Journal of Alloys and Compounds 446–447 (2007) 376–379

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

H(D)-lattice interactions in single wall carbon nanotubes

O. Palumbo [a,b,*], A. Paolone [a,c], R. Cantelli [a], U. Dettlaff [d], S. Roth [d]

[a] Università di Roma “La Sapienza”, Dipartimento di Fisica, Piazzale A. Moro 2, I-00185 Roma, Italy
[b] Consorzio Interuniversitario per le Scienze Fisiche della Materia—CNISM, Unità di Roma “La Sapienza”,
Dipartimento di Fisica, Piazzale A. Moro 2, I-00185 Roma, Italy
[c] Laboratorio Regionale SuperMat, CNR-INFM, Salerno, Italy
[d] Max Planck Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany

Received 18 September 2006; received in revised form 17 November 2006; accepted 1 December 2006
Available online 29 December 2006

Abstract

A thermally activated relaxation process has been found in the anelastic spectrum of HiPco carbon nanotubes at 25 K. This peak is depressed in the hydrogenated samples, but grows after subsequent thermal treatments which partially remove hydrogen. The activation energy obtained by the peak shift with frequency is $E_a = 54.7$ meV, and the pre-exponential factor of the Arrhenius relaxation time is $\tau_0 = 10^{-14}$ s, which is typical of point defect relaxation. The observation of an isotope peak shift confirms that the relaxation is due to hydrogen. The height of the peak firstly increases with decrease of c_H as more free sites are made available for the H jumps. On further reducing the hydrogen content, the peak height decreases, as a small number of relaxing species is left in the sample. The high mobility of the species giving rise to this peak indicates that it can hardly be ascribed to a hydrogen molecule. Moreover, classical models cannot reproduce the peak, suggesting a dynamics of atomic hydrogen governed by quantum tunneling.

Keywords: Nanostructured materials; Hydrogen absorbing materials; Point defects

1. Introduction

Carbon nanotubes have unique one-dimensional characteristics in atomic and electronic structures due to their diameter of the order of the nanometers; a single walled carbon nanotube (SWCNT) can be metallic, semiconducting or semimetallic, depending on its chirality [1]. Their special geometry and interesting properties offer great potential applications, including nanoelectronic devices, energy storage, chemical probes, biosensors, field emission displays [2–4]. The change of electric resistivity with the concentration of adsorbed gases is promising for the production of sensors. Moreover, it has been recently shown that sidewall functionalization of the SWCNT by atomic hydrogen transforms the electronic structures from metallic to semiconducting by removing π states near the Fermi level [5]. Carbon nanotubes are known to be able to adsorb various gases [6,7]; in particular, high hydrogen adsorption values ranging between 0.4 and 67 wt% have been reported. However, recent literature suggests that the highest values previously measured are due to experimental artifacts. Nevertheless, values of 4–6 wt% have been obtained for chemically processed nanotubes at liquid nitrogen temperature and a few bars of hydrogen pressure [8,9]. It is also suggested that the storage properties may be significantly increased by metal doping functionalization. Although a high number of papers has been produced on CNT’s, a detailed understanding of their adsorption mechanisms and properties is still lacking. In this framework, the knowledge of the diffusion and motion parameters of H adsorbed on single-walled carbon nanotubes is of relevant importance, but in spite of that only a few results have been reported up to now [10,11].

In a previous paper [12] the anelastic spectrum of HiPco carbon nanotubes was measured and two relaxation processes, found at 140 and 25 K, have been ascribed to the dynamics of hydrogen in the molecular and atomic form, respectively. That study showed that hydrogen is present in carbon nanotubes even if they are not intentionally hydrogenated and that molecular hydrogen strongly interacts with the hexagonal lattice.

