

Raman Spectroscopy of Carbon Nanostructures in Strong Magnetic Field

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Abstract—One- and two-dimensional carbon nanostructures with sp^2 hybridization of carbon atoms (single walled carbon nanotubes and graphene) are promising materials in future electronic and spintronics devices due to specific character of their electronic structure. In this paper we present a comparative study of graphene and single-wall carbon nanotubes by Raman spectro-microscopy in strong magnetic field. This unique method allows to study changes in electronic band structure of the two types of carbon nanostructures induced by a strong magnetic field.

Keywords—Carbon nanostructures, magnetic field, Raman spectroscopy.

I. INTRODUCTION

CARBON nanostructures with sp^2 hybridization of carbon atoms (single-walled carbon nanotubes - SWCNTs and graphene) are recently widely studied due to their potential applications in many fields of nanodevices. The electronic band structure of the graphene shows a typical Dirac cone located at around the K-point of the two-dimensional (2D) hexagonal Brillouin zone. The graphene is often named as zero gap semiconductor due to the presence of the Dirac point, which separates the valence and conduction band in neutral state.

In defect free material, the Dirac fermions propagate through the 2D crystal as massless particles and determine the unique physical properties of graphene such as high electrical and thermal conductivity.

In high magnetic fields (above 10 Teslas) additional plateaus of the Hall conductivity at $\sigma_{xy} = \nu e^2/h$ with $\nu = 0, \pm 1, \pm 4$ are observed [1]. Recently, a plateau at $\nu = 3$ and the fractional quantum Hall effect at $\nu = 1/3$ were also reported [2]. These observations with $\nu = 0, \pm 1, \pm 3, \pm 4$ indicate that the four-fold degeneracy (two valley and two spin degrees of freedom) of the Landau energy levels is partially or completely lifted.

The graphene is also proposed as ideal candidate for spintronics due to its small spin-orbit interaction, negligible of nuclear magnetic moments in carbon and weak hyperfine interaction. Possibility of electrical spin current injection and detection has been demonstrated up to room temperature. Spin coherence length above 1 micrometer was observed at room temperature, and control of the spin current polarity with an

electrical gate was achieved at low temperature [3]. Recent prediction of carbon pseudospin in graphene stimulated formulation of the novel concept of electronics, the pseudo-spintronics.

In carbon nanotubes, one-dimensional (1D) analogues of the graphene derived as rolled graphene sheets, the band structure shows typical van Hove singularities and either a small gap (semiconducting tube) or a non-zero density of states at the Fermi level (metallic tubes), defined by the characteristic chiral vector of the tube [4]. Application of external magnetic field causes changes of the band structure depending on the mutual direction of the applied field and the tube axis. The carbon nanotubes have been also considered for spintronic applications [5].

The electronic structure of nanotubes can be related to the band structure of graphene as follows. Considering the two points in momentum space (K and K') due to the inversion symmetry of the graphene lattice, the only allowed states for a nanotube are those that comply with the quantization condition of fitting an integer number of Fermi wavelengths around the circumference of the nanotube.

When the first quantization line misses the K point, a band gap appears along with hyperbolic electron-like and hole-like dispersions near the K point. Neglecting the spin, time-reversal symmetry implies a complementary set of energy bands with exactly the same energy at the K' point. The valley degeneracy results in a discrete, two-state quantum degree of freedom (named isospin). The isospin, combined with spin, gives a four-fold degeneracy in the electronic spectrum.

One implication of the Dirac-cone picture is that stationary states formed from one valley carry a persistent current around the nanotube circumference, while the opposite valley carries the opposite current.

Magnetic moments associated with these “clockwise” and “counterclockwise” currents are expected in order of few Bohr magnetons, and therefore couple strongly to external magnetic fields applied parallel to the nanotube axis. External fields can thus be used to tune both the band gap and the energy separation of opposite valley states.

Hence the information on the evolution of the band structure of the graphene and carbon nanotubes under high magnetic field is of enormous importance for development of spintronic applications.

It was shown previously that magnetic flux parallel to carbon nanotube axis can modulate the band gap due to Aharanov-Bohm effect. In addition the magnetic field was suggested to activate the originally dark exciton. Indeed it was shown that the magnetic field can strongly enhance the

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photoluminescence of carbon nanotubes [6].

