Low-temperature electrical resistivity of carbon-black-loaded polyethylene

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Measurements of the electrical resistivity of carbon-black-loaded polyethylene for various concentrations are reported at room temperature. The apparent 'non-ohmic' behaviour is discussed and the possible use of the electrical resistivity measurements for sample characterization is also suggested. The temperature dependence from 2 to 300 K was also investigated in the ohmic range and a drastic increase in resistivity with decreasing temperature was shown in the liquid helium range.

Keywords Electrical resistivity; carbon-black; filled polyethylene; low temperature; self heating; sample homogeneity

INTRODUCTION

Over the last decade a few works have been reported in the literature on the electrical properties of carbon-black-filled polymers[1-7]. One of the main technological interests pertains to the enhancement of the electrical conductivity of these polymers due to carbon black addition. An obvious application is where there is a need to prevent the accumulation of static electricity on the surface of vessels containing inflammable or explosive products. In that case electrical discharges or sparks should be avoided. Static electricity may also attract dust. Sometimes polymers may also be used as electrical conductors in applications where relatively low conductivities are tolerated.

Also of fundamental and practical interest is the very sharp transition from a conductive to an almost insulating behaviour, observed at room temperature, when the carbon black content is reduced by a few per cent[1,5,6,8]. The carbon black content at which the transition occurs, as well as the width of the transition, depends on the origin of the carbon black, the crystallinity rate of the host polymer, the sample preparation and other parameters.

In this paper we report the results of measurements on the temperature variation from 2 to 300K of samples of polyethylene loaded with various amounts of carbon black. This overlaps with and extends to lower temperature the work of Klason *et al.*[6], which was performed on low- and high-density polyethylene from nearly 100K to 450K. These authors found that, in the range 100K up to room temperature, the electrical resistivity is almost temperature insensitive. This is in contrast to what happens at higher temperature where a rapid increase in resistivity with temperature (positive thermal coefficient: *PTC*) is observed just below the melting point[7-11]. In the lower temperature range investigated here we found a drastic increase in resistivity with decreasing temperature. The resistivity increases by more than four orders of magnitude when the temperature is lowered from 77K to 2K. This is one of the most pronounced continuous variations of resistivity ever observed in this temperature range. It suggests that the effect could be usefully applied in low-temperature resistance thermometry. Though these are the first observations reported on carbon-black-loaded polyethylene below 100K, the same temperature range was recently investigated with poly(vinyl chloride)[3,5].

EXPERIMENTAL

Sample preparation

The starting material samples were prepared by the Phillips Petroleum Technical Center (Brussels). The high-density polyethylene (HDPE) used is their Marlex 47100. The carbon black was obtained from the gasification of a heavy oil; the XE-2 carbon black manufactured by Phillips Petroleum (Brussels) and the Ketjenblack manufactured by Akzo Chemie (Netherland). It had a specific area ranging from 800 to 1100 $m^2 g^{-1}$ as determined from BET (nitrogen) measurements. The particle size, as determined by electron microscopy, amounted to 3×8^{-8} m and the specific volume in the polymer compound was 1.9×10^3 kg m^{-3}. It should be noted that the carbon black aggregates are formed by hollow shell-like particles[12]. With 100 parts of powdered HDPE was mixed one part of the antioxidant Santonox and different parts of carbon black. The starting temperature of the mixing procedure was 130°C and the dump temperature 200°C. After the mixing procedure, which lasted 5 min, the mixture was granulated and then obtained in the form of a plate by compression moulding. This procedure was achieved in two steps: first a preheating at 180°C under a small pressure and then the moulding for 5 min at 180°C and under 8 MPa. The system was then allowed to cool to room temperature for approximately 15 min. The various samples, the characteristics of which are given in *Table 1*, were cut from these plates by means of a hot wire. This procedure was found necessary since any mechanical treatment, such as sawing or abrasion, was found to decrease to a great extent the surface conductivity of the sample leading to very high contact resistances.

