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LETTER TO THE EDITOR

## Thermal transport in hard carbon prepared from C<sub>60</sub> fullerene

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**Abstract.** We report measurements of thermal conductivity in the 30–350 K range of hard fullerene-based carbon. The material has been prepared by pressure–temperature treatment of C<sub>60</sub> fullerene. It shows an unusual combination of high hardness and relatively high electrical conductivity. Its thermal conductivity is about 5.7 W mK<sup>-1</sup> at room temperature and decreases almost linearly in the investigated temperature range. Excellent linearity in a wide temperature range may arise from some sort of crystalline order in the transformed substance. Obtained data are compared with thermal properties of C<sub>60</sub>, glassy carbon and diamond. The applicability of recent theoretical models for explanation of recorded data is discussed.

Investigation of thermal transport in various forms of carbon is of principal importance from a theoretical as well as a practical point of view. The thermal conductivity of perfect crystalline diamond is  $\lambda = 3500 \text{ W mK}^{-1}$  at room temperature [1], the highest value known for crystalline solids. Scattering of phonons on defects and imperfections of a crystal lattice substantially decreases the thermal conductivity of the substance. That is why in amorphous carbon the thermal conductivity has a smaller magnitude and normally lies in the range 2–400 W mK<sup>-1</sup> [2]. Finally, C<sub>60</sub> crystals or fullerites usually described as solids of the Van der Waals type due to their molecular nature have very small thermal conductivity ( $\lambda = 0.4 \text{ W mK}^{-1}$ ) [3]. Detailed investigation of the thermal conductivity of C<sub>60</sub> measured under pressure enabled the mapping of its phase diagram and gave some new elements for clarifying the possibility of polymerization of fullerene molecules [4].

Recently a transformation of C<sub>60</sub> into a very hard form of carbon (HC) has been reported [5]. The material was obtained at relatively soft conditions (pressure, 3 GPa; temperature, 700 °C) in the form of bulk specimens. It shows the unusual combination of remarkable micro-hardness (more than 4000 kg mm<sup>-2</sup>) and substantial electrical conductivity (about 100 (Ω cm)<sup>-1</sup>). The estimated density of HC,  $\rho \approx 1.9 \text{ g cm}^{-3}$ , is bigger than the density of initial C<sub>60</sub> (1.7 g cm<sup>-3</sup>), but significantly lower than the density of diamond (3.5 g cm<sup>-3</sup>). X-ray diffraction study shows a lack of long-range crystalline order in the transformed material. Films prepared from HC using laser sputtering in vacuum reveal, however, distinct evidence of microcrystalline diamond [6]. Electron diffraction and Raman measurements of the films allow us to suggest the existence of some crystalline order in the substance at least in a short-range scale. It may be relevant to such a hypothetical form of carbon as hollow diamonds [7], the material predicted theoretically, that comprises arrays of covalently interconnected fullerene cages and should have an excellent thermal conductivity. As a continuation of the

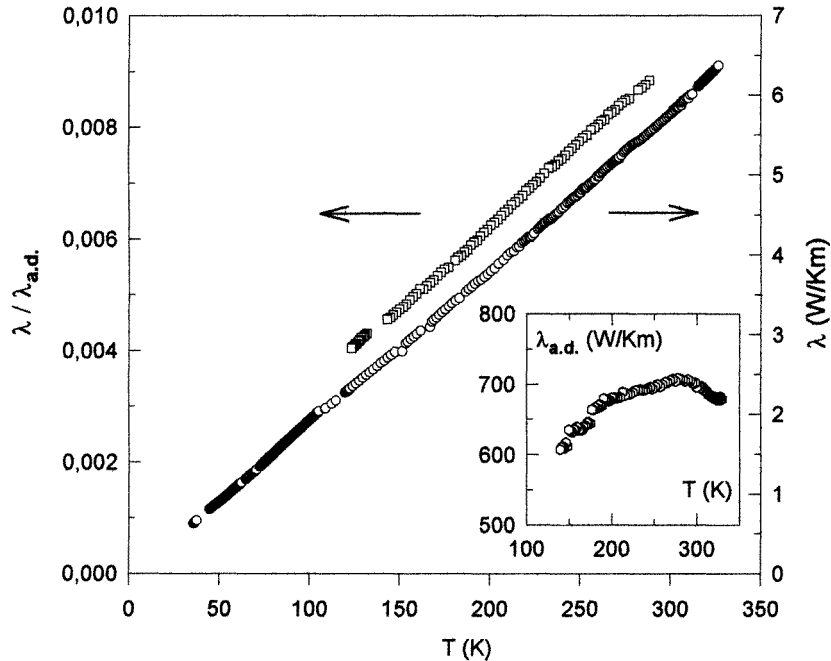
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characterization of HC we report data on thermal transport and compare them with those for glassy carbon, artificial diamond and  $C_{60}$  crystals.