The modulation of the photoluminescence intensity is not expected for the magnetic field perpendicular to carbon nanotube axis. In this case, however, the periodic modulation of the bandstructure was suggested. This effect is difficult to study by photoluminescence spectroscopy due to its relatively low sensitivity to changes in the electronic structure. Recently, the in-field Raman spectro-microscopy has been used for studying the Landau levels through magneto-phonon resonances in single-layer graphene and few-layer graphene [7]. A smart technique for studying the band structure of carbon nanotubes is the resonance Raman spectroscopy. Because of the resonant condition of the scattering process, the observed spectra involve not only the information on phonons but also the electronic states.

The Raman active modes of carbon nanotubes are briefly discussed below, followed by description valid for the graphene.

The RBM band is of particular importance in SWCNTs since its frequency scales with tube diameter d_t according to the relation:

$$\omega_{\text{RBM}} = C_1/d_t + C_2 \quad (1)$$

where the constant C_1 has been reported to be in the range of 217 to 251 $\text{cm}^{-1}\cdot\text{nm}$ [8]. The constant C_2 ($\approx 15 \text{ cm}^{-1}$) is generally used to include the effect of interactions between nanotubes in bundled samples, and therefore in the case of individual isolated tubes, we expect $C_2 \approx 0 \text{ cm}^{-1}$. For small diameter tubes, the knowledge of the diameter and resonance profile is sufficient to determine the chiral indices (n,m) of the particular nanotubes. All other Raman modes for SWCNTs give relatively little information which can be used for their (n,m) assignment. Thus in most Raman studies of SWCNTs, only the RBM band is used to assign the tube (n,m) indices and this information is then used for the interpretation of the chirality dependence of other Raman modes.

Group theory predicts six Raman-active features in the TG band region for chiral nanotubes: $2A_{1g} + 2E_{1g} + 2E_{2g}$, which are reduced to three Raman-active bands for the symmetric zig-zag or armchair tubes. For semiconducting tubes, the $E_{1\text{TO}}$ and $E_{2\text{TO}}$ modes are predicted to be stiffer than the $E_{1\text{LO}}$ and $E_{2\text{LO}}$ modes, while the $A_{1\text{TO}}$ mode is softer than the $A_{1\text{LO}}$ mode due to the different stiffness for the axial and circumferential bonds [9]. For unpolarized Raman studies of semiconducting tubes, only two main components of the TG band are often considered in the analysis. They are usually referred to as the G^+ and G^- lines, which are found at around 1590 cm^{-1} (composed of $A_{1\text{LO}}$, $E_{1\text{TO}}$ and $E_{2\text{TO}}$) and 1560 cm^{-1} (composed of $A_{1\text{TO}}$, $E_{1\text{LO}}$ and $E_{2\text{LO}}$), respectively. The E_1 and E_2 modes have a much weaker Raman intensity than the totally symmetric A_1 modes [10]. Thus for semiconducting tubes, the G^+ line is attributed mainly to the diameter independent $A_{1\text{LO}}$ modes, while the G^- line is assigned to the $A_{1\text{TO}}$. A proper interpretation for the TG band spectra for metallic SWCNTs has been recently established based on the presence of a Kohn anomaly, arising from the electron-phonon interaction in

metallic tubes [11], [12].

The D and G' modes are observed in all kinds of polycrystalline carbon materials with sp^2 hybridization. However, their physical origin has been explained only recently in terms of double-resonance theory [13]. The D and G' modes are observed in the spectral regions of 1250-1450 cm^{-1} and 2500-2900 cm^{-1} , respectively. The one-phonon second-order Raman D-band appears only if there is a breakdown in translational crystal symmetry, which can be caused by defects in the structure. On the other hand, the two-phonon second-order Raman G' feature occurs independently of the presence of structural defects. The two phonons contributing to the G' feature have wave vectors q and $-q$, and thus the momentum conservation constraint is automatically preserved.

