Electrical and Optical Properties of Ultra-small Carbon Nanotubes Arrayed in Channels of Zeolite Single Crystals

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0.4 nm-sized single-walled carbon nanotubes (SWNTs) were produced by means of pyrolysing hydrocarbon molecules in 1 nm-sized channels of AlPO_4-5 (AFI) single crystals. These small SWNTs are highly aligned and uniform in size. They behave as a good polarizer, having strong absorption for the light polarized parallel to the tube direction, and nearly transparent for the light polarized in perpendicular direction. The absorption bands are assigned to the dipole transitions between the van-Hove singularities. Resonant Raman scattering measurement confirmed these van-Hove singularity structures. Investigation of the magnetic and transport properties of these SWNTs revealed that at temperatures below 20 K, the 0.4 nm tubes exhibit superconducting behavior manifest as an anisotropic Meissner effect, with a superconducting gap and fluctuation supercurrent.

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1. Introduction

A single-walled carbon nanotube (SWNT) is wrapped from a two-dimensional graphite sheet. The diameter of each freestanding SWNT ranges from 0.7 nm to a few ten nanometers. Within the band-folding scheme, the diameter and the chirality of a SWNT are believed to determine whether the nanotube is metallic or semiconducting.\(^1\) Their electronic density-of-states (DOS) have van-Hove singularities, which have been directly observed by scanning tunneling spectroscopy,\(^2\) and optical transitions between the van-Hove singularities have been seen in absorption spectra of SWNTs bundles as well as nanotube thin films.\(^3,4\) More controlled experimental studies on the optical and electric transport properties for SWNTs are, however, not easy to carry out because of the technical difficulty in fabricating \textit{mono-sized} and \textit{well-aligned} nanotubes. We have recently produced SWNTs with diameter as small as 0.4 nm in the 1 nm-sized channels of AlPO_4-5 single crystals (AFI).\(^5\) These nanotubes have been observed directly by transmission electron microscopy,\(^6-8\) as well as indirectly by diffuse x-ray scattering\(^9\) and micro-Raman measurements of the nanotube breathing mode.\(^10\) The data consistently indicate a nanotube diameter of 0.4 nm. Investigation of the magnetic and transport properties of these SWNTs revealed that at temperatures below 20 K, the 0.4 nm tubes exhibit superconducting behavior manifest as an anisotropic Meissner effect, with a superconducting gap and fluctuation supercurrent.\(^11\)

In this paper, we report the electronic and superconductivity properties of the 0.4 nm SWNTs arrayed in the one-dimensional channels of an AFI single crystal. AFI is a type of porous aluminophosphate single crystals. Its framework consists of alternate tetrahedra of (AlO_4)^- and (PO_4)^3- which form open one-dimensional channels packed in the hexagonal structure. Figure 1 schematically shows the framework structure of the AFI single crystal viewed along [001] direction. Typical dimension of the AFI crystals used in our experiment is about 100 \(\mu\)m in diameter and about 500 \(\mu\)m in length. The AFI single crystals are transparent from near infrared to ultraviolet region, and are good insulator. They are therefore ideal hosts for studying optical and electric transport properties of nanostuctures formed inside. The SWNTs formed inside the channels of AFI are highly aligned and uniform in size. Because the SWNTs are isolated from each other, they constitute an almost ideal 1D system. The observed superconductivity are consistent with the manifestations of a 1D BCS (phonon-mediated) superconductor with a mean-field \(T_C = 15\) K.

2. Experimental

The SWNTs were synthesized by pyrolysis of tripropylamine (TPA) molecules which were pre-encapsulated in the channels of AFI crystals. To measure electric transport, the sample was fixed by epoxy inside a small hole drilled on a machinable ceramic, and then was polished into a thin layer.
Electrical contacts were made by evaporating a thin layer of gold on the two ends of the AFI-SWCN crystal. The conductance of the nanotubes was measured in the two-probe configuration at temperatures ranging from 300 to 0.3 K. For optical measurements, sample was polished mechanically then using Ar-ion milling to as thin as 10 μm. Transmission spectra were measured at room temperature, using a tungsten-halogen incandescent lamp as a light source. The incident polarized light was focused onto the sample by a reflecting microscope objective. The transmission light was collected by another reflecting objective coupled with an optical fiber and dispersed by a 275-mm single-grating monochromator.