Thermal conductivity was measured by a steady-state comparative method in the temperature range 30–300 K. It was performed relative to a constantan foil [8] and, independently, relative to a crystal of artificial diamond (a.d.) of Ib type. The latter was grown by Sumitomo Electric Industries, had dimensions  $2 \times 2 \times 0.3 \text{ mm}^3$  and orientation (100). For comparison measurements were carried out also on a sample of glassy carbon fabricated by Nikon Carbon Ltd, company brand VCP-5, of a size  $3 \times 1 \times 1 \text{ mm}^3$ . The sample of HC prepared from pure  $C_{60}$  as described previously [6] was cut in the form of a baton ( $3.5 \times 1 \times 0.6 \text{ mm}^3$ ). It was attached with GE varnish to the referent sample that was also used as a thermal link between the sample and the heater. On the other side the sample was glued directly to a thermal sink. The sample character was maintained in vacuum better than  $10^{-4} \text{ Pa}$ . The heat flow was estimated from the voltage difference between two chromel wires ( $\Phi = 15 \text{ }\mu\text{m}$ ) point-soldered to the constantan foil, so the link was also used as a thermocouple element. The thermal gradient in the sample was measured by a thin chromel–constantan thermocouple ( $\Phi = 15 \text{ }\mu\text{m}$ ) glued to the sample with GE varnish. The temperature difference measured on the sample was always smaller than 1 K when constantan was used as reference. Due to the higher thermal conductivity of a.d., independently used as a reference, the measured temperature difference on the sample was slightly larger depending on the temperature range. This was determined by the lowest voltage difference of the thermocouple on the a.d. sample ( $\sim 1 \text{ }\mu\text{V}$ ) necessary to achieve sufficient resolution. In order to minimize the radiation heat losses, the sample holder was closely surrounded by the heat shield, kept at almost the same temperature. The cooling (heating) rate was generally  $\sim 5 \text{ K h}^{-1}$  or less. The relative accuracy of the measurement (1–2%) was much better than that for absolute values (about 20% due to uncertainty in geometrical factors of the sample and the reference). Electrical resistivity was measured independently on the same sample by a conventional four-probe method. Contacts were made using conducting silver paste directly on the surface of the sample.

The thermal conductivity of HC at room temperature (R.T.) is about  $5.7 \text{ W mK}^{-1}$ . The value is much higher than for crystalline  $C_{60}$  [3], but significantly lower than for diamond crystals [1]. The thermal conductivity of HC measured relative to an a.d. crystal in the temperature range 120–290 K is more than two orders of magnitude lower and it decreases monotonically towards lower temperatures as shown in figure 1. The inset in figure 1 exhibits the temperature dependence of the thermal conductivity of the a.d. (measured relative to constantan). The absolute value at R.T. does not exceed  $700 \text{ W mK}^{-1}$  indicating substantial amounts of impurities. The two sets of data for HC measured relative to constantan and relative to a.d., regardless of very different measuring conditions, agree very well. A small difference in the absolute values apparently originates from the estimation of geometrical factors. The comparative measurement of the sample of glassy carbon shown in figure 3 demonstrates similar temperature behaviour but a 50% smaller R.T. value than for HC. The most intriguing fact is an almost perfect linear temperature dependence of the thermal conductivity of HC in the whole temperature range and we are going to discuss this.

