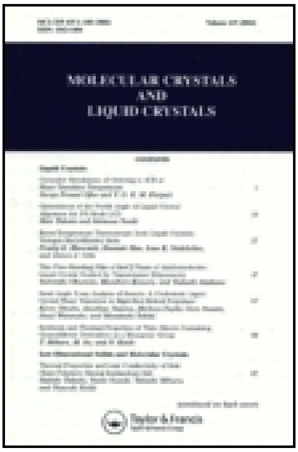

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The Superconductivity at Room Temperature and Much Higher in New Polymer Films

Leonid N. Grigorov [a] & Dmitry N. Rogachev [a]
[a] Institute of Synthetic Polymeric Materials of Russian Acad. of Sci. Profsoyuznaya st.70, Moscow, 117393, Russia

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THE SUPERCONDUCTIVITY AT ROOM TEMPERATURE AND MUCH HIGHER IN NEW POLYMER FILMS

LEONID N.GRIGOROV and DMITRY N.ROGACHEV
Institute of Synthetic Polymeric Materials of Russian Acad.of Sci.
Profsoyuznaya st.70, Moscow, 117393, Russia

Abstract Quasi-one-dimentional superconductivity of oxidized PP , discovered in 1988, is discussed. The low limit of T_c is found > 700 K. The transgression of Wiedemann-Franz law and unusual Meissner effect at 293 K are considered as proofs of true superconductivity.

INTRODUCTION

The local electronical conductivity of films of the polymer dielectric polypropylene (PP) was found in 1986.[1] Later we have understood the films become locally conductive if PP is in elastic state only and contains the dipole groups which appear after its oxidation.[2] (Subsequent UV-irradiation used by us[2-4] and later in[5,6] accelerates the conductive points formation only.[7] The waiting after oxidation for some weeks leads to the same results.) The diameter of conductive points is estimated[6,8,9] < 1μ.

The most surprising thing is that conductive points in dielectric PP matrix have features at > 300 K which are known for superconductors only. The first one is very low point resistance R which doesn't depend on the film thickness up to 0.1 mm[2-4] and is practically the same like the contact resistance.[2-4,6] The second one is the delayed transition of R from the technique zero to the high value and back as a result of magnetic field H ~ 0.1 T switching on and off.[4] Moreover, some samples demonstrate anomalously great diamagnetism which corresponds to the superconductive phase content up to 0.3 vol.% (Fig.1). It disappears slowly if H exceeds the critical value $H_c \sim 0.1$ T.[2,3]

The direct current (or temperature) slow increasing doesn't allow to find J_c (or T_c) due to the melting of indium microelectrode at 429 K. If the copper microelectrode is used the thin copper wire (≈0.1 mm), connecting it with the power supply, is melted at J = 2-3 A but polymer has no damage because there is no heat generation in conductive point.

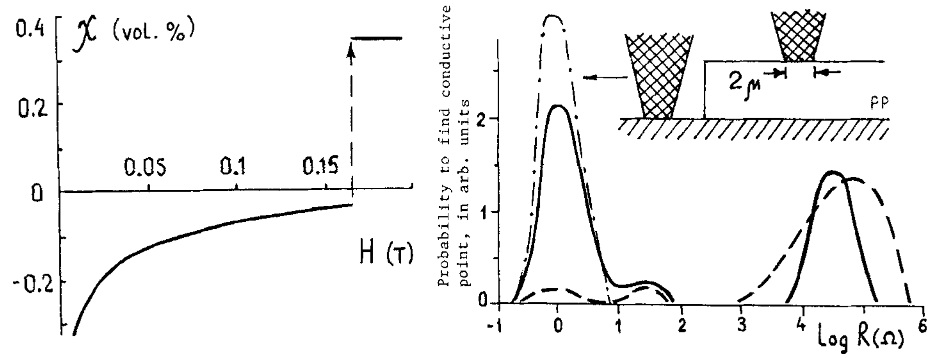

FIGURE 1 Field H dependencies of the magnetic sucseptibility χ (left) and the point's R distribution function (right) at 293 K : —— - H = 0; --- after 10 days at H∼0.1 T. The R distribution -·- corresponds to the direct contact of the copper support (shadowed) and very soft indium microelectrode (double shadowed).

