Absence of Impurity Bands in Conjugated Polymers

K. Harigaya and Y. Wada
Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

K. Fesser
Physikalisches Institute, Universität Bayreuth, D-8580 Beyreuth, Federal Republic of Germany

(Received 12 June 1989)

Electronic states in conducting polymers containing impurities are analyzed. The influence of backward- and forward-scattering (bond and site) impurities is studied using the coherent-potential approximation. Because of the 1D nature of the problem, the formation of impurity bands in the gap, as known in different circumstances such as semiconductors and superconductors, is suppressed if the strength of the bond impurity is larger than that of the site impurity. Consequences for the interpretation of experiments are discussed.

PACS numbers: 71.20.Hk, 71.25.−s, 73.20.Dx

The physical properties of conjugated polymers change drastically upon addition of donors or acceptors. This has been discussed, so far, only by considering additional electrons or holes in the electronic structure of the *undoped* material and has led to the concept of nonlinear *solitonic* excitations[1] in these systems. Earlier, this was questioned by Bryant and Glick[2] who drew analogies to conventional semiconductors, where it is known that impurities lead to the formation of impurity states (or bands) in the forbidden energy region of the undoped material. It is, therefore, worthwhile to know whether impurities do significantly change the electronic structure.

There have been some attempts to address this question. Using the Su, Schrieffer, and Heeger (SSH) model[3] and its continuum version[4] [the Takayama-Lin-Liu-Maki (TLM) model] for the undoped polymer, the influence of randomly distributed impurities has been studied by various techniques.[5-7] The impurities act as backward- ($k \rightarrow -k$) ("bond impurity") or forward- ($k \rightarrow k$) ("site impurity") scattering centers of the π electrons. The exact-diagonalization work for finite systems[5] has not obtained information on the electronic structure. The supersymmetric treatment[6] of the random potential and the (equivalent) Born approximation[7] for the self-energy yield a decrease of the energy gap, similar to the case of magnetic impurities in superconductors. On the other hand, it is known that this approximation cannot discuss the emergence of impurity bands. The coherent-potential approximation (CPA) can be used to investigate such a problem.[8] Here, we apply it to doped conjugated polymers.

To fix the notation, we start from the continuum TLM model,

$$H_{\mathrm{TLM}} = \sum_s \int_{-\infty}^{\infty} dx\, \Psi_s^\dagger(x)[-i\sigma_3(\partial/\partial x) + \sigma_1\Delta(x)]\Psi_s(x) + (1/2\pi\lambda)\int_{-\infty}^{\infty} dx\, \Delta^2(x)\,, \qquad (1)$$

and include impurities,

$$H_{\mathrm{imp}} = \sum_{is} \int dx\, \Psi_s^\dagger(x) V\delta(x-x_i)\Psi_s(x)\,, \qquad (2)$$

$$V = I\sigma_1 + J1\,,$$

where the impurity sites x_i are random; I and J are the strengths of bond and site contributions, respectively; the quantity $\Psi_s(x)$ is a two-component spinor describing left- and right-moving electrons; the σ_i's are the Pauli matrices; $\Delta(x)$ is the order parameter describing the dimerization amplitude; and λ is the dimensionless electron-phonon coupling constant. Here, we take the transfer matrix element between intercarbon atoms $t_0 = 1$ and the size of the unit cell in terms of the continuum model $2a = 1$, and then, the Fermi velocity is $v_F = 1$. The system size is $2aN = N$. We assume uniform dimerization, $\Delta(x) = \Delta$. We study the influence of isoelectronic disorder, i.e., without changing the total number of electrons in the system. Therefore, we expect that the formation of kinks or polarons is suppressed since, in the pure case, these distortions are formed as excited states upon the addition of charges into the system. When the site impurities are always between the $2n$th and $(2n+1)$th sites, in the SSH model, giving them the same potential strength, we have the Hamiltonian (2) without a $J\sigma_2$ term.

