Executive Summary for the SRC Forum on Highly Conductive Polymers (HCP)

In 2007 SRC conducted a fundamental study on Highly Conductive Polymers (HCP). The objectives of the study were:

- To review publications in the field (a 'pro et contra' approach)
- To summarize quantitative experimental results reported on highly conductive polymers and to address alternative interpretations of experimental results
- To explore universal mechanisms of electrical conduction in solids, which are applicable to e.g. both normal conductors and superconductors

On October 4, 2007 a forum was held in Georgia Institute of Technology. The forum concluded the 2007 SRC Fundamental study on Highly Conductive polymers.

HCP phenomenon
The focus of the study was on polymer films between two metal electrodes, which after special treatment exhibit areas of very low resistivity in the direction normal to the surface. Some groups claimed that a superconducting state exists in these polymer films at room temperature.

1. Key Experimental Results for HCP

There is a significant body of literature on the topic of HCP. In this report we review several the most representative publications.

In 1989, a group from Institute of Synthetic Polymeric Materials, Moscow, Russia reported on very low resistivity of thin polymer film in the direction normal to the surface (N. S. Enikolopyan, 1989 [1]). The work was reproduced by a group in Ioffe Physico-Technical Institute, St.-Petersburg, Russia, which conducted experiments both at room temperature and cryogenic temperatures (to achieve superconducting state on metal electrodes).

In 1992, the group of the Ioffe Institute concluded that the low resistance state was due to *metallic bridge formation from electrode material* (A. N. Ionov, 1992 [2]).

In 1998 a group from Bar-Ilan University, Israel conducted an additional study. The main aim of their work was "to verify whether or not the low-resistance state in the above experiments can be explained by the formation either metallic or carbon bridge between the contacts" (Shlimak I, Martchenkov V. , 1998 [3]). In experiments, with poly(dimethylsiloxan) - PDMS, two switching regimes were found*:*

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[1] N. S. Enikolopyan, et al., *Possible Superconductivity near 300-K in Oxidized Polypropylene*, JETP LETT. 49: 371-375 (1989)
[2] A. N. Ionov et al, *Low-Resistance State in Polydipheylenephtalide at Low Temperature*, Solid State Com. 82, 609 (1992)
[3] Shlimak I, Martchenkov V, *Switching phenomena in elastic polymer films*, Solid State Com. 107 (1998): 443-446

1) **<u>High voltage switching</u>**: If the applied voltage exceeded some threshold value V_{th} >*100* V, the sample resistance switched from the normal high resistance state (R ~ 10^9 Ohm) to the low-resistance state with typical resistance of a few Ohm. Formation of a metal bridge from the electrode atoms (copper in their case) was clearly observed. In this regime, the maximum current in low-resistance state was I_{max}<100 mA and it was limited by melting of the metal bridge.

2) **<u>Low voltage switching (LVS)</u>**: In these experiments the voltage applied to the polymer films did not exceed 1 Volt, which is much smaller than for the electrical breakdown in the previous case of high voltage switching. The resistance of films with thickness in the range d = 5-12 μm was observed to switch randomly between the high-resistance OFF state (about 10^9 Ohm) and the low-resistance ON state (about 0.4-0.5 Ohm) The ON state remained after the voltage is switched off (the "memory" effect), however it disappeared and reappeared spontaneously. Typical time dependence of the resistance of polymer film in the low voltage switching experiments is shown in Fig. 1. *The switching from high-resistance to low-resistance state occurs after ~8-10 hours of low-voltage conditioning.* For thicker films (*d*> 15 μm), the ON state was not observed during several days of observation.

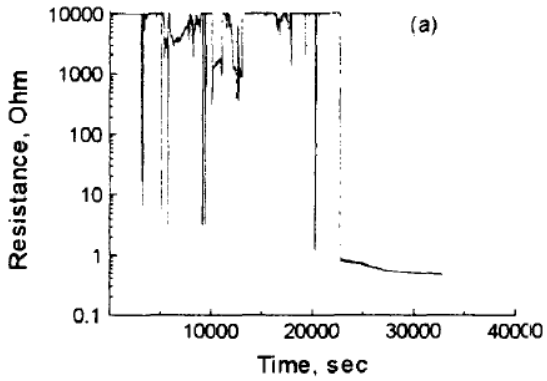

Fig. 1. Typical time dependence of the resistance of thin PDMS film in the low voltage switching experiments (Schlimak, 1998)

