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The amorphous nature of C_{60} hard carbon manifested in its specific heat, sound velocity and heat conduction

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Abstract
Detailed measurements of the specific heat, thermal conductivity and relative
variation of the sound velocity in the temperature range 2–280 K for hard
fullerene-based carbon are reported. The novel material was obtained from
pressure–temperature treatment of C_{60} fullerene and is known for a unique
combination of its diamond-like hardness and high electrical conductivity. The
substance was found to possess an unconventional, close-to-linear temperature
dependence of the thermal conductivity over almost the entire temperature
range. The specific heat of hard carbon exhibited a very large linear contribution
to the specific heat at low temperatures, but no excess contribution to C_p/T^3,
and a deviation from the Debye dependence above 6 K. The sound velocity
decreased linearly from 4 up to 120 K. These results are consistent with the
concept of a glassy solid formed by polymerized and partially transformed
fullerene clusters.

1. Introduction

The range of novel materials has greatly increased in the last decade. Characterization of the
substances frequently smears boundaries between well-established families of compounds,
requiring readjustment of our understanding of conventional physics–property relationships.

One of the most exciting developments in the field of materials science is related to the
remarkable expansion of the carbon family. Traditional studies of graphite and diamond
now look incomplete without references to fullerenes [1] and carbon nanotubes [2], the
fascinating new carbon modifications. Another interesting representative of the family is
so-called hard carbon (HC), peculiar in showing the coexistence of high hardness and high
electric conductivity [3].

HC is obtained from C_{60} fullerenes under moderate pressure of 3 GPa and at a temperature
of 700 °C [3]. The microhardness of the material was found to be comparable to that of

diamond and its density was only slightly higher than the density of solid fullerites, which locates it halfway between fullerites and diamond. Macroscopically, the specimens of HC were conductive, exhibiting semimetallic temperature dependence. X-ray diffraction and Raman measurements [3] have shown the lack of long-range crystalline order. Recent STM and STS measurements [4] reveal a mesoscopic lattice, which consists of electrically conductive nanograins interconnected with covalent bonds. The typical nanograin radius ranges from 2 to 4 nm.

The thermal conductivity of HC exhibits an unusual linear temperature dependence over a very wide temperature range, from 30 to 320 K [5], deviating from the thermal properties of graphite and diamond and consistent with the concept of a glassy solid. Such behaviour is interesting from theoretical point of view and might be of importance for applications.

In the present paper we report temperature dependences of the specific heat, thermal conductivity and variation of the sound velocity of HC. The results provide further characterization of the unconventional thermal properties of HC.

2. Experimental details

The HC sample had the shape of a half-disc, about 5 mm in diameter and 1 mm in thickness, with the mass of $m = 15.6$ mg. Three different characterization techniques have been employed. The temperature dependence of the relative change of the longitudinal sound velocity was recorded using the standard pulse-echo method with longitudinal waves generated along the smallest dimension of the sample. LiNbO$_3$ transducers were attached to the flat surfaces of the sample. The change of sound velocity, Δv, at a given temperature T was measured at 15 MHz using a phase-coherent detection method and normalized by the value at 4 K ($\Delta v/v$). Because of the small thickness of the sample, reliable assessment of absolute values of the sound velocity was difficult.

Thermal conductivity was measured along the thickness direction of the disc. Using GE varnish, a small heater was attached to one side of the sample and a 200 μm thick Cu foil on the other side, providing a link to a thermal sink. Temperature differences ranging from 0.1 to 0.5 K were detected with a 50 μm Au (0.07% Fe)–chromel thermocouple. Before beginning the experiment, the sample space was evacuated to 10^{-6} mbar. The sample was cooled down to 2 K and subsequently heated to room temperature. It was found that upon heating, the vacuum in the chamber improved to 1.3×10^{-7} mbar resulting in slightly reduced heat loss. Therefore only data collected in the heating run will be reported from now on.

With a slight modification of the geometry of the thermometry on the sample, we measured the specific heat using a quasi-adiabatic transient heat pulse technique. The difference in sample temperature relative to the heat sink was determined by leaving one side of the thermocouple on the sample face opposite to the heater side and moving the other one from the sample to the thermal sink. A short current pulse was applied to the heater, and the quasi-adiabatic jump of the sample temperature was estimated from the extrapolation of the long-time exponential decay. The contribution from the heater to the heat capacity was neglected.