The samples, with typical dimensions $0.3 \times 1.0 \times 6.0$ cm^3, were usually prepared for a four-contact bridge d.c. electrical resistivity measurement. The electrical leads

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Table 1 Carbon black concentrations in the various samples used

Sample identification no.	Carbon content (wt %)
11	9.82
10	9.01
9	8.18
7	6.48
9–6	6.22
10–7	8.00
11–8	8.93
13–10	8.93

were glued to the sample by means of a flexible SC 18 S silver ink, a micropaint manufactured by Microcircuits Co., New Buffalo, Michigan, USA. This paint was found to retain its flexibility at low temperature and ensured very stable contacts down to the liquid helium range, in spite of the large difference in expansion coefficient between the metallic wires and the polyethylene sample.

Variable-temperature cryostat

The samples were mounted in a vertical variable-temperature liquid-helium cryostat, which is a modified version of a system which was used in our laboratory for about 12 years to measure transport phenomena. This new version was found particularly adapted for the investigation of the transport properties of polymeric materials. The main body of the cryostat including the sample chamber is shown schematically in *Figure 1*. Its essential features are the double shielding arrangement (A and A′) and the fact that the experimental chamber (C) could be evacuated independently from the surrounding space (D) enclosed in the external vessel (B), which is directly immersed in the cryogenic bath (liquid helium or liquid nitrogen). This allows the introduction of an exchange gas, usually helium, in the experimental chamber (C), while keeping the latter thermally insulated from the bath. In this way the time for the low thermal conductance sample to reach thermal equilibrium is considerably reduced. The dual radiation shield system (A and A′) was designed in order to reduce to insignificance the stray thermal gradients on the sample and the experimental chamber while ensuring close temperature control of the latter. This is particularly important in the study of polymers, since the samples investigated have a very low thermal conductivity and the property measured is very sensitive to temperature at low temperatures.

The needle valve (E) allows the introduction of the cryogenic liquid contained in the dewar flask into the heat sink (F). This is mainly useful in the liquid helium range. By reducing the vapour pressure on the helium bath and stabilizing it within 10^{-3}K by means of a home-made Walker manostat, the important range from 2 to 4.2K could be carefully explored. For operation above 4.2K the needle valve was closed and the heat sink evacuated. The temperature of the sample chamber was then electronically regulated, within 5×10^{-2}K, by means of a model 3010 II Thor cryogenics temperature controller. In the same way, liquid nitrogen could be introduced into the sink from the surrounding dewar flask to work around 77K. It was then evacuated again to cover the range 77–300K by means of the electronic temperature controller. The temperature controller was actuated by an Au(0.03 at% Fe)–chromel P thermocouple which was previously calibrated and has its reference junction matched to the temperature of the cryogenic bath.