<u>Characteristics of the low-resistance state:</u>

1) The sample resistance in the ON state does not depend on the cross section of the polymer film available for the current flow (the sample area in these experiments varied from 0.1to 0.4 cm^2)
2) The most intriguing property of the LVS ON state is its ability to carry a high current. A current exceeding 2 A was passed through "sandwich''-like sample for a few hours without sample damage. The maximum current was limited by the electrode burn-out. The *I-V* characteristics in LVS ON state are linear up to the maximal current (which may suggest either that there is no heating or that resistivity is temperature independent).
3) .Resistance of the US ON state *R* = 0.4-0.5 Ohm.

The measured resistance of the ON state R = 0.4-0.5 Ohm can be attributed either to the polymer film itself or to the contact between the film and metal electrode:
$R_{ON}=R_{film}+R_{cont}$

The Joule heat was released in the metal electrodes and not in the polymer film. Therefore, one can conclude that $R_{film}<<R_{cont}$ (otherwise, for example if one assumes conductive bridge formation inside the polymer film, generation of Joule heat in the bridge made of any metal for I = 2 A would result in a temperature increase of ~10^4 K).

The authors concluded that the low-voltage switching is a new effect, which can not be explained in terms of conventional breakdown. They suggested that further investigation is needed. *The authors did not refer to a superconducting state in polymer film.*

In 2005-2007, the group of Ionov et al. from *Ioffe Physico-Technical Institute, Russia,* which argued against the concept of HCP in 1992 (see Ionov, 1992) published a new series of articles on the subject in collaboration with the *Freie Universitat Berlin, Germany (*Ionov, 2005 [4] , Ionov, 2007 [5]). In these articles, Ionov et al., have reversed their opinion and now maintain that the HCP phenomenon is real. Their experiments with superconductive electrodes indicated the non-dissipative transport of charge carriers in the polymers.

Summary of experimental results on HCP

- Low resistance state at room temperature
  - *Experimental challenge:* Resistivity measurements in the structure with metal electrodes
- High current in the low resistance state without destruction of the polymer film
- Superconductive state at cryogenic temperatures (in the structure with superconducting electrode)

2. Theory

Quasi-one-dimensional conductors, in particular, conducting polymers, are always attracted significant attention as promising candidates for realization of high-temperature superconductivity (HTS). In the early work by Little (Little, 1964 [6], Davis, 1976 [7]) and followed up by Ginzburg (Ginzburg and Kirzhnits, 1982 [8]), the possible HTS of polymers was associated with the exciton mechanism, which was described in the frame of the Bardeen-Cooper-Schrieffer (BCS) approach.
Modern physics of superconducting materials indicates many common features of HTS cuprates and polymers (Lee, 2006 [9]): (i) without doping these materials are insulators

[4] A. N. Ionov et al, *High Conductivity and Supercurrent in Superconductor-Polymer-Superconductor Systems*, Physica B (2005) 506
[5] A. N. Ionov et al, *Local distribution of high-conductivity regions in polyamide thin films*, JEPT Lett. (2007) 636
[6] W. A. Little, *Possibility of synthesizing organic superconductor*, Phys. Rev. A 134 (1964): 1416&
[7] D. Davis, H. Gutfreund, W. A. Little, *Proposed model of a high-temperature excitonic superconductor*, Phys. Rew B 13 (1976): 4766-4779 1976
[8] V.L. Ginzburg and D.A. Kirzhnits, *High-Temperature Superconductivity* (Springer 1982)
[9] P.A. Lee, N. Nagaosa, X.G. Wen, *Doping a Mott insulator: Physics of high-temperature superconductivity*, Rev. Mod. Phys. **78** (2006) 17

due to interaction effects, (ii) with doping they became conductors, and HTS cuprates show the phase separation and formation of quasi-one-dimensional conducting channels (stripes); (iii) in the normal phase, the correlation effects in both materials are very strong and cannot be described in the frame of the Landau-Fermi-liquid theory; (iv) interaction effects can provide various phase transitions, including the superconducting transition, and phase competition is very sensitive to a number of material parameters. Moreover, the ideas developed early for polymers (Kivelson and Emery, 1994 [10]) are widely used in modern attempts to describe the superconducting transition in cuprates (Emery and Kivelson, 1995 [11]).

