

# Anomalous electron instability of polymers due to uniaxial pressure

A. N. Lachinov, A. Yu. Zherebov, and V. M. Kornilov

*Physics Department, BNTs, Ural Branch of the Academy of Sciences of the USSR*

(Submitted 15 April 1990)

*Pis'ma Zh. Eksp. Teor. Fiz.* **52**, No. 2, 742–745 (25 July 1990)

The electrical properties of thin films of polyaromatic compounds—polyarylenephthalides—are highly sensitive to pressure. At anomalously low pressure, not exceeding  $2 \times 10^5$  Pa, an insulator–metal phase transition is observed in test samples. The conductivity changes by 11 orders of magnitude at the point of the transition. A model of a Mott phase transition is proposed to explain this effect.

Recent papers have reported a spontaneous anomalous increase in the conductivity of initially insulating polymer films upon a decrease in their thickness.<sup>1,2</sup> The meaning may be that, because of factors which are not yet clear, there should be a region of critical thicknesses  $d_{cr}$  within which an insulator–metal phase transition occurs.

Polymer systems have a strong electron–phonon interaction, which leads in particular to a high pressure sensitivity of the electron energy spectrum,<sup>3,4</sup>  $\sim 0.17$  eV/GPa. It is logical to suggest an increase in this sensitivity near  $d_{cr}$ .

In this letter we are reporting a study of the electrical properties of thin polymer films near the insulator–metal phase transition, induced by an anomalously low uniaxial pressure.

As the test samples we used a polyaromatic compound: polydiphenylenephthalide. This compound was chosen because it is soluble film-forming polymer which exhibits a spontaneous conductivity at film thicknesses below 200 nm (Ref. 5). In addition, it was found in Ref. 6 that the electron energy spectrum undergoes important changes at pressures of  $10^8$  Pa in bulk samples.

The samples were prepared by centrifuging polymer solutions on the surfaces of various metal electrodes (Cu, Al, Cr, Au), which had been formed by vacuum diffusion deposition on the surface of polished glass. Several methods were used to fabricate the second electrode (diffusion deposition in vacuum, clamping, rolling a foil, etc). Electrodes with an area of 0.25–1 cm<sup>2</sup> were used for the most part. No effect of the electrode material, shape, or area on the characteristics of the effects under study was observed. Before and after the electrical measurements, the uniformity of the polymer films was checked by transmission electron microscopy on an ÉMMA-100 electron microscope. It was found that there were no apertures going completely through the film at the resolution of this microscope.

A voltage was applied to the sample in the direction across the film, along the direction of the uniaxial pressure. The current flowing through the sample was found

by measuring the voltage drop across a standard resistance in series with the sample. The pressure was varied by means of a shaft connected to the movable core of an electromagnet; the pressure change was determined from the current flowing through the electromagnet. To determine the pressure which was developed, we constructed a calibration characteristic  $P = f(I)$ , where  $P$  is the magnitude of the pressure developed, and  $I$  is the current through the electromagnet. The elastic modulus of polymer films of this class is about  $3000 \text{ Mn/m}^2$ , so it can be asserted that the change in thickness caused by the pressure is negligible.

Figure 1 shows the current through a sample  $300 \text{ nm}$  thick versus the uniaxial pressure  $P$ . In the initial state ( $P = 0$ ) the polymer film has a conductivity of  $10^{-14} \text{ S/cm}$ . When the critical pressure,  $P_{\text{cr}} = 1.1 \times 10^5 \text{ Pa}$  in this case, is reached, the conductivity increases sharply, reaching<sup>1)</sup>  $10^{-3} \text{ S/cm}$ . As a result of the phase transition, a state with a metal-like conductivity arises in the polymer film.

Interestingly, the conducting state induced by the pressure is unstable in an electric field. Figure 2 shows a current-voltage characteristic of a sample  $5600 \text{ nm}$  thick subjected to a pressure above the threshold for the transition. On this curve we can clearly see the critical nature of the behavior of the current through the sample,  $I$ , as a function of the applied voltage  $U$ . Above a certain voltage, the  $I = f(U)$  curve drops sharply, and the sample reverts to its original state. The highly conducting state can be

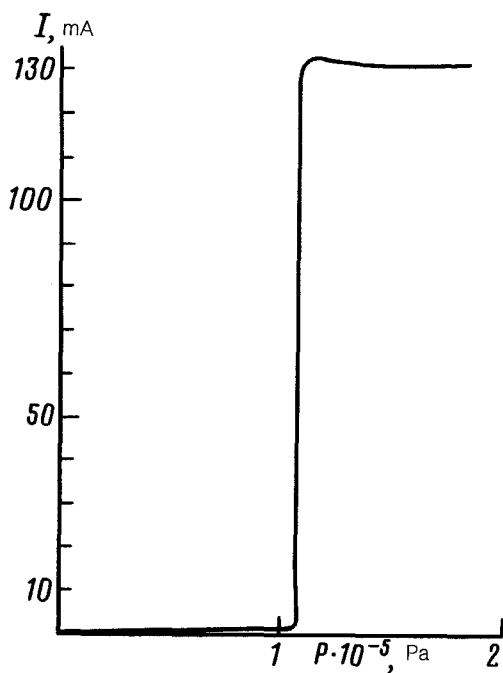


FIG. 1. Current flowing through polymer film  $0.3 \mu\text{m}$  thick versus the magnitude of the uniaxial pressure. The voltage across the sample is  $3.5 \text{ V}$ .