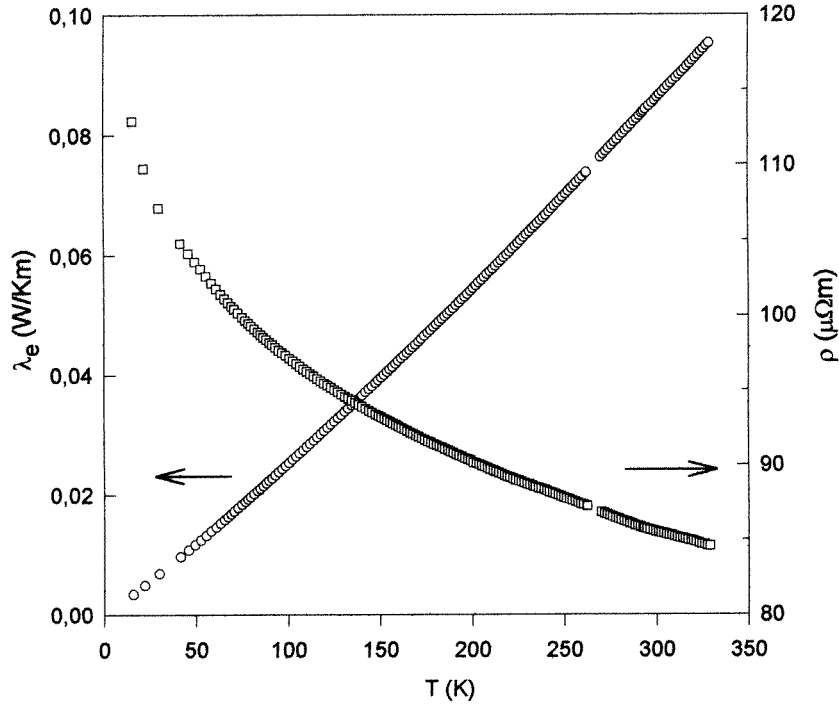
Usually total thermal conductivity,  $\lambda_T$ , is considered as the sum of the lattice,  $\lambda_g$ , and the electronic,  $\lambda_e$ , contributions:  $\lambda_T = \lambda_g + \lambda_e$ . As HC is electrically conducting, an estimation of the possible contribution of free carriers becomes necessary. In ordinary metals, it would suffice to evaluate  $\lambda_e$  at high temperatures from the Wiedemann–Franz law:  $\lambda_e \rho / T = L_0$ , where  $L_0 = 2.45 \times 10^{-8} \text{ W }\Omega \text{ K}^{-2}$  is the Lorentz number and  $\rho$  is the dc resistivity. The electrical resistivity of our sample at room temperature is relatively low,



**Figure 1.** The temperature dependences of the thermal conductivity of HC measured relative to constantan (○) and relative to a crystal of a.d. (□). The inset shows data for a.d. measured relative to constantan.

about  $85 \mu\Omega \text{ m}$ . While cooling down to 40 K it increases by about 30% (figure 2). The temperature dependence is in agreement with previously published data [5] and substantially deviates from the activated regime typical for usual glassy carbon [9]. It resembles a semimetallic behaviour rather than a semiconducting one [10]. Nevertheless, the small overlap of the valence and conduction bands appearing in semimetals can be regarded as a negative energy gap and some possible effects as in the heat conduction of semiconductors should be taken into account. In addition to the electronic contribution (electrons and holes), there is also so called bipolar diffusion originating from recombination of electrons and holes [11]. The free carrier contribution can be treated through the Wiedemann–Franz law but with a so called effective Lorentz number that can greatly exceed the above-given Lorentz value. However, it seems to be unlikely that the effective Lorentz number in this almost semimetallic material could surpass the value of 10 [12]. Even in this extreme condition the free carrier contribution should be in the range of the absolute accuracy of our measurement. The electronic contribution  $\lambda_e$  for our sample calculated using the simple Wiedemann–Franz law and experimental resistivity data is shown in figure 2. Although the  $\lambda_e$  temperature dependence is similar to that for the total thermal conductivity, its contribution to  $\lambda_T$  is less than 1%.