3. Results

3.1. Specific heat

The temperature dependence of the specific heat of the HC recorded in the range 2–280 K is shown in figure 1. The experimental results are compared with the measurements on graphite [6, 7] and diamond [7], as well as several C$_{60}$-based systems such as compressed C$_{60}$/C$_{70}$ powder [8], molecular C$_{60}$ [9] and 1D and 2D polymerized C$_{60}$ [9] obtained through pressure/temperature treatment.
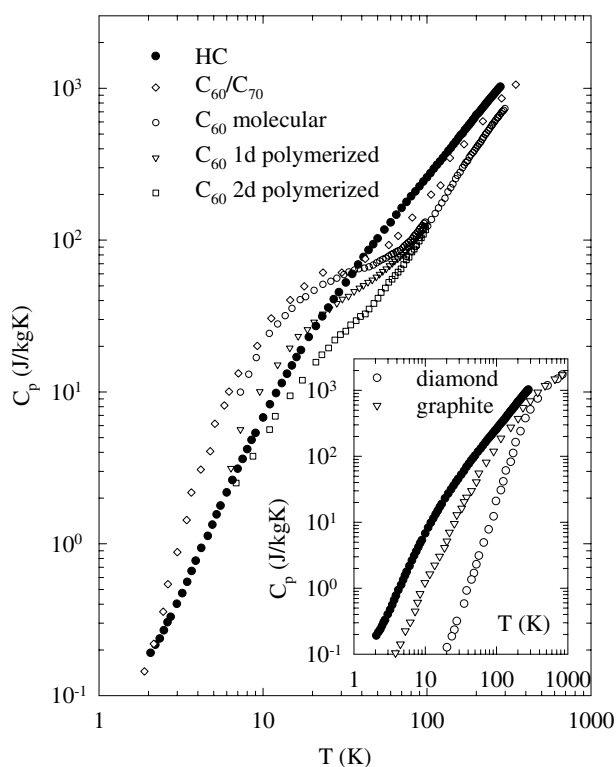
Figure 1. The specific heat of HC measured from 2 up to 280 K compared with data obtained on compressed C_{60}/C_{70} [8], molecular C_{60} [9] and 1D and 2D polymerized C_{60} [9]. The comparison to graphite [6] and diamond [7] is given in the inset.

The specific heat (C_p) of HC exhibits very unusual temperature dependence. It exceeds C_p for diamond and graphite over the entire temperature range, as shown in the inset of figure 1. It evidences that some additional degrees of freedom, besides the acoustic vibrations, exist in the configurational part of the free energy. The room temperature (RT) value of C_p is slightly higher than in other C_{60}-based materials presented in figure 1 and follows almost the same temperature dependence down to $T \approx 100$ K. However, below 100 K, HC does not show the excess contribution in the form of a low-temperature wing, which seems to be typical for other C_{60}-based systems presented in figure 1. As the excess contribution is well explained by the vibrational modes of C_{60} molecules [8, 9], this indicates the lack of corresponding modes in HC.

The analysis of the temperature dependence of C_p is given in figure 2 in the usual presentation as C_p/T^3 versus T. Our data show a pronounced low-temperature upturn. A C_p/T versus T^2 plot given in the inset of figure 2 shows that up to 6 K C_p is well described by the $\gamma T + \beta T^3$ law, with $\gamma = 0.051$ J kg^{-1} K^{-2} and $\beta = 9.5 \times 10^{-3}$ J kg^{-1} K^{-4}.

