

FINAL EXAM - SOLID STATE PHYSICS FALL 2019

1. ISOLATED CHAINS.

Some organic compounds like TTF-TCNQ are made up of weakly coupled chains. In TTF-TCNQ, tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) chains are weakly bound. This gives these compounds a 1D aspect. The aim in this problem is to study some characteristic features of these 1D compounds.

In a very simple approximation, we shall describe these compounds as single chains of N identical molecules, each the same distance a from the next, as shown in Fig. 1. Let R_ℓ be the coordinate of the ℓ th molecule, so $R_\ell = \ell a$. We assume the usual periodic boundary conditions. We calculate the band structure of each chain in the tight-binding approximation. The quantum states of the electrons in the last occupied orbital of molecule ℓ are modelled by a single non-degenerate orbital state $|R_\ell\rangle$ of energy E_0 with $\langle R_\ell | R_m \rangle = \delta_{\ell m}$. We assume that the Hamiltonian \hat{H} of one electron in the chain can be written in the form

$$\hat{H} = \frac{p^2}{2m} + \sum_{\ell=1}^N V(r - R_\ell),$$

where $V(r - R_\ell)$ is the potential at site ℓ . We only take into account hopping integrals involving the two nearest neighbours. These are denoted as $-t_0$ and $-t_1$ (with t_0 and t_1 positive).

1. Recall the general form $|\Psi_k\rangle$ for an eigenstate of this Hamiltonian together with the associated energy eigenvalue E_k . Sketch the shape of the dispersion curve in the first Brillouin zone.
2. Sketch the wave functions $|R_\ell\rangle$ with s symmetry, together with the potential contributing to the various hopping integrals entering the expression for E_k .
3. Assume that each molecule gives a conduction electron to the band. What can be deduced about the electrical transport properties of this chain? Find the Fermi wave vector k_F and the Fermi energy E_F .
4. Calculate the total electronic energy of the chain. Hint: It simplifies to integrate over k .

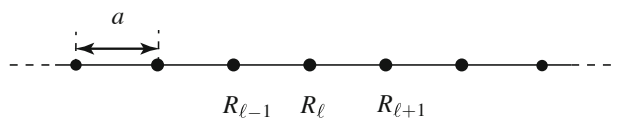


Fig. 1 Simple model for a molecular chain

2. EXPERIMENTAL

The structure of TTF-TCNQ is shown in Fig. 2. The TTF and TCNQ molecules are stacked in the direction b , aligned with the chains. (The parameter b is identified with a in 1 and 3). The temperature dependence of the conductivity parallel to the TTF-TCNQ chains is shown in Fig. 3.

1. What can be said about the electrical resistivity of this compound?

Figure 4 shows topographical images obtained by scanning tunnelling microscopy of the surface of a TTF-TCNQ crystal in the plane ab at two different temperatures (70 and 36 K).

2. On Fig. 4a, indicate the primitive cell at the surface. Do you recognise the material basis of Fig. 2?

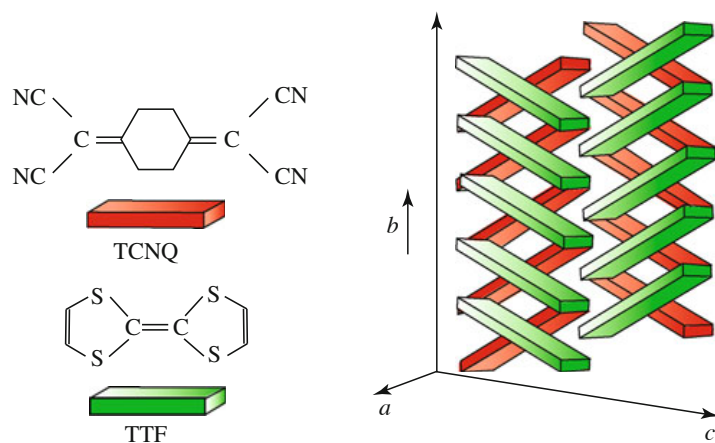
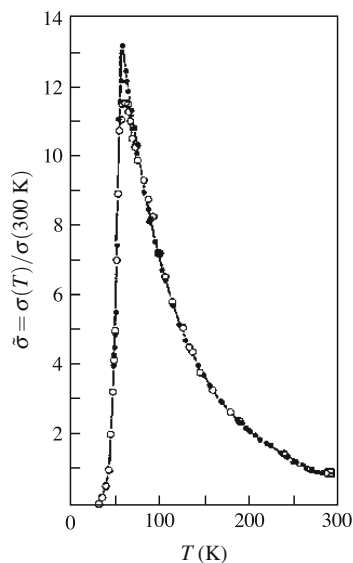