Thermal conduction in HC originates mainly from lattice vibrations and it has temperature behaviour very different from that of crystalline  $\text{C}_{60}$  [3]. They are compared in figure 3. The conventional behaviour of  $\lambda(T)$  of crystalline materials is a roughly  $1/T$  decrease at higher temperatures (above the Debye temperature) and a peak at low temperatures (not shown for  $\text{C}_{60}$  due to lack of low-temperature data in [3]). This is

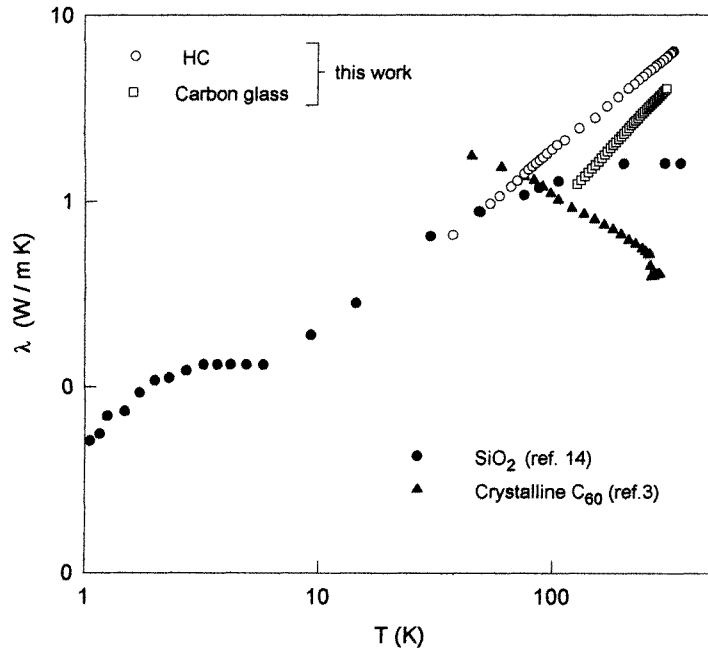


**Figure 2.** The temperature dependences of the electrical resistivity of HC ( $\square$ ) and the estimated electronic contribution to the thermal conductivity  $\lambda_e$  ( $\circ$ ).

characteristic of heat carried by phonons with a mean free path limited by ordinary ‘umklapp’ scattering. On the other hand, liquids and amorphous materials represent systems in which phonons are not well defined and they exhibit unconventional  $\lambda(T)$ . There are also some other examples of unconventional behaviour of  $\lambda(T)$  in the case when the unit cells become very complicated. The lack of local periodicity may cause a change from crystalline behaviour into the amorphous one as has been found for  $\text{YB}_{68}$  [13].

The typical behaviour of thermal conductivity for amorphous solids and certain disordered crystals is illustrated in figure 3 by the example of  $\text{SiO}_2$  [14]. It follows approximately the  $T^2$  law at low temperatures ( $T < 1$  K), has an almost temperature-independent ‘plateau’ between 1 K and 10 K and increases with  $T$  at higher temperatures. The low-temperature ( $T < 1$  K) part of  $\lambda(T)$  has been explained by a phenomenological model in which the two-level-state (TLS) excitations [15] are the principal scatterers for the phonons. TLSs are believed to arise from quantum tunnelling of atoms or molecules but their microscopic origin is still unknown. For temperatures above the plateau, there are still some controversies and open questions.