According to the modern views on HTS in cuprates (Wang, 2003 [12]), the mean field superconducting transition temperature in these materials is in fact close and even higher (depending on doping) to the room temperature. However, strong phase fluctuations destroy the global coherence of the superconducting state in cuprates, local superconductivity manifests itself in the form of magnetic vortices far above the *observable* T_c.

The SRC study group explored universal mechanisms of electrical conduction in solids, which are applicable to both normal conductors and superconductors. The analysis, based on the quantum conductance model yields results consistent with experimental data reported both with conventional superconductors and HCP (see APPENDIX).

3. Forum Discussion Points

1) The conductivity switching in PDMS films is very interesting and unexpected result. PDMS is known as insulator, and if indeed the behavior shown in Fig. 1 could be reproduced, this would suggest new physical mechanisms of conductivity switching in insulating polymers.

2) Quantitative resistivity measurements are difficult
    a. Standard techniques, such as 4-probe measurements cannot be used because of extreme conductance anisotropy
    b. Effects of metal contacts may dominate at room temperature

4. Forum outcome

It was decided, that the SRC/FCRP Interconnect Focus Center will conduct experimental work to attempt to reproduce the switching phenomena in PDMS, shown in Fig.1 (Shlimak, 1998).

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[10] A. Kivelson and V. J. Emery, *Strategies for finding superconductivity in conducting polymers*, SYNTHETIC METALS 65 (1994): 249-254

[11] V.J. Emery and S.A. Kivelson, *Importance of phase fluctuations in superconductors with small superfluid density*, Nature 374 (1995) 434

[12] Y. Wang, S. Ono, Y. Onose et al., *Dependence of upper critical field and pairing strength on doping in cuprates*, Science 299 (2003) 86

5. References

D. Davis, H. Gutfreund, W. A. Little, *Proposed model of a high-temperature excitonic superconductor*,Phys. Rew B 13 (1976): 4766-4779 1976

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A. N. Ionov et al, *Local distribution of high-conductivity regions in polyamide thin films*, JEPT Lett. (2007) 636

S. A. Kivelson and V. J. Emery, *Strategies for finding superconductivity in conducting polymers*, SYNTHETIC METALS 65 (1994): 249-254

P.A. Lee, N. Nagaosa, X.G. Wen, *Doping a Mott insulator: Physics of high-temperature superconductivity*, Rev. Mod. Phys. **78** (2006) 17

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APPENDIX

Physics of Highly Conductive Materials

V. V. Zhirnov, A. A. Kiselev, R. K. Cavin

This report examines highly conductive polymer materials, which according to some reports exhibit, in certain cases, very low room-temperature resistance, e.g. much lower than the resistance of copper. The mechanics of conduction in certain polymers is not understood, and it should be noted, that the reported results on highly conductive polymers are not universally accepted.

On the other hand, if materials could be designed with near zero electrical resistance at room temperature, the benefits to society, in many different applications, would be tremendous. Therefore it seems to be worthwhile to examine the reported results on the highly conductive polymers with respect to their compliance with fundamental physics.

1. Brief Summary of Reported Electrical Characteristics of Highly Conductive Polymers

- The maximum measured current density is 10^8 A/cm^2
- The highest measured current through the polymer film is 1700 Amperes (in approx 1cm^2 sample)
- The resistivity of the polymer film in the direction normal to the surface is 10^{-11} – 10^{-24} Ohm·cm (for comparison, the resistivity of bulk Cu is 1.7x 10^{-6} Ohm·cm)

In the next section, we examine, the compliance of the reported resistivity data with fundamental physics.

2. What is the *RESISTIVITY* of a superconductor?

The most common answer to the above question would be “zero”. However, in reality the conductivity must be a very small but finite number. For example, if we consider an extremely short-length single-electron conductor connecting points *A* and *B*, the resistance will be determined by the time, needed for an electron to move from *A* to *B*. An upper bound for the time can be obtained from the Heisenberg relation:

$$\Delta E \Delta t \geq \frac{h}{2} \qquad (1)$$

Correspondingly,

$$\Delta t \geq \frac{h}{2\Delta E} \qquad (2)$$

Eq. 2 gives an estimate of minimal time of dynamical evolution of a physical system (see e.g. [1]).