The electron Green's function is defined by $G(k,p,\tau) = -\langle T_\tau \Psi_k(\tau)\Psi_p^\dagger(0)\rangle$ and reads for the undoped system

$$G^0(k,iE_n) = (iE_n + \mu - k\sigma_3 - \Delta_0\sigma_1)^{-1}\,,$$

where $E_n = (2n+1)\pi T$, T being the temperature and μ the chemical potential. For the case of one single impurity at $x=0$, we can define the t matrix by

$$G(k,p,iE_n) = G^0(k,iE_n)\delta_{kp} + G^0(k,iE_n)t(k,p,iE_n)G^0(p,iE_n)$$

and obtain $t = (V/N)(1-gV)^{-1}$, with $g = (1/N)$

$\times\sum_k G^0(k,iE_n)$. The localized states around the impurity are determined by the singularities of t at $T=0$ K. This condition yields

$$(\Delta_0^2-\omega^2)^{1/2}=-4(I\Delta_0+J\omega)/(4+I^2-J^2)\,, \tag{3}$$

$iE_n+\mu$ being replaced by ω. We find that there is no solution, i.e., no impurity state, if $|I|>|J|$ and $I\Delta_0>0$. Thus, the existence of such an impurity state depends on the relative sign of the order parameter Δ_0. This is similar to the case of a charge-density wave (CDW) in the presence of an impurity, where it was shown[9,10] that the phase of the CDW determines the existence of bound states. [Lin[10] considers only the case $I=J$ which is included in our formula (3).]

For the many-impurity case, we study the averaged Green's function $\bar{G}^{-1}=(G^0)^{-1}-\Sigma$, with self-energy Σ. In the CPA, Σ is determined through

$$c(V-\Sigma)[1-\bar{g}(V-\Sigma)]^{-1}-(1-c)\Sigma(1+\bar{g}\Sigma)^{-1}=0\,, \tag{4}$$

with

$$\bar{g}=(1/N)\sum_k \bar{G}(k,iE_n)=(1/N)\sum_k[(G^0)^{-1}-\Sigma]^{-1}\,, \tag{5}$$

and c the impurity concentration. All quantities are 2×2 matrices. This is a generalization of previous treatments.[6,7]

For a qualitative understanding of the results, it is sufficient to expand (4) for small impurity concentration. One then gets $\Sigma=c(I\sigma_1+J1)$, which can be absorbed in the unperturbed Green's function G^0 by regarding Δ_0 and ω as $\tilde{\Delta}=\Delta+cI$ and $\tilde{\omega}=\omega-cJ$, respectively. Consequently, when calculating the total energy per site $E=2\int d\omega\,\omega\rho(\omega,\Delta)+\Delta^2/2\pi\lambda$, with the ρ density of states, we use

$$\rho(\omega,\Delta)=|\tilde{\omega}|/\pi(\tilde{\omega}^2-\tilde{\Delta}^2)^{1/2}\,. \tag{6}$$

The energy difference between the present state and the undimerized impurity-free state is

$$\delta E=-(\tilde{\Delta}^2/\pi)\ln(2\Lambda/|\tilde{\Delta}|)+2cJ\Lambda/\pi+\tilde{\Delta}^2/2\pi+\Delta^2/2\pi\lambda\,, \tag{7}$$

where Λ is the cutoff. The $\tilde{\Delta}$ dependence breaks the $\Delta\rightarrow-\Delta$ symmetry. The minimum of the total energy occurs at the side $I\Delta>0$, since the main contribution comes from the first term. Consequently, when $|I|>|J|$, there are no bound states in the gap and hence no impurity bands.

In order to establish the above argument, we present numerical results for the case of positive I and J. The parameters are $\lambda=0.183$ and $c=0.01$. Electronic states are half filled. The order parameter Δ is determined by the condition

$$\partial E/\partial\Delta=0\,. \tag{8}$$

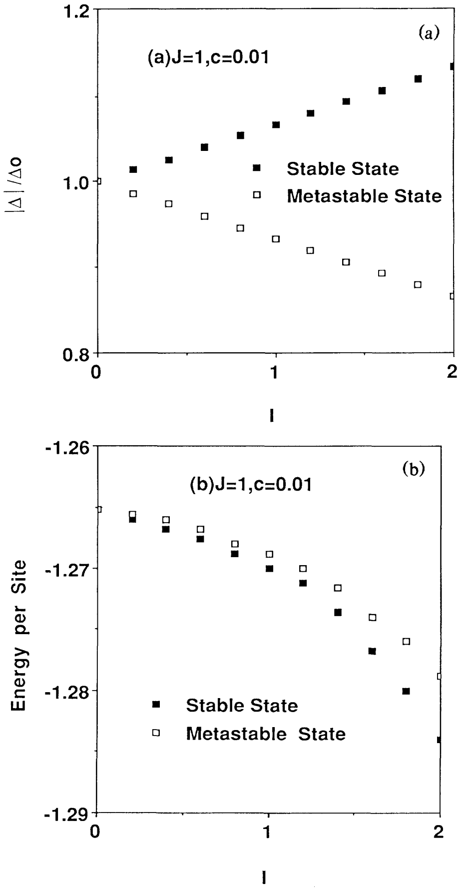

FIG. 1. (a) Two solutions of $|\Delta|$ as functions of the strength of the bond impurity I. The quantity Δ_0 is the order parameter without the impurities. The strength of the site impurity is $J=1$. Concentration is $c=0.01$. The symbols ■ and □ correspond to the positive and negative Δ's, respectively. (b) Total energy per site for the two solutions. The positive and negative Δ's give stable and metastable states, respectively.