The peak at 25 K is thermally activated and characterized by a very fast dynamics (10^3 jumps per second at 25 K) [12]. The activation energy obtained by the peak shift with frequency is

---

* Corresponding author. Tel.: +39 06 49914400; fax: +39 06 4957697.
E-mail address: oriele.palumbo@roma1.infn.it (O. Palumbo).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.12.006

$E_a = 54.7$ meV, and the pre-exponential factor of the Arrhenius relaxation time is $\tau_0 = 10^{-14}$ s. The latter value is typical of point defect relaxation and suggests that the process is originated by the dynamics of hydrogen or by H complexes. The high mobility of the species giving rise to this peak indicates that it can hardly be ascribed to a hydrogen molecule, and suggests atomic hydrogen as a possible relaxing species. Moreover, the process is depressed in the hydrogenated nanotubes, but progressively increases with hydrogen outgassing. When further thermal treatments deplete the H content, the peak decreases and vanishes. These features have been interpreted in terms of an unblocking mechanism. This peak might also be explained assuming that the mobile species causing the process is different from hydrogen and that H blocks its dynamics. A high local mobility might be possible for atoms residing in multiwell potentials separated by a low barrier, as in glasses.

To identify the effective role of hydrogen in the process originating the peak at 25 K, in case it is both present in the relaxing units or only responsible for the blocking mechanism, we carried out new experiments on deuterated HiPCo SWCNT. In the present work we report the isotope shift of the 25 K peak, which confirms that the process is originated by the dynamics of hydrogen or H complexes.

2. Experimental

HiPco single walled carbon nanotubes were purchased from Carbon Nanotechnologies Inc. The material containing ~5 wt% catalytic Fe was suspended in a 1% water solution of sodiumdodecylsulphate (SDS) and filtrated, producing pieces of bucky paper. Two samples, H and D, were prepared with the form of prismatic bars of about 38 mm × 6 mm × 0.1 mm. Both samples after preparation and before the measurements were heated for 1 h at 500 K in order to remove water and subsequently they were hydrogenated (sample H)/deuterated (sample D) at a pressure of 72/80 bar, respectively.

Anelastic spectroscopy measurements are conducted suspending the bars on thin wires located at the nodal lines of flexural vibration modes, and electrostatically exciting the corresponding mechanical resonance of the samples. The sample vibration produces an alternate stress which interacts with the local lattice distortions introduced by the mobile entities and perturbs their site energies in such a way that the sites that are energetically favored in the first half period become unfavored in the second half. The system then looks for the equilibrium redistribution among the perturbed levels. At the temperature at which the relaxation rate τ^{-1} of the species is equal to the angular vibration frequency ω ($\omega\tau = 1$) the stimulated atomic migration is able to follow, by thermal activation, the sample vibration, and the coefficient of elastic energy dissipation Q^{-1} reaches its maximum value. The energy dissipation (or reciprocal of the mechanical quality factor Q) is measured from the decay of the free oscillations or from the width of the resonance peak. The measurement of the dynamic Young modulus E' is simultaneously obtained from the angular vibration frequency $E' = \omega^2/k\rho$ where ρ is the mass density, and k a numerical factor depending on the sample geometry [13]. The independent and concomitant measurements of Q^{-1} and E' allow the complex modulus $E = E' + iE''$ to be derived, being $Q^{-1} = E''/E'$. For a single relaxation time, τ, Q^{-1} is given by:

$$Q^{-1} = g v_0 (\lambda_1 - \lambda_2)^2 \frac{c n_1 n_2}{kT} E' \frac{(\omega\tau)^{\alpha}}{1 + (\omega\tau)^{2\alpha}} \tag{1}$$

where c is the molar concentration of the jumping atoms and n_1 and n_2 their equilibrium fractions in sites 1 and 2; λ_1 and λ_2 are the elastic dipoles [13] of the defects in their two configurations; g is a factor of the order of (1/2) depending on the geometry of the jump and the type of sample vibration, v_0 the unit cell volume, and k the Boltzmann constant. The parameter α is equal to 1 for a single-time Debye process and lower than 1 for a Fuoss–Kirkwood process.