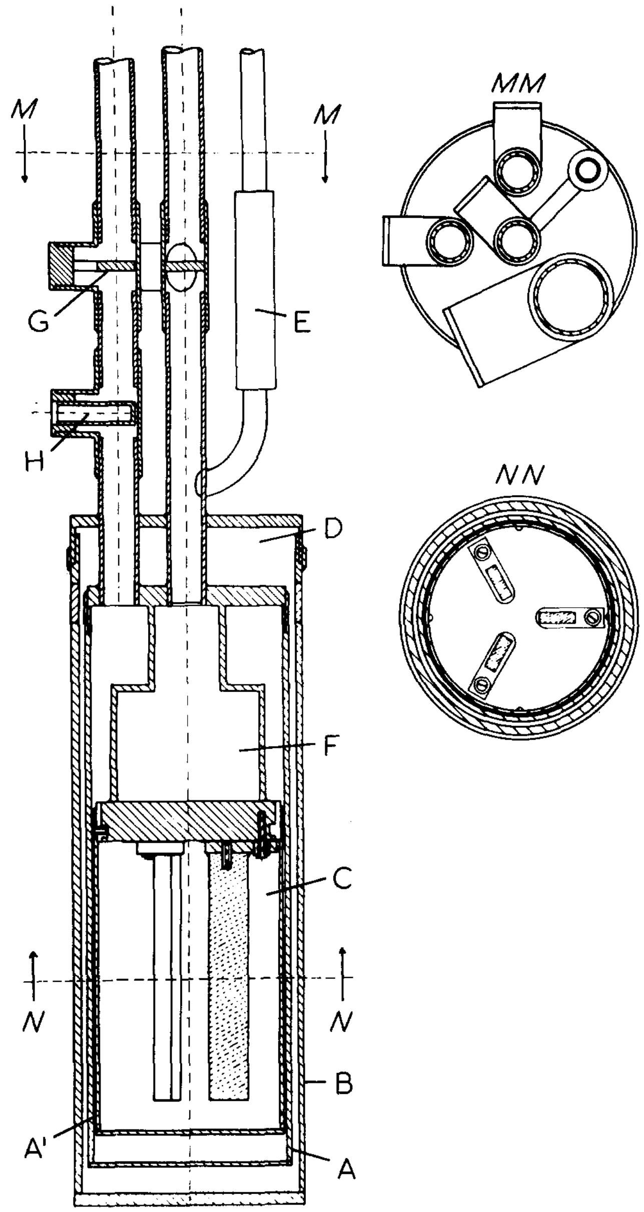

Figure 1 **Variable-temperature liquid helium cryostat: A, radiation shield and inner vacuum-tight enclosure; A′, radiation shield around the experimental chamber; B, external vacuum-tight vessel; C, experimental chamber; D, external thermal insulating enclosure; E, needle valve; F, heat sink; G, radiation shield; H, thermal anchoring column**

Special care was taken to avoid stray heat inputs to the experimental chamber. A copper radiation shield (G) in good thermal contact with the cryogenic bath prevented room-temperature radiation. Conduction from the electrical leads entering the sample chamber was considerably reduced by carefully anchoring twice all the leads, once to the liquid bath (H) and then to the heat sink (F). The sample temperature relative to that of the heat sink and the temperature of the sink were also measured by means of Au(0.03 at% Fe)–chromel P thermocouples. The e.m.f.s from the thermocouples were read on a Keithley 174 digital voltmeter with a resolution of 10^{-7} V. The sample currents were supplied by a Hewlett–Packard d.c. stabilized power supply and their values read on a Keithley 177 multimeter. The corresponding voltage drops across the e.m.f. arms of the samples were read on Keithley 174 voltmeter, provided the resistance measured did not exceed 10^2 Ω m. For higher sample resistances a Keithley 602 electrometer was used.

Some samples were also studied by direct immersion into the cryogenic baths covering the temperature range 2–4.2K (liquid helium) and to 77K (liquid nitrogen). Room-temperature measurements were also performed by immersing the samples into silicone oil.

RESULTS AND DISCUSSION

In order to characterize electrically all our samples (*Table 1*) and allow comparison with previous works[3,4,6,9,10], we have first measured their room-temperature electrical resistivity. Only four of these samples were subsequently investigated as a function of temperature down to about 2K. We have also tested the range of validity of Ohm's law at various temperatures as well as sample homogeneity and sample-to-probe contact resistance.

Room-temperature resistivity versus carbon black concentration

The room-temperature electrical resistivities *versus* carbon black contents are shown in *Figure 2*. All concentrations are expressed in weight. We may see from *Figure 2* that, when the carbon black content varies from 6.2 to 9.8%, the electrical resistivity swings from ~10^2 Ω m to less than 0.20 Ω m. The fact that for larger concentrations the resistivity varies in a slower manner with carbon black content is consistent with the data previously reported in the literature[5,6,8], where it is shown that the electrical resistivity becomes almost concentration insensitive for more than 15 wt% carbon black. The scatter in the data may be due to differences in the carbon black structure, porosity and specific area for a given concentration[12].

In view of the apparent 'non-ohmic behaviour' of the samples (see later), all measurements represented in *Figure 2* were performed in the limit of very low current densities, i.e. the range for which the voltage varied linearly with current.