We solve (4), (5), and (8) by an iteration method, replacing $iE_n+\mu$ by $\omega+i\delta$ and starting from an arbitrary initial set of values for Δ and Σ. Analytical properties of the retarded Green's function are required.

The results are to be reported mainly for $J=1$. The strength of I is varied within $0\leq I\leq 2$. When $I\neq0$, two solutions are found for Δ. Figure 1(a) shows them as functions of I. Filled squares have positive Δ's, while open squares have negative Δ's. The corresponding total energies are shown in Fig. 1(b). Positive Δ's correspond to the energy minimum, which is stable. This coincides with the above conclusion for small concentration.

Electronic densities of states are shown in Figs. 2 and 3 for the stable and metastable solutions, respectively. The chemical potential μ is always in a region where the density of state vanishes, as indicated by the arrow. In the stable solution, at $I=0$, there is an impurity band, more or less distinct, in the gap. As I increases, it moves

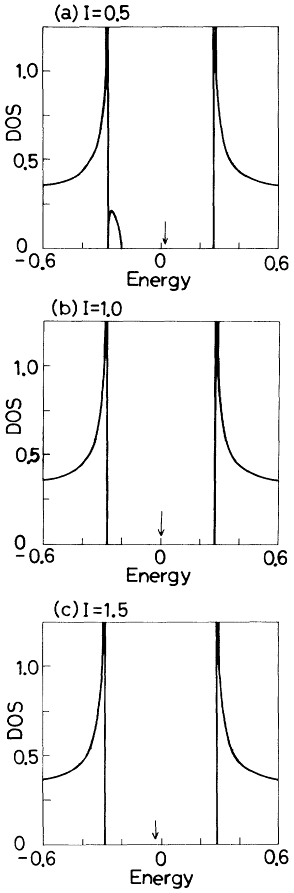

FIG. 2. Density of states per site of the stable solution. The strength of the site impurity is $J=1$. The units along the ordinate and abscissa are t_0^{-1} and t_0, respectively. The strength of the bond impurity is (a) $I=0.5$, (b) $I=1$, and (c) $I=1.5$. The arrow indicates the chemical potential μ.

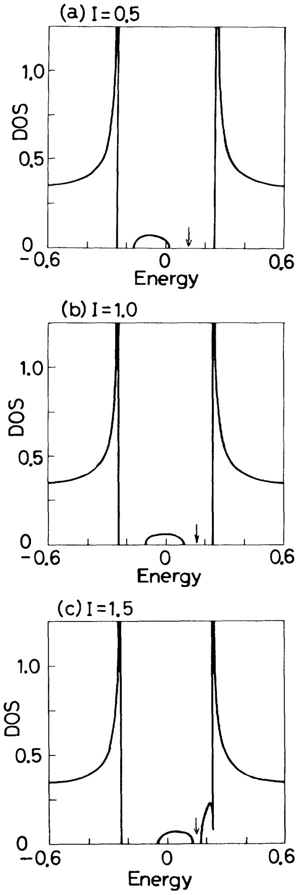

FIG. 3. Density of states per site of the metastable solution. The strength of the site impurity is $J=1$. The strength of the bond impurity is (a) $I=0.5$, (b) $I=1$, and (c) $I=1.5$.

toward the valence band to be absorbed finally at $I=J$. There is no impurity band when $I>J$. In the metastable solution, there is one impurity band at $I=0$. As I increases, it moves toward the gap center. When I becomes larger than J, a new impurity band is emitted from the conduction band.

We show a phase diagram for the stable state in Fig. 4, I and J being the variables. In region I, there is no impurity band. We find an impurity band which is connected to the valence band in region II. It is isolated in region III. The boundary between I and II is $I=J$. The boundary between II and III turns out to be nearly parallel to $I=J$.

We have shown that, differently from conventional systems such as semiconductors and superconductors, there are no impurity bands in the gap in conducting polymers if the strength of the bond impurity is larger than that of the site impurity. The main reason is the one-dimensional nature of the Fermi surface which reduces drastically the allowed phase space for scattering processes. Similar results are valid for CDW systems where the absence of impurity bands has been verified experimentally.