Graphene can be viewed as un-rolled single wall nanotube. The Raman spectra thus contains the G and G' mode and in case of defective samples also the D mode. On the other hand the RBM mode is missing in the Raman spectra of graphene. In addition the G mode is not split into two bands as in case of carbon nanotubes in unstrained graphene [14]. Here we propose to use resonant Raman spectroscopy to study the effect of magnetic field on single walled carbon nanotubes and compared it to the graphene. Due to the resonance enhancement of the Raman signal we have been able to observe subtle changes in the electronic structure of these materials

II. RESULTS AND DISCUSSION

The carbon nanotube samples were purchased from Sineurop. Graphene was prepared using a modified CVD growth method. A copper foil (25 μm thick, 99.9%, Alfa Aesar) was used as a catalyst which was cleaned by dipping the copper into Ni etchant (Nitric acid, Transeneinc.) for 30 seconds. The growth procedure was as follows: the substrate was heated to 1000 $^\circ\text{C}$ under 10 sccm H_2 for 30 min for annealing the substrate. Subsequently, the $^{12}\text{CH}_4$ was introduced for 40 min, and then it was cooled down under the flow of gasses. To transfer the samples onto the SiO_2/Si substrate we used PMMA according to previously reported procedures. In brief: Graphene on copper was coated with diluted 50:50 Poly(methyl methacrylate) (PMMA, 950 A9, Microchem, 4.5% in anisole) followed by removing the copper from the copper etchant (CE-100, Transene). Then the PMMA/graphene was washed by DI water to remove the residual copper etchant and the PMMA was removed by thermal annealing at 350 $^\circ\text{C}$ for 3 h under a 200 sccm $\text{H}_2/200$ sccm Ar atmosphere.

In order to measure the Raman spectra in magnetic field we used a custom setup: the Witec Raman spectrometer combined with confocal Raman spectro-microscope insert by attoCube. The insert was placed in a cryostat equipped with superconducting magnet with the possibility to vary the magnetic field between 0-14T. The Raman spectra were excited by either 2.33 eV (532 nm) or 1.92 eV (633 nm) laser energy. The measurements were performed at 300 K.

Fig. 1 shows an example of the Raman spectra of graphene and SWCNT. The Raman spectra of SWCNT are strongly enhanced due to the resonance effect and therefore the intensity of the SWCNTs spectrum is very strong.

The Raman signal is also relatively strong but the enhancement originates also from light interference in thin silicon dioxide layer. In the case of the Raman spectra of SWCNTs there is the RBM mode at about 200cm^{-1} , which suggest that the diameter of studied tubes is about 1.2 nm. It can be recognized that the TG mode at about 1600cm^{-1} consist of two peaks G^- and G^+ . The asymmetric line shape of G^- mode is suggesting that metallic tubes are in resonance with 633 nm laser excitation.

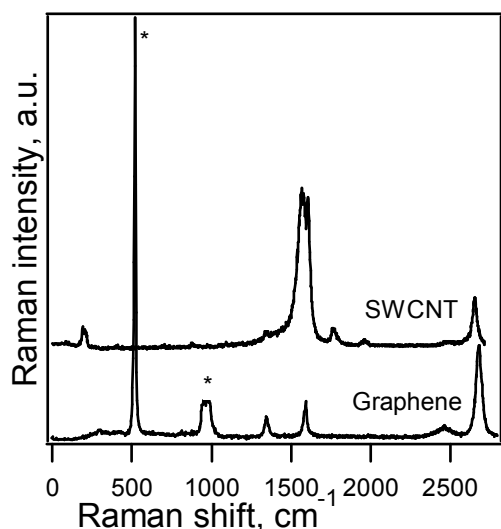


Fig. 1 Typical Raman spectra of graphene and SWCNTs. The spectra were excited using 532 nm laser excitation energy. The bands marked by asterisk correspond to Si substrate

The Raman spectrum of graphene sample contains the D, G and G' modes. The D mode is relatively weak; hence, the sample does not contain a substantial amount of defects. The G mode is found at about 1593cm^{-1} which points to a slight doping of graphene. This doping is probably due to the Si/SiO₂ substrate and air. The G' mode is found at about 2680cm^{-1} . Hence the sample is slightly stressed. The stress in the graphene is often seen in real samples and can be induced for example by transfer procedure. The doping of graphene is also manifested by a reduced G/G' intensity ratio.

