

Pressure dependence of the optical absorption spectra of single-walled carbon nanotube films

S. Kazaoui,^{1,*} N. Minami,¹ H. Yamawaki,¹ K. Aoki,¹ H. Kataura,² and Y. Achiba²

¹National Institute of Materials and Chemical Research, AIST 1-1 Higashi, Tsukuba, Ibaraki, 305-8565 Japan

²Faculty of Science, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan

(Received 3 February 2000)

We have experimentally observed that the optical absorption spectra of single-walled carbon nanotube (SWCNT) films change drastically and reversibly by pressure up to 4.1 GPa. The main absorption feature at 0.68 eV attributed to the interband optical transition in semiconducting nanotubes [chiral (n, m) and zigzag ($n, 0$), with $n - m \neq 3i$] shifts to lower energy and eventually vanishes with increasing pressure. Accordingly, we infer that the electronic structure and the electronic properties of SWCNTs in the solid state are highly sensitive to intertube interactions and/or to symmetry breaking.

I. INTRODUCTION

The solid-state physics of single-wall carbon nanotubes (SWCNTs) is of great interest because of their unique one-dimensional structure and outstanding electronic properties.¹⁻³ A tremendous number of theoretical calculations on the electronic structures of ideally isolated SWCNTs with various chiral indexes (n, m) were carried out in order to predict their electrical and optical properties.⁴⁻⁹ However, because a SWCNT forms a two-dimensional triangular close-packed lattice weakly bound by van der Waals forces in the solid state,¹⁰ effects of intertube interactions and symmetry breaking can no longer be neglected. Indeed, if these effects were included in theoretical calculations, significant changes of the electronic structures were predicted and different properties were expected.¹¹⁻¹³

In the present contribution, we have clarified these issues by experimentally investigating the effects of high pressure on the optical absorption spectra of SWCNT films using a diamond anvil cell. The utilization of high pressure is a powerful technique to tune intertube distances and/or to induce deformation of the structure of SWCNTs, as was very recently observed by an *in situ* x-ray diffraction experiment.¹⁴ It should be stressed that, different from resistivity^{15,16} and Raman¹⁷ measurements, optical absorption spectroscopy directly probes and detects changes in specific electronic states of SWCNTs.^{18,19}

We have experimentally observed that the main optical absorption features of SWCNT films are strongly and reversibly pressure dependent. This experimentally proves that the electronic structures and the electronic properties of nanotubes in the solid state are highly sensitive to intertube interactions and/or symmetry breaking. Changes in the electronic properties of SWCNT films are presented and discussed in connection with the most recent experimental and theoretical developments.

II. EXPERIMENTS AND RESULTS

SWCNT samples were synthesized by the electric arc discharge method using a Ni/Y catalyst.¹⁸ The as-prepared material consists mainly of carbon nanotubes, with a significant quantity of carbon particles and traces of the catalysts. From

transmission electron microscopy and scanning tunnel microscopy (STM), it was observed that the samples were made of individual and bundles of nanotubes. Bundles were a few tens of nanometers in diameter and a few micrometers in length, containing hundreds of close-packed individual nanotubes. The diameter of the latter were found to be distributed from 1.2 to 1.6 nm with various helicity.

A. Optical absorption spectra of SWCNT films at ambient pressure

The optical absorption spectra of SWCNT films (prepared as described in Ref. 18 and 19) were collected in a wide spectral range from the far infrared (50 cm^{-1} or $6.2 \times 10^{-3} \text{ eV}$) to UV ($5 \times 10^4 \text{ cm}^{-1}$ or 6.2 eV) in transmission mode at ambient pressure and temperature (Fig. 1).