Fig. 2 Chemical structure of TTF-TCNQ (*left*) and three dimensional stacking of the molecules (*right*)

Fig. 3 Temperature dependence of the conductivity parallel to TTF-TCNQ chains. From Cohen, M.J., Coleman, L.B., Garito, A.F., Heeger, A.J.: Phys. Rev. B **10**, 1298 (1974). With the permission of the American Physical Society (© 1974 APS). <http://link.aps.org/doi/10.1103/PhysRevB.10.1298>



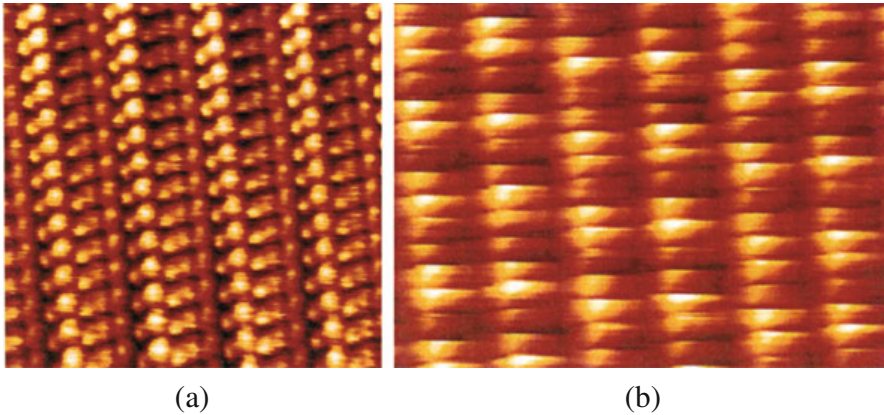


Fig. 4 Topographical images obtained by scanning tunnelling microscopy of the surface of a TTF-TCNQ crystal in the plane ab at two different temperatures: (a) 70 K and (b) 36 K. Images courtesy of Wang, Z.Z.: LPN, Marcoussis

3. *The structure is radically different at 36 K. How would you characterise it along the chains? Across the chains?*

2. DIMERISED CHAINS

Although the experimental situation in Fig. 4b is more complicated, we shall use a simple model of structural deformation to describe changes in electronic properties. We assume that the chains dimerise at low temperatures, with each molecule moving a distance $\pm u$ as shown in Fig. 5.

1. *What is the primitive cell for this structure and the size of the first Brillouin zone?*

The aim now is to calculate the new band structure of this compound, still using the tight-binding approximation. The Hamiltonian for an electron in the chain can now be written

$$\hat{H} = \frac{p^2}{2m} + \sum_{\ell=1}^{N/2} [V(r - R_{\ell}^+) + V(r - R_{\ell}^-)] .$$

2. *Explain why solutions of the Hamiltonian will have the form*

$$|\Psi_k\rangle = \sqrt{\frac{2}{N}} \sum_{\ell=1}^{N/2} e^{2ik\ell a} (a_k |R_{\ell}^+\rangle + b_k |R_{\ell}^-\rangle) ,$$

with $|a_k|^2 + |b_k|^2 = 1$.

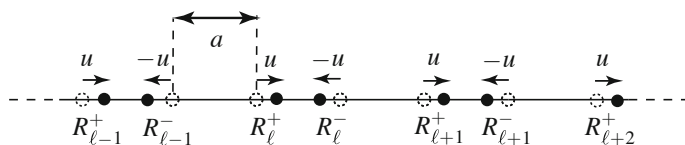


Fig. 5 Dimerisation of the chain

In order to find the functions $|\Psi_k\rangle$ and their associated energies E_k , we write down the eigenvalue equation $\hat{H}|\Psi_k\rangle = E_k|\Psi_k\rangle$ for the energies and project onto each of the states $|R_\ell^+\rangle$ and $|R_\ell^-\rangle$ in turn. We still assume that the only nonzero hopping integrals are those involving nearest neighbours, and use the notation