The Raman signal of graphene is strongly affected by doping and stress. The stress and doping may vary depending on the Raman spot location. Therefore to correctly quantify a changes intensity of Raman signal several spectra must be measured, ideally Raman mapping of the sample should be used. Fig. 2 shows Raman map of the intensity of the G mode of graphene at 0T. The spectra were excited using 532 nm laser excitation energy. Indeed, one can see large variation of the G mode signal intensity. The Raman map thus allows monitoring the changes at different location of the substrate. Fig. 2 also shows the Raman map of the G mode intensity of same sample in the magnetic field of 14T. By comparing the

Raman maps at 0T and 14T one can observe that the overall intensity is increased at magnetic field.

Fig. 3 shows Raman map of the intensity of the G mode of SWCNTs at 0T and in the magnetic field of 14T. The spectra were excited using 633 nm laser excitation energy. Again we measured Raman map to ensure that the results is not affected by local conditions. By comparing the average signal intensity at 0T and in the field of 14T one can see that the Raman signal of the G mode is enhanced similarly as in the case of graphene.

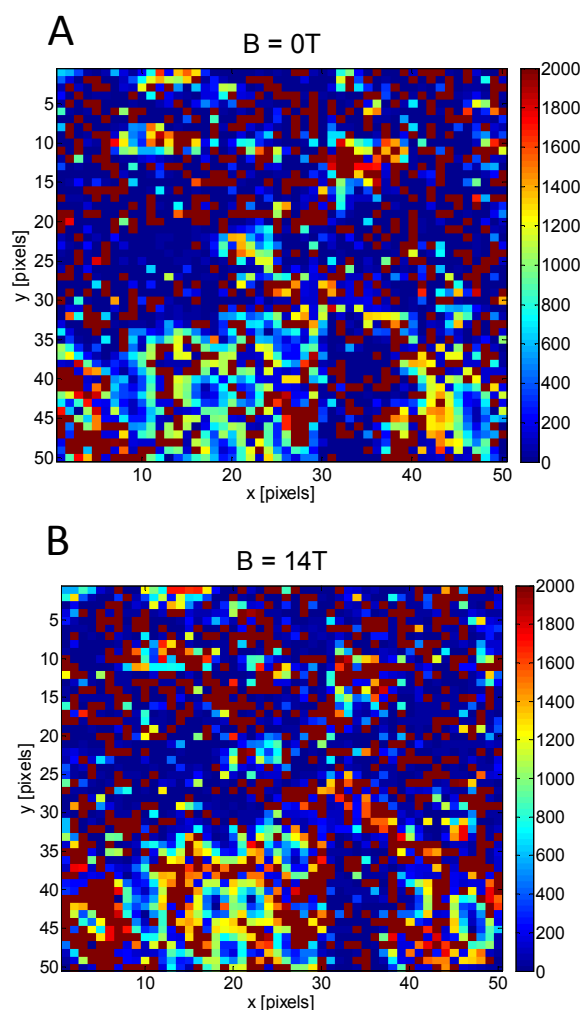


Fig. 2 Raman map of the intensity of the G mode graphene at A) 0T and B) 14T. The spectra were excited using 532 nm laser excitation energy

Although the activation of the dark states in the electronic structure of carbon nanotubes is not expected in the magnetic field perpendicular to nanotube axis, we see the enhancement of the Raman signal. This enhancement is also observed for graphene.

Finally the in-field evolution of the Raman intensity and Raman shift of the D, G and G' modes of the graphene and the G and G' modes of the single-wall carbon nanotubes, respectively, were investigated. The results are shown in Fig. 4. The behavior observed for the graphene is in agreement

with the previously published results and shows typical features related to the magneto-phonon resonance.

For the nanotubes, there is no evidence of Landau levels mixing up to 14 T, however a significant change of the intensity of the bands can be observed. The origin of the enhancement is not clear yet and can be attributed either to oscillations of the band width of the van Hove anomalies seen through the resonance enhancement or influenced by oscillations of the luminescence contribution observed previously. Nevertheless, the proposed interpretation is not fully supported by the available band structure calculation, which yields about one order larger magnitude of the applied magnetic field needed to see the oscillatory behavior.