It is worthwhile to bear in mind plausible values for impurity strengths in relativistic polyacetylene in view of the above new finding. The Coulomb potential of a charged impurity, used by Conwell and Jeyadev,[11] gives $|J|\sim 0.42$ in the units $2a=1$ and $t_0=1$. It has a matrix element which modifies the electron transfer, giving $|I|\sim 0.14$, with the help of the tight-binding wave functions[12] Jeyadev and Conwell[13] have discussed the effects of sp^3 defects to find that the conjugation is severely interrupted. The transfer integral for the π electrons could be 1% of t_0 at the sp^3 site, which implies $|I|\simeq 1$. The parameter J has not been estimated, since off-plane hydrogen atoms introduce an additional p_z-like state into the Hamiltonian. The *cis* segments in the *trans* chain should be an example of the bond-type impurities, as Brazovskii and Kirova have suggested.[14] The parameter I is of the order of $\Delta_e\sim\Delta_0\sim 0.26$, while $J\simeq 0$. Here, Δ_e is a parameter introduced in Ref. 14. The strong bond-type impurities can also be found at morphological de-

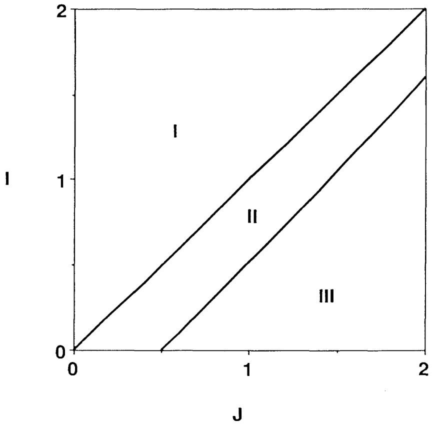

FIG. 4. Phase diagram of the stable solution. In region I, there is no impurity band. The impurity band is connected to the valence band in region II. It is isolated in region III.

fects, such as irregular bendings of the polyacetylene chain. They would primarily give rise to I, keeping J practically zero.

The shortcoming of the present theory is the assumption of a homogeneous order parameter Δ in the presence of impurities. One would expect Δ to vary around the impurity. A self-consistent treatment of a space-dependent $\Delta(x)$ appears to be necessary. This task is difficult but work in this direction is in progress.

This self-consistent treatment is also required if one wants to understand in detail what happens during the doping process. The doping introduces additional charges into the system and alters the electronic structure of the undoped material through scattering processes. A different perspective of this problem has been discussed recently.[11] Consequences for the conductivity mechanism are not yet well understood, but the overlap of (localized) impurity states and band states of the polymer seems to be of importance.

Numerical work has been performed on M-380Q of the International Center for Elementary Particle Physics, University of Tokyo. This work was supported by Deutsche Forschungsgemeinschaft through Sonderforschungsbereich No. 213 (TOPOMAK, Bayreuth), by Research Association for Basic Polymer Technology under the sponsorship of NEDO, and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

---

[1] For a review, see A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, Rev. Mod. Phys. **60**, 781 (1988).

[2] G. W. Bryant and A. J. Glick, Phys. Rev. B **26**, 5855 (1982).

[3] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980).

[4] H. Takayama, Y. R. Lin-Liu, and K. Maki, Phys. Rev. B **21**, 2388 (1980).

[5] Y. Ono, K. Iwano, A. Terai, Y. Ohfuti, and Y. Wada, J. Phys. Soc. Jpn. **58**, 2450 (1989).

[6] B. C. Xu and S. E. Trullinger, Phys. Rev. Lett. **57**, 3113 (1986).

[7] K. Fesser, J. Phys. C **21**, 5361 (1988); K. Iwano and Y. Wada, J. Phys. Soc. Jpn. **58**, 602 (1989).

[8] See, for example, J. M. Ziman, *Models of Disorder* (Cambridge Univ. Press, Cambridge, 1979), Chap. 9.

[9] I. Tüttö and A. Zawadowski, Phys. Rev. B **32**, 2449 (1985).

[10] J. C. Lin, J. Phys. C **20**, 4917 (1987).

[11] E. M. Conwell and S. Jeyadev, Phys. Rev. Lett. **61**, 361 (1988).

[12] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. **17**, 1248 (1949).

[13] S. Jeyadev and E. M. Conwell, Phys. Rev. B **37**, 8262 (1988).

[14] S. A. Brazovskii and N. N. Kirova, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 6 (1981) [JETP Lett. **33**, 4 (1981)].