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Hydrogenated Single-Wall Carbon Nanotube Material as a Cold-Neutron Moderating Medium

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Abstract

Carbon has excellent neutron properties. Carbon nanotubes provide a morphology for high-volume adsorption/filling of hydrogen or methane on a multi-dimensional architecture over the nanometer-to-micrometer scale. The excess phonon density at low energies in a one-dimensional single-wall nanotube leads to enhanced heat capacity at low temperatures. The high Debye energy of phonons propagation along the nanotube axis affords a very high intrinsic thermal conductivity comparable to that of diamond. Furthermore, very high content (~88 at%) of hydrogen can be stably chemisorbed in single-wall carbon nanotubes (SWNT) by a novel synthesis method. Hoping to capitalize these unique properties towards a possible design of high-performance cold neutron moderators that use carbon nanotubes as an interspersed medium, we have measured the phonon spectrum and the heat capacity of SWNT. The dynamics of physisorbed hydrogen molecules in pure SWNT and chemisorbed hydrogen atoms in hydrogenated SWNT was characterized. In contrast to the weak physical adsorption of molecular hydrogen in pure SWNT, we observed three distinct vibrational peaks, two in the region of 130-175 meV and one at 350 meV in hydrogenated SWNT, corresponding to C-H bending and stretching vibrations of the CH_x complexes, respectively. At energies below 5 meV the measured inelastic neutron scattering spectra show noticeable increase of intensity compared to the case of physisorbed hydrogen in pure SWNT. These observations suggest that hydrogenated SWNT may be a candidate for use as a cold-neutron moderating medium.

1. Introduction

The demand for high production of cold and very cold neutrons at spallation sources merits advanced design of moderators using novel materials. Solid methane has been proved to be a very efficient cold-moderator material because of its high hydrogen density and favorable low-energy dynamic properties, namely the availability of rotational modes below 5 meV for energy exchange with neutrons [1]. Solid and liquid methane moderators have been in use at moderate-flux sources (e.g., IPNS and KENS) for many years and the application of solid methane has been proposed for higher flux sources [2-3]. Mesitylene also shows prospects of similar usefulness, as might N-isotope-separated ammonia, $^{15}NH_3$.

The relatively low thermal conductivity of solid methane necessitates the interspersion of an aluminum foam within the moderator container, which takes up about 10% of the volume. Important factors are, in addition to the neutron properties of the foam material, the nuclear heating power, and the thermal conductivity and volume density of the methane-foam configuration [2].

Carbon has excellent neutron properties, e.g., essentially free of neutron absorption. It is inexpensive in principle, naturally abundant, and environmentally benign. The recent advent of nanostructured carbons has prompted the consideration of a possible interspersed methane and single-wall carbon nanotubes configuration for a high-performance cold-neutron moderation. Here, we report the nanoscale morphology and atomic dynamics of pure SWNTs and a novel kind of SWNTs that contains a high content of

chemically adsorbed hydrogen atoms. The structural and thermodynamic properties of such hydrogenated SWNTs capable of accommodating a high-volume of adsorbed and filled methane may provide uniquely favorable conditions for a cold and very cold neutron moderator.

2. Materials

2.1 Open-ended single-wall carbon nanotubes

An open-ended SWNT can be visualized as a curved tube with a roll-up graphite-like wall and an empty interior of a typical 14 Å cylindrical diameter and of microns in length [4]. Roughly ~10-100 SWNTs assemble in a bundle, forming a cross-sectional hexagonal lattice. This configuration can be observed by high-resolution electron microscopy and neutron diffraction, as illustrated in Figure 1 for one of our high-purity SWNT samples synthesized at the MER Corp. The SWNT bundles are randomly oriented and dispersed in very low density, typically 2-5% of the maximum theoretical density of close-packed bundles. Therefore, the material provides in principle the 1D, 2D and 3D topology for adsorption and filling of methane molecules up to 95% of the total volume.