From the value of β we can calculate the Debye temperature which we need in order to estimate the expected temperature dependence of C_p as well as for comparison with other C_{60}-based materials. Taking the molar mass of the parent C_{60} compound $M = 720$, we obtain $\beta = 6.8 \times 10^{-3}$ J mol^{-1} K^{-4}, and finally[4] $\theta_{Dac} = 66$ K. The solid circles in the main plot

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[4] For the estimation of the conventional Debye temperature θ_D, we have to take into account that there are $r = 60$ C atoms in the formula unit, so from the formula $\theta_D = (1944r/\beta)^{1/3}$, we get $\theta_D = 66$ K.
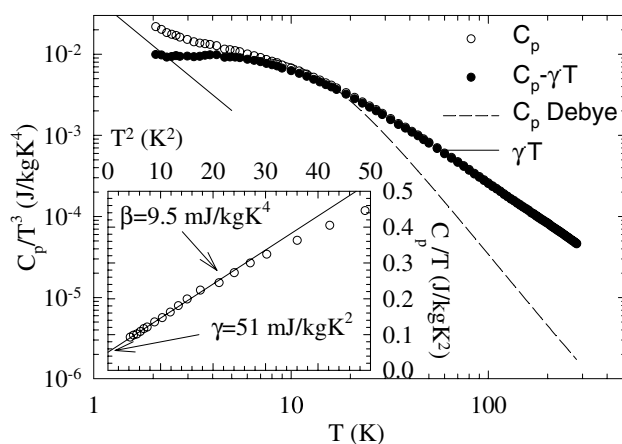
Figure 2. Specific heat data for HC plotted as C_p/T^3 versus T on log–log scales. The solid line represents the linear contribution estimated from the C_p/T versus T^2 plot as the C_p/T axis intersection (shown in the inset). The full symbols are obtained after the subtraction of the linear term, and show a $\sim T^3$ dependence up to 6 K, where it starts to deviate smoothly. The dashed curve corresponds to the expected Debye-like behaviour.

were obtained by subtraction of the linear term from the experimental data. They evidence that a deviation from the T^3 law appears at $T \sim \theta_{Dac}/10$, not far from the expected Debye-like behaviour (indicated by the dashed curve). However, at higher temperatures the deviation becomes more pronounced.

The Debye temperature $\theta_{Dac} = 66$ K deduced from β is smaller than $\theta_{Dac} = 80$ K reported for compacted C_{60}/C_{70} [8]. Experimental data for C_{60} pressed pellets [10, 11], which are very close to the data in [8], have been analysed within the model containing Debye terms, Einstein oscillators and a linear contribution. Two Debye terms representing vibrational–acoustic modes yielded corresponding Debye temperatures of 49 and 67 K. If the orientational ordering was neglected, one single Debye temperature of 74 K was obtained [10, 11]. Note that these values are very close to our estimation of θ_{Dac} for HC.

On the other hand, the low values of θ_{Dac} reported for C_{60} pressed pellets [10, 11] are consistent with the low value of the sound velocity in C_{60} [12], whereas in the case of HC, the sound velocity of $v_D = 1900$ m s^{-1} calculated from θ_{Dac} is much lower than the sound velocity of about 5900 m s^{-1} measured by one of us [13] for a similar HC sample. In this respect, the observed Debye-like contribution is higher than would be expected from the velocity of sound.

Finally, we discuss the unusually large linear component $\Delta C_p = \gamma T$ with $\gamma = 51$ mJ kg^{-1} K^{-2}. As HC exhibits semimetallic behaviour [5], this contribution could be assigned to the free carriers. However, a simple comparison with metallic materials such as Cu that have RT conductivities several orders of magnitude higher, but lower values of $\gamma \approx 10$ mJ kg^{-1} K^{-2}, shows that this would be inconsistent as regards the much lower density of free carriers.

