Final Report

Resonant Raman spectroscopy in novel two-dimensional materials

NKFI-K115608, (2016.02.01 – 2021.07.31) principal investigator: Jenő Kürti

I) Aim of the research

During our previous research we acquired great experience in theoretical investigation of the electronic and vibrational properties of carbon nanostructures (carbon nanotubes, graphene) using first principles methods. Our aim was to continue these kind of calculations for various two-dimensional systems, similar to graphene. Many novel materials belong to this family. Some of them consist of only one kind of atom (graphene, silicene, germanene, phosphorene), but most of them are hetero structures (MoS_2; BiTeX where X=I, Br, Cl; etc). For the calculations with density functional theory (DFT) we used mainly the VASP (Vienna Ab-initio Simulation Package) code.

Our results are related mainly to Raman and also to some transport and magnetic properties of some novel materials with two dimensional structure. In addition to the 2D materials we continued also the investigation of the 1D carbon nanotubes.

The materials are grouped in five classes and the corresponding results are summarized below, more or less in order of time within the classes. The five classes are: Carbon nanotubes (A: 6 papers), 2D monolayers (graphene, silicene, germanene, MoS_2, BiTeI) (B: 7 papers), 2D heterostructures (BiTeX-graphene) (C: 4 papers), Magnetic heterostructures (D: 3 papers) and Special materials (E: 2 papers).

II) RESULTS

The [numbers] correspond to the list in NKFI-EPR page. CIT = total number of independent citations.

A) Carbon nanotubes [1,2,4,5,6,22] CIT=17

A1) Controlled Isotope Arrangement in ^{13}C Enriched Carbon Nanotubes [1]

Koltai J, Mezei G, Zólyomi V, Kürti J, Kuzmany H, Pichler T, Simon F

J PHYS CHEM C 120: (51) 29520-29524 (2016) | https://pubs.acs.org/doi/10.1021/acs.jpcc.6b11367

In cooperation with our experimental colleagues, we studied a compelling novel isotope engineered carbon material: single-walled carbon nanotubes made of ^{13}C enriched clusters which are embedded in natural carbon regions. The material is synthesized with a high temperature annealing from ^{13}C enriched benzene and natural C_{60}, which are coencapsulated inside host SWCNTs in an alternating fashion. We observe an unexpected downshift of the Raman modes, which is best visible for the 2D Raman line: the downshift is much larger than expected for a homogeneously distributed isotope enrichment. A semiempirical method based modelling of the Raman mode energies for ^{13}C isotope enrichment suggests that the experimental observation is compatible with a significant clustering of the isotopes. We believe that our observation opens the way for further combined molecular-isotope engineering, i.e., when several different molecules are filled in the host

nanotubes as inner tube precursors with different levels of isotopes. This could result in an inner tube whose isotope distribution is controlled to a high degree.

A2) Resonance Raman Optical Activity of Single Walled Chiral Carbon Nanotubes [2]

Nagy Péter, Koltai János, Surján Péter, Kürti Jenő, Szabados Ágnes

J PHYS CHEM A 120: 5527-5538 (2016) DOI: https://pubs.acs.org/doi/10.1021/acs.jpca.6b04594

We developed a computational protocol for calculation of the vibrational Resonance Raman Optical Activity (RROA) spectra of chiral singlewalled carbon nanotubes (SWCNTs). The calculations were performed imposing line group symmetry. Polarizability tensors, computed at the π-electron level, are differentiated with respect to DFT normal modes to generate spectral intensities. This computational protocol yields a RROA spectrum in good agreement with the only experiment on SWCNT, available at present, namely on (6,5) chiral nanotube. Besides the recently measured (6,5) tube, RROA spectra of five more chiral SWCNTs were calculated. These may aid forthcoming experiments in absolute configuration determination (right or left handedness). Involvement of fundamental vibrations in the region of the intermediate frequency modes is found to be more notable in ROA than in Raman spectra. Calculations indicate exceptionally strong resonance enhancement of SWCNT ROA signals that may assist nanotube identification. We mention that multilayer graphenes and multiwalled nanotubes can also exhibit ROA if the mirror planes of their (achiral) monomers are not coinciding.