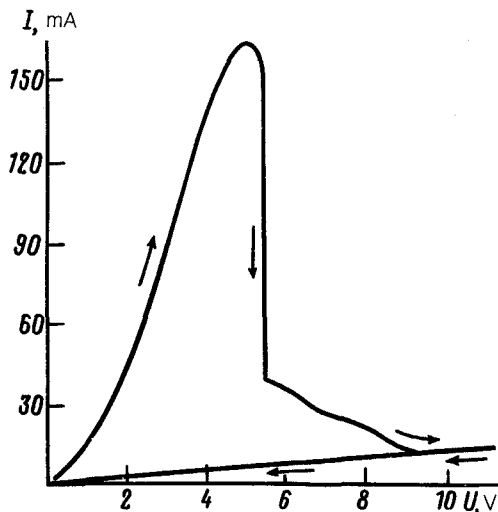


FIG. 2. Current-voltage characteristic of a film sample subjected to a uniaxial pressure above the threshold value of  $2 \times 10^5$  Pa. The arrows show the direction in which the voltage across the sample is varied.

restored either by switching the polarity of the applied voltage or by increasing the pressure applied to the sample. The effect of the electric field on the conductivity of a sample under pressure (Fig. 2) indicates that there is no direct contact between the electrodes.

Although further experiments will be required to determine the nature of this effect and its mechanism, it is apparently pertinent to offer the following comments at this point. There are at least two basic models describing the effect of pressure on the electrical properties of polymers. The first is based on an increase in the interchain exchange integral and assumes that the probability for the chains to move closer together because of the pressure is higher than the probability for a change in the length of the links within a molecule. This effect is seen optically as a decrease in the width of the optical gap,<sup>3,4</sup> and it is accompanied by a conductivity increase proportional to  $P^{1/2}$  (Ref. 7). The second is a modified Mott model,<sup>8</sup> which deals with a change in the distance between hopping centers and predicts a linear dependence of the conductivity on the applied pressure. The first of these models apparently does not apply in our case, because of the low threshold pressures. The second model can in principle explain the observed effect, provided that we assume that the concentration of hopping centers is close to the percolation threshold. In this case, a very weak external agent could cause a phase transition similar to a Mott transition.<sup>8</sup>

The charge instability observed in certain polymers is of a general nature. It is manifested in insulator-metal phase transitions during the application of relatively weak external agents: electric fields<sup>5</sup> and a decrease in thickness<sup>2</sup> caused by pressure. In the case at hand we are apparently dealing with a case of mutual effects of surface and volume properties, since all these effects are observed at thicknesses below a certain critical value.

<sup>1</sup>The changes in the conductivity did not exceed 300% per  $10^8$  Pa in samples thicker than  $1 \mu\text{m}$ .

---

<sup>1</sup>N. S. Enikolopyan, L. N. Grigorov, and S. G. Smirnova, *Pis'ma Zh. Eksp. Teor. Fiz.* **49**, 326 (1989) [*JETP Lett.* **49**, 371 (1989)].

<sup>2</sup>V. M. Arkhangorodskii, E. G. Guk, A. M. El'yashevich *et al.*, *Dokl. Akad. Nauk SSSR* **309**, 603 (1989) [*Sov. Phys. Dokl.* **34**, 252 (1989)].

<sup>3</sup>D. Moses and A. Felblum, *Phys. Rev. B* **26**, 3361 (1982).

<sup>4</sup>A. Brillante, M. Hanfland, K. Syassen *et al.*, *Physica B* **139-140 B**, 533 (1986).

<sup>5</sup>O. A. Skaldin, A. Yu. Zherebov, A. N. Lachinov *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **51**, 141 (1990) [*JETP Lett.* **51**, 159 (1990)].

<sup>6</sup>A. A. Petrov, M. G. Gonikberg, S. N. Salazkin *et al.*, *Izv. Akad. Nauk SSSR Ser. Khim.* **2**, 279 (1968).

<sup>7</sup>H. A. Pohl, *J. Polym. Sci. (C)* **17**, 13 (1967).

<sup>8</sup>B. Lundberg, B. Sundqvist, O. Inganas *et al.*, *Mol. Cryst. Liq. Cryst.* **118**, 155 (1985).

Translated by D. Parsons