The current associated with electron movement from *A* to *B* is:

$$I = \frac{e}{\Delta t} \tag{3}$$

From Ohm's law:

$$I = \frac{V}{R} \tag{4}$$

From (3) and (4):

$$R = \frac{V\Delta t}{e} \tag{5a}$$

Taking into account $\Delta E = eV$, obtain

$$R = \frac{\Delta E \Delta t}{e^2} \tag{5b}$$

Or, using (1) obtain the resistance of a single-electron conductance channel

$$R_1 = \frac{h}{2e^2} = 12.9 \text{ kOhm} \tag{5c}$$

Eq. 5c is a well known quantum resistance of a single-electron channel [2], and is the minimum resistance of the channel. It corresponds to "ballistic" electron transport between A and B. In most practical cases, the electron transport is non-ballistic and the channel resistance is larger than (5c).

To examine the relations between the quantum resistance and superconductivity we now calculate the expected resistivity of a piece of metal conductor (for example copper) in the ballistic regime. Consider a copper cube 1cm side. Each Cu atom contributes one conductivity electron [3], and thus the number of conductivity electrons is approximately equal to the number of atoms in the cube. For copper, the atomic density is n=8.44x10^{22} at/cm^3.

The cross-section of the 1cm-cube conductor contains many atoms, and therefore many parallel single-electron conductance channels. The corresponding resistance is

$$R = \frac{R_1}{N}, \tag{6}$$

where N is the number of independent channels in the crossection. It follows from 3D atomuc density that:

$$N = n^{\frac{2}{3}}. \tag{7}$$

By definition, resistivity, is the resistance of the unit side cube, and therefore the 'ballistic resistivity' of copper is:

$$\rho_{bal} = \frac{h}{2e^2} n^{-\frac{2}{3}} \quad (8)$$

For Cu (n=8.44x10^{22} at/cm^3) and ρ_{bal}=6.7x10^{-12} Ohm-cm.
For comparison, the resistivity of metal copper at room temperature is ρ_{Cu}=1.7x10^{-6} Ohm-cm, which is six orders of magnitude larger. It is tempting to relate the ballistic resistivity to the superconductive state (and it is occasionally made by some researchers).

However, the reported experimental data on the resistivity of superconductors is 3.6x10^{-23} Ohm-cm [4]. This number is many orders of magnitude smaller that the ballistic resistance, and thus there is an apparent contradiction between the superconductivity phenomena and quantum transport. To resolve this contradiction, we revisit the quantum resistance model (Eqs 1-8). Note, that R_1=12.9 kOhm is the minimum resistance of a *single-electron* conductance channel. The assumption of *N* independent single-electron channels was also used in the derivation of ballistic resistivity of a bulk material (Eqs. 6-8).

If instead, we consider the case that electrons participate in conductance not individually, but collectively, the above result for the ballistic resistivity should be modified. Consider *M* electrons forming a quasiparticle of charge *q=Me*, which moves from point *A* to point *B*. The current associated with the movement of *M* electrons from *A* to *B* is:

$$I_M = \frac{q}{\Delta t} = \frac{Me}{\Delta t} \quad (9)$$

Repeating derivations (4)-(8), and taking into account $\Delta E = qV = MeV$, we obtain:

$$R_M = \frac{h}{2(eM)^2} \quad (10)$$

Consider again the cross-section of 1 cm-cube conductor, which contains N electrons (7). Let the electrons form groups with M electrons in each group. Thus, the total number of groups in the cross-section is $K = \frac{N}{M}$. The resistance associated with coherent movement of one group (quasiparticle) is RM, and ballistic resistivity of the conductor is

$$\rho_{bal}(M) = \frac{R_M}{K} = \frac{h}{2e^2M^2} \cdot \frac{M}{N} = \frac{h}{2e^2M} n^{-\frac{2}{3}} \quad (11)$$

As follows from (11), the minimum resistivity could be much less than (8). In the limit, when all *N* electrons in the cross-section form one group, the resistivity will be:

$$\rho_{bal}(M = N) = \frac{h}{2e^2} \frac{n^{-\frac{4}{3}}}{A} \quad (12),$$

where A is cross-sectional area.