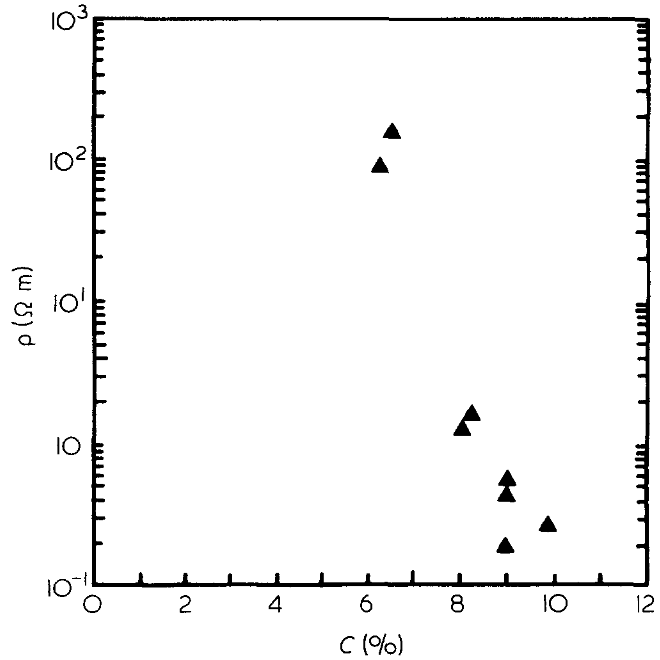

Figure 2 Room-temperature electrical resistivities of the samples *versus* carbon black contents (in wt%)

Contact resistance and sample homogeneity

Though in principle the four-point bridge method that we used eliminates the contact resistance in the measurement of the electrical resistivity, it is interesting to have an estimate of the probe-to-sample resistance. This is of practical importance if the order of magnitude of this resistance is higher than that of the sample. In that case the input impedance of the measuring voltmeter and the design of the current source should be adapted accordingly. We have thus measured the voltage drop between a current contact and various points on the samples. In *Figure 3* the room-temperature resistance is represented *versus* length for one of the samples and the extrapolation of the straight line to zero length yields the contact resistance. As expected, the contact resistance was found not to be reproducible and as a general trend varied with the resistivity of the sample. However, it was found that, at room temperature, the contact resistance is always negligible for the samples investigated compared to the 10^7 Ω voltmeter impedance which we used.

Also, since the sample resistivity is very sensitive to carbon black contents for small concentrations, the curves in *Figure 3* are a test of the homogeneity of the samples at a macroscopic scale. It may be seen from *Figure 3* that within the sample the various regions are homogeneous. In *Table 2* we have represented the values of the resistivities for different samples of the same starting