If the linear term is assigned to the contribution of low-energy excitations (LEE) characteristic for conventional disordered systems [14], it would have almost 20 times larger magnitude than that for (amorphous) a-SiO$_2$ (1.5–3 mJ kg^{-1} K^{-2}) [15]. This would mean that the number of corresponding two-level systems (TLS) should be also 20 times larger. If we pursue the comparison with glasses, the so-called boson peak [17] contribution to C_p/T^3 situated at about 10 K is missing in HC. It is interesting that SiO$_2$ aerogels [16] also exhibit very large linear terms (15–150 mJ kg^{-1} K^{-2}), but no boson peak.
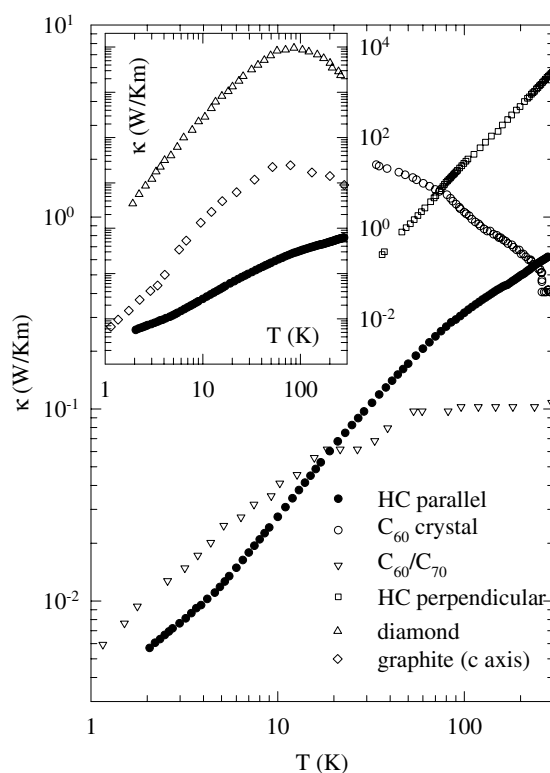
Figure 3. The thermal conductivity of HC measured along the direction of the pressure application during sample preparation compared with compressed C$_{60}$/C$_{70}$ [8], crystalline C$_{60}$ [20] and another HC sample [5] measured perpendicular to the direction of the pressure application. The inset shows the comparison with the crystalline behaviour of diamond [21] and graphite [22].

Similarly large values of γ have been also found for other carbon-based compounds such as amorphous graphite [18], single-wall nanotubes [19] and C$_{60}$ [10]. In the latter case, it was shown to diminish upon additional thermal and pressure treatment [11]. Therefore the linear contribution to C_p might have the same nature in these compounds.

3.2. Thermal conductivity

The temperature dependence of the thermal conductivity of HC in the direction of the pressure application recorded in the range 2–280 K is shown in figure 3 and compared with the thermal conductivities of several carbon-based compounds, diamond [21], graphite [22] (in the inset), crystalline C$_{60}$ [20], compacted C$_{60}$/C$_{70}$ [8] and another sample of HC [5].

The main contribution to the thermal conductivity is from the lattice, as the free carriers contribute less than <10% [5]. The lattice thermal conductivity is particularly sensitive to the degree of disorder, which affects the phonon dispersion and the mechanism of the phonon scattering. It demonstrates the existence of substantial differences in phonon spectrum between an amorphous solid and a perfect crystal. Comparison of the temperature dependence of the thermal conductivity of a HC sample with those for crystalline materials such as C$_{60}$ [20], diamond [21] and graphite [22] indicates its disordered nature. For instance, the thermal conductivities of HC and C$_{60}$ have very similar values at RT, but exhibit completely different trends on temperature decrease.

On the other hand, it is known that the application of moderate pressure reduces heat conduction in C_{60} [23], as does the inclusion of C_{70} clusters (in C_{60}/C_{70} compacts). Also, the conductivity of C_{60}/C_{70} compacts is almost constant down to $T \sim 50$ K, and follows a similar, linear temperature dependence at lower temperatures, as in HC. The difference between C_{60}/C_{70} compacts and HC above 50 K is definitely caused by a difference in texture of the materials, which results from different conditions of pressure–temperature treatment. Although moderate pressure (0.1 GPa) reduces conduction in fullerenes, it was shown that further increase in the applied pressure up to 1 GPa causes a substantial rise of thermal conductivity [23].

The previous measurements of the thermal conductivity of HC [5] revealed pronounced linearity in the temperature range 30–320 K. Qualitatively similar, close-to-linear behaviour of the thermal conductivity was now recorded down to 2 K, however with a smooth curling over above 80 K (figure 3). The two samples had been prepared in similar conditions [3], but the measurement in [5] was performed in the direction perpendicular to the pressure application. This could signify anisotropy in the thermal conductivity, with higher conductivity perpendicular to the direction of the pressure application. We plan to investigate the anisotropy of HC in the near future.

