Electrical Resistivity of Fullerenes at High Pressures

EUROPHYSICS LETTERS 1 January 1993

Europhys. Lett., 21 (1), pp. 49-53 (1993)

Electrical Resistivity of Fullerenes at High Pressures.

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(received 13 July 1992; accepted in final form 20 October 1992)

PACS. 62.50 – High-pressure and shock-wave effects in solids.
PACS. 72.20 – Conductivity phenomena in semiconductors and insulators.

Abstract. – We have measured the electrical resistivity as a function of temperature up to pressures of 25 GPa of pure fullerenes C_{60}, C_{70} and the compound $C_{60}I_4$. For the three materials the best fit in our temperature range corresponds to a three-dimensional variable-range hopping conductivity, signature of an important disorder. A dramatic decrease of the resistivity, by two orders of magnitude per GPa, is observed at low pressures. However, no metallic state is attained as all the samples present a phase transformation in the high-pressure range, probably originated by the crossover from sp^2 to sp^3 hybridization of the carbon orbitals at high pressures.

Recently, a new family of carbon allotropes, the fullerenes, have become available [1] for conventional solid-state characterization with surprising results. These materials can be viewed as graphite plans folded into spherical (C_{60}) or egg-shaped (C_{70}) structures by means of twelve pentagons. In graphite the planes formed by the highly stable hexagonal bonding of predominantly sp^2 hybridized carbon orbitals are held together by van der Waals forces. However, there is sufficient interaction to allow a band crossing rendering graphite semi-metallic. In fullerenes the cohesion is obtained also by van der Waals interactions between the spheroids, but the weak overlap between them keeps the gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) almost unaltered [2]. Both C_{60} and C_{70} are semiconductors. When doped with alkalis the more prominent member of the family, C_{60}, transforms from a semiconducting molecular solid into a metal [3], which becomes superconducting [4] at temperatures as high as 33 K. On the other hand, though the room pressure C_{60} state is extremely soft on account of the weak van der Waals interactions between molecules, calculations of the bulk modulus

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of C_{60} show that, at pressures higher than 50 GPa, it can be the most incompressible solid known [5]. In this perspective a characterization of, firstly, the electrical properties as a function of temperature of the undoped material, and, secondly, the behaviour of fullerenes at high pressures is of key importance for their understanding and eventual practical applications. In this letter we present measurements of the electrical resistivity as a function of temperature and pressure that give a first overview of these properties in three members of the fullerene family. The results are: *a*) the electrical resistivity follows an $\exp[T^{-1/4}]$ dependence that corresponds to a three-dimensional variable-range hopping mechanism; *b*) the resistivity is extremely sensitive to the application of pressure, thus suggesting a possible metallization of the materials by band gap closure; *c*) however, under the quasi-hydrostatic conditions of our measurements this behaviour saturates at high pressures. For C_{60} and C_{70} this corresponds to a transformation into an insulating state which suggests a change of the bonding between carbon atoms.

A soot containing different fullerenes was obtained in a procedure similar to that described by Haufler *et al.* [6]. A mixture of approximately 80% of C_{60} and 20% of C_{70} was extracted from the soot with boiling toluene. C_{60} and C_{70} were then separated by column chromatography on neutral alumina column followed by solvent drying. Their purity was checked by high-pressure liquid chromatography, infra-red, ultraviolet, and mass spectrography. No signal attributed to impurities was detected. The $C_{60}I_4$ sample was prepared from the mixture with saturating I_2 vapour pressure at 250 °C for one week. Its X-ray spectrum could be indexed on a simple hexagonal cell with $a = 9.962$ Å and $c = 9.984$ Å in excellent accordance with the intercalation molecular compound obtained by Zhu *et al.* [7]. No other phases were detected with X-rays. The C_{60} and $C_{60}I_4$ samples were pressed from the powder into 40 μm thick platelets, that were then cut into rectangular shape ($(300 \times 700)\,\mu m^2$, the C_{60} sample being much more friable than the $C_{60}I_4$). The C_{70} samples were simply faceted polycrystals obtained by dissolving the powder in toluene and crystallizing by controlled evaporation. The dimensions were approximately $(50 \times 50 \times 500)\,\mu m^3$.