The important questions which arise as a result[2-4] are :

1. What is a reason of free carriers generation in the oxidized PP ?
2. Why do these films conduct in local points only ?
3. Is the phenomenon observed the true superconductivity or not ?

GENERATION OF CARRIERS AND FORMATION OF CONDUCTING CHANNELS

The generation of carriers in polar elastomers is studied[8,10] theoretically. It is shown that even weak inhomogeneous electrical field can easily orient and replace the carboxyl group dipoles in elastic matrix. Due to this any ion has to be effectively solvatated by 3-4 dipoles if their concentration exceeds $10^{20} cm^{-3}$. The energetic gain of such solvatation is found to exceed the polymer dielectric gap. Thus, the irreversible self-ionization of polar elastomers is thermodynamically profitable process which leads to the gradual accumulation of free polarons in the matrix.

In order to understand the local conductivity we have assumed[8,12] that in polar elastomers, which have high dielectric constant, polarons can join together due to low Coulomb repulsion and exchange interaction gain caused by the overlap of their wave functions. The quantum-mechanical calculations[11,12] show that stable thread of joined polarons (so-called "superpolaron") can exist if the electron spins are parallel, i.e. the superpolaron has to be ferromagnet. This thread (Fig.2) behaves like quasi-one-dimensional conductive channel because any electron wave function in it is a running wave. The complete overlap of such quasi-one-

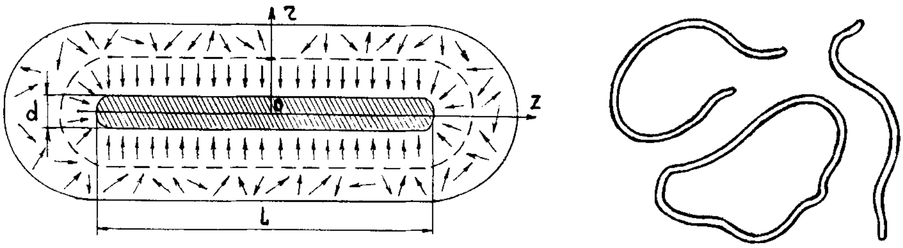

FIGURE 2 Theoretical structure of the superpolaron (left): electronic thread (shadowed) surrounded by oriented dipoles (arrows). Positive ions are assumed to be spreaded in a matrix homogeneously. Right side - real structures supposed (including closed circuits).

dimensional waves makes their exchange interaction the most strong one. It guaranteesthe stability of superpolaron independently on its length L . Thus, in elastic matrix it is possible (now theoretically only) to obtain the conductive electronic wire of any L.

The model proposed answers the questions 1,2 and predicts the ferromagnetism of oxidized PP detected.[2,3] It doesn't involve the exact chemistry of elastomers. This predicts that PP has not to be a unique one. Really, the same properties are found for poly(dimethylsiloxane).[13] It allows us to discuss the 3rd question from view point of the same model.

PROOFS OF TRUE SUPERCONDUCTIVITY OF SUPERPOLARONS

Resistance R jump at $T = T_c$ or at $J = J_c$ and Meissner effect are usually considered as the best proofs of any true superconductivity.