A3) Arrayed Arrangement of ^{13}C Isotopes During the Growth of Inner Single-Walled Carbon Nanotubes [4]

János Koltai, Hans. Kuzmany, Thomas Pichler, and Ferenc Simon

Phys. Status Solidi B 254:11, 1700217 (2017) | DOI: 10.1002/pssb.201700217

We studied a compelling isotope engineered carbon material: single-wall carbon nanotubes which are grown from ^{13}C enriched benzene or toulene and natural carbon containing C60. We observe an unexpected downshift of the Raman modes. The semierimpical based modelling explains that this observation is compatible with a significant clustering of the isotopes.

A4) The growth of new extended carbon nanophases from ferrocene inside single-walled carbon nanotubes [5]

Hans Kuzmany, Lei Shi, Jenő Kürti, János Koltai, Andrey Chuvilin, Takeshi Saito, and Thomas Pichler

Phys. Status Solidi RRL 2017, 1700158 (2017) | DOI: 10.1002/pssr.201700158

The Raman response of new structures grown after filling SWCNTs with ferrocene and transformation at moderate high temperatures is demonstrated to be very strong, even stronger than the response from the tubes. Transmission electron microscopy demonstrates that the new objects are flat and exhibit a structure similar to short fragments of nanoribbons. The growth process is controlled by two different activation energies for low and high transformation temperatures, respectively. Immediately after filling Raman pattern from a precursor molecule are detected. Two different types of nanoribbons were identified by selecting special laser energies for the Raman excitation. These ribbons have the signature of quaterrylene and terrylene, respectively.

A5) Molecular Dynamics Simulation of Carbon Structures Inside Small Diameter Carbon Nanotubes [6]

István László, Bálint Gyimesi, János Koltai, and Jenő Kürti

Phys. Status Solidi B 2017, (2017) 1700206 | DOI: 10.1002/pssb.201700206

Motivated by recent experimental results of hydrocarbon formation in small diameter carbon nanotubes filled with ferrocene molecules, we performed molecular dynamics simulations with a DFT-adjusted tight binding method. At lower temperatures we obtain graphene ribbons, and at higher temperatures fullerenes or nanotubes are formed – in agreement with experimental results.

A6) Well-defined sub-nanometer graphene ribbons synthesized inside carbon nanotubes [22]

Hans Kuzmany, Lei Shi, Miles Martinati, Sofie Cambré, Wim Wenseleers, Jenő Kürti, János Koltai, Gergő Kukucska, Kecheng Cao, Ute Kaiser, Takeshi Saito, & Thomas Pichler

Carbon 171, 221-229 (2021) DOI: https://doi.org/10.1016/j.carbon.2020.08.065

Our experimental coworkers were able to synthesize graphene nanoribbons inside carbon nanotubes by high-temperature vacuum annealing of ferrocene molecules inside single-walled carbon nanotubes. We performed first principles density functional theory (DFT) calculations to obtain the vibrational frequencies and mode-specific Raman intensities for various nanoribbons. Raman intensities were evaluated using the frequency dependent Placzek approximation, optical excitation energies were calculated by solving the Bethe-Salpeter equation within the frame of a quasiparticle selfconsistent GW calculation. The combination of our calculations and an extensive wavelength-dependent Raman scattering characterization allowed the identification of the structure of the nanoribbons inside the nanotube. These findings enable a facile and scalable approach leading to the controlled growth and detailed analysis of well-defined sub-nanometer graphene nanoribbons.

B) 2D monolayers (graphene, silicene, germanene, MoS_2, BiTeI) [**7**,16,10,11,**3**,**15**,**9**] CIT=87

B1) Preparing local strain patterns in graphene by atomic force microscope based indentation [7]

Péter Nemes-Incze, Gergő Kukucska, János Koltai, Jenő Kürti, Chanyong Hwang, Levente Tapasztó & László P. Biró

Scientific Reports | 7: 3035 (2017) | DOI:10.1038/s41598-017-03332-5

In cooperation with experimentalists we studied the effect of preparing local strain patterns in graphene by atomic force microscope based indentation. Patterning graphene into various mesoscopic devices such as nanoribbons, quantum dots, etc. by lithographic techniques has enabled the guiding and manipulation of graphene's Dirac-type charge carriers. Graphene, with well-defined strain patterns, holds promise of similarly rich physics while avoiding the problems created by the hard to control edge configuration of lithographically prepared devices. Our experimental colleagues developed an atomic force microscope based technique by which strain can be created in substrate supported graphene layers. This method opens up new possibilities in tailoring the properties of graphene using mechanical strain. The effect of strain on the orbital motion of electrons in graphene can be described using a vector potential, corresponding to a time reversal symmetric

pseudo-magnetic field. We carried out tight binding calculations to obtain the pseudo magnetic field in accordance with the combined AFM and Raman measurements. This field has a threefold symmetric structure with the maximum of the field in the range of 100 tesla.

