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# ELECTRON DENSITY OF STATES OF THE DISTORTED ONE DIMENSIONAL SYSTEM WITH BOND DISORDER*

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We present results from investigations of a distorted one-dimensional electron system with "bond impurities". We determined the positions of impurity levels for a single impurity and we calculated the electron density of states in the single bond CPA, for random perturbed hopping integrals.

## 1. *Introduction*

KCP and NMP-TCNQ are quasi-one-dimensional crystals, their flat molecules are arranged in chains [1, 2]. Some ions in KCP molecules (e.g. Br) are arranged in a random way [2]. In the NMP molecule the methyl group has two equivalent positions and in the NMP chain these positions are randomly occupied [3]. These materials have a similar temperature dependence of an electrical conductivity [4] with the characteristic smeared out phase transition.

The electrical conductivity of doped semiconductor materials considerably differs from that of pure crystals, even in the low impurity concentration limit. At a low temperature below a critical temperature quasi-one-dimensional crystals have similar properties to semiconductors [1] and we may expect impurity levels to lie somewhere between the conduction and valence bands.

In this paper we report on a distorted one-dimensional electron system. The single impurity model is a realistic description of crystals with a low impurity concentration, and moreover, it gives qualitative information for higher concentrations. In Section 2 straightforward calculations for a single "site" and a single "bond impurity" are presented. Next, in Section 3, the model with an arbitrary "bond impurity" concentration is investigated. We focus our interest on the energy gap region. We present the electron density of states calculations, in the single bond coherent potential approximation (sbCPA) [5].

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## 2. *One "impurity" in the distorted chain*

Here we consider a distorted linear atomic system with a half-filled electronic band. In this case we have two types of bonds: one between a pair of ions situated closer to each other (the C-bond) and the second one between a pair of ions situated farther away from each other (the F-bond). This system is shown in Fig. 1, where electron hopping integrals between neighbour sites are noted. The Hamiltonian of this system has the form [2, 6]:

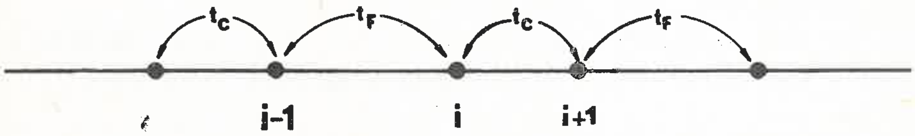

Fig. 1. Distorted atomic chain with one electron per atom. The electron hopping integrals between neighbour sites are noted

$$H_0 = -\sum_i (t+(-1)^i\delta)a_i^\dagger a_{i+1}, \tag{1}$$

where $t_C = t+|\delta|$, $t_F = t-|\delta|$.

The Hamiltonian of the system with a single "impurity" can be written as:

$$H_1 = H_0 + V a_0^\dagger a_0, \tag{2}$$

or

$$H_2 = H_0 + V(a_0^\dagger a_1 + a_1^\dagger a_0). \tag{3}$$

$H_1$ and $H_2$ describe the distorted system, in which one site has a different atomic potential (the "site impurity"), or one pair of neighbour atoms has a different electron hopping integral (the "bond impurity"), respectively. Electron Green's functions are defined by:

$$\hat{g}(E) = \frac{1}{E-H_0}, \tag{4}$$

$$\hat{G}_1(E) = \frac{1}{E-H_1} = \frac{\hat{g}(E)}{1-\hat{g}(E)\hat{V}_1} \tag{5}$$

and

$$\hat{G}_2(E) = \frac{1}{E-H_2} = \frac{\hat{g}(E)}{1-\hat{g}(E)\hat{V}_2}, \tag{6}$$

where $\hat{V}_1 = H_1 - H_0$ and $\hat{V}_2 = H_2 - H_0$. Poles of the Green functions $\hat{G}_1(E)$ and $\hat{G}_2(E)$ different than poles of $\hat{g}(E)$ are obtained from equations:

$$\det(1-\hat{g}(E)\hat{V}_1) = (1-Vg_{00}(E)) = 0, \tag{7}$$

$$\det(1-\hat{g}(E)\hat{V}_2) = \begin{vmatrix} 1-Vg_{00}(E) & -Vg_{01}(E) \\ -Vg_{10}(E) & 1-Vg_{11}(E) \end{vmatrix} = 0. \tag{8}$$