The pressure measurements were performed using a sintered diamond cell. We used a pyrophillite gasket of 1 mm internal diameter. The fullerene sample and a lead strip were introduced between soft steatite lids that served as the pressure medium ensuring quasi-hydrostatic conditions. Both samples were measured with a four-contact technique ensured by 33 μm platinum wires that passed through the pyrophillite gasket. The lead sample served as a manometer by monitoring its superconducting transition temperature. The width of the transition gave us an estimate of the pressure gradient inside the cell, which was around 1 GPa.

We show in fig. 1 the resistivity of the three materials as a function of temperature for different pressures. We observe that there is a gradual decrease of the resistivity as we go over from C_{60} to C_{70} to $C_{60}I_4$. Comparing the band structure calculations [2] for C_{60} with a recent analysis of the C_{70} molecule [8], one observes that the HOMO-LUMO energy difference of C_{70} is 0.7 times that of the C_{60} molecule. The C_{70} solid should then be more conducting than the C_{60} one, as we do find. We remark that there is an increase of conductivity with increasing pressure for the three materials. This is the result expected if there is a weak orbital overlap at ambient pressure that is increased by the reduction of volume under pressure. We see in fig. 2 the variation of the resistance for the three materials. We were not able to measure the C_{60} nor the C_{70} samples below about 6 GPa, due to the high value of the resistance. We can compare our data to those obtained from C_{60}-C_{70} mixture evaporated films [9] of $10^{14}\,\Omega\cdot$cm. Our value of about $10^6\,\Omega\cdot$cm implies a very steep decrease of the resistivity with a few GPa. This dramatic behaviour is confirmed by the $C_{60}I_4$ sample, which could be measured from lower pressures, and whose resistance drops by five

