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Effects of phonon dimensionality in the specific heat of multiwall carbon nanotubes at low temperatures

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Abstract.

We have measured the specific heat at constant pressure, C_p , of three different samples of multiwall carbon nanotubes (MWNT). For all samples, C_p departs from a graphitic behavior at $T < 120$ K. C_p measurements show a temperature threshold from a linear regime for intermediate temperature to a higher-order power law for low temperatures. Moreover, it was found that this crossover only depends on the internal structure of the individual MWNT and not on the spatial order of the MWNT within a bundle.

1. Introduction

Carbon nanotubes have attracted great attention due to their potential technological applications. They present a variety of interesting physical properties that have been studied extensively over the past years. Particularly, the knowledge of the vibrational properties of these systems is of technological interest since the electron-phonon interaction is one of the mechanisms that determine their electronic transport properties. In spite of the intense experimental work done on single-wall carbon nanotubes (SWNT) and multiwall carbon nanotubes (MWNT), their specific heat at constant pressure (C_p) at low temperatures has not been comprehensively studied, specially if we refer to MWNT.

Within the few experimental works on the specific heat of MWNT, Yi *et al* [1] measured C_p in a bundle of MWNT, and found that it varied linearly with temperature in the range 10-300 K. It was attributed to a prevalence of the out-of-plane modes in the essentially bidimensional vibrational excitation spectrum within each tube, with a weak intertube coupling. Later on, Mizel *et al* measured bundles of SWNT and MWNT [2], finding that for the latter the specific heat was similar to that of graphite, meaning that the intertube coupling was comparable to interplane coupling in graphite. Finally, Masarapu *et al* worked with a bundle of aligned

MWNT [3] and obtained a linear specific heat for $T > 40$ K, and a dimensional crossover to a higher power law at lower temperatures. This was assigned to a dimensional change in the excitation spectrum from 3D at low temperatures to a reduced dimensionality at higher temperatures.

In this work, we present a systematic survey on the specific heat at constant pressure in three samples of MWNT with different geometries as a function of temperature. We observed a crossover whose characteristic temperature depends on the internal structure of the individual MWNT that constitute the sample.

To our knowledge, a systematic study of this feature in different kinds of MWNT has not been done previously. Due to the scarce and disperse specific heat data on MWNT and the lack of a theoretical or numerical framework, we expect the work presented in this paper to help understand the basic physical phenomena involved.

2. Experimental

Three different classes of MWNT were studied: sample *A* (90 nm external diameter) sample *B* (30 nm) and sample *C* (25 nm). Samples *A* and *B* were synthesized by CVD of analytical grade iron(II) phthalocyanine, under Ar/H₂ atmosphere in a flow reactor consisting of a quartz glass tube. It was heated by a dual furnace fitted with independent temperature controllers, following the procedure reported elsewhere [4]. Growing conditions involved temperatures of around 880°C, a total gas flow rate of 30 ml/min and Ar/H₂ ratio of 1:1. Carbon nanotubes of sample *C* were synthesized using a catalyst of Fe nanoparticles diluted in a SiO₂ matrix. The nanoparticles were reduced in a 9% H₂/N₂ flux (110 cm³/min, 180 Torr) at 600°C for 5 hs. Carbon was deposited using acetylene gas diluted in H₂ at 9% maintaining the same flow and pressure, at 700°C for 3 hs. The nanotubes of sample *C* were purified using an excess of HF/H₂SO₄ (1:1 v/v) in order to eliminate the silica support and rinsed with HCl to solubilize the iron nanoparticles. Then, the sample was filtered, washed with distilled water, and dried at 80°C for 24 hs.

As a result of the different growing conditions of samples *A* – *B* and *C*, they have different structural properties. SEM microscopy shows that samples *A* and *B* growth in aligned bundles, whereas sample *C* has a forest distribution. TEM images also reveal in the former an internal bamboo-like structure within each MW, not present in the latter.

The specific heat measurements were made with a thin silicon nitride membrane microcalorimeter. It consists in a silicon frame of 11x11 mm² with a 5x5 mm² SiN membrane, 1 μm thick [5]. On the front side of the membrane, a platinum resistor heater and a NbSi composite thermometer were made by sputtering and photolithography. On the back side of the membrane, a gold conduction layer is deposited in order to thermalize the thermometer and the heater, and the sample is attached on it with a thermally conductive compound. The film thermometers on the membrane were calibrated in temperature against a factory-calibrated Cernox thermometer. The method used to measure specific heat is the thermal relaxation time technique [6].