Estimation of T_c and J_c by the measurement of resistance jump

Taking into account that T_c and J_c of oxidized PP can't be found using direct current[3] the short current pulses are used.[9,11] Just at the pulse begining R falls below the technique zero and remains the same for 1-2 min after the pulse if its amplitude is $J_1 < J_c$. In such a case the polymer heat degradation is not detected even after $\sim 10^3$ repetitions of J_1 pulses shown in Fig.3 . This leads to estimations $R < 10^{-6}$ Ohm and, assuming channel diameter < 1µ , its specific conductivity $\sigma > 10^{11}$-10^{12} S/cm. After[11] the same estimation of σ low limit is obtained[6] by other method

Every pulse J_1 heats the tip of the needle electrode and the polymer T_{max} is found to attain ≈ 700 K just near the tip.[9] (The PP is not degradated due to short time < 1 µs of T_{max} only - see Fig.3). But there

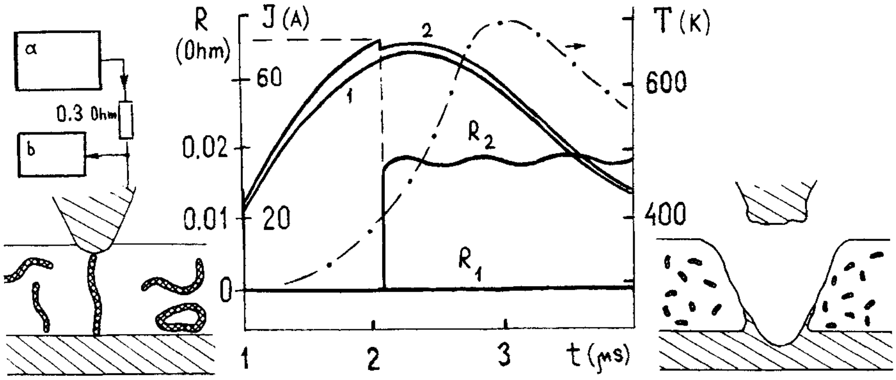

FIGURE 3 Resistance R jump observation using short current pulse (1 - a little bit less than J_c , 2 - a little bit more than J_c). Copper electrodes are used as well as pulse voltage generator (a) and digital oscillograph (b) remembering the sample's voltage and current kinetics. The curve -•- shows the kinetics of the PP temperature for pulse 1 just near the needle tip ($\approx$10 μ). Right side - the result of the heat generation caused by single pulse 2 .

is no R jump near T_{max} shifted about 0.7 μs after maximum of J_1 pulses. This gives the estimation of the critical temperature low limit T_c>700 K.

But if a single pulse $J_2(t)$ crosses the value $J_c \sim 70$ A the channel jumps immediately to the resistive state and strong heat generation destroys locally PP and both electrodes.[9,11] It looks, indeed, like the destruction of true superconductivity by critical current $J_c \gg 10^8 A/cm^2$.

Nature of current carriers in the channels

In order to investigate this nature the channel's heat resistance r_{heat} is measured at $T \simeq 340$ K using the heated electrode equipped by microscopical thermocouple just near the needle tip[7] (Fig.4). The comparison of temperatures T_2 and T_1 (at conductive and dielectrical points correspondingly) allows to subtract the matrix heat flow and to express r_{heat} by formula[7]

$$r_{heat} \geq \frac{h}{\pi D(h+\frac{D}{2})\lambda}\left(\frac{T_0-T_1}{T_0-T_3}\right)\left[\frac{T_2\left(1-\frac{T_3}{T_0}\right)-T_3\left(1-\frac{T_2}{T_0}\right)\frac{d}{D}}{T_1-T_2}\right] \quad (1)$$

(λ - specific heat conductivity of dielectrical PP matrix, $h \simeq 20$ μ - film thickness, D = 10 μ , d = 3 μ - it is clear from Fig.4 , what it is). The results[7] obtained show that $r_{heat} \to \infty$ and doesn't obey the Videman-Franz law at least by 7 orders of magnitude. It means that charge carriers in conductive channel do not obey the Fermi-distribution and are not able to transport the heat like any superconductive carriers.