B2) Large intravalley scattering due to pseudo-magnetic fields in crumpled graphene [16]

Péter Kun, Gergő Kukucska, Gergely Dobrik, János Koltai, Jenő Kürti, László Péter Biró, Levente Tapasztó, Péter Nemes-Incze

npj 2D Mater Appl 3, 11 (2019). https://doi.org/10.1038/s41699-019-0094-6

Here we show that pseudo-magnetic field fluctuations present in crumpled graphene can induce significant intravalley scattering of charge carriers. We detect this by measuring the confocal Raman spectra of crumpled areas, where we observe an increase of the D'/D peak intensity ratio by up to a factor of 300. We reproduce our observations by numerical calculation of the double resonant Raman spectra.

B3) Characterization of epitaxial silicene with Raman spectroscopy [10]

G. Kukucska, V. Zólyomi, and J. Koltai

Phys. Rev. B 98, 075437 (2018) | DOI: 10.1103/PhysRevB.98.075437

Silicene, the silicon equivalent of graphene, is most commonly grown on Ag(111) substrates where it undergoes reconstruction due to the strong interaction between the Si and Ag atoms. We demonstrated through first-principles density functional theory (using the VASP code) for eight reconstructions that the Raman spectrum is unique for each configuration.

B4) Resonance Raman Spectroscopy of Silicene and Germanene [11]

G. Kukucska, V. Zólyomi, and J. Koltai

J. Phys. Chem. C 123, 1995−2008 (2019) DOI: 10.1021/acs.jpcc.8b11943

We modeled Raman processes in silicene and germanene involving scattering of quasiparticles by either two phonons or one phonon and one point defect. We identified features in the Raman spectra that are unique to the studied materials or the defects therein. We used our model to predict scattering cross sections for defect-induced Raman scattering involving adatoms, substitutional impurities, Stone–Wales pairs, and vacancies, and argued that the presence of each of these defects in silicene and germanene can be qualitatively matched to specific features in the Raman response.

B5) Theoretical Investigation of Strain and Doping on the Raman Spectra of Monolayer MoS_2 [3]

G. Kukucska and J. Koltai

Phys. Status Solidi B 2017, 00, 1700184 (2017)| DOI: 10.1002/pssb.201700184

Two-dimensional heterostructures are generally extremely sensitive to perturbations due to the large surface–volume ratio. A widely used non-destructive experimental technique to characterize these perturbations is

the Raman spectroscopy. In this work, we demonstrate that the intensity ratio depends strongly on the strain - thus it can be used as a supplementary method to characterize strain in the samples.

B6) Moderate strain induced indirect bandgap and conduction electrons in MoS_2 single layers [15]

János Pető, Gergely Dobrik, Gergő Kukucska, Péter Vancsó, Antal A Koós, János Koltai, Péter Nemes-Incze, Chanyong Hwang, Levente Tapasztó

npj 2D Mater Appl 3, 39 (2019). https://doi.org/10.1038

In order to experimentally determine the amount of mechanical strain induced in the MoS_2 lattice in the bubble areas, confocal Raman spectroscopic measurements were performed. We have performed simulations of the Raman spectrum of MoS_2 single layers subjected to biaxial tensile strain using the frequency-dependent Placzek approximation. The comparison of experimental and calculated Raman spectrum shows the best agreement for 2% biaxial tensile strain in agreement with other results in the literature.