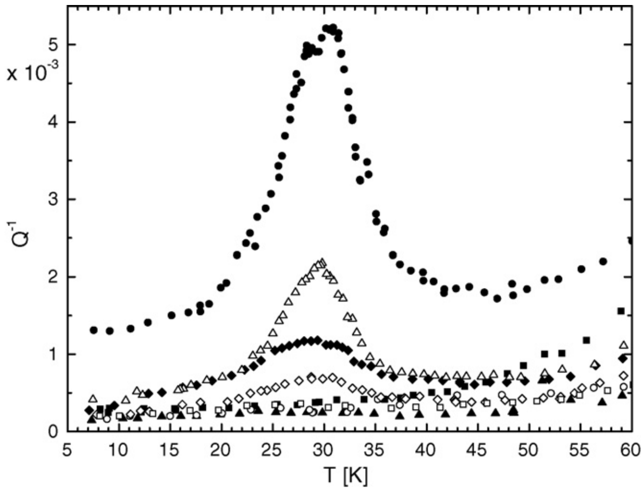

Fig. 1. Elastic energy loss of the deuterated sample; full squares, as received; full triangles, after thermal treatment (TT) at 450 K for 60 min; open dots, after second TT at 450 K for 120 min; full rhombuses, after third TT at 500 K for 90 min; open triangles, after fourth TT at 500 K for 60 min; full dots, after fifth TT at 500 K for 75 min; open rhombuses, after sixth TT at 500 K for 120 min; open squares, after seventh TT at 500 K for 60 min.

For classical processes $\tau = \tau_0 e^{E_0/kT}$, where E_0 is the activation energy. As τ is temperature dependent for thermally activated processes, the relaxation condition ($\omega\tau = 1$) is satisfied at low temperatures for fast processes and at high temperatures for slow processes.

3. Results and discussion

The anelastic spectrum of the as received and intentionally deuterated sample (sample D), measured in vacuum between 60 and 5 K, is shown in Fig. 1 (full squares), where it is seen that the dissipation monotonically decreases with decreasing temperature. This absence of any relaxation process below 60 K was observed also for the fully hydrogenated samples [12]. In order to test whether thermal treatments introduce a peak, as observed for hydrogen, the present sample D was subjected to subsequent high temperature annealings as specified below, and each one was followed by a measurement down to the liquid helium temperatures. All the thermal treatments were carried out in a vacuum better than 10^{-5} mbar.

The first thermal treatment performed at 450 K for 60 min did not change the anelastic spectrum of the sample (Fig. 1, full triangles), and no change was observed also after increasing the annealing time to 2 h (open dots). Instead, after a third TT at 500 K for 60 min (full rhombuses) a peak appeared at 30 K (for $f = 0.9$ kHz). The peak height continued growing after subsequent annealings at 500 K for 60 min (open triangles) and 75 min (full dots), but started decreasing after a TT at 500 K for 120 min (open rhombs) and disappeared after a sixth TT (500 K for 60 min; open squares).

The correlation between deuterium evolution out of the sample and peak height is the same reported for the hydrogenated samples. The main difference is in the annealing temperatures, which are shifted of nearly 50 K for deuterium; typically 500 K for deuterium instead of 450 K. The same variation of the peak height with both the hydrogen and deuterium contents con-