On the high-energy side, it was established that the main features at approximately 0.68 eV (labeled S1), 1.2 eV (S2), 1.8 eV (M1), and around 2.4 eV (S3) superimposed on the broad π -plasmon absorption band centered at about 5 eV derive from the bulk properties of SWCNTs.¹⁸ Furthermore, by comparing with theoretical calculations, these features

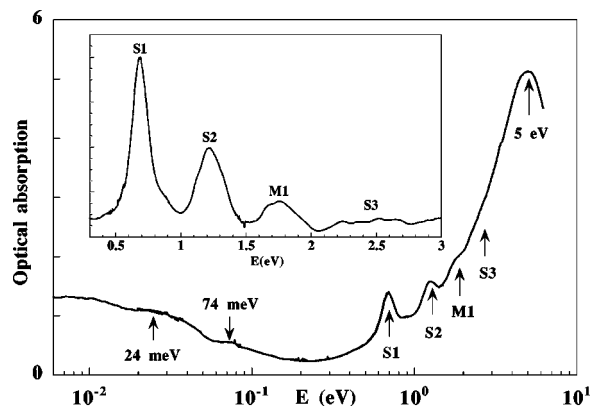


FIG. 1. Optical absorption spectrum of SWCNT film in air at atmospheric pressure [different substrates (quartz, KBr, polyethylene, diamond) and spectrometers were used to cover this energy range]. Inset: for convenience, by subtracting the large absorption background due to π plasmon, the absorption features labeled (S1, S2, S3) and (M1) are clearly displayed.

were assigned to optical transitions between van Hove singularities of the density of states (DOS) of SWCNTs.^{5,18} Specifically, S1, S2, and S3 were respectively attributed to allowed electronic transitions between the first, second, and third pairs of singularities in semiconducting nanotubes [chiral (n,m) and zigzag $(n,0)$, with $n-m \neq 3i$], whereas M1 was assigned to an allowed electronic transition between the first pairs of singularities in metallic nanotubes [armchair (n,n) , zigzag $(n,0)$, or (n,m) chiral nanotubes with $n-m = 3i$]. Armchair nanotubes are expected to contribute significantly to M1 because they are characterized by a small unit cell and large density of states.⁵

The above-mentioned assignments in the energy range 0.5–3 eV are consistent with STM studies of individual nanotubes,²¹ and optical absorption spectroscopy on purified and chemically modified SWCNTs in CS_2 solution,²² as well as with high-resolution momentum-dependent electron energy loss spectroscopy (EELS) experiments of bulk SWCNTs.²³

On the low-energy side, several broad optical absorption features are clearly observed at approximately 74 meV (600 cm^{-1}) and 24 meV (200 cm^{-1}) superimposed on a Drude-type absorption background. Although further experiments are in progress to elucidate the origin of the above-mentioned features, we suggest that the features at 74 and 24 meV probably correspond to the expected small energy gap or pseudogap in metallic nanotubes.^{11,24}

B. Optical absorption spectra of SWCNT films under pressure

Now that the origins of the absorption bands are relatively well established, we can systematically study their pressure dependence. We used a diamond anvil cell, where the sample compartment was a small cylindrical hole (diameter $d = 0.3 \text{ mm}$ and height $h = 0.1 \text{ mm}$) in a metal gasket of Inconel X-750. Chemically inert KBr powder including a ruby crystal (for pressure determination) was initially packed into the hole. Subsequently, a thin film of SWCNTs was deposited on KBr according to the following procedure: SWCNT powder was dispersed in ethanol by sonication, then sprayed using an airbrush and finally dried. Figure 2 presents the optical absorption spectra of SWCNT film on KBr recorded in a transmission mode through the diamond anvil cell using a microspectrophotometer (Zeiss UMSP-80 and Jasco MFT 2000) in the energy ranges 2.6–1.5, 1.4–0.6, and 0.65–0.10 eV, in the pressure range from 0.2 to 4.1 GPa, and at room temperature.