The Green functions $g_{00}(E)$, $g_{01}(E)$, $g_{10}(E)$ and $g_{11}(E)$ have the form:

$$g_{00}(E) = g_{11}(E) = 2 \sum_{|k| \leqslant \pi/2a} \frac{E}{E^2 - E_k^2}, \tag{9}$$

$$g_{01}(E) = g_{10}^*(E) = 2 \sum_{|k| \leqslant \pi/2a} \frac{-t \cos ka - i\delta \sin ka}{E^2 - E_k^2} e^{-ika}, \tag{10}$$

where $E_k = \{t^2 \cos^2 ka + \delta^2 \sin^2 ka\}^{1/2}$, $a$ is the lattice constant.

We look for impurity levels in the energy gap. For $E^2 < \delta^2$, we may write:

$$g_{00}(E) = \frac{-E}{[(t^2 - E^2)(\delta^2 - E^2)]^{1/2}}, \tag{11}$$

$$g_{01}(E) = \frac{1}{t + \delta}\left[1 + \frac{\delta t + E^2}{[(t^2 - E^2)(\delta^2 - E^2)]^{1/2}}\right]. \tag{12}$$

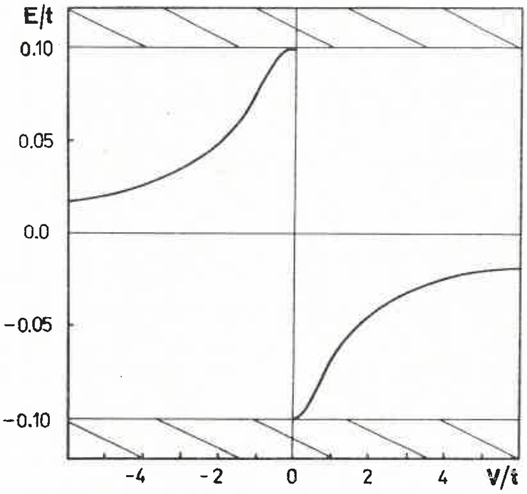

Fig. 2. The position of the "site impurity" level ($|\delta| = 0.1t$)

The roots of Eqs. (7)–(8) may be obtained easily. In Fig. 2 and Fig. 3 the functions:

$$V = \frac{1}{g_{00}(E)} = \frac{[(t^2 - E^2)(\delta^2 - E^2)]^{1/2}}{-E} \tag{13}$$

and

$$V = \frac{1}{g_{00}(E) \pm |g_{01}(E)|} = \frac{(t + \delta)[(t^2 - E^2)(\delta^2 - E^2)]^{1/2}}{-E(t + \delta) \pm |[(t^2 - E^2)(\delta^2 - E^2)]^{1/2} + \delta t + E^2|}, \tag{14}$$

are plotted, where $E$ is the root of Eq. (7) or Eq. (8), respectively.

For a single "site impurity" and for any atomic potential $V \neq 0$, the electron state exists in the energy gap (Fig. 2). More interesting is the case of a single "bond impurity" (Fig. 3). The $V$ dependence of the position of the impurity state in the energy gap is different for a variation of the hopping integral between the F-atoms (i.e., the pair of atoms situated farther away from each other) — the curve *a*, than between the C-atoms (i.e., the pair of atoms situated closer to each other) — the curve *b* (Fig. 3). For the strong "bond impurity" potential $|V| > V_0 = t+\delta$ and for $\delta > 0$, i.e. for the "C-bond impurity", there are no electron states in the energy gap. For $\delta < 0$, i.e., for the "F-bond impurity" and for $|V| > V_0 = t+\delta$ two electron states exist in the gap.

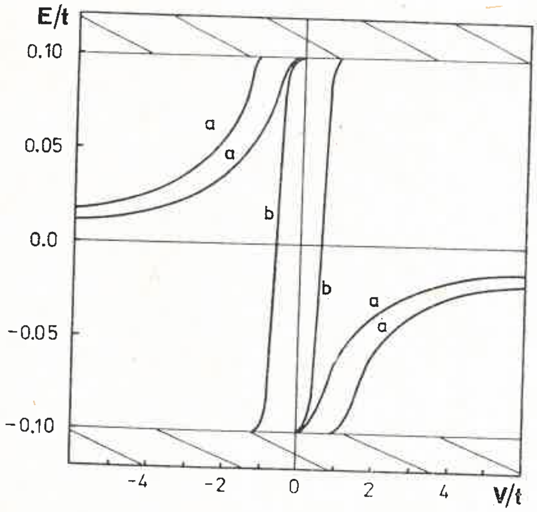

Fig. 3. The position of the "F-bond impurity" level (curve *a*) and of the "C-bond impurity" levels (curve *b*) — $|\delta| = 0.1t$