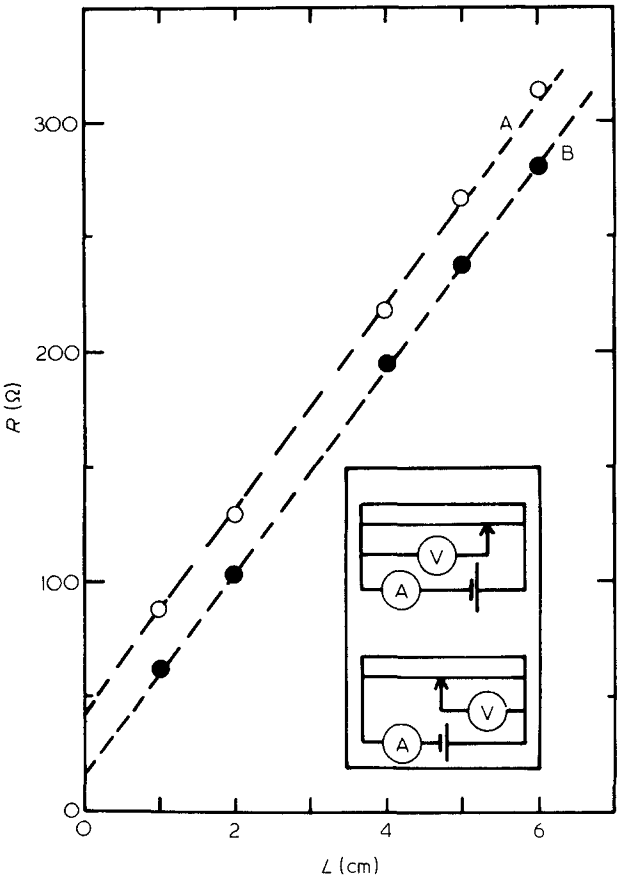

Figure 3 Resistance of sample no.11 *versus* length at room temperature. One of the voltage probes was connected to one of the current leads near one of the contacts to the sample and the other voltage probe was connected on the sample at different distances from this contact (curve A). For curve B, the same procedure was followed by starting from the other contact to the sample (see inset)

Table 2 Electrical resistivity of various carbon-loaded polyethylene samples cut from two different plates: ρ_{293} indicates the room-temperature value, while $\rho_{77.2}/\rho_{293}$ and $\rho_{4.2}/\rho_{293}$ are the resistivity ratios with respect to liquid nitrogen and liquid helium temperatures respectively

Starting material no.	Sample no.	ρ_{293} (Ω m)	$\rho_{77.2}/\rho_{293}$	$\rho_{4.2}/_{293}$
13–10	1	0.1772	1.404	126.60
	2	0.3206	1.342	186.60
	3	0.2877	1.278	183.72
	4	0.2904	1.438	–
	5	0.2757	1.565	–
	6	0.2803	1.392	–
	7	0.3003	1.375	–
	8	0.2880	1.428	–
	9	0.2903	1.454	–
	10	0.2853	1.443	–
11	1	0.2435	1.455	159.0
	2	0.3893	1.406	200.66

material. The various samples were cut from two different plates; no.13–10 and no.11. We may see from *Table 2* that for the plate 13–10, except for two of the samples (13–10–1 and 13–10–2), the various samples have the same room-temperature resistivity within less than 10%. Also the ratio of liquid-nitrogen to room-temperature and liquid-helium to room-temperature resistivities are in good agreement. For the plate no.11, from which only two samples were cut, the differences are larger. These tests show that within a region of a few centimetres the samples are very homogeneous (see *Figure 3*), while on a larger scale there is a larger inhomogeneity which does not usually exceed 10% (see *Table 2*). Room-temperature electrical resistivity measurements are thus a direct and simple means to characterize the samples and test their homogeneity on a macroscopic scale.

Current–voltage characteristics

When voltage *versus* current measurements are performed the qualitative features observed are as follows. At 4.2K and 77.2K when the current density exceeds a critical value J_m the experimental points are below the extrapolated ohmic characteristic (*Figure 4*). This indicates that the resistivity apparently decreases with increasing electrical field. The value of J_m is higher at 77.2K than at 4.2K. At 253K, up to the higher field investigated ($\sim$900 V m^{-1}) the experimental data follow exactly the ohmic characteristic, while at 295K, above J_m, the experimental points are above the extrapolated ohmic characteristic. A straightforward explanation is to ascribe the observed experimental facts to self-heating of the sample. If we anticipate the results of *Figure 6*, we may see that up to about 200K the sample resistivity, in the ohmic range, decreases with increasing temperature. Thus, if the sample temperature is increased with increasing Joule heating resulting from the sample current, then the observed sample resistivity should decrease with increasing current. At 253K, since the $\rho(T)$ characteristic is flat, one should not expect significant effects for moderate current intensities, as observed. When the sample is at room temperature one comes nearer to the region of *PTC* reported elsewhere[2,6–11] and one would expect an apparent increase of resistivity with increasing current. This is exactly what is observed. The above experiments were performed by directly immersing the investigated sample into different liquid baths: liquid helium (4.2K), liquid nitrogen (77.1K) and silicone oil (253 and 293K). For this reason one should have expected to work close to isothermal conditions. However, because of the very low thermal conductivity of polymeric materials, isothermal conditions are approximately achieved only when the current densities are sufficiently low. At higher current densities the central part of the sample has its temperature raised with respect to the outer part which is in direct contact with the bath.