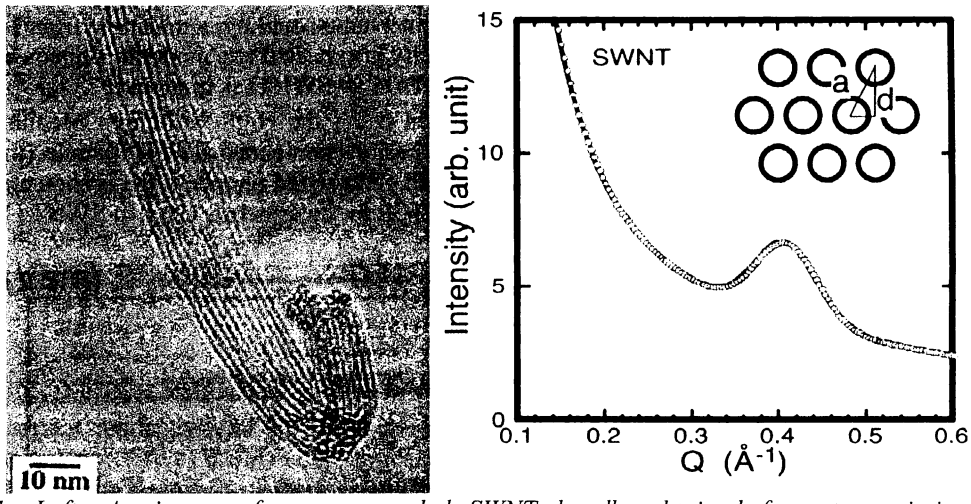

Figure 1: Left: An image of an open-ended SWNT bundle obtained from transmission electron microscopy. The cross section resembles a hexagonal lattice with a lattice parameter a = 17.5 Å. Right: Neutron diffraction from SWNTs revealing a peak at ~0.4 $Å^{-1}$, corresponding to the spacing d between the lattice plans shown schematically in the inset.

Phonons influence directly the thermodynamic properties of carbon nanotubes because electronic excitations as compared to phonons are expected to be negligibly small below room temperature [5]. Owing to the 1D-character of isolated or weakly coupled SWNTs, the phonon dispersion curves and density of states exhibit unique features which may result in excess heat capacity and thermal conductivity at low temperatures. We shall discuss the consequences in the utilization of SWNTs as the interspersed component in a cryogenic neutron moderator.

2.2 Hydrogenated SWNT

In 2004 Bashkin and co-workers [6] reported the synthesis of hydrogenated SWNTs and carbon nanofiber samples that are capable of stably storing 6.8 wt% of hydrogen up to 500°C at ambient pressure in an inert atmosphere. The charging of hydrogen was carried out by a novel technique by which the sample was held under a hydrogen pressure of 9 GPa via thermal decomposition of AlH_3 at temperatures up to 400°C for a period of ~24 h. The appearance of a peak in the x-ray diffraction pattern only after hydrogenation indicated a change of the interatomic C-C spatial correlation, suggesting a distortion of the C-C network structure of the SWNT wall. Chemical analysis suggested the possible formation of CH_x complexes and determined a chemical formula of $CH_{0.88}$ of the average composition.

These special CH_x complexes in the hydrogenated SWNT give rise to new dynamic characteristics in terms of extra vibrations of adsorbed hydrogen atoms at very low energies. We have measured the vibrational spectrum of hydrogenated SWNT by neutron spectroscopy and shall discuss the opportunities in cold neutron production by integrating hydrogenated SWNTs in the moderator design.

3. Phonons, Low-Energy Vibrational Modes, thermodynamic Properties

3.1 Phonon density of states (DOS), heat capacity and thermal conductivity of SWNT

The phonon dispersion relations and DOS of SWNTs have been studied both theoretically and experimentally by many workers [7-8]. First, an isolated SWNT exhibits four acoustic phonon branches that disperse linearly with respect to wavevector $\vec{q}$. This gives rise to a finite, constant phonon density at zero energy. Furthermore, the low-energy 1D optical modes result in van Hove singularities in the DOS, with the lowest spiky feature expected to occur at ~3 meV (25K) [7]. Secondly, the corresponding specific heat of isolated SWNTs shows extra capacity at low temperatures as compared to the typical Debye behavior for 3D solids such as 3D graphite [9]. The large heat capacity is favorable in a moderator design for reducing the temperature rise in a pulse of radiation-induced heating. Finally, the bundling of the SWNTs has to be considered. Regardless of the strength of inter-tube coupling, a transition from 1D-like to 3D behavior in the phonon DOS and hence in the heat capacity is expected at a moderate phonon energy or temperature [7]. Therefore, a characterization of the phonon DOS of SWNTs is important.

Our measurements of the phonon DOS were performed using the High-Resolution Medium-energy Chopper Spectrometer (HRMECS) at IPNS on a 3g high-purity open-ended SWNT sample (inner tube diameter ~14 Å) synthesized at the MER Corp. The observed generalized phonon DOS is shown in Figure 2. It compares well, albeit qualitatively, with the calculated DOS for an armchair (10, 10) SWNT [10].

