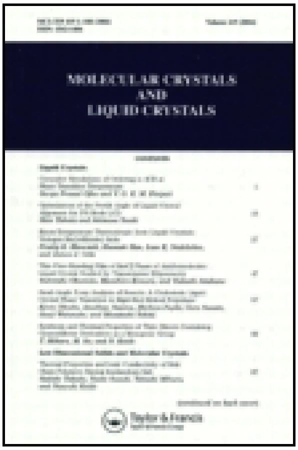

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Effects of Doping Induced Disorder in Polyacetylene

M. Kabbaj [a], J. P. Albert [a] & C. Jouanin [a]
[a] Groupe d'Etudes des Semi-conducteurs, Universite des Sciences et Techniques du Languedoc, 34060, Montpellier, France

To cite this article: M. Kabbaj , J. P. Albert & C. Jouanin (1985): Effects of Doping Induced Disorder in Polyacetylene, Molecular Crystals and Liquid Crystals, 117:1, 205-208

To link to this article: http://dx.doi.org/10.1080/00268948508074625

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 205-208
0026-8941/85/1174-0205/$10.00/0

Printed in the United States of America

EFFECTS OF DOPING INDUCED DISORDER IN POLYACETYLENE

M. KABBAJ, J.P. ALBERT and C. JOUANIN
Groupe d'Etudes des Semi-conducteurs
Université des Sciences et Techniques du Languedoc
34060 Montpellier, France.

Abstract In this paper, the effects of disorder on the electronic structure of doped trans-polyacetylene are evaluated. In effect, at the high doping levels currently obtained on $(CH)_x$, it is not realistic to consider the dopant molecules as isolated impurities. Therefore we have examinated in this work how a random distribution of dopant molecules broadens the impurity levels lying within the band gap. We consider a model where the molecules form covalent bonds with the neighbouring π orbitals. Making use of the SSH model for $(CH)_x$ chain, the electronic density of states is obtained by averaging the Green's function over the random distribution of dopants along the lines of a cluster CPA. From our results, we discuss the formation of impurity bands in the gap and their dependence on both the doping concentration and the chemical nature of the doping molecules.

INTRODUCTION

In recent years, many theoretical works have been devoted to the study of polyacetylene since the hamiltonian considered by Su, Schrieffer and Heeger (SSH)[1] has been able to provide a successfull description of many of its unusual properties. Generally, these theoretical studies assume that the effects of impurities introduced by doping is only to transfer charges of the $(CH)_x$ chains. Recently, some attention has been devoted to the effects of the dopant potential[2-4] on the electronic structure and on the impurity states which appear in the gap. A further complication comes from the fact that at the high doping levels currently attained in polyacetylene, the impurities can no more be considered as isolated units. Our intent in this work is to study the effects on the electronic density of states of the disorder introduced by a random distribution of such impurities.

ISOLATED IMPURITY

We will first recall here the main results obtained when considering an isolated impurity interacting with a $(CH)_x$ chain. More details can be found in Ref. 4. The interaction of the impurity with the chain will be modeled by the following hamiltonian

$$H_e = H_o + \varepsilon_I \, (|i\rangle \langle i|) + V \, (|i\rangle \langle 0| + h.c.)$$

H_0 is the electronic part of the SSH hamiltonian, ε_I is the self energy of the extra level introduced by the impurity and V models the hybridization of this level with the chain.

The bound states of the system are then given as solutions of:

$$\varepsilon - \varepsilon_I - V^2 \, \mathrm{Re} \, (G^o_{oo}(\varepsilon)) = 0$$

where $G^o_{oo}(\varepsilon)$ is the diagonal element of the Green's function of the chain at the site directly coupled with the impurity.

FORMATION OF IMPURITY BANDS

The interaction between a $(CH)_x$ chain and an isolated impurity is a limiting case corresponding to weak dopant concentration. However, as the concentration of impurities increases, their interaction increases and the impurity level, if it lies inside the gap brodens into a band. We will first describe the model used to calculate the density of states of the system in the case of a random distribution of dopants.

Let us consider, for this purpose, a perfectly dimerized chain interacting with a regular repartition of impurities, one impurity being incorporated with two (CH) groups in each unit cell of the lattice. The resulting system can be described by a hamiltonian partitionned into homomorphic subunits^5 as shown in Fig. 1.a.

$$H = \sum_c |c\rangle h_c \langle c|$$

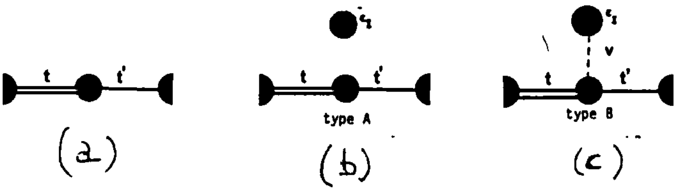

FIGURE 1 Different partitions quoted in the text
(a) Undoped cluster (b) Type A cluster (c) Type B cluster

where $|c\rangle$ denotes a set of basis orbitals spanning the individual unit and h_c is the corresponding matrix hamiltonian. In our case h_c can be chosen as

$$h_c = \begin{pmatrix} 0 & t & 0 & 0 \\ t & 0 & V & t' \\ 0 & V & \varepsilon_I & 0 \\ 0 & t' & 0 & 0 \end{pmatrix}$$

where t and t' are the transfer integral for the perfectly dimerized chain. The doped polyacetylene chain can then be considered as a binary alloy whose elements are these homomorphic clusters of the two types A and B as shown in Fig. 1.b and c.