First, we consider the pressure effect on the absorption features labeled S1, S2, and S3. It is remarkable that the S1 feature [Figs. 2(a) and 2(c)] exhibit a pronounced broadening and a significant reduction in intensity with increasing pressure from 0.2 up to 4.1 GPa. Indeed, the optical absorption at constant energy $E = 0.68 \text{ eV}$ decreased quasilinearly with pressure. Moreover, the energy corresponding to the maximum of the S1 band shifted with pressure as shown in the inset of Fig. 2(a). Admittedly, the energy shift was very small but significant and reproducible. This result suggests that the optical band gaps of semiconducting SWCNTs nar-

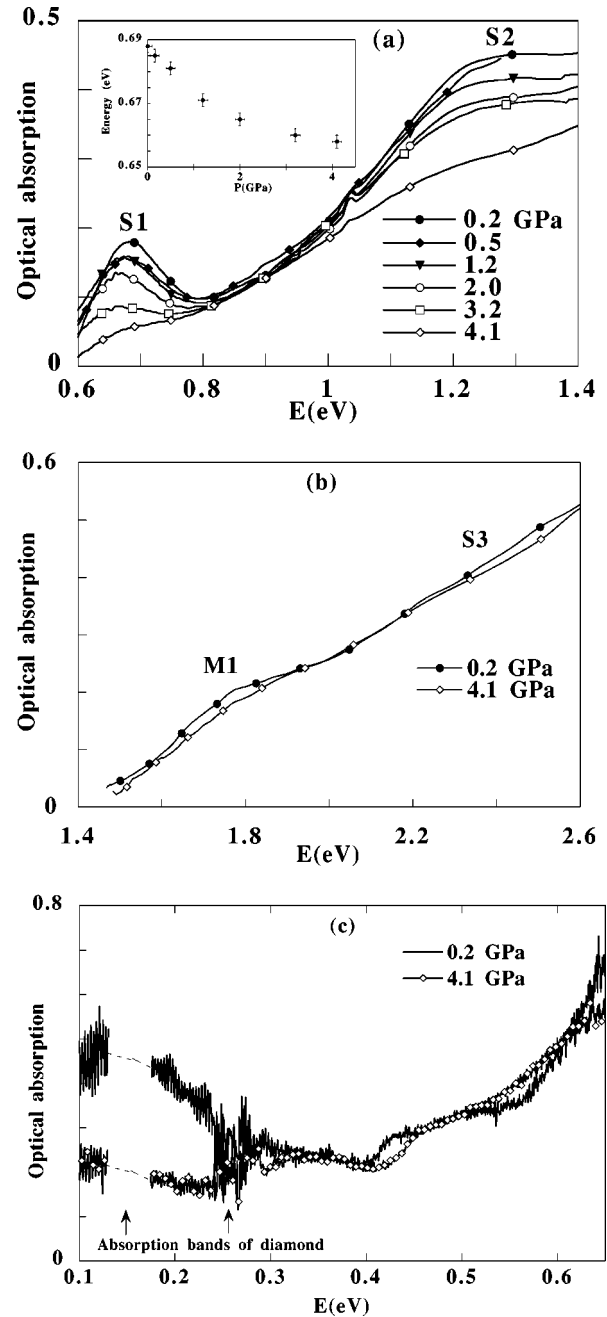


FIG. 2. Optical absorption spectra of SWCNT film under pressure ($p = 0.2$ – 4.1 GPa) in the energy ranges (a) 0.6–1.4 eV, (b) 1.5–2.6 eV and (c) 0.1–0.65 eV. The inset shows the energy shift of the S1 feature vs pressure.

row with pressure. The features labeled S2 and S3 were also significantly reduced with increasing pressure [Figs. 2(a) and 2(b)].

Second, we turn to examine qualitatively the pressure effect on the absorption features labeled M1. Although less resolved, they were significantly reduced and smoothed with increasing pressure from $p = 0.2$ to 4.1 GPa [Fig. 2(b)]. The absorption features in the M1 region were still observed even at 4.1 GPa, whereas at the same pressure the S1 features almost vanished. These results underline that M1 exhibits a

distinct pressure dependence compared to S1, because these features originate from nanotubes with different electronic structures and symmetries.

Finally, Fig. 2(c) shows the optical absorption spectra for photon energy 0.1–0.65 eV (the measurement range was mainly limited by the absorption bands of diamond). Interestingly, the absorbance in the range 0.1–0.25 eV dramatically decreased with increasing pressure. Since this range corresponds to the tail of the absorption feature at approximately 74 meV, which was tentatively assigned to electronic transitions in metallic nanotubes as already mentioned, this result indicates that the electronic transition in these nanotubes is also strongly pressure dependent.