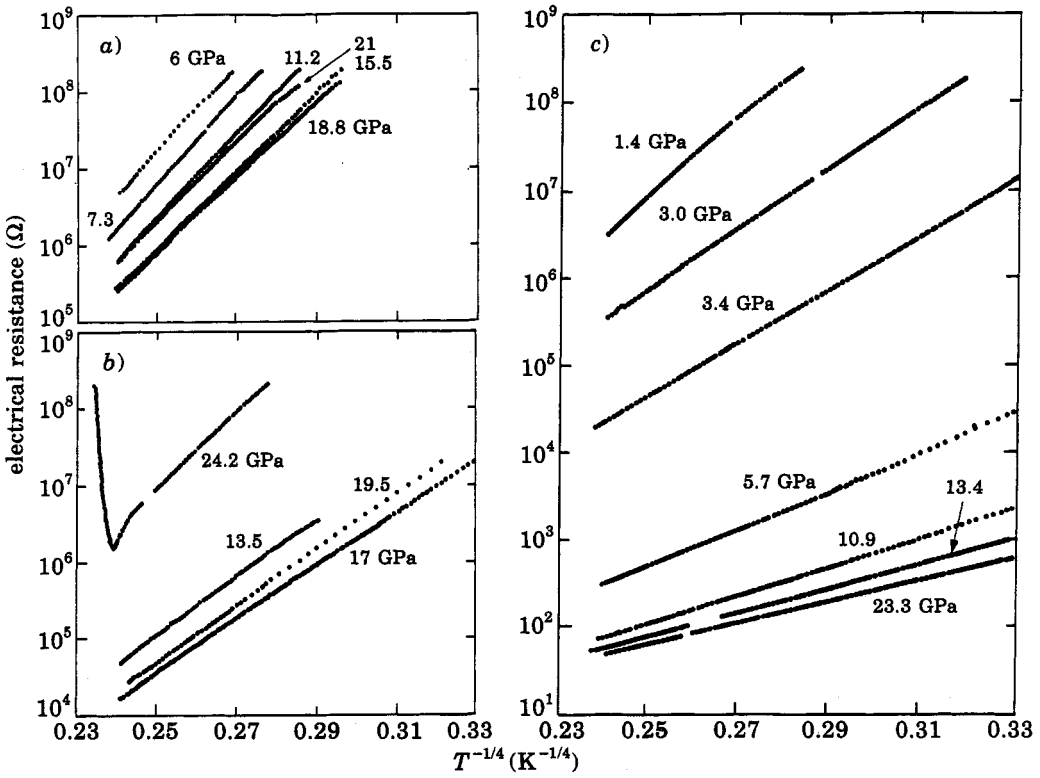

Fig. 1. – Logarithm of the resistivity of fullerenes as a function of $T^{-1/4}$ for different pressures in GPa: *a*) C_{60}; *b*) C_{70} and *c*) $C_{60}I_4$. The observed linear behaviour corresponds to a variable-range hopping conductivity. For the highest pressure on C_{70} we observe the transformation to an insulating state while heating above room temperature. The change in slope before the sudden increase in resistivity is probably the result of a too quick heating rate.

orders of magnitude within 3 GPa. A transition to a semi-metallic state similar to graphite seems close at hand. However, the rate of change of the pressure coefficient of the resistivity decreases in absolute values and even becomes slightly positive at higher pressures. At the maximum pressure of 25 GPa for both C_{60} and C_{70}, the samples undergo a transition to an insulating state, whose kinetics is substantially increased by heating the cell above room temperature. With $C_{60}I_4$ we observe a similar change of rate of increase of conductivity, but the sample remains semiconducting up to the highest pressure.

For an ideal semiconductor we should observe a temperature dependence $R = R_0 \exp[E_g/k_B T]$, with E_g equal to the band gap. Preliminary measurements on C_{60} samples [10] showed that within this scheme there was a very strong temperature dependence of the gap. A detailed analysis within our measuring range favours a three-dimensional variable-range hopping dependence $R = R_0 \exp[2(T_0/T)^{1/4}]$ for all our fullerene samples, as can be verified by the linear behaviour on the appropriate plot of fig. 1. In general, this type of temperature dependence is caused by electrical conduction due to states localized by disorder, and has been observed in a large number of systems [11] including high-temperature superconductors [12]. Different types of disorder seem to be present in fullerenes. O_2 is found to dissolve [13] in C_{60}, and can be an obvious source of disorder. Vacancies and other types of structural defects, like stacking faults, which are

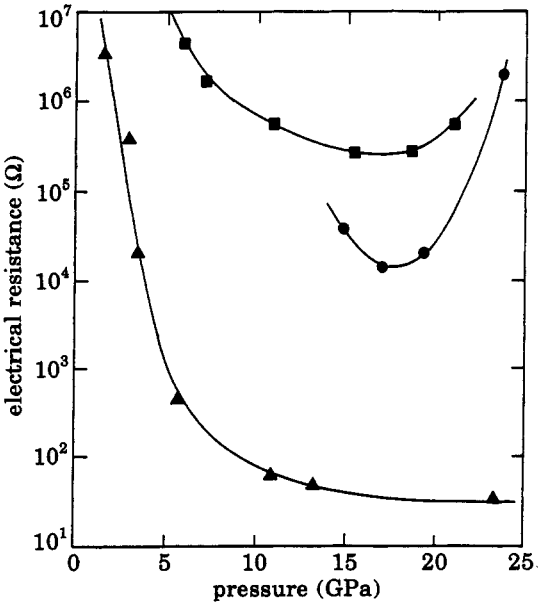

Fig. 2.

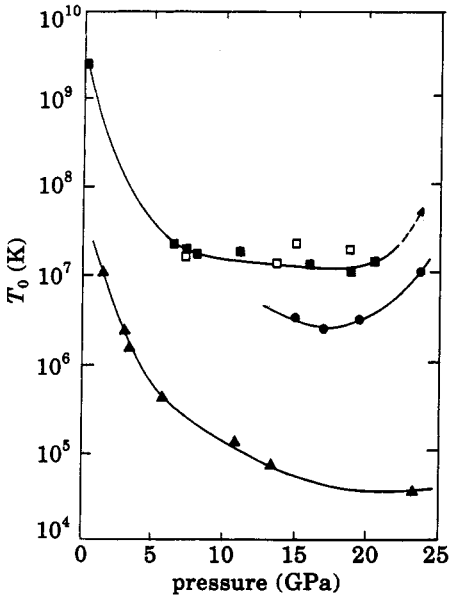

Fig. 3.