The linear dependence of the thermal conductivity is reminiscent of the linear conductivity in glasses [24] (for instance amorphous or a-SiO$_2$), together with the high-temperature curling over. However, there is a substantial difference in low-temperature behaviour. In glasses the thermal conductivity enters a plateau at about 10 K (and eventually turns to showing a $\sim T^2$ dependence below 1 K), whereas in HC it only starts to flatten below 4–5 K. Again, it would be interesting to pursue the temperature dependence to lower temperatures to see whether a true plateau occurs. Such a low-lying plateau, both in temperature (below 1 K) and in amplitude, as well as (quasi-) linear temperature dependence above the plateau, has been observed in silica aerogels [16]. Generally, it seems that in less dense materials the plateau occurs at lower temperatures and has lower amplitude.

Finally, the extrapolation of the linear contribution towards low temperatures tends to zero at $T = 0$, or a value only slightly above this. This shows that it represents an independent channel of heat transport, in agreement with recent theories of linear thermal conductivity in amorphous systems that we will present in our discussion.
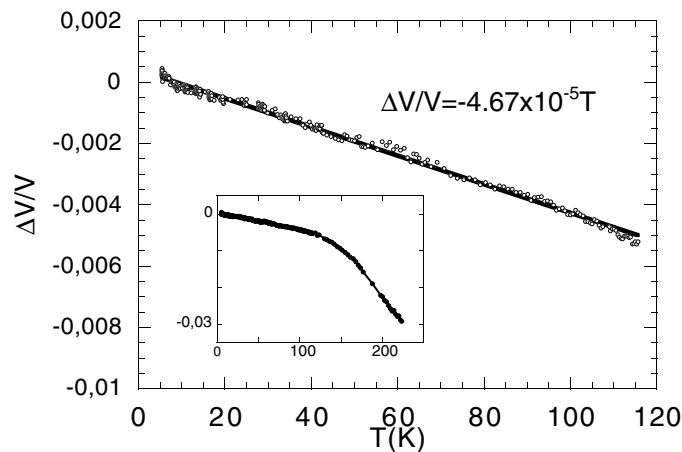
3.3. Sound velocity

Another striking difference between amorphous and crystalline solids is in the temperature variation of the sound velocity. In a variety of amorphous solids, the sound velocity has been found to decrease linearly with temperature and can be described by

$$\Delta v/v_0 = -b(T - T_0) \tag{1}$$

where v_0 is the velocity of sound at some reference temperature T_0. This is called the Bellessa effect, after the work [25]. In our case, $T_0 = 4.2$ K. As noted before, the absolute value of the sound velocity was difficult to obtain in the present sample geometry.

Our results shown in figure 4 demonstrate very continuous, linear dependence on T up to 120 K. The estimated coefficient $b = 4.67 \times 10^{-5}$ is very close to the value measured by Bellessa for amorphous metallic Pd–Si [25]. If the various materials exhibiting linear sound velocity variation are compared [26], HC is placed close to the top of the amorphous solids (compared to the ten-times-larger b-value for SiO$_2$) and also almost at the top of the quasicrystals (comparable with Al$_{65}$Cu$_{20}$Fe$_{15}$) or near ZrO$_2$(20% CoO), a disordered crystal, which is not considered to be glass-like in the conventional definition.

Figure 4. The linear variation of the sound velocity measured relative to the unknown value at 4.2 K. The inset shows the variation over the entire temperature range.

4. Discussion

As we mentioned in the introduction, the structural investigation of HC revealed its amorphous nature. Our results on the temperature dependence of the thermal capacity, the thermal conductivity and the sound velocity support this conclusion. The lack of a well-defined contribution from vibrational modes of C$_{60}$ molecules indicates that they are at least partially destroyed in HC, in agreement with the fact that they have not been observed in TEM measurements. As HC has such high microhardness [3], the destruction of C$_{60}$ molecules is accompanied by three-dimensional covalent bonding. The temperature dependence of the thermal conductivity and sound velocity, particularly the linearity over the wide temperature region, is again consistent with the amorphous nature of HC. Therefore, it would be appropriate to try to understand the properties of HC within the framework of other amorphous systems.