We attempted to establish the pressure behavior of the features at 74 and 24 meV. Since the pressure medium (KBr) could not be used due to its absorption in the energy range 6.2–86.7 meV and the microspectrophotometer was not available, we used a diamond press (2 mm diameter) on which SWCNT film was directly deposited. But no significant change was detected probably due to the insufficient strength of the available pressure (only 0.1 GPa maximum).

We also observed pressure-induced changes of the Raman spectra of SWCNTs using different excitation energies such as 1.95 and 2.4 eV, which correspond to the M1 and S3 features, respectively. Combining the results of the optical absorption and Raman measurements, we firmly proved that pressure reversibly affects the photophysical properties of SWCNTs at least up to 4.1 GPa, within our experimental resolution. (The Raman data will be reported separately.)

III. DISCUSSION

A comprehensive analysis of the pressure effect on SWCNT is readily achieved by combining the above experimental results with structural information and theoretical calculations. The pressure effects on the crystal structure and on the symmetry of nanotubes were already discussed on the basis of the compressibility,²⁰ Raman,¹⁷ and *in situ* synchrotron x-ray diffraction experiments.¹⁴ In substance, with increasing pressure the intertube distance decreases with a concomitant enhancement of intertube interactions and distortion of the cross section of the nanotubes (such as polygonal or elliptical). As a result of these structural changes, significant effects on the electronic properties of SWCNTs are expected. Indeed, we have experimentally observed that the interband optical transitions and vibrational modes of SWCNTs are pressure dependent.

Theoretical calculations on the electronic structure of SWCNT bundles under pressure (applied to the bundle's cross section) using the local density approximation in the framework of the density functional theory were very recently reported.²⁵ These calculations show that the electronic band structure of (6,6) and (8,0) SWCNT bundles is dramatically affected by decreasing intertube distance and concurrently lowering the symmetry of both the nanotubes and the crystal lattice. Moreover, it was predicted that with increasing pressure the band gap opens in (6,6) armchair metallic nanotubes, whereas it closes in (8,0) zigzag semiconducting nanotubes [calculations on (*n,m*) nanotubes are not yet

available].²⁵ A similar prediction was made by theoretically considering the effects of distortion of ideally isolated and thus essentially noninteracting nanotubes.¹³ It was shown that the lowest unoccupied and highest occupied molecule orbit (LUMO-HOMO) band gap at the Γ point of semiconducting zigzag (10,0) nanotubes closes by pentagonal distortions, whereas metallic zigzag (12,0) nanotubes under hexagonal distortions reveal an optical band gap.¹³ If the above calculations (carried out for small nanotubes with diameter about 0.6–0.9 nm) can be extrapolated to a large one (the diameter of our nanotubes is in the range 1.2–1.6 nm), then they should provide considerable support to elucidate the basic properties of SWCNTs under pressure. Compiling all the above discussions, we expect that the electronic structures and consequently the electronic properties of SWCNTs in the solid state are highly sensitive to intertube interactions and/or symmetry breaking.

Experimentally, the main absorption feature at around 0.68 eV assigned to the interband transition in (*n,m*) chiral and (*n,0*) zigzag nanotubes showed a pressure-induced shift to lower energy. The striking correspondence of our results with the theoretical predictions mentioned above^{13,25} suggests that (*n,0*) zigzag and probably (*n,m*) chiral SWCNTs undergo a pressure-induced semiconductor to metal transition. However, another possibility would be pressure-induced three-dimensional overlap of the wave functions that leads to a decrease and smearing out of the pronounced absorption peaks originating from the one dimensionality of SWCNTs. The establishment of the predicted insulator-metal transition should await more elaborate experimental information.

Bozhko *et al.* and Gaal *et al.* reported the pressure dependence of the electronic transport properties of bulk SWCNT samples.^{15,16} However, since the samples inevitably contained a variety of nanotubes and since transport properties reflect both intrinsic and extrinsic mechanisms, it should be admitted that such measurements only reflect averaged properties. The pressure effects on SWCNTs remain the subject of further experimental studies. Ultimately, electrical measurements under pressure on a single or bundle of nanotubes are of great interest to elucidate the pressure dependence of the conductivity, although they are technically challenging.