3. Results and Discussion

3.1 Optical absorption spectra

Figure 2 shows a series of optical absorption spectra of the SWNT-containing AFI crystal for different polarization configurations. The top curve labeled $0^\circ$ corresponds to the absorption of light polarized parallel to the tube axis ($E \parallel c$). In this spectrum, we see a sharp peak at 1.37 eV with a shoulder at 1.19 eV, and two broad bands centered at 2.1 eV and 3.1 eV, respectively. The intensities of these absorption bands gradually decrease with increasing polarization angle (the increment is $10^\circ$). For the perpendicular configuration ($E \perp c$), the absorption bands vanish eventually and the nanotube is nearly transparent in the whole measured energy region, as indicated by the rather flat curve labeled $90^\circ$. We could not carry out the measurement in the energy region higher than 4.0 eV, because the epoxy used to hold the sample has strong absorption in the ultraviolet region. It is noticed that in the $E \parallel c$ configuration, the nanotubes have a finite optical density within the whole photon energy region, which implies that these ultra-small nanotubes are of metallic behavior ($\pi$-electron plasma absorption background). The metallic behavior along the tube direction was also seen from the electric transport measurements. The 0.4 nm nanotubes only have three possible chiralities: the zigzag (5,0), the armchair (3,3) and the chiral (4,2). Based on the band-folding scheme, tube (5,0) should be semiconducting. The large curvature effects, however, leads to a hybridization of $\sigma^*$ and $\pi^*$ orbitals, so the electronic structures can no longer be predicted by the simple band-folding picture. To understand the electronic properties of such small nanotubes, we performed ab-initio calculations for these three nanotubes, using a plane-wave pseudopotential formulation within the framework of local density approximation (LDA). The energy band structural calculation showed that the (3,3) nanotube is metallic as expected, the (5,0) nanotube is metallic, too, resulting from the strong curvature effect, while the (4,2) nanotube has a small indirect energy gap at the Fermi energy. The optical absorptions result from the dipole transitions from the bonding $\pi$ bands to the anti-bonding $\pi$ bands. Although there are many possible pairs for bonding and anti-bonding $\pi$ bands, the dipole allowed pairs of energy sub-bands are limited to only a few. Thus we can assign the chiralities and the sub-bands energy to the observed absorption spectra. Since the energy dispersion is relatively large, the absorption bands are relatively broad.

3.2 Resonant Raman spectra

The inset of Fig. 3 shows representative Raman spectra in the radius breathing mode (RBM) region of a SWNT/AFI sample excited by a dye laser of wavelength 616 nm. The spectrum is dominated by two peaks at 510 cm$^{-1}$ and 550 cm$^{-1}$, which are attributed to the (5,0) and (4,2) tubes, respectively. The RBM of the (3,3) tube near 580 cm$^{-1}$ is too weak to be identified. In the regime of elastic approximation, the frequency of the RBM scales inversely proportional to the tube diameter. Because of the strong curvature effect in the 0.4 nm SWNTs, however, the frequency of the RBM tends to deviate from the inverse relation. Calculation using the frozen phonon method showed that frequencies of three SWNTs are in order of $\omega_{(5,0)} < \omega_{(4,2)} < \omega_{(3,3)}$, although geometrically $d_{(3,3)} \approx d_{(4,2)}$. The relative intensity of the RBM is very sensitive to the energy of the excitation laser line. Figure 3 shows the integrated intensity in the spectral range between 450 cm$^{-1}$ and 650 cm$^{-1}$, after background subtraction plotted as a function of the excitation laser energy. The results were corrected for the sensitivity of the Raman system in addition to the laser power normalization. Two dominating peaks are clearly seen at $\sim 2.0$ eV and $\sim 2.4$ eV. The Raman signal is obviously resonance enhanced for the two particular energies. This means the energies match an electronic transition between two van Hove singularities in the electronic density of states. The result shown in Fig. 3 is in very good agreement with optical absorption measurements where a broad absorption peak at 2.1 eV was found. Recent calculations of the dielectric function for the 0.4 nm nanotubes yielded two maxima for the imaginary part in the energy region covered with our experiment. The observed maxima are located at 1.9 eV and 2.3 eV and were derived for (4,2) and (5,0) tubes, respectively. They correspond directly to the maxima in optical absorption and thus determine for which
energies Raman spectra are resonantly enhanced. We may safely assign the resonance observed at 1.9 eV to the (4,2) tubes and the resonance observed at 2.4 eV to the (5,0) tubes.