3. Results and discussions

It is known that the electronic specific heat of carbon nanotubes is more than two orders of magnitude lower than the phonon counterpart [7], even when the nanotubes are metallic. Therefore, the specific heat measured at constant pressure can be regarded as coming entirely from the vibrational degrees of freedom of the system, and has a strong relation with the phonon density of states.

The measured C_p for the three samples is displayed in Fig. 1. We include also the curve of C_p of graphite as a reference [8]. The curves depart from the graphite curve for $T < 120$ K. It is clear that samples *A* and *B* follow almost the same curve, whereas sample *C* presents

differences at low temperatures with respect to the others. First of all, samples *A* and *B* have a marked peak at $T_P = 60$ K, not present in sample *C*. This peak will be extensively studied in a forthcoming paper, so we will not discuss its origin here. Secondly, we observe a shoulder that is produced at $T_{DC} = 33$ K in samples *A* and *B*, and $T_{DC} = 52$ K in sample *C*. All these characteristic temperatures are marked in Fig. 1.

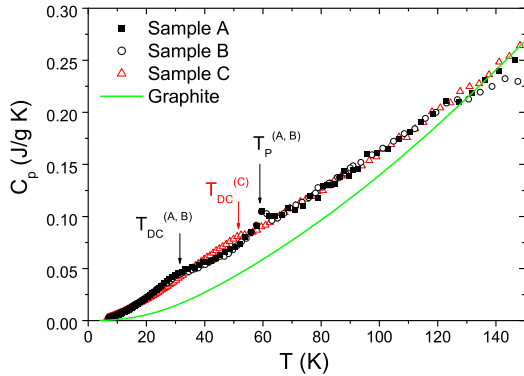


Figure 1. Specific heat of sample *A*, *B* and *C* as a function of temperature. The C_p of graphite is shown for comparison [8]. The characteristic temperatures T_{DC} and T_P are marked.

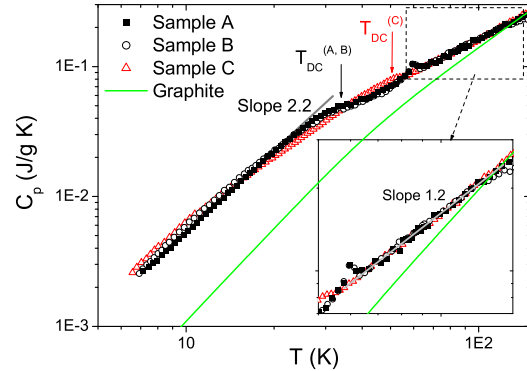


Figure 2. The same data on Fig. 1 with logarithmic axes. The different slopes and characteristic temperatures are marked. The inset shows an expansion of the rectangle.

In Fig. 2 the same curves are displayed in a bilogarithmic graph. The curves present an approximate slope of 2.2 below T_{DC} . As the temperature is increased, the slope changes to 1.1 above T_{DC} (see the expanded region in the inset of Fig. 2). This crossover is seen clearly in the plot of C_p/T vs. T showed in Fig. 3. In this figure, the characteristic temperature manifests as a maximum in C_p/T . Above T_{DC} , the curves become almost flat indicating a pseudo-linear regime in all samples. Below T_{DC} , the vibrational behavior is different among them, as seen in the figure. The crossover at T_{DC} is similar to that observed by Masarapu et al [3], but we obtained a sample dependent shifting of the temperature T_{DC} , that has not been observed previously.

A similar crossover occurs in graphite, in which C_p has a cubic behavior at very low temperatures. Since the graphene layers are weakly coupled, phonon modes with displacements perpendicular to the layers have a very low Debye energy, causing a saturation of the specific heat associated with those modes when the temperature is raised. Hence, the specific heat at intermediate temperatures has a quadratic variation [9]. In our case, we observed a similar behavior, but the crossover is more pronounced, so that we can assign a well-defined crossover temperature T_{DC} for each sample.

For an isolated perfect nanotube, considered as a graphene layer rolled up, it is known that at very low temperatures it can be considered a perfect 1D system [9]. As the temperature is raised (or the radius is increased) radial modes can be excited and the system undergoes a dimensional crossover to a 2D regime. The order of magnitude for the temperature at which this change takes place is $T_{CR} \approx \hbar v/k_b R$, with v being the typical sound velocity and R de radius of the tube [7]. For our samples, this temperature is less than 5 K for all diameters, so we effectively have MWNT formed by essentially 2D individual tubes.