In conclusion, we have experimentally demonstrated that the electronic structure and the optical properties (interband optical transitions and vibrational modes) of SWCNTs in the solid state are affected by intertube interactions and/or symmetry breaking. This work should provide important information for further understanding of the basic properties of SWCNTs as well as for its potential applications to electronic devices.

ACKNOWLEDGMENTS

We acknowledge useful discussions with Dr. S. Okada (Tsukuba University) on the electronic structure of SWCNTs under pressure (prior to publication). We also thank all the members of the High-Pressure Chemistry Laboratory (NIMC) for technical assistance on high-pressure experiments and Dr. T. Itatani (ETL) for far-infrared experiments.

- * Author to whom the correspondence should be addressed: Fax: +81-298-61-6232; e-mail: kazaoui@nimc.go.jp
- ¹C. Dekker, *Phys. Today* **52(5)**, 22 (1999).
- ²M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996).
- ³R. Saito, G. Dresselhaus, and M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, Singapore, 1998).
- ⁴R. Saito, M. Fujita, G. Dresselhaus, and M.S. Dresselhaus, *Appl. Phys. Lett.* **60**, 2204 (1992).
- ⁵R. Saito, G. Dresselhaus, and M.S. Dresselhaus, *Phys. Rev. B* **61**, 2981 (2000).
- ⁶J.W. Mintmire, B.I. Dunlap, and C.T. White, *Phys. Rev. Lett.* **68**, 631 (1992).
- ⁷J.W. Mintmire and C.T. White, *Phys. Rev. Lett.* **81**, 2506 (1998).
- ⁸N. Hamada, S. Sawada, and A. Oshiyama, *Phys. Rev. Lett.* **68**, 1579 (1992).
- ⁹C.L. Kane and E.J. Mele, *Phys. Rev. Lett.* **78**, 1932 (1997).
- ¹⁰A. Thess *et al.*, *Science* **284**, 1508 (1999).
- ¹¹P. Delaney *et al.*, *Nature (London)* **391**, 466 (1998); P. Delaney *et al.*, *Phys. Rev. B* **60**, 7899 (1999).
- ¹²Y.K. Kwon, S. Saito, and D. Tomanek, *Phys. Rev. B* **58**, R13 314 (1998).
- ¹³J.C. Charlier, Ph. Lambin, and T.W. Ebbesen, *Phys. Rev. B* **54**, R8377 (1996); J.C. Charlier, *J. Mater. Res.* **13**, 2368 (1998).
- ¹⁴J. Tang *et al.*, in *Amorphous and Nanostructured Carbon*, edited by J. Robertson *et al.*, Materials Research Soc. Symp. Proc. No. 593 (Materials Research Society, Pittsburgh, 2000).
- ¹⁵A.D. Bozhko *et al.*, *Appl. Phys. A: Mater. Sci. Process.* **67**, 75 (1998).
- ¹⁶R. Gaal, J.-P. Salvétat, and L. Forro, *Phys. Rev. B* **61**, 7320 (2000).
- ¹⁷U.D. Venkateswaran *et al.*, *Phys. Rev. B* **59**, 10 928 (1999).
- ¹⁸H. Kataura *et al.*, *Synth. Met.* **103**, 2555 (1999).
- ¹⁹S. Kazaoui *et al.*, *Phys. Rev. B* **60**, 13 339 (1999).
- ²⁰S.A. Chesnokov *et al.*, *Phys. Rev. Lett.* **82**, 343 (1999).
- ²¹J.W.G. Wildoer *et al.*, *Nature (London)* **391**, 59 (1998).
- ²²J. Chen *et al.*, *Science* **282**, 95 (1998).
- ²³T. Pichler *et al.*, *Phys. Rev. Lett.* **80**, 4729 (1998).
- ²⁴A. Ugawa, A.G. Rinzler, and D.B. Tanner, *Phys. Rev. B* **60**, R11 305 (1999).
- ²⁵S. Okada, A. Oshiyama, and S. Saito (private communication).