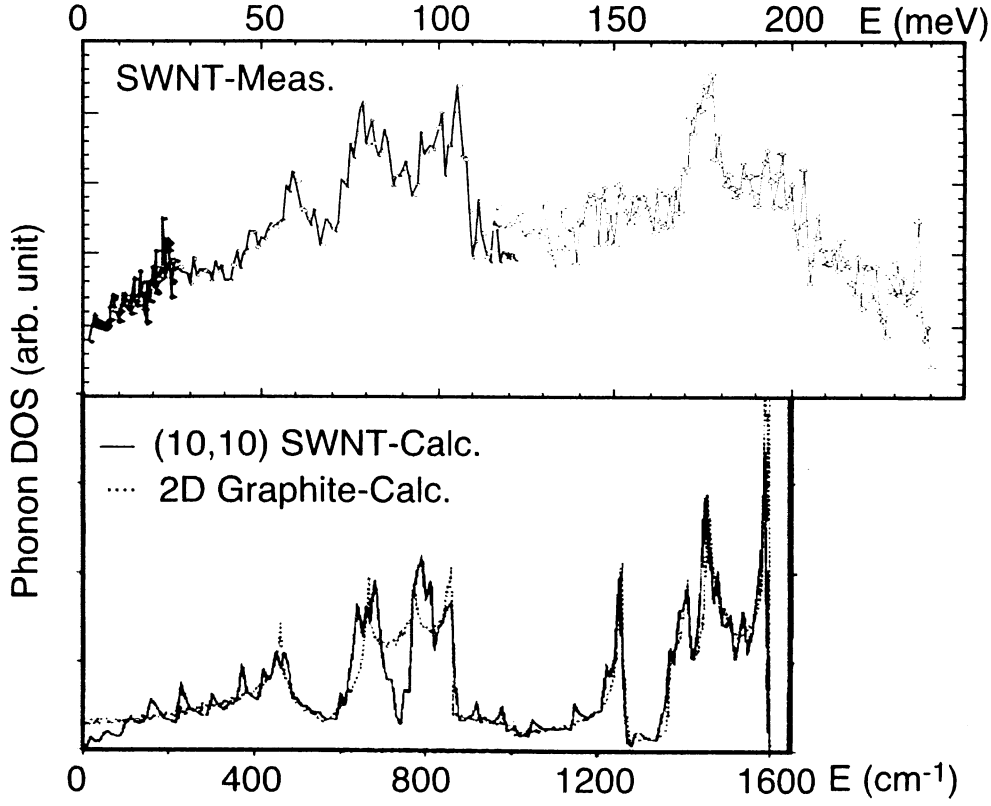

Figure 2: Top: Measured phonon DOS of open-ended SWNTs. The spectrum was composed from HRMECS data obtained from 3 incident neutron energies, 50, 140 and 280 meV. Bottom: The calculated phonon DOS of a (10,10) SWNT (solid line) and a 2D graphite sheet (dotted line) [10].

We attempted to measure the heat capacity of a sample of high-purity open-ended SWNT. The measurements were carried out at Institute of Physics, Beijing using a Quantum Design Physical Properties Measurement System. The observed heat capacity, as shown in Figure 3, in general is about 10-25% higher than that measured by Hone *et al.* [7] The discrepancy is probably due to the presence of moisture in the sample. More heat capacity measurements are underway.

