

Interband and plasma excitations in single-walled carbon nanotubes and graphite in inelastic x-ray and electron scattering

C. Kramberger,¹ E. Einarsson,² S. Huotari,³ T. Thurakitserree,² S. Maruyama,² M. Knupfer,⁴ and T. Pichler¹¹*Faculty of Physics, University of Vienna, Strudlhofgasse 4, A-1090 Vienna, Austria*²*Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*³*European Synchrotron Radiation Facility, Boîte Postale 220, F-38043 Grenoble Cedex 9, France*⁴*IFW Dresden, Helmholtzstraße 20, D-01069 Dresden, Germany*

(Received 25 January 2010; revised manuscript received 9 April 2010; published 7 May 2010)

The dynamical structure factor $S(q, \omega)$ in graphite, freestanding thin-bundled single-walled carbon nanotubes and bulk aligned nanotubes is probed by means of inelastic x-ray and electron scattering. We utilize the equivalency and complementarity of the two techniques in our combined approach. Both independent methods may be joined seamlessly. The joint extended experimental access to the plasmon dispersion exposes vividly the transition from screened plasmons at low momenta to uniform interband transitions at high momentum transfers.

DOI: [10.1103/PhysRevB.81.205410](https://doi.org/10.1103/PhysRevB.81.205410)

PACS number(s): 73.22.Lp

I. INTRODUCTION

The atoms in a flat, sp^2 -bonded carbon sheet are arranged in a hexagonal honeycomb structure. The graphene sheet is the basic building block of hierarchical materials such as graphite or single-walled carbon nanotubes (SWNTs), which are essentially rolled-up strips of graphene. Different densities and dimensionalities may be constructed from the versatile carbon sheets. The local dimensionality as well as the macroscopic density are crucial for collective phenomena, such as charge-density waves^{1,2} or effective exciton binding energies.^{3,4} Charge-density waves can propagate in a solid, and possess a momentum state.^{5,6} They may be accessed experimentally by inelastic scattering events, and stem from the loss function that is readily derived from the complex dielectric function $\epsilon(\omega)$ as $\phi(\omega) = \text{Im}\{-1/[\epsilon(q, \omega)]\}$. The integral in the f -sum rule $\frac{\pi}{2}\omega_p^2 = \int d\omega \omega \phi(\omega)$, where the plasma frequency is introduced as $\omega_p^2 = n_e e^2 / m_e \epsilon_0$, scales with the density of electrons n_e . Thus, plasmon frequencies are upshifted at higher electron densities. Due to this screening, a plasmon's energy always lies above the corresponding interband transition.

A material's loss function is composed of individual plasmons that in conventional matter arise at the zeros of the real part of the generalized dielectric function $\text{Re}[\epsilon(q, \omega)] = 0$. In very thin media or in individual molecules, as well as, isolated nano-objects, there is however no sufficient collective charge-carrier density to corroborate a vanishing $\text{Re}[\epsilon(q, \omega)]$. In this case the observed plasmons can no longer be envisaged as density waves in a plasma but they are constituted of material-specific electronic interband transitions.⁷

To date, there have been two entirely independent approaches to experimentally probe the momentum-dependent loss function $\phi(q, \omega)$. These two approaches use either inelastically scattered x-rays or electrons, both of which may excite propagating plasmons for energies of several eV and momentum transfers of a few \AA^{-1} . Both methods probe the loss-function in their own unique way. From an experimental point of view the most crucial distinction lies in the magni-

tude as well as the different scaling of the cross section with the scattering angle or momentum transfer q . The scalings are $\propto q^2$ for Thomson scattering and $\propto 1/q^2$ for Rutherford scattering of x-rays and electrons, respectively.