B7) Exfoliation of single layer BiTeI flakes [9]

Bálint Fülöp, Zoltán Tajkov, János Pető, Péter Kun, János Koltai, László Oroszlány, Endre Tóvári, Hiroshi Murakawa, Yoshinori Tokura, Sándor Bordács, Levente Tapasztó and Szabolcs Csonka

2D Mater. 5 031013 (2018) | DOI: 10.1088/2053-1583/aac652

In this work the first successful isolation and characterization of a single layer of BiTeI using a novel exfoliation technique on stripped gold was reported. Our first principles calculations also predict the formation of SL BiTeI due to the strong bonding between Te and I to Au substrate. Moreover, BiTeI strongly hybridizes with the Au substrate, which results in a finite DoS in the gap, in accordance with the differential conductance measurements.

C) 2D heterostructures (BiTeX-graphene) [8,18,19,21] CIT=11

C1) Transport Properties of Graphene-BiTeI Hybrid Structures [8]

Z. Tajkov, D. Visontai, P. Rakyta, L. Oroszlány, and J. Koltai

Phys. Status Solidi C 2017, 00, 1700215 (2017) | DOI: 10.1002/pssc.201700215

Recent studies have shown that heterostructures comprised of graphene and certain chalcogenides are robust two-dimensional (2D) topological insulators. We developed a simplified model Hamiltonian for such systems and investigated their properties as the function of various parameter values. We mapped the phases of the system that can behave as an insulator, metal or topological insulator. We used this simplistic model to calculate transport characteristics on experimentally relevant sample sizes.

C2) Uniaxial Strain Induced Topological Phase Transition in Bismuth-Tellurohalide–Graphene Heterostructures [18]

Zoltán Tajkov, Dávid Visontai, László Oroszlány, János Koltai

Nanoscale 11, 12704-12711 (2019) https://doi.org/10.1039/C9NR04519H

We explored the electronic structure and topological phase diagram of heterostructures formed of graphene and ternary bismuth tellurohalide layers. We constructed an effective tight binding description for low energy excitations and fitted the model's parameters to ab initio band structures. We proposed a simple approach for predicting phase boundaries as a function of mechanical distortions.

C3) Topological Phase Diagram of BiTeX–Graphene Hybrid Structures [19]

Zoltán Tajkov, Dávid Visontai, László Oroszlány, János Koltai

Appl. Sci., 9(20), 4330 (2019) https://doi.org/10.3390/app9204330

Strong spin-orbit coupling in BiTeX compounds and the recent fabrication of a single layer of BiTeI points towards a feasible experimental realization of a Kane–Mele phase in graphene-based heterostructures. In this paper we theoretically demonstrated the tunability of the topological phase by mechanical strain.

C4) Competition of topological and topologically trivial phases in patterned graphene based heterostructures [21]

Zoltán Tajkov, János Koltai, József Cserti, and László Oroszlány

Phys. Rev. B 101, 235146 (2020) DOI: https://doi.org/10.1103/PhysRevB.101.235146

We explored the effect of mechanical strain on the electronic spectrum of patterned graphene based heterostructures. We focused on the competition of Kekulé-O type distortion favoring a trivial phase and commensurate Kane-Mele type spin-orbit coupling generating a topological phase. We derived a simple low-energy Dirac Hamiltonian incorporating the two gap promoting mechanisms and include terms corresponding to uniaxial strain. The derived effective model explains previous ab initio results through a simple physical picture. We showed that while the trivial gap is sensitive to mechanical distortions, the topological gap stays resilient.

D) Magnetic heterostructures [**12**,13,14] CIT=16

D1) Topological and trivial magnetic oscillations in nodal loop semimetals [12]

László Oroszlány, Balázs Dóra, József Cserti, and Alberto Cortijo

Phys. Rev. B 97, 205107 (2018) | DOI: 10.1103/PhysRevB.97.205107

Topological nodal semimetals are three dimensional semimetallic systems where the valence and conduction bands closest to the Fermi level cross each other in momentum space. In the case of Weyl/Dirac semimetals, the crossing consists of a discrete set of points, while in the case of nodal loop semimetals (NLSM), the crossing takes the form of a closed loop. In this work we presented a comprehensive theoretical description of magnetic oscillations present in these novel systems. Based on simple topological arguments backed by a semiclassical analysis we constructed the phase diagram for finite chemical potential and arbitrary field orientation and contrasted it to numerical calculations.