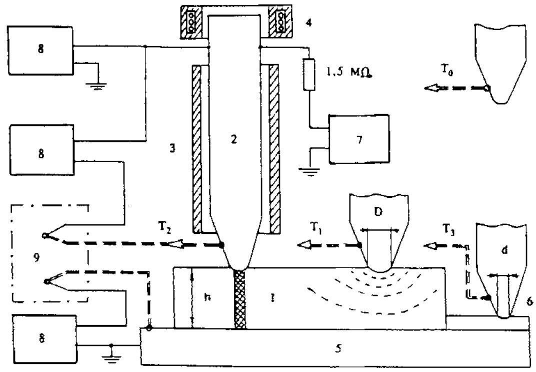

FIGURE 4 The scheme of r_{heat} measurements: 1 - PP, 2 - copper zond equipped by thermocouple near the tip, 3 - heat screen, 4 - oven , 5 - copper support, 6 - soft indium layer near PP, 7 - battery 12V, 8 - μV meters for the temperature and conductivity measurements, 9 - thermostabiliser for precise measurements of the temperature, which are made in 4 different positions of the same tip shown above

<u>Observation of the Meissner effect</u>

Let's remember Meissner effect is spontaneous appearance of the undamping ring current which pushes superconductor out of magnetic field H = Const if two conditions are fulfilled: 1) $T < T_c$ and 2) closed electrical circuit exists in substance mentioned. Condition 2) is usually forgotten due to its automatical fulfilling for any three-dimensional conductor.

But in our one-dimensional case, evidently, it means that two opposite endsof the superpolaron have to be in contact. We have supposed that closed ring configuration of the thread (like in Fig.2) can appear sometimes because all the data obtained show the continuous changes of its structure due to heat fluctuation of the elastomer matrix.

Thus, some probability exists to find the moment of closed circuit formation. If the sample is placed in constant $H \neq 0$ and $T < T_c$ (this is not a problem due to estimation $T_c > 700$ K) the undamping ring supercurrent must be exited by Meissner effect just at this moment. Experimentally it has to look like spontaneous appearance of additional force which pushes the sample out of field for the whole time until this ring exists.

The continuous measurements of PP interaction force F with H=Const at 293 K, carried out with magnetical balance, allow to detect events predicted (Fig.5). The sign of ΔF obtained corresponds to pushing out force only. No events are detected at H = 0 or $H > H_c$. Statistical treatment of these results shows that the probability to imitate them by oc-

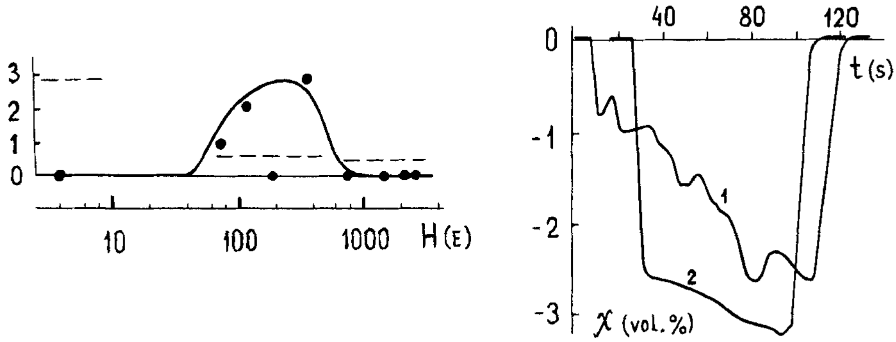

FIGURE 5 Meissner effect in PP at 293 K : 1,2 - kinetics of spontaneous appearance of the force pushing the samples out of field H = 400 E given in units of sucseptability (right). Left side - numbers of events detected at each H value applyed. Dotted lines show the same numbers expected statistically if false events are assumed caused by uncontrolled external factors like seismic shocks

casional factors (like seismic shocks) is negligibly low $\approx 4 \cdot 10^{-4}$.

This allows to conclude that Meissner effect is really observed for PP samples, and it proves the true superconductivity of superpolarons in polar elastomers at room temperature and higher.

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