$$\begin{aligned} -t'_0 &= \langle R_\ell^+ | V_\ell^+(r) | R_\ell^+ \rangle = \langle R_\ell^- | V_\ell^-(r) | R_\ell^- \rangle, \\ -t'_1 &= \langle R_\ell^+ | V_\ell^+(r) | R_\ell^- \rangle = \langle R_\ell^+ | V_\ell^-(r) | R_\ell^- \rangle, \\ -t''_1 &= \langle R_{\ell-1}^- | V_\ell^+(r) | R_\ell^+ \rangle = \langle R_{\ell-1}^- | V_{\ell-1}^-(r) | R_\ell^+ \rangle, \end{aligned}$$

where $V_\ell^+ = V(r - R_\ell^-) + \sum_{m \neq l} V(r - R_m)$ and similarly for V_ℓ^- .

3. Show that we obtain a system of two equations in a_k and b_k , one of which is

$$a_k(E_0 - E_k - t'_0) + b_k(-t'_1 - t''_1 e^{-2ika}) = 0,$$

and derive an expression for the other.

4. Calculate the two energy eigenvalues E_k^1 and E_k^2 in terms of E_0 , t'_0 , t'_1 , and t''_1 . Sketch the band structure, specifying the values at the center and the edge of the Brillouin zone. What happens to the band structure when $u = 0$?

5. Would you say this result is compatible with the observations of Fig. 3?

For a more accurate analysis of the temperature dependence of the conductivity σ of TTF-TCNQ, Fig. 6 shows the logarithm of σ as a function of $1/T$ down to the lowest temperatures.

6. What can you say about the temperature dependence of the conductivity at the lowest temperatures?

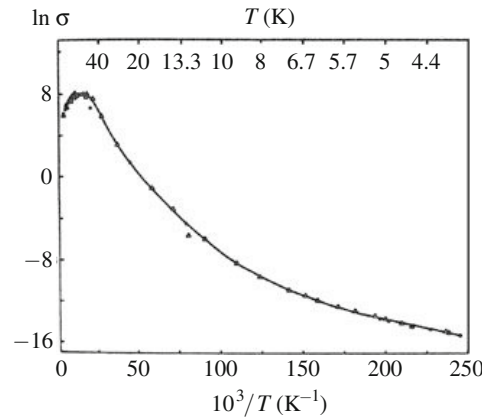


Fig. 6 Temperature dependence of the conductivity σ of TTF-TCNQ down to the lowest temperatures. From Ferraris, J., Cowan, D.O., Valatka, N., Jr., Perlstein, J.H.: J. Am. Chem. Soc. **95**, 948 (1973). With permission of the American Chemical Society, © 1973

2. PIERLS TRANSITION

In this section the aim is to investigate the stability of the dimerised state at $T = 0$. From now on, we consider only the nearest-neighbour contribution to the potentials V_ℓ .

1. For small displacements u compared with a , justify the following approximations: $t'_0 \approx t_0$, $-t'_1 \approx -t_1 - \alpha u$, and $-t''_1 \approx -t_1 + \alpha u$ with $\alpha > 0$.
2. Calculate the change in the total electronic energy resulting from dimerisation and show that the gain in electron energy compared with the situation $u = 0$ can be written in the form

$$\Delta E = -ANu^2 \left(\ln \frac{B}{u} - \frac{1}{2} \right),$$

specifying the values of A and B in terms of t_1 and α .

It is given that

$$\int_0^{\pi/2} \left[1 - (1 - z^2) \sin^2 x \right]^{1/2} dx = 1 + \frac{1}{2} z^2 \left(\ln \frac{4}{|z|} - \frac{1}{2} \right),$$

for small z .

3. Assuming that the atoms are coupled harmonically by an elastic force with stiffness constant K , calculate the static deformation energy of the chain as a function of N , K , and u .
4. Discuss the instability of the ion–electron system with regard to dimerisation of the chain. Find the static displacement u_{eq} at equilibrium as a function of K , t_1 , and α .

In TTF-TCNQ, charge transfer between chains is such that a chain carries 0.50 electrons per molecule rather than 1 as assumed above.

5. Can you explain the structure actually observed in Fig. 4b?