D2) Site-Resolved Contributions to the Magnetic-Anisotropy Energy and Complex Spin Structure of Fe/MgO Sandwiches [13]

Ramón Cuadrado, László Oroszlány, András Deák, Thomas A Ostler, Andrea Meo, Roman V Chepulskii, Dmytro Apalkov, Richard FL Evans, László Szunyogh, Roy W Chantrell

Phys. Rev. Applied 9, 054048 (2018) | DOI: 10.1103/PhysRevApplied.9.054048

In this work we presented a fully relativistic electronic structure study of the exchange interactions and the site-resolved MAE of ⋯MgO/nFeFe/MgO⋯ [nFe=4, 8] sandwiches. Our results reveal a dominant contribution to the MAE from the two-ion exchange anisotropy. Furthermore, we show that the competing ferromagnetic and antiferromagnetic interactions at the Fe/MgO interface lead to an overall ferromagnetic ground state but which includes a frustrated spin spiral at the interface, which destabilizes the magnetization of the interfacial layer at elevated temperatures, leading to a reduction of the Curie temperature of the system.

D3) A multiscale model of the effect of Ir thickness on the static and dynamic properties of Fe/Ir/Fe films [14]

Ramón Cuadrado, László Oroszlány, László Szunyogh, Gino Hrkac, Roy W. Chantrell & Thomas A. Ostler

Scientific Reports, 8, 3879 (2018) | DOI: 10.1038/s41598-018-21934-5

The focus of this work was on the effects of the Ir thickness and how the exchange interactions govern the ground state and thermal properties of the system. The tensorial exchange interactions were calculated within the Korringa–Kohn–Rostoker (SKKR) code in the spirit of Liechtenstein.

E) Special materials [17,**20**] CIT=15

E1) Magic Number Theory of Superconducting Proximity Effects and Wigner Delay Times in Graphene-Like Molecules [17]

Peter Rakyta, Asma Alanazy, Andor Kormanyos, Zoltan Tajkov, Gergo Kukucska, Janos Koltai, Sara Sangtarash, Hatef Sadeghi, Jozsef Cserti, and Colin J. Lambert

J. Phys. Chem. C, 123 , 11, 6812-6822 (2019) DOI: https://pubs.acs.org/doi/10.1021/acs.jpcc.8b11161

We demonstrated that ratios of transport properties can be predicted easily using tables of 'magic numbers,' which capture the connectivity dependence of superconducting proximity effects and Wigner delay times within molecules. These numbers are calculated easily, without the need for large-scale computations. For normal-molecule-superconducting junctions, we find that the electrical conductance is proportional to the fourth power of their magic numbers, whereas for superconducting-molecule-superconducting junctions, the critical current is proportional to the square of their magic numbers.

E2) Signature of Large-Gap Quantum Spin Hall State in the Layered Mineral Jacutingaite [20]

Konrád Kandrai, Péter Vancsó, Gergő Kukucska, János Koltai, György Baranka, Ákos Hoffmann, Áron Pekker, Katalin Kamarás, Zsolt E. Horváth, Anna Vymazalová, Levente Tapasztó, and Péter Nemes-Incze

Nano Lett. 20:7 5207–5213 (2020) DOI: https://doi.org/10.1021/acs.nanolett.0c01499

In this work, we showed that the layered mineral jacutingaite (Pt_2HgSe_3) is a candidate quantum spin Hall (QSH) material, realizing the long sought-after Kane–Mele insulator. During the work, we investigated the jacutingaite with first principles density functional theory, with special emphasis on its topological properties. We simulated several spectral properties such as topographic STM images, Raman spectrum or differential tunneling conductivity (STS). The obtained results were discussed and compared with the experimental findings of the MTA Lendület group led by Péter Nemes-Incze.

Most of the research were done in collaboration with experimental partners. The most important partners were prof. Hans Kuzmany (Vienna University, Vienna, Austria) and Levente Tapasztó and Péter Nemes-Incze (Centre for Energy Research, Institute of Technical Physics and Materials Science, Nanotechnology Department, Budapest).

The number of publications with reference to the NKFI-115608 project is 22. The cumulative impact factor of these publications is 106,564. The number of independent citations is 146 until now, according to MTMT2.

The two most highly cited papers are B1 and B5, the number of independent citations is 18 for each.

Budapest, 30th August 2021.

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Jenő Kürti, PI