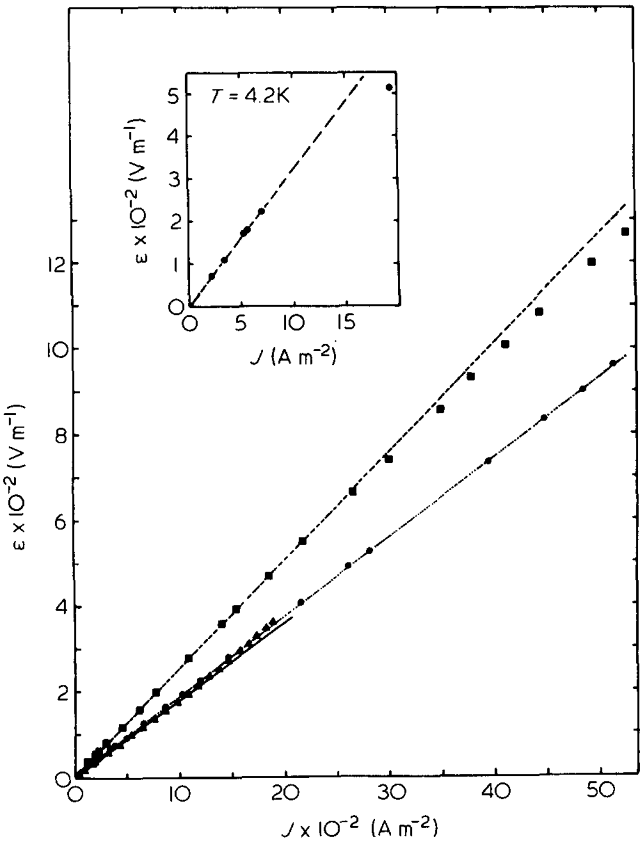

Figure 4 Electric field *versus* current density measured on sample no.13.10 at 77.2K (■), 253K (●) and 295K (▲). The inset is relative to the 4.2K values (also ●). The straight lines indicate the extrapolated ohmic behaviour

In order to check this assumption, we have investigated a sample in which the hot junction of a thin chromel–

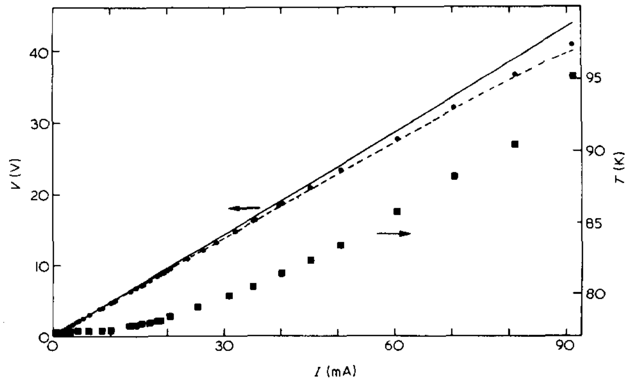

Figure 5 Voltage–current characteristic for sample no.13–10 at liquid nitrogen temperature. It may be seen that the departure from ohmic behaviour is accompanied by an increase in the temperature of the inner part of the sample. The broken curve represents the computed value (see text)

alumel thermocouple was sensing the temperature in a small hole in the centre of the sample. We have recorded the voltage resulting from a slowly increasing current as a function of current (*Figure 5*). At the same time the temperature indicated by the thermocouple was also recorded as a function of the current. Knowing the temperature variation of the resistivity in the limit of low currents (*Figure 6*) we could estimate the resistivity ρ_1 for any given current I_1 corresponding to the temperature T_1 indicated by the thermocouple and thus calculate the voltage V_1 corresponding to I_1. This is also represented in *Figure 5* (broken curve).