III. CONCLUSION

In conclusion we applied a new technique – in situ Raman mapping in high magnetic fields – to study subtle changes in Raman spectra of selected carbon nanostructures. We demonstrated the power of the method on the study of carbon nanostructures (single walled carbon nanotubes, and graphene) since it allows monitoring in situ the changes in electronic structure induced by magnetic field.

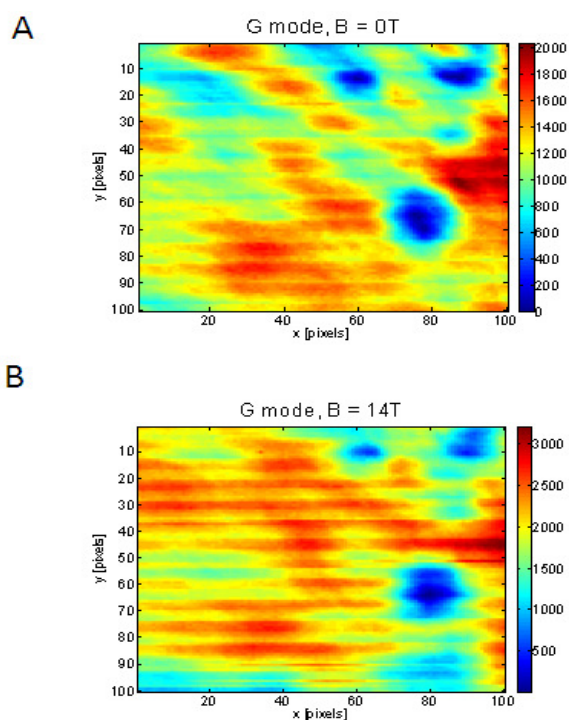


Fig. 3 Raman map of the intensity of the G mode of SWCNTs at A) 0T and B) 14T. The spectra were excited using 633 nm laser excitation energy

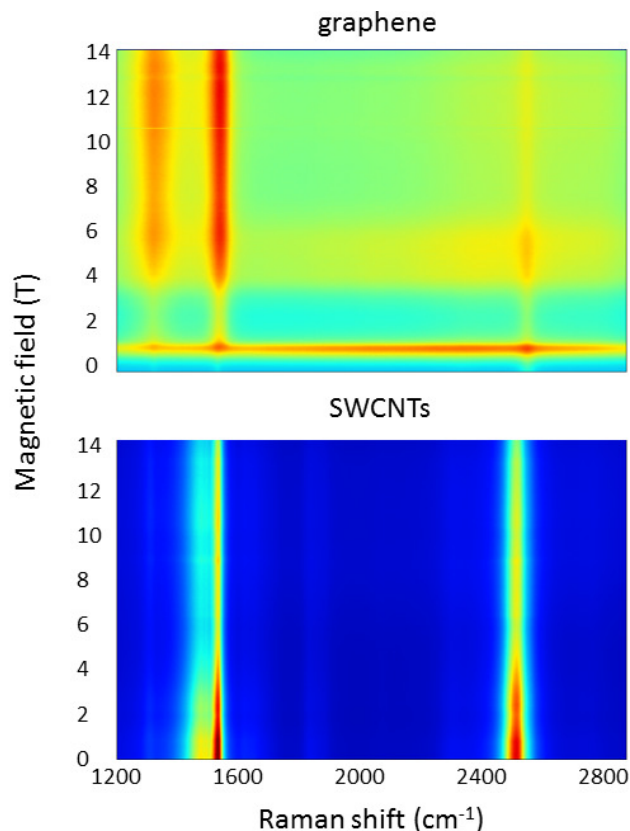


Fig. 4 Evolution of the characteristic modes of the graphene (upper panel) and single-wall carbon nanotubes (lower panel) in magnetic field. The spectra were excited using 532 nm laser excitation energy

ACKNOWLEDGMENT

The work was supported by Czech grant agency, project No.: P204/10/1667. The in-field Raman spectroscopy measurements were performed in MLTL (see: <http://mltl.eu>), which is supported within the program of Czech Research Infrastructures (project no. LM2011025).