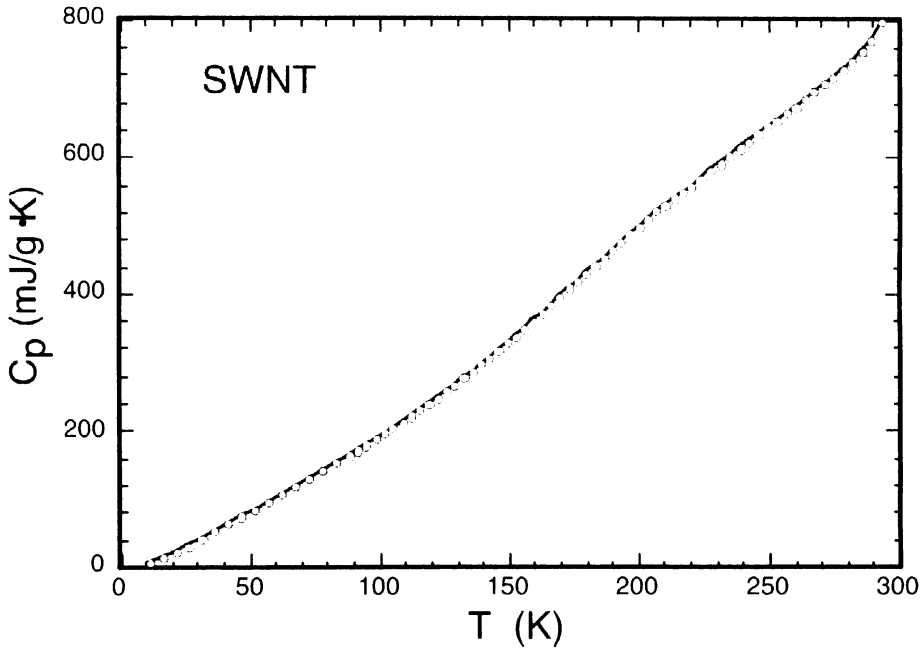

Figure 3: Measured heat capacity of open-ended SWNTs.

The thermal conductivity of SWNT is governed to a large extent by the phonon conductivity over the nano-to-micro structure of the material. In general, a high thermal conductivity of the interspersed medium is desirable for the reduction of thermal gradient across the moderator. Here, the nanostructure of open-ended SWNT over a micrometer length scale becomes attractive to an optimal moderator design. First, diamond and graphite exhibit the highest 3D and in-plane thermal conductivity ($\geq$ 2000 W/m•K) known among all materials. The graphite-like wall of the nanotubes and the micron-size length favor the propagation of long-wavelength phonons along the tube axis with a high sound speed (Debye energy) which in turn leads to very high thermal conductivity [5]. A recent theoretical prediction of the longitudinal conductivity along the tube was as high as 2980 W/m•K [11]. When taken into account of the bundling and volume density, an estimated thermal conductivity of ~35 W/m•K at room temperature was obtained [5]. However, the effective thermal conductivity of methane-adsorbed or filled SWNT at nanometer scale has not yet been considered.

3.2 Hydrogen/methane adsorption in SWNT and vibrational spectra of hydrogenated SWNT

The high porosity and large surface area of SWNTs are ideal for molecular adsorption. Previous adsorption isotherm measurements [12, 13] and neutron diffraction studies [14] showed that CH_4 (CD_4) molecules can easily be adsorbed physically on SWNTs, first in the grooves and the interstitial channels within the bundles and then on the outer surface of the bundles. Continuing condensing of CH_4 gas below 50K will lead to filling the voids in the material by solid methane. Dynamically, CH_4 molecules physisorbed on weakly bound sites retain liquid-like diffusion down to about 70 K [15]. At lower temperature solid molecular motion prevails.

We were motivated by the high hydrogen content (~88 at%) in the hydrogenated SWNT and its stability over the entire temperature range for moderator operation. In particular, the C-H bonds of the CH_x complexes created by dissociative chemisorbed hydrogen on SWNTs is thought to be different (sp^3-like) from that (σ-type covalent bonds) of traditional hydrocarbons including methane. As a result, the vibrational motions of hydrogen in hydrogenated SWNTs may display distinct characters that benefit a new moderator design.

We have therefore investigated the dynamics of the chemisorbed hydrogen in a 1.2g sample of hydrogenated SWNTs prepared at the Institute of Solid State Physics RAS, Chernogolovka. The inelastic spectrum shows no detectable molecular hydrogen in terms of any ortho-para rotational peak. But a two-peak structure and a broad band were observed around 130-180 and 350 meV, respectively, from the QuasiElastic Neutron Spectrometer (QENS) and HRMECS (see Figure 4). These bands are assigned to C-H bending and stretch vibrations of the CH_x complexes produced by dissociative chemical adsorption of hydrogen on SWNTs. However, the stretch vibrational frequencies are distinctly lower than those in conventional hydrocarbons. Furthermore, there appeared to be excess inelastic intensity extending from the elastic position to finite energies (~5 meV). This is probably due to the high concentration of hydrogen atoms that are not subject to the conformation of the para-state of molecular hydrogen.