The large number in electrons in one group, *M*, implies that there must be a minimum width of the conductor to accommodate large *M*.

For a conductor with a cross-sectional size W, the number of electrons in cross-section is

$$N = n^{\frac{2}{3}} W^2 \quad (13)$$

The number of group electrons *M* cannot exceed the total number of electrons N. Correspondingly, the minimum size to accommodate *M* group electrons is (one group per cross-section, *M*=*N*):

$$W_{\min} = M^{\frac{1}{2}} n^{\frac{1}{3}} \quad (14)$$

Table I shows range of possible resistivities for different group size M and corresponding minimum width of conductor. As can be seen, the range of possible resistivities is very consistent with the resistivities reported for highly conductive polymers (see page 1) and with experimental results reported for conventional superconductors [4].

Table I.

M	***R(M)*, Ohm**	***K***	ρ_{min}	**W_{min}, cm**
1	12929.69	1.92E+15	6.72E-12[13]	2.28E-08
10	129.2969	1.92E+14	6.72E-13	7.21E-08
100	1.292969	1.92E+13	6.72E-14	2.28E-07
1000	0.01293	1.92E+12	6.72E-15	7.21E-07
10000	0.000129	1.92E+11	6.72E-16	2.28E-06
100000	1.29E-06	1.92E+10	6.72E-17	7.21E-06
1000000	1.29E-08	1.92E+09	6.72E-18	2.28E-05
10000000	1.29E-10	1.92E+08	6.72E-19	7.21E-05
1E+08	1.29E-12	1.92E+07	6.72E-20	2.28E-04
1E+09	1.29E-14	1.92E+06	6.72E-21	7.21E-04
1E+10	1.29E-16	1.92E+05	6.72E-22	2.28E-03
1E+11	1.29E-18	1.92E+04	6.72E-23[14]	7.21E-03

Conclusion: The reported data on HCP doesn't contradict to the quantum conductance model. The reported wide range of resistances can be explained based on the size effects for minimum resistivity.

3. Connection between Quantum Conductance Model and canonical theory of superconductivity

Based on literature analysis and consultations with authoritative experts in superconductivity, we offer a connection between the above simple ballistic or quantum

[13] Reported for highly conductive polymers (see page 1)
[14] Reported for conventional superconductors [4]

conductance model and the canonical theory of superconductivity. The summary of our findings is as follows:

1) The ballistic model (1)-(14) corresponds to temperatures much lower than critical temperature, $T<<T_c$. This is why temperature does not appear in the model.
2) In the ballistic model, the group of M electrons (quasiparticle) has an characteristic size given by (14). It appears that the equivalent characteristic size in the canonical theory of superconductivity is the Landau-Ginzburg coherence length $\xi = \frac{\hbar}{\sqrt{2m\alpha}}$, where α is a phenomenological parameter.

The two immediate predictions from the ballistic model are:

1) The resistance of superconductive state is a very small but finite value, R_0
2) The superconductive "zero-state" resistance depends on the cross-section of the conductor: $R_0=f(W)$

Both these results are anticipated by the superconductivity community, however, there experimental exploration is still work in progress.

Finally, we performed a direct test of the applicability of the ballistic model to superconductivity. In [4] the resistivity of the superconducting lead film was reported to be $\rho \sim 3.6\text{x}10^{-23}$ Ohm-cm. The thickness of the film was 1.2 μm and the width of the cross-section ~3cm. The atomic density of Pb, $n_{Pb}=3.3\text{x}10^{22}$ at/cm^3. Putting these numbers in (12) results in $\rho_{bal}=3.4\text{x}10^{-23}$ Ohm-cm – almost exactly the experimental number!

Conclusion

The concept of Highly Conductive Polymers has passed the fundamental physics check. Of course the result of this study doesn't guarantee the validity of the reported data on the conductive polymers. Nevertheless, it sends an encouraging message that such systems are in principle possible. There remain many questions including the structure of the material necessary to support the collective behavior of the electrons indicated above and it may be that insight into this structure could be captured from well-designed experiments on highly conductive polymers.

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