### 3. *Electron density of states in the single bond coherent approximation (sb CPA)*

Now we investigate the distorted one-dimensional electron system with random perturbations of the electron hopping integrals. This system is described by the Hamiltonian:

$$H = -\sum_i (t+(-1)^i\delta)a_i^\dagger a_{i+1} + V\sum_i c_i a_i^\dagger a_{i+1}. \tag{15}$$

The symbol $c_i = 1$ if the hopping integral from $i$-th site to $i+1$-th site is disturbed and $c_i = 0$ otherwise.

We calculate the electron density of states in the single bond CPA proposed by Niizeki [5]. For this model we have two types of bond, the F-bonds (for even $i$) and the C-bonds (for odd $i$). Coherent potentials $h_{e\pm}(E)$ and $h_{o\pm}(E)$ (e — even, o — odd) are calculated from equations:

$$x\frac{\pm(h^X_{e(o)}-h_{e(o)\pm}(E))}{1-(h^X_{e(o)}-h_{e(o)\pm}(E))F_{e(o)\pm}(E)}+y\frac{\pm(h^Y_{e(o)}-h_{e(o)\pm}(E))}{1-(h^Y_{e(o)}-h_{e(o)\pm}(E))F_{e(o)\pm}(E)}=0, \qquad (16)$$

where

$$h^X_e=-t-\delta+V, \quad h^X_o=-t+\delta+V,$$
$$h^Y_e=-t-\delta, \quad h^Y_o=-t+\delta. \qquad (17)$$

($x$ is the concentration of the "bond impurities", $x+y=1$). The Green functions $F_{e\pm}(E)$ and $F_{o\pm}(E)$ are in the form (see [5]):

$$F_{e\pm}(E)=4\sum_{0\leqslant k\leqslant\pi/2a}\frac{E-\Delta(E)\pm h(E)\cos^2 ka+\sigma(E)\sin^2 ka}{(E-\Delta(E))^2-h^2(E)\cos^2 ka-\sigma^2(E)\sin^2 ka},$$
$$F_{o\pm}(E)=4\sum_{0\leqslant k\leqslant\pi/2a}\frac{E-\Delta(E)\pm h(E)\cos^2 ka-\sigma(E)\sin^2 ka}{(E-\Delta(E))^2-h^2(E)\cos^2 ka-\sigma^2(E)\sin^2 ka}, \qquad (18)$$

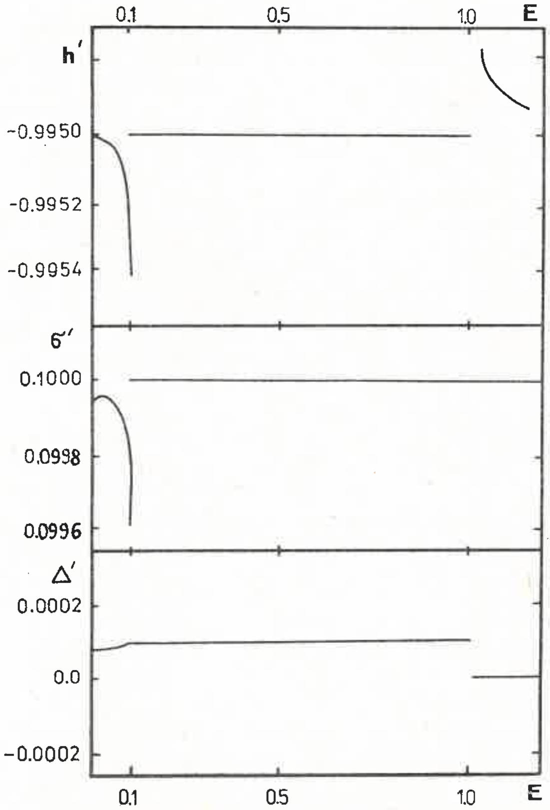

Fig. 4. Real parts of the coherent potentials $h$, $\sigma$ and $\Delta$ for $\delta=0.1$ and $V=0.01$

where

$$\begin{aligned} h(E) &= \tfrac{1}{4}\left[h_{o+}(E)+h_{o-}(E)+h_{e+}(E)+h_{e-}(E)\right], \\ \sigma(E) &= \tfrac{1}{4}\left[(h_{e+}(E)+h_{e-}(E))-(h_{o+}(E)+h_{o-}(E))\right], \\ \Delta(E) &= \tfrac{1}{2}\left[(h_{e+}(E)+h_{o+}(E))-(h_{e-}(E)+h_{o-}(E))\right], \end{aligned} \tag{19}$$

denote the hopping integral, the gap and the atomic potential for the Hamiltonian of the effective medium.

