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## Thermal conductivity of hard carbon prepared from $C_{60}$ fullerene

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## Abstract

We report measurements of thermal conductivity in 30–350 K range of hard fullerene-based carbon. The material has been prepared from  $C_{60}$  fullerene under pressure and has an unusual combination of large hardness and relatively high electrical conductivity. Its thermal conductivity is about 5.5 W/mk at room temperature and decreases almost linearly in the investigated temperature range. The data obtained bear resemblance to the thermal properties of amorphous materials. It is consistent with the structural investigation that allows one to suggest the existence of short-range crystalline order in this transformed substance.

Recently many works have been devoted to the study of  $C_{60}$  fullerene especially after it has been shown that under pressure it can be directly transformed into diamond [1]. Unlike diamond with pure sp<sup>3</sup> hybridisation and  $sp^2$  hybridisation in graphite, the bonding in  $C_{60}$ molecules has an aromatic character [2]. In addition, a quasi-tetrahedral co-ordination of carbon atoms in pentagons of buckyballs [1] is sterically quite close to that of the diamond. Therefore the formation of intermolecular bridges and a small rearrangement of the atoms can cause an essential modification of structural properties of this material. At relatively moderate conditions (nonhydrostatic pressure 2.6-3 Gpa and a temperature of 700°C) a very hard form of carbon can be obtained. The treatment of ordinary graphite at similar conditions does not produce a material with the comparable hardness [3]. Although there is no clear evidence of crystalline diamond ingredients, this material shows the

ry graphite at similar erial with the compais no clear evidence of its material shows the conducting; it electrical conductivity was  $10^2 (\Omega \text{ cm})^{-1}$  at room temperature and while cooling it increased (~ 20%) almost linearly down to 40 K [3]. The value of

coexistence of the remarkably high hardness and relative-

ly high electrical conductivity. It is probably related to its

complex bonding by which the saturated sp<sup>3</sup> bonds bring

about high strength of the compound, whereas regions

with three-fold carbon co-ordination originating from

the hybridisation of the initial C<sub>60</sub> cages contribute to the

transport properties [3]. Owing to its remarkable hard-

ness this compound could be interesting for industrial

application, so that in addition to the hardness and the

electrical transport, a heat transport investigation is ne-

heat transport measurements was quite homogenous,

without voids and pores, visible even with optical and

The sample of superhard form of carbon used in our

cessary for a better characterisation.

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Fig. 1. Thermal conductivity of superhard carbon measured by steady-state comparative method relatively to constantan [5]. The inset shows the electrical resistivity ( $\bigcirc$ ), measured on the same sample together with the estimated electronic contribution to the thermal conductivity ( $\bigcirc$ ) which is negligible compared to the total thermal conductivity.

the conductivity is typical for glassy carbon [4], but the temperature dependence does not follow the usual activated behaviour. The measured resistivity,  $\rho(T)$ , shown on inset in Fig. 1, resembeles a semimetallic behaviour rather than a semiconducting one. Thermal conductivity,  $K_{\rm T}$ , was measured by a steady-state comparative method relatively to a constant foil [5] on the sample of typical dimensions  $3.5 \times 1.4 \times 0.6$  mm<sup>3</sup>. K<sub>T</sub> shows nearly linear temperature behaviour (see Fig. 1). The total thermal conductivity,  $K_{\rm T}$ , can be considered as the sum of the lattice,  $K_{g}$ , and the free carrier,  $K_{e}$ , contribution:  $K_{\rm T} = K_{\rm g} + K_{\rm e}$ . Since  $\rho(T)$  measured on the same sample show a semimetallic behaviour, the free carrier contribution should be estimated using the Wiedemann-Franz law  $K_e = L_0 T / \rho$  but with the so-called effective Lorentz number,  $L_{eff}$ , that can greatly exceed the value of Sommerfeld-Lorentz number,  $L_0$ , due to bipolar diffusion originating from recombination of electrons and holes [6]. Taking into account our experience with the estimation of the free carrier contribution in charge density wave materials, that can be assumed to be semiconductors with a small temperature-dependent gap [7], we do not believe that in this almost semimetallic material  $L_{\rm eff}$  could surpass the value of few  $L_0$ . Even in the extreme condition ( $L_{eff} = 5$ ) the free carrier contribution would be in the range of the absolute accuracy of our measurement [5].  $K_e$  as calculated by using the



Fig. 2. Comparative plot of thermal conductivities of different materials illustrating conventional thermal conductivity  $(\triangle)$  for single crystal C<sub>60</sub> [8], the unconventional behaviour ( $\bullet$ ) of typical amorphous material SiO<sub>2</sub> [9] and our measured data for superhard form of carbon ( $\Box$ ).

Wiedemann–Franz law with  $L_0$  (inset in Fig. 1) has similar temperature behaviour as the total thermal conmductivity but it represents less than 1% of  $K_T$ .

Thermal conductivity of superhard carbon comes mainly from lattice vibrations and it shows an anomalous behaviour compared to single crystal  $C_{60}$  [8] (shown together in Fig. 2). The conventional behaviour of K(T)of crystalline materials is roughly a 1/T decrease at higher temperatures  $(T \gg \Theta_D)$  and a maximum at low tempertures. This is characteristic of heat carried by phonons with a mean free path limited by ordinary "umklapp" scattering. On the other hand amorphous materials represent the systems in which phonons with well-defined wave vector "do not exist" and they show unconventional behaviour of K(T). Their thermal conductvity K(T) between roughly 1 and 10 K displays a nearly temperatrure-independent "plateau" above which it smoothly increases at higher temperatures. This behaviour is illustrated in Fig. 2 for  $SiO_2$  as a prototype amorphous material [9] in comparison with the behaviour of single crystal C60 in more restricted temperature range (taken from Ref. [8]). The thermal conductivity of superhard carbon follows the behaviour of vitreous silica above its plateau, before it starts to deviate from nearly linear temperature dependence.

Unlike crystalline insulators where propagating shortwavelength phonons scattered by anharmonic interactions at higher temperatures cause  $K(T) \propto 1/T$ , in the case of amorphous solids  $K(T) \propto T$ , in approximately the same temperature range. It has been demonstrated that beyond the edge of the plateau the dominant vibrations propagate distances shorter than the hypothetical wavelength, so that the dominant modes in amorphous solids at higher temperature are localised. The linear dependence might be explained in the representation of an additional heat conduction channel [10] where the spatially localised vibrational modes contribute to the heat current. Superhard carbon displays the linear heat conductivity in a very wide temperature range without any indication of deviation at higher temperature. Unfortunately, we were not able to reach the plateau region. However, the estimated value of the thermal conductivity at T = 10 K corresponds to about the same magnitude of the thermal conductivity of the plateau of very different amorphous materials falling roughly within the same temperature window.

In conclusion, a superhard form of carbon shows a linear temperature dependence of thermal conductivity in even larger temperature range than it has been found in the thermal conductivity of the densified a-SiO<sub>2</sub> [11]. We suppose that the density inhomogenities produced by applied pressure in both dense materials play some role in suppressing the anharmonic quenching of the hopping which cause the curling over K(T) from its linear temperature dependence in other amorphous solids. These materials might be a good model systems for proving the thermal conductivity of localised modes in amorphous solids.

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