A multiwall nanotube can be regarded as a set of concentric tubes with increasing diameter. Then, there will be a coupling between the internal tubes. If the nanotubes are ordered in bundles, as in the case of samples *A* and *B*, there is also coupling between neighbor tubes.

Both couplings introduce phonon dispersion perpendicular to the tube axis. Hence, at very low temperature the system will behave as three-dimensional. As the temperature increases, the transversal modes will saturate their contribution to the specific heat, and the internal phonon structure of the constituents will show up. The mode relevant in a graphene layer is the out-of-plane acoustic mode that has a quadratic dispersion relation, giving a nearly constant phonon density of states and, consequently, a linear specific heat. In the case of tubes large enough this behavior will show up at intermediate temperatures. That is what we observed in Figs. 1, 2 and 3. At $T < T_{DC}$, the system tends to show a $T^{2.2}$ behavior, but with an increasing slope at lower temperatures. Above T_{DC} , the linear behavior in all samples is a consequence of the dominant phonon modes of the individual tubes. The reason why the crossover is not smooth, like in graphite, is unknown to us.

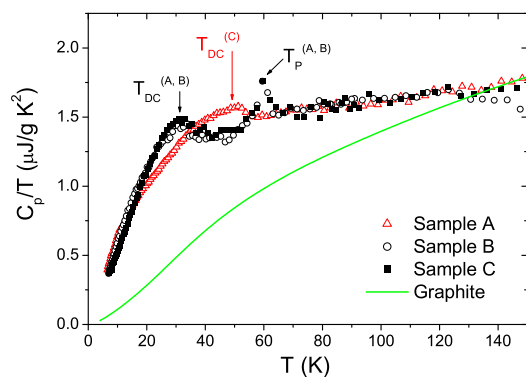


Figure 3. C_p/T vs. T for sample A , B and C . The temperature T_{DC} and T_P are marked.

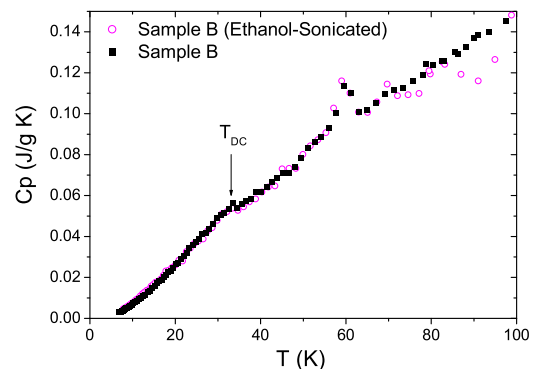


Figure 4. Comparison between C_p of sample B and ethanol-sonicated sample B .

From the measurements we can realize that the characteristic crossover temperature is different for samples $A - B$ ($T_{DC} = 33$ K) than for sample C ($T_{DC} = 52$ K). The different temperatures could be due to different internal structure of the MWNT or different arrangement of the MWNT within a bundle. We already mentioned that samples $A - B$ were synthesized by the same process, having an ordered bundle structure. In order to determine whether this structural order is relevant in this problem, we dispersed and sonicated sample B in ethanol and measured again. The spatial order of the MWNT was eliminated by this process, as seen by SEM micrography. The results are shown in Fig. 4, where a plot of the original sample B (full symbols) is displayed alongside the ethanol-sonicated sample (open symbols). The fact that both curves almost coincide in the whole range measured confirms that the spatial order of the individual MWNT within a bundle is not a relevant parameter for the observed crossover.

4. Conclusion

We present specific heat measurements at low temperatures in three different MWNT samples. For all cases a crossover at a well defined temperature, T_{DC} , was observed, separating a low temperature quadratic from a high temperature linear dependence. The main factor that influences T_{DC} is the internal structure of the individual MWNT. This could explain the differences between T_{DC} of samples $A - B$ and T_{DC} of sample C . The latter undergoes the crossover at a higher temperature, possibly due to the enhanced coupling between internal tubes caused by the absence of bamboo-like defects. Further work is needed to prove that it is

the change in phonon dispersion relation rather than a change in dimensionality what describes our results.

Acknowledgments

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