For NMP-TCNQ the methyl group has two equivalent positions. Thus, the probability $x = y = 1/2$. From Eq. (16) we obtain

$$h_{e(o)\pm}(E) = -(t\overset{+}{(-)}\delta)+\tfrac{1}{2}V-\left[1-\{1+V^2F^2_{e(o)\pm}(E)\}^{1/2}\right]/(2F_{e(o)\pm}(E)). \tag{20}$$

We solved numerically the selfconsistent equation (20) by an iteration method. We carefully integrated the integrals (18) (the integrands are complex functions of the complex variable $E = E'+iE''$ and for a small value of $E''$ they are of the Gaussian type with a sharp peak). For $V \neq 0$ the variation of $E''$ from $E'' = 10^{-4}$ to $E'' = 10^{-5}$ induced the variation of results which were less than 0.1%.

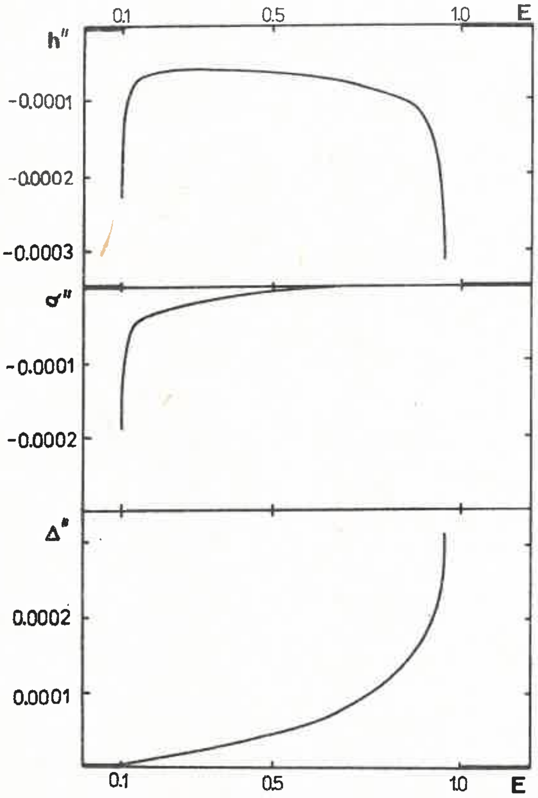

Fig. 5. Imaginary parts of the coherent potentials $h$, $\sigma$ and $\Delta$ for $\delta = 0.1$ and $V = 0.01$

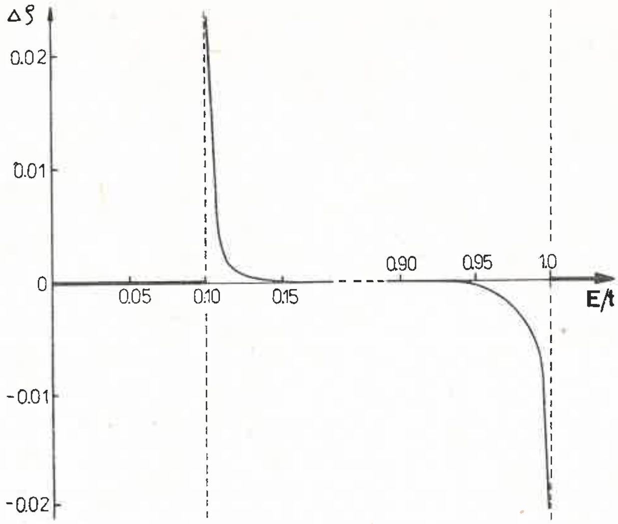

Fig. 6. Difference in the electron density of states for the disordered and the ordered system, $\Delta\varrho = \varrho_{\text{disorder}} - \varrho_{\text{order}}$ for $\delta = 0.1$ and $V = 0.01$