Thermal properties of a variety of glassy materials normally reveal three well-defined regions. In the low-temperature region below a few kelvins $\kappa \sim T^2$, a temperature dependence which is well explained by inelastic phonon scattering on a TLS [14]. In the same temperature range, TLS give a linear contribution to C_p above the Debye contribution. At higher T, above 10 K, κ enters a plateau region, where C_p/T^3 exhibits a so-called boson peak [17]. And finally, above the plateau, or 30 K, κ starts to increase in a linear manner, with a curling over at higher temperatures [24].

Two approaches to the origin of the plateau and the linear dependence above it have been proposed. One attributes the origin of the plateau to resonant scattering of phonons on localized modes of some characteristic frequency ω_c due to structural defects [27], which reduce their mean-field path to values close to the interatomic distance. The same local modes contribute to the excess density of states responsible for the boson peak [28]. The increase of the thermal conductivity above the plateau is due to the reappearance of extended (phonon-like) modes, which scatter again on TLS [29]. The linear dependence is a consequence of the depopulation of TLS states at higher temperatures.

The second, more recent approach relies on the fact that the short-wavelength phonons cannot propagate in the disordered structure of glasses. In this respect, two types of excitation are postulated: extended (phonon-like) and localized ones [30, 31]. They do not coexist; instead there is a length scale ξ and a corresponding frequency ω_c at which the crossover

between the extended (low-frequency) and localized (high-frequency) modes occurs. ω_c acts now as a mobility edge for the phonons and the plateau occurs at temperatures where all phonons up to ω_c are thermally excited. The linear contribution in this approach is due to the phonon-assisted hopping of localized excitations [32, 33] and represents a new channel of heat transport. We should note that the analyses have been carried out assuming fractal geometry at short length scales, so the localized excitations are called fractons [30], but the results, as the authors of [30] discuss, should be applicable to any system in which short-wavelength excitations are localized [33]. The coupling between phonons and localized excitations is via anharmonic interaction, which should be fairly large to fit the experimental data. The excess density of states of the localized modes is responsible for the boson peak.

First we discuss the temperature dependence of the thermal conductivity. Our results differ considerably from the results for glasses; the linear contribution to κ is extended towards lower temperatures, and we observe only an indication of the possible plateau region below a few kelvins. As both aforementioned approaches introduce a characteristic frequency ω_c which determines the plateau temperature, we can conclude that ω_c for the case of HC is much lower than in glasses. A simple scaling of the plateau offset temperature gives ω_c for HC of the order of $\nu \leqslant 100$ GHz compared to $\sim$THz [34] for glasses. As we have already noted, our results are similar to those for the silica aerogels [16], both as regards the low amplitude and the extension of the linear regime towards lower temperatures. Small-angle neutron scattering has demonstrated that the structure of aerogels is indeed fractal at mesoscopic length scales up to 10 nm [35], much longer than what has been estimated for a-SiO$_2$ [32]. The similarity with aerogels might suggest that in HC the crossover length scales are also of the order of few nm, which is also the dimension of the nanograins observed in TEM [4]. If we consider ω_c as a cut-off frequency for propagating phonons, a low value of ω_c would be consistent with high ξ. It is hard to differentiate between the two approaches to the origin of the thermal conductivity. However, the fact that our results interpolate to a finite positive value at $T = 0$ favours the localized mode hopping model which introduces a new channel of heat conduction.

Considering now the temperature dependence of C_p, there are two pronounced differences in comparison with glasses. First, there is no boson peak. This is actually consistent with the suppression of the plateau in the thermal conductivity, as the boson peak is due to the same modes as are responsible for the plateau [28]. The second difference is the contribution from LEE which is unexpectedly large compared to those for other disordered materials, as we noticed for a-SiO$_2$. We could, in a very formal framework, in which TLS are responsible for the universal low-T properties shared by all configurationally disordered systems, explain this contribution by an unusually high density of TLS. However, in this case these TLS do not interact with phonons in a similar way to in conventional glasses, i.e. there is no evidence of their scattering with phonons giving rise to $\kappa \propto T^2$. The only way this can be reconciled is to accept that all propagating modes (phonons) are already thermally excited at a few kelvins (the second approach described previously), so the increased number of TLS only decreases the amplitude of thermal conductivity and does not affect the temperature dependence. We have already mentioned that SiO$_2$ aerogels also have a very large linear contribution to the low-temperature C_p. The explanation is again based on their fractal structure, through the 'coarse-grained' fractal structure model [16] in which flexural modes are of dominant importance.