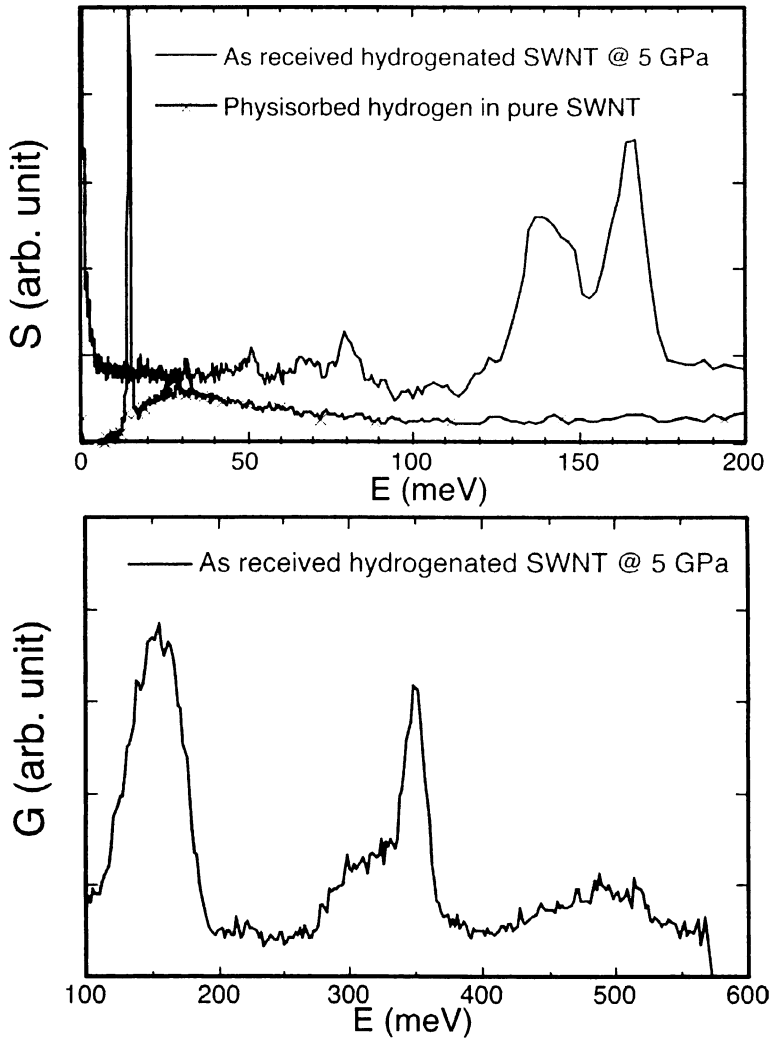

Figure 4: Top: The scattering functions of physisorbed hydrogen molecules in pure SWNTs and as-received hydrogenated SWNTs, (with an applied pressure of 5 GPa during synthesis) both at 15 K measured on QENS. The double peaks at 130-180 meV are assigned to C-H bending modes of the CH_x complexes which are unique to hydrogenated SWNTs. Bottom: The generalized vibrational DOS of hydrogenated SWNTs at 15 K measured on HRMECS where a band at ~350 meV of C-H stretch vibrations was observed. The two-peak structure of the C-H bending modes (centered at ~150 meV) was unresolved.

4. Conclusions

Carbon nanotubes feature a variety of physical properties that are attractive in principle for being an interspersed medium in cold-neutron moderators. In addition to the desirable neutron scattering properties pertaining to carbon, the multi-dimensional architecture of carbon nanotubes over the nanometer-to-micrometer length scale may offer new opportunities for optimization of hydrogen density and operation conditions of a cryogenic moderator. We have initiated a basic characterization of two kinds of single-wall carbon nanotubes. For pure SWNTs, we measured the phonon DOS over the entire one-phonon spectrum and the heat capacity from 5 to 300 K. The non-Debye-like phonon behavior due to the low-dimensionality of a SWNT and the consequences in the low-temperature heat capacity and thermal conductivity have yet to be explored in more details. We also investigated the dynamics of physisorbed hydrogen molecules in pure SWNTs. For a novel hydrogenated SWNT sample that contains up to 88 at% of chemisorbed hydrogen, we verified the formation of special CH_x complexes and the absence of molecular hydrogen in this material. Furthermore, much enhanced intensity was observed in the elastic and near-elastic regions of the spectrum, apparently stemming from the atomic rather than molecular ground state of hydrogen. We believe that these properties in conjunction with the very high intrinsic thermal conductivity along the nanotube axis merit further characterization and modeling studies toward a realization of an optimized cold-neutron moderator. In addition, for production of very cold neutrons, it would be desirable to evaluate the deuterated versions of this class of materials.

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