3.3 1D Meissner effect

Temperature-dependent magnetic susceptibilities for the ultra-small SWNT samples were obtained with the Quantum Design superconducting quantum interference device magnetometer (MPMS-5S) equipped with a 5T magnet. The c axes of the crystallites were aligned by hand to form a parallel array and fixed. The magnetization was measured as a function of temperature while warming from 1.8 to 50 K. At each temperature, the magnetization was measured after the temperature was stabilized for 60 seconds. The measured magnetization is anisotropic with respect to the field orientation. After a simple deduction of the pure zeolite crystallite contribution (using the data obtained from pure zeolite crystals) and normalizing to the nanotube volume, the temperature dependence of the SWNTs' magnetic susceptibility is shown in Fig. 4, for five values of applied field perpendicular to the c axes. A strongly temperature-dependent diamagnetism is seen below 10 K, at 0.02 or 0.2 T applied field. The magnitude of the susceptibility decreases monotonically with increasing field and is very small at 5 T. The result is in quantitative agreement with the Meissner effect of 1D fluctuation superconductivity, shown below.\(^\text{[1]}\) The susceptibility of the parallel field case is one order of magnitude less, within the error caused by the crystallites' misalignment and consistent with the observation that there is no Meissner effect under a parallel field for 1D systems. The Meissner effect associated with 1D superconductivity differs substantially from the conventional behavior of an abrupt susceptibility jump at \(T_c\). Here, the dominance of 1D fluctuations means that the critical phenomenon around \(T_c\) is replaced by smooth temperature and magnetic-field variations.

3.4 1D superconductivity

To observe the supercurrents, it is necessary to fabricate thin samples to ensure that there is no imperfection (potential barrier) within the length of the SWNTs. This is done by reducing the thickness of the AFI foil to about 50 nm by argon ion milling both sides of the sample. After etching (using HCl) and cleaning (using distilled water) of the foil, Pt electrodes were made on both sides of the foil by FIB deposition. The size and location of the Pt electrodes were precisely controlled by FIB, ensuring good contact between the electrodes and the ends of SWNTs. Detailed description of the measurement process is reported in.\(^\text{[1]}\) In Fig. 5 the conductance \(J/E\) (evaluated at the experimental \(E_{\text{exp}} \approx 2 \times 10^5 \text{ V/cm}\)) is plotted as a function of temperature. To explain this conductance behavior (at \(T \sim 15 \text{ K or less}\), we calculated of the ensemble-averaged current using the Monte Carlo approach.\(^\text{[1]}\) The calculated (normalized) conductivity (open circles) \(J/E\) (evaluated at the experimental \(E_{\text{exp}} \approx 2 \times 10^5 \text{ V/cm}\)) is in excellent agreement with the experiment (solid circles). The sample at \(T \geq T_c\) cannot be at zero resistance (even without potential barriers) because at any given instant there is always some probability that fluctuations would locally drive the superconducting state to the normal state. In a 1D system, any normal segment is in series with the rest of the sample, and hence there is always a finite resistance at finite temperatures. Because such a
probability decreases with temperature, the fluctuation supercurrent, and hence the conductance, increases. Zero resistance is reached only at $T = 0 \text{K}$. 

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