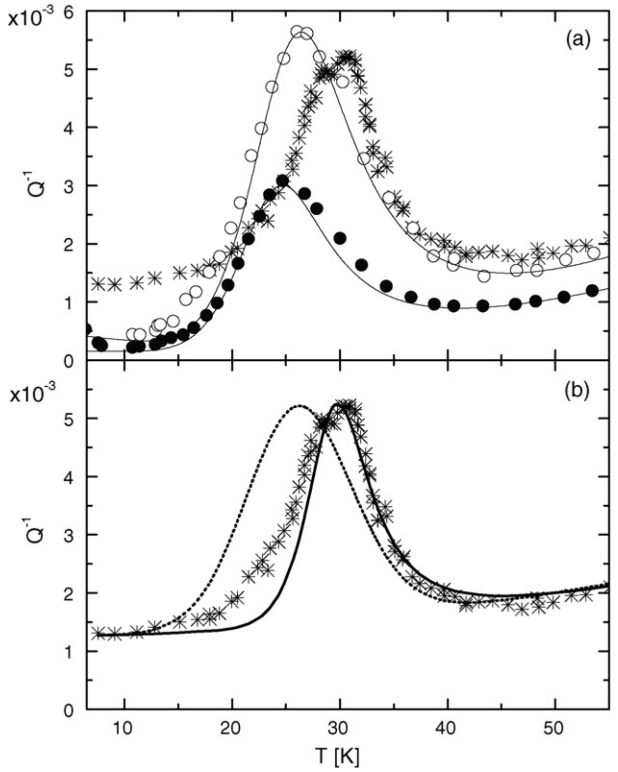

Fig. 2. Panel (a): elastic energy loss of the hydrogenated sample measured at 360 Hz (full dots) and 2.1 kHz (open dots) and of the deuterated sample measured at 0.9 kHz (asterisks); continuous lines are Fuoss–Kirkwood fits. Panel (b): elastic energy loss of the deuterated sample measured at 0.9 kHz (asterisks); the continuous line is the Fuoss–Kirkwood fit with $E_D = 59.9$ meV; the dashed line is a Fuoss–Kirkwood simulation calculated with $E = 54.7$ meV (as for hydrogenated sample).

firms the unblocking mechanism we proposed for hydrogen [12]. Precisely, the D(H) dynamics would be blocked at high concentrations, as D(H) needs unoccupied neighboring interstitial sites for reorientation. With proceeding D(H) outgassing, progressively more sites are made available for D(H) jumps and hence more complexes can relax and contribute to the peak height. With deuterium/hydrogen depletion the peak keeps decreasing and vanishes when no hydrogen is left in the sample.

The peak measured at 25 K in the hydrogenated sample is originated by a thermally activated relaxation process, as it shifts towards higher temperature with the frequency increase (Fig. 2(a)). For comparison, the dissipation curve of sample D which shows the maximum peak intensity has been reported in Fig. 2(a) together with the curves of the hydrogenated sample measured at two different frequencies. The peak of sample D is visibly shifted to higher temperature with respect to the peak of the hydrogenated specimen. In fact, it appears at 30 K for 0.9 kHz, compared with 26.5 K for 2.1 kHz in sample H.

The experimental curves of sample H resulted to be markedly broader than a single Debye peak. This implies a distribution of the relaxation parameters (E_a and τ_0), which is generally caused by elastic interactions, as it is expected in a highly disordered system like the present one. A quantitative analysis was carried out [12] by the Fuoss–Kirkwood fitting procedure. The best fitting values, after subtraction of the background dissipation by a parabolic law [12], were found to be $E_a = 54.7$ meV, $\alpha = 0.26$, and $\tau_0 = 10^{-14}$ s (drawn in Fig. 2(a) with a continuous lines). The strong deviation of the Fuoss–Kirkwood parameter from the unity and the impossibility to fit the data for both frequencies with a unique value of the relaxation strength (the prefactor in Eq. (1)), arose serious doubts that the observed process can be described by the classical hopping expressed by the Arrhenius law for τ.

It was not possible to measure the dissipation curve of sample D at two frequencies. Therefore, in order to strictly compare the peak temperatures of H and D, we calculated the relaxation curve of hydrogen at the same frequency of the deuterium sample (0.9 kHz), using the fitting parameters for sample H reported above (dotted line in Fig. 2(b)). The obtained peak shift of 4 K with respect to H is well above the experimental uncertainty of measurement. This isotope effect clearly demonstrates that the peak is caused by the dynamics of a species involving some hydrogen complex.