REFERENCES

- [1] Y.Zhang, Z.Jiang, J.P.Small, M.S.Purewal, Y.W.Tan, M.Fazlollahi, J.D.Chudow, J.A.Jaszczak, H.L.Stormer, P.Kim, "Landau-level splitting in graphene in high magnetic fields," *Phys.Rev.Lett.* vol.96, 2006, pp. 136806-
- [2] X.Du, I.Skachko, F.Duerr, A.Luican, E.Y.Andrei, "Fractional quantum Hall effect and insulating phase of Dirac electrons in graphene," *Nature*, vol.462, 2009, pp. 192-195.
- [3] N.Tombros, C.Jozsa, M.Popinciuc, H.T.Jonkman, B.J.van Wees, "Electronic spin transport and spin precession in single graphene layers at room temperature," *Nature*, vol.448, 2007, pp. 571-5U4.
- [4] S.Piscanec, M.Lazzeri, F.Mauri, A.C.Ferrari, J.Robertson, "Kohn anomalies and electron-phonon interactions in graphite," *Phys.Rev.Lett.* vol.93, 2004, pp. 185503-1-185503-4.
- [5] F.Kuemmeth, H.Churchill, P.Herring, C.Marcus, "Carbon nanotubes for coherent spintronics," *Materials Today*, vol.13, 2010, pp. 18-26.
- [6] J.Shaver, J.Kono, O.Portugall, V.Krstic, G.L.Rikken, Y.Miyauchi, S.Maruyama, V.Perebeinos, "Magnetic brightening of carbon nanotube photoluminescence through symmetry breaking," *Nano Letters*, vol.7, 2007, pp. 1851-1855.
- [7] S.Bercaud, M.Potemski, C.Faugeras, "Probing Electronic Excitations in Mono- to Pentalayer Graphene by Micro Magneto-Raman Spectroscopy," *Nano Letters*, vol.14, 2014, pp. 4548-4553.

- [8] P.T.Araujo, S.K.Doorn, S.Kilina, S.Tretiak, E.Einarsson, S.Maruyama, H.Chacham, M.A.Pimenta, A.Jorio, "Third and fourth optical transitions in semiconducting carbon nanotubes," *Phys.Rev.Lett.* vol.98, 2007, pp. 067401-1-067401-4.
- [9] A.Jorio, M.A.Pimenta, A.G.Souza, G.G.Samsonidze, A.K.Swan, M.S.Unlu, B.B.Goldberg, R.Saito, G.Dresselhaus, M.S.Dresselhaus, "Resonance Raman spectra of carbon nanotubes by cross-polarized light," *Phys.Rev.Lett.* vol.90, 2003, pp. art-107403.
- [10] S.D.M.Brown, A.Jorio, P.Corio, M.S.Dresselhaus, G.Dresselhaus, R.Saito, K.Kneipp, "Origin of the Breit-Wigner-Fano lineshape of the tangential G-band feature of metallic carbon nanotubes," *Phys.Rev.B* , vol.6315, 2001, pp. 155414-1-155414-8.
- [11] S.Piscanec, M.Lazzeri, J.Robertson, A.C.Ferrari, F.Mauri, "Optical phonons in carbon nanotubes: Kohn anomalies, Peierls distortions, and dynamic effects," *Phys.Rev.B* , vol.75, 2007, pp. 035427-1-035427-22.
- [12] M.Kalbac, H.Farhat, L.Kavan, J.Kong, M.S.Dresselhaus, "Competition between the Spring Force Constant and the Phonon Energy Renormalization in Electrochemically Doped Semiconducting Single Walled Carbon Nanotubes," *Nano Letters* , vol.8, 2008, pp. 3532-3537.
- [13] R.Saito, A.Jorio, A.G.Souza, G.Dresselhaus, M.S.Dresselhaus, M.A.Pimenta, "Probing phonon dispersion relations of graphite by double resonance Raman scattering," *Phys.Rev.Lett.* vol.88, 2002, pp. 027401-1-027401-4.
- [14] O.Frank, G.Tsoukleri, J.Parthenios, K.Papagelis, I.Riaz, R.Jalil, K.S.Novoselov, C.Galiotis, "Compression Behavior of Single-Layer Graphenes," *Acs Nano* , vol.4, 2010, pp. 3131-3138.