As mentioned, unlike crystalline insulators, where propagating short-wavelength phonons scattered by anharmonic interactions at high temperatures cause a dependence  $\lambda(T) \propto 1/T$ , noncrystalline solids seem to reveal a behaviour  $\lambda(T) \propto T$  in approximately the same temperature range. The thermal conductivity for HC in the temperature range available fits very well a linear dependence  $\lambda(T) = 0.022T^{(1.00 \pm 0.03)}$ . The comparative measurement of the sample of glassy carbon also shows the quasilinear behaviour  $\lambda(T) = 0.002T^{(1.33 \pm 0.03)}$  in the temperature range 120–350 K. HC has a certain degree



**Figure 3.** A comparative plot illustrating the conventional  $\lambda(T)$  for a crystalline sample of  $C_{60}$  ( $\blacktriangle$ , from [3]), and the unconventional behaviour of a typical amorphous material  $a\text{-SiO}_2$  ( $\bullet$ , from [14]) and our measured data for HC ( $\circ$ ) and glassy carbon ( $\square$ ).

of amorphization as evidenced by very broad diffuse peaks obtained by x-ray diffraction as well as by Raman scattering [5]. However, the material is not completely amorphous. It has the sort of crystalline order that sometimes reveals itself in Raman and electron diffraction measurements. This is probably the main reason that  $\lambda(T)$  of this material fits approximately the same frame as for  $\text{SiO}_2$  and glassy carbon above their plateau.

The problem of the heat transport above the plateau has been widely discussed in the last decade (see review [16] and references therein). There have been two different concepts for the explanation of the linear temperature dependence of  $\lambda(T)$  above the plateau: the ‘resonance’ interpretation [17] and the picture of an additional heat conduction channel [18]. In the first approach the anharmonic modes that can carry heat are supposed to be introduced at a temperature above the plateau. They are scatterers for TLSs and as the population of TLSs decreases linearly with  $T$  the scattering of anharmonic modes decreases in the same manner, causing  $\lambda(T) \propto T$ . The second model [18] although originally based on the fracton model should also be valid for more conventional localized vibrations [19]. The recent simulations by means of the nonequilibrium molecular-dynamics (MD) method [16] support the model of anharmonicity-induced hopping heat transfer in glasses. Presuming that the aperiodicity of amorphous solids is their only common feature, the MD simulation has demonstrated the presence of localized vibrational modes that are the source of the strong anharmonicity in amorphous solids. It has been shown in addition that the influence of quasiperiodicity on  $\lambda(T)$  is the same as that for a simple aperiodicity.

To our knowledge HC is the unique material obeying a linear  $T$  dependence of the thermal conductivity in such a wide temperature range. Unfortunately we did not reach the plateau region that is necessary for the estimation of some parameters in the model of

anharmonicity-induced localized vibrational state hopping. However, it looks as if in this specific material there is no departure of the thermal conductivity from linear dependence upon temperature as observed in some amorphous systems. According to the same model this means that there is no violation of the temperature-dependent condition on the hopping lifetimes of the localized vibrational excitations that might cause the curling over of  $\lambda(T)$  from its linear temperature dependence and this fact is related to the degree of anharmonicity [18]. HC reveals some sort of crystalline order at least in the short-range scale. The unusual mechanism of thermal transport in HC is presumably caused by the characteristic microstructure (or mesostructure) of this material. It provides an anharmonic interaction that is sufficient to invoke the hopping conductivity but not large enough to quench it. Further structural investigation of HC should clarify this point.

In summary, the main characteristics of the thermal transport in the new material HC have been discussed. A comparative study of the thermal conductivity in HC, crystalline diamond, glassy carbon and molecular  $C_{60}$  crystals shows that it correlates with the density of these compounds. Covalent linking of  $C_{60}$  cages is apparently responsible for the drastic increase of the thermal conductivity in HC at 300 K compared with pristine  $C_{60}$ . A substantial number of  $sp^3$  sites in its 'polymerized' structure causes the increase of the thermal conductivity relatively to glassy carbon. However the disordered structure of HC makes the room-temperature values much smaller than those in crystalline diamond. The existence of the short-range crystalline order in HC can be related to the excellent linearity of  $\lambda(T)$  in a broad temperature range. This material seems to be very promising for the verification of actual theories of thermal transport in amorphous solids.

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