Case A with $\varepsilon_I \to \infty$ and $V = 0$ corresponds to an impurity induced level artificially put at $+\infty$ and decoupled from the chain while case B corresponds to an extra level at energy ε_I interacting with its nearest neighbor on the chain via the potential V.

Doping polyacetylene thus amount, in this model to substitute clusters A by clusters B.

A random distribution of dopants with concentration c is then simulated by an alloy of clusters A and B with respective concentration 1-2c and 2c. The configuration averaged density of states $N(\varepsilon)$ is defined in the usual manner

$$N(\varepsilon) = - \frac{1}{\pi} \operatorname{Im} \operatorname{Tr} \langle G \rangle$$

where <G> denotes the average of the Green's function over all the alloy's configurations. When using the homomorphic cluster CPA method, the average Green's function G is obtained by introducing an effective periodic medium hamiltonian $H_{eff} = \sum_c |c\rangle \sigma_c \langle c|$ such that a cluster embedded in this effective medium does not produce any scattering. The Green's functions needed in this cluster CPA calculation were obtained by a recursive procedure. In Figure 2.a, we display the density of states obtained for a concentration $c = 0.05$ of impurities with $\varepsilon_I = 0.1$ eV and $V = 0.1$ eV. When isolated, this impurity introduces a localized level at mid-gap. When the impurity concentration increases, the individual impurity levels broaden and form an impurity band while the discontinuities at the band-edges are rounded. We also show in Figure2b the density of states obtained in the case of a more strongly interacting impurity with concentration $c = 0.025$ and $V = 0.8$ eV (for comparison the mean value of the intrachain interaction is $t_0 = 2.5$ eV) and $\varepsilon_I = 1$ eV (donor case). As it can be seen, there is no more gap between the impurity band and the conduction band. As a consequence the fundamental energy gap is reduced by an amount which is concentration dependent. Similar effect must occur in the acceptor case where the impurity band lies near the valence band edge. These results indicate, however that moderate doping induced isorder is not expected to contribute significantly to the eventual closing of the Peirls gap.

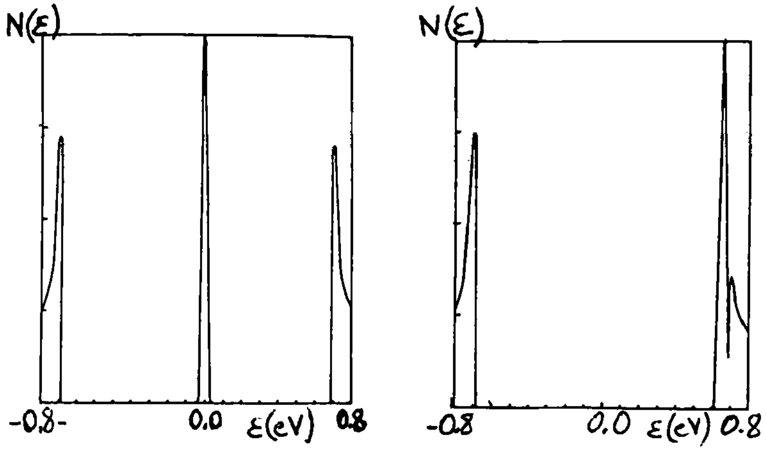

FIGURE 2 Density of states vs energy near the gap
a) ε_I = 0.1 eV ; V = 0.1 eV ; c = 0.05
b) ε_I = 1 eV ; V = 0.8 eV ; c = 0.025

CONCLUSION

In this work, we have studied the effects of a disordered distribution of covalent type impurities on the electronic structure of a $(CH)_x$ chain. Within a simple Huckel formalism and the homomorphic cluster version of the CPA, we have shown how the disorder effects can lead to the formation of impurity bands around the localized level corresponding to an isolated impurity. In some cases, overlap between the conduction or valence band and the impurity band may be expected. This should contribute yet only slightly to the closing of the gap.

REFERENCES

1. W.P. Su, J.R. Schrieffer and A.J. Heeger, Phys. Rev. B 22, 2099 (1980).
2. G.W. Bryant and A.J. Glick, Phys. Rev. B 26, 5885 (1982).
3. D. Baeriswyl, J. Phys. (France), 44, C3-381 (1983).
4. J.P. Albert and C. Jouanin, 47, 825, (1983).
5. T. Odagaki and F. Yonezawa, J. Phys. Soc. Jpn, 47, 379 (1979).