The phonon-assisted fracton hopping model also accounts for the linear decrease of the sound velocity $\Delta v/v(T)$ and provides the linear relation with κ through the formula [32]

$$\Delta v/v = -0.1(\xi^2/2\pi^2 v)[\kappa(T)/T]k_B^{-1}T. \qquad (2)$$

For a-SiO$_2$, comparison with experimental data yields ξ of the order of 1–2 nm. As we have performed measurements of the thermal conductivity and variation of sound velocity on

the same sample, we can estimate the value of ξ in the case of HC on the basis of equation (2). With the coefficients of the linear temperature dependence for κ (3.4×10^{-3} W m^{-1} K^{-2}) and $\Delta v/v$ (-4.7×10^{-5} K^{-1}) obtained in our experiments, together with $v = 5900$ m s^{-1} obtained for another HC sample [13], the formula yields $\xi \approx 4.7$ Å. This about three times smaller than the value obtained for a-SiO$_2$ [32], and more than an order of magnitude smaller than those for aerogels.

Consequently, such a small value of ξ presents a problem regarding the consistency of our explanation. However, the numerical prefactor given in equation (2) is evaluated in the quasi-static limit, $\omega \ll \omega_c$, whereas it has been shown that in Pd–Si [25], where ω_c is of the order of THz, the amplitude of $\Delta v/v(T)$ decreases slightly for frequencies between 10 and 190 MHz. In our case the measurements have been done at 15 MHz and ω_c is estimated to be below 100 GHz. Therefore the frequency dependence of the prefactor (i.e. its decrease) might be significant. Whether this can give a ten-times-higher ξ we will try to decide once a more reliable value of ω_c is obtained from thermal conductivity measurements at lower temperatures.

On the basis of the discussion of C_p- and κ-data, we conclude that HC shares many features with aerogels. As the TEM data have shown that in HC the C_{60} molecules are at least partially destroyed in order to build much larger nanograins several nanometres in size, we can readily suppose some kind of porosity/hollowness within nanograins and corresponding fractal structure at lengths below the nanograin size. This is consistent with the estimates of the crossover frequency and length based on the comparison with aerogels and a-SiO$_2$. However, the fractal structure of aerogel is attributed to its low density below 1 g cm^{-3}. In this respect HC, with at least two-times-higher density—comparable even to that of a-SiO$_2$—would hardly fit in this category, and we might be looking at a new class of dense fractal systems.

5. Conclusions

Our investigation of the specific heat, thermal conductivity and relative variation of the sound velocity of HC has demonstrated the amorphous nature of this material. There are some peculiarities that distinguish it from typical glassy materials.

The temperature dependence of the thermal conductivity and that of the sound velocity are linear over a wide temperature range, as is also the case in glasses. However, the linearity of the thermal conductivity extends below the region where a plateau is usually found in glasses. We observe only a slight levelling off below 5 K. As the plateau in glasses originates from the resonant scattering of the localized modes that contribute also to the maximum in C_p/T^3 around 10 K, it is not a surprise that we do not see such a maximum in our C_p/T^3 data. On the other hand, the large linear contribution to C_p at low temperatures is larger by almost an order of magnitude than that for glasses, which would mean that the density of TLS is correspondingly higher. As such a large contribution is also seen in glassy carbon and carbon nanotubes, it might be a feature common to all carbon-based materials.

Comparison with aerogels shows many similarities which can be accounted for by assuming fractal structure on length scales shorter than several nanometres, which is the size of the nanograins observed in TEM. This fractal structure is a consequence of the disorder in the covalent bonding introduced by partial destruction of the C_{60} cages.

We hope that this work will contribute to the understanding of the character of excitations that result in the linear temperature dependence of the thermal conductivity and stimulate new theoretical approaches, or verification of existing ones.

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