To obtain quantitative information on the relaxation process observed in sample D, we tried to fit the data of a single frequency using the Fuoss–Kirkwood fitting procedure, after subtracting a parabolic background. The value of τ_0 was fixed to that previously obtained for the hydrogenated sample (namely $\tau_0 = 10^{-14}$ s). The best-fit parameters obtained are $\alpha = 0.5$ and $E_D = 59.9$ meV; the latter value is higher than the activation energy for relaxation found for the hydrogenated sample. The best fit curve (continuous line in Fig. 2(b)), does not match the low temperature side of the peak, suggesting a possible contribute of some unintentionally absorbed hydrogen or of the fraction of hydrogen present in the gas used for deuteration.

The isotope peak shift, the very fast dynamics of the relaxing units, and the value of the pre-exponential factor (10^{-14} s), which is typical of a point defect relaxation, indicate that the observed process cannot be ascribed to molecular hydrogen. Hence, we conclude that the peak is due to hydrogen in the atomic state. Furthermore, the remarkable height reached by this peak suggests the possibility that hydrogen may display also a strong interaction with the CNT different from the physisorption and chemisorption processes. Such an interaction may be originated by the trapping effect exerted on hydrogen by lattice imperfections, as we recently proposed [12]. In this case the mechanism of the process observed at 25 K for H (30 K for D) would consist in the thermally assisted relaxation of trapped hydrogen (deuterium).

4. Conclusions

The anelastic spectrum of HiPco carbon nanotubes shows a thermally activated relaxation at 25 K. The activation energy obtained by the peak shift with frequency is $E_a = 54.7$ meV, and the pre-exponential factor of the Arrhenius relaxation time is $\tau_0 = 10^{-14}$ s, which is typical of point defect relaxation. These parameters and the deuterium isotope peak shift we observed suggest the attribution of the process to the dynamic of atomic hydrogen. This peak is depressed in the hydrogenated nanotubes, but grows after subsequent thermal treatments, which partially remove hydrogen. When further thermal treatments deplete the

H content, the peak decreases and vanishes. These features have been interpreted in terms of an unblocking mechanism.

References

[1] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, Science 287 (2000) 622.

[2] M.S. Dresselhaus, G. Dressehaus, P.C. Eklund, Science of Fullerenes and Carbon Nanotubes, Academic Press, New York, 1996 (Chapter 19).

[3] T. Ebbesen, Carbon Nanotube: Preparation and Properties, CRC, Boca Raton, FL, 1997.

[4] R. Saito, G. Dressehaus, M.S. Dresselhaus, Physics Properties of Carbon Nanotubes, World Scientific, New York, 1998.

[5] K.S. Kim, D.J. Bae, J.R. Kim, K.A. Park, S.C. Lim, J.-J. Kim, W.B. Choi, C.Y. Park, Y.H. Lee, Adv. Mater. 14 (2002) 1818.

[6] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, Science 287 (2000) 622.

[7] P.G. Collins, K. Bradley, M. Ishigami, A. Zettl, Science 287 (2000) 1801.

[8] B.K. Pradhan, A.R. Harutyunyan, D. Stojkovic, J.C. Grossman, P. Zhang, M.W. Cole, V. Crespi, H. Goto, J. Fujiwara, P.C. Eklund, J. Mater. Res. 17 (2002) 2209.

[9] E. Poirier, R. Chahine, P. Bénard, D. Cossement, L. Lafi, E. Mélançon, T.K. Bose, S. Désilets, Appl. Phys. A 78 (2004) 961.

[10] D.G. Narehood, J.V. Pearce, P.C. Eklund, P.E. Sokol, R.E. Lechner, J. Pieper, J.R.D. Copley, J.C. Cook, Phys. Rev. B 67 (2003) 205409.

[11] C.M. Brown, T. Yildirim, D.A. Neumann, M.J. Heben, T. Gennett, A.C. Dillon, J.L. Alleman, J.E. Fischer, Chem. Phys. Lett. (2000) 311–329.

[12] A. Paolone, O. Palumbo, R. Cantelli, S. Roth, Mat. Sci. Eng. A 442 (2006) 314–318.

[13] A.S. Nowick, B.S. Berry, Anelastic Relaxation in Crystalline Solids, Academic Press, New York, 1972.