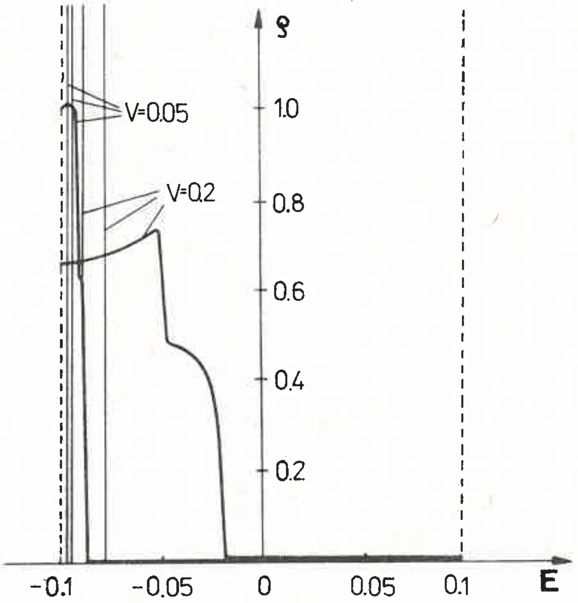

Fig. 7. The electron density of states in the energy gap for $\delta = 0.1$ and for $V = 0.05$ and $V = 0.2$. The single "bond impurity" levels are also noted

Figs. 4 and 5 exhibit the real and the imaginary parts of the coherent potentials for the case of a weak random potential, $V = 0.01$. All quantities are in units of the hopping integral ($t = 1$). Fig. 6 shows the change of the electron density of states, $\Delta\varrho = \varrho_{\text{disorder}} - \varrho_{\text{order}}$. For this case (small $V$) the electron density of states is greater near the energy gap than in the case of the ordered system. According to our considerations in Section 2 the impurity states are expected to lie at a small distance above the top of the valence band. However, these states lie too close to the band edge (Fig. 3) and we could not reach these points in our numerical calculations.

For greater values of $V (V = 0.05$ and $V = 0.2)$ we repeated this procedure. Much more iteration steps were needed for larger $V$. For the energy $0.1 < |E| < 1.0$ the numerical procedure was not convergent within 60 steps of iteration and, therefore, we confined calculations to energy in the gap.

For these values of $V$ we found the electron density of states near the top of the valence band. Fig. 7 exhibits the results of these calculations as well as the single "bond impurity" levels, for $V = 0.05$ and $V = 0.2$. The impurity states form the band and the width of this band depends on the value of the potential $V$. The density of states has two jumps, which, as we suppose, are originated from the "F-bond" and the "C-bond impurity" states. The single impurity states lie closer to the band edge than the jumps of the density of states (see Fig. 7). For a higher impurity concentration, we expect, there are created more impurity states, which are shifted from the position of the single impurity level.

## 4. *Conclusions*

In our considerations many approximations are involved. For example, we assumed that for an arbitrary impurity concentration and for any potential $V$ our system is stable. For strong impurity perturbations a stability problem of the distorted phase must be considered also.

However, we might assert that even for a weak impurity potential (for small $V$) two types of impurity states exist in the energy gap. If a one electron hopping integral between neighbour atoms, situated farther away from each other (the F-atoms) or situated closer to each other (the C-atoms), is perturbed, then we have the "F-bond impurity" level (curve *a* in Fig. 3) or the "C-bond impurity" level (curve *b* in Fig. 3). We assert that these two types of states build up the impurity band which has two jumps (Fig. 7). For a very weak random potential ($V = 0.01$) we have calculated the electron density of states for the whole energy range. We have observed that near the gap, in the valence and in the conduction band, the electron density of states is greater than in the case of the ordered system.

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## REFERENCES

[1] J. J. André, A. Bieber, F. Gautier, *Ann. Phys.* (Paris) **1**, 145 (1976).
[2] L. N. Bulaevski, *Usp. Fiz. Nauk* **115**, 263 (1975).
[3] B. Moris, *Phys. Lett.* **A53**, 455 (1975).
[4] A. N. Bloch, R. B. Weisman, C. M. Varma, *Phys. Rev. Lett.* **28**, 753 (1972).
[5] K. Niizeki, *J. Phys. C.* **10**, 211, 2131, 2141, 3351 (1977).
[6] B. R. Bułka, *Acta Phys. Pol.* (1980), in press.