These observations strongly suggest that d.c. measurements are totally inadequate in our case to interpret deviations from Ohm's law as an intrinsic mechanism. Though such mechanisms might exist the dependence of the results on the experimental conditions are by far the most important factor which leads to the observed non-linearity in the V–T characteristics. This is why, since we are interested here in d.c. conductivities, all the current densities used were well below the critical limit J_m.

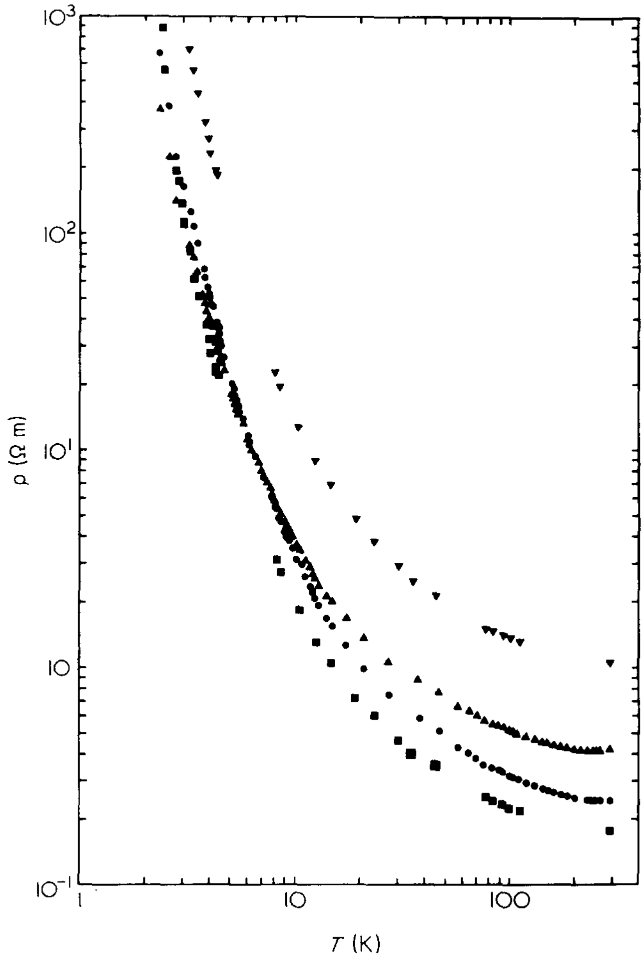

Figure 6 Temperature variation of the electrical resistivity of four samples of carbon-loaded polyethylene: ▼, no.10–7; ▲, no.11–8; ●, no.11; ■, no.13–10

Moreover, if instead of immersing the sample in a bath we place it into the evacuated chamber of the cryostat (*Figure 1*), we are then closer to adiabatic conditions and, as expected, the values of J_m are then shifted downwards.

Resistivity versus temperature

The temperature variation of the electrical resistivity of the four samples nos. 11, 11–8, 10–7 and 13–10 is shown in *Figure 6*. While around and below room temperature the resistivity is almost temperature insensitive, it starts to increase with decreasing temperature in the vicinity of 200K. In the liquid helium range, there is a drastic increase in resistivity per unit temperature decrease. This is indeed one of the highest sensitivities of resistance to temperature ever observed in a solid, together with that of carbon glass and carbon-loaded poly(vinyl chloride) if we exclude abrupt transitions (superconductivity, metal–insulator transitions, ...).

The resistance–temperature characteristic of carbon-black-loaded polyethylene is very similar to that of carbon resistor (Allen Bradley or Speer type) or carbon-impregnated glass, known as carbon glass resistor[13]. The latter has recently been used as a low-temperature thermometer because it combines high sensitivity, reproducibility and low reproducible dependence on magnetic fields up to 5 T[14]. We are now in the process of checking whether carbon-loaded polyethylene, which is a little more sensitive than carbon glass, could be used as a low-temperature sensor.

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