Fig. 2. – Variation of the resistance at room temperature of fullerenes with pressure: ■ C_{60}; ● C_{70} and ▲ $C_{60}I_4$. Note the very steep variation with pressure at low pressures, that for $C_{60}I_4$ almost reaches metallic values.

Fig. 3. – Dependence of the activation temperature T_0 on pressure: ■,□ different samples of C_{60}; ● C_{70} and ▲ $C_{60}I_4$. The increase at high pressures for C_{60} and C_{70} announces the transition to an insulating state that is observed at the highest pressure. The value at ambient pressure for C_{60} is extracted from ref. [9].

easily generated in these materials, can also localize electronic states. Another more interesting origin for the disorder comes from the actual observation [14] of an orientational glass at high pressures in C_{60} and of orientational disorder [15] in C_{70}. According to these reports our samples would always be in an orientationally disordered state that can localize states in the gap.

We show in fig. 3 the variation of T_0 as a function of pressure for the three samples. For C_{60} at ambient pressure we have extracted T_0 from the data of Mort *et al.* [9], which, in our view, also follow a three-dimensional variable-range hopping behaviour. We know that $T_0 = \{\alpha^3/k_B N(E_F)\}$, where α is the localization distance, k_B the Boltzmann constant and $N(E_F)$ the density of states at the Fermi energy, arising from the localized states in the gap [11]. We can make the reasonable assumption that α is approximately constant and of the size of a fullerene molecule, *i.e.* the carriers are localized in the spheroids. T_0 then represents the variation of $N(E_F)^{-1}$. Within this analysis the three materials show a similar behaviour for $N(E_F)$, with a steep increase at low pressures followed by a saturation at higher pressures. For the pure fullerenes we have, at the highest pressure, a transformation towards an insulating state, *i.e.* $N(E_F) = 0$.

In X-ray diffraction measurements on C_{60} Duclos *et al.* [16] observed that, under nonhydrostatic conditions, there was a transition to a low symmetry phase. We believe that we have measured the same type of transition to a high-pressure phase in our

quasi-hydrostatic cells at high pressures. We remark that this high-pressure phase was not observed in conditions of almost ideal hydrostaticity [14]. A hexagon-against-hexagon relative position of the molecules should favour sp^3 bonding between the molecules [17]. David *et al.* [18] have shown that in the orientationally ordered phase (and most probably in the orientational glass observed at high pressure in Raman experiments [14]) the basic position is double-bond-against-hexagon. We can speculate that this is the reason for the stability of the low-pressure phase in good hydrostatic conditions. Only under uniaxial or shear stresses favouring deformations or slipping of spheroids are new phases with an increasing sp^3 character formed. The ultimate step of this evolution under pressure is the transformation into a totally sp^3 cubic diamond, as recently reported by Núñez-Regueiro *et al.* [19]. These authors show how, in strong dynamic nonhydrostatic conditions, the fullerene structure collapses above 15 GPa. It would be of interest, however, to study and stabilize the intermediate phases, as they could have interesting properties.

We can now draw the following picture for the electrical properties as a function of pressure of the fullerenes that we have measured. At low pressures the existence of some type of disorder, orientational or structural, causes a variable-range hopping mechanism of conductivity. Naively, conduction is done by carriers that hop from spheroid to spheroid, which have states of slightly different energies due to the existing disorder. With increasing pressures, this conductivity gradually increases. However, we do not reach a metallic state as, at high quasi-hydrostatic pressures, the interaction between molecules becomes strong, and the materials phase-transform into an insulating state, which probably implies a change of the predominantly sp^3 bonding observed in isolated molecules to an sp^3 bonding between molecules.

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We have greatly benefited from the help of A. ZAHAB during fullerene preparation. We also thank J. E. FISHER for early communication of results on the iodine compound and D. NÚÑEZ-REGUEIRO for numerous discussions.

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