Here, we utilize archetypical sp^2 carbon systems like graphite and SWNTs to experimentally access the momentum resolved loss function as probed in inelastic x-ray scattering (IXS). The results are merged with earlier studies of the momentum dependent loss-function as probed by angle-resolved electron energy-loss spectroscopy (AR-EELS) on graphite,⁸ bulk SWNT (Ref. 9), and thin bundled and vertically aligned SWNT (VA-SWNT).¹⁰ In comparison to other's earlier studies¹¹⁻¹³ we present the full angle resolved dispersion relation combining both methods. Regarding the plasmon dispersion, thin-bundled SWNTs (Ref. 14) reveal in comparison to bulk material a fundamental change in the shapes as well as a shift in the absolute positions. The very different plasmon dispersions at small to intermediate momentum transfers q are strongly contrasted by a uniform plasmon response in the limit of high q . These stark effects can be understood in terms of a wavelength dependent effective charge carrier density. They are ultimately imprints of the varied macroscopic charge-carrier densities as well as the internal morphologies in the different superstructures of carbon sheets. Nanostructured sp^2 carbon architectures are a showcase example of a precisely tunable plasmon response and hence offer a significant potential for engineering purposes.

II. EXPERIMENTAL

Forests of vertically aligned and $\sim 50 \mu\text{m}$ long SWNTs were grown by chemical vapor deposition using static alcohol vapor and a binary Co/Mo catalyst.¹⁵ Two as-grown films were removed from their quartz substrates using warm water and transferred onto standard Cu TEM grids.¹⁶ The total thickness of the stacked vertically aligned SWNTs is $\sim 100 \mu\text{m}$. The grid-supported SWNTs as well as empty TEM reference grids were mounted over a 2-mm-wide slit in a $20 \times 20 \times 1 \text{ mm}$ steel plate. A $500 \mu\text{m}$ thick sample of

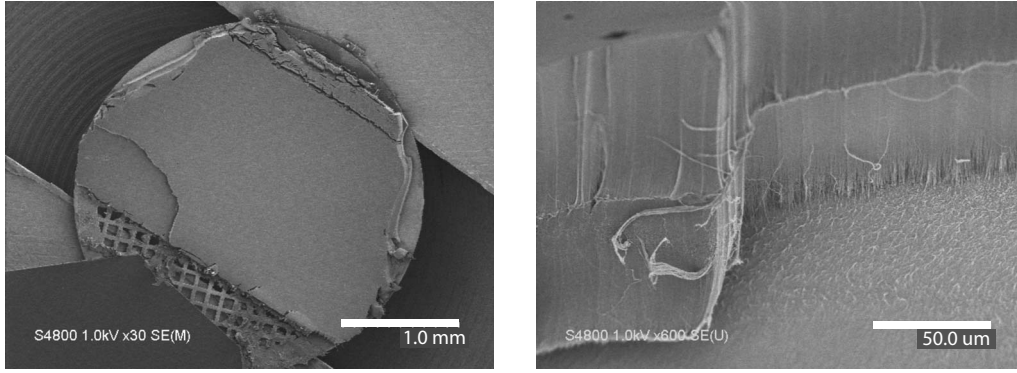


FIG. 1. Left panel overview SEM micrograph of the homogeneous double-layered sample on a TEM grid crossing the 2-mm-wide gap in the sample holder. The only single-layered region can be seen on the left. Right panel: perspective view of the bilayer structure of thin-bundled VA-SWNT forests. The micrographs were taken after the IXS measurements.

turbostratic graphite was used as a reference for archetypical bulk sp^2 carbon.

IXS experiments were conducted at beamline ID16 of the ESRF in Grenoble.¹⁷ The radiation from three consecutive undulators was monochromatized by a cryogenically cooled Si(111) premonochromator and a Si(220) channel-cut secondary monochromator. Si(660) analyzer crystals were used in the Rowland-circle geometry (bending radius 1 m). The total energy resolution in the measurements was 0.75 eV. Depending on the orientation of the samples, spectra were either recorded in transmission or reflection geometry. In the former the momentum transfer is perpendicular to and in the latter q is parallel to the net alignment of the SWNTs in the stacked films. The momentum transfer spread along the analyzer crystals was limited by slitting the analyzers down to $\Delta q = 0.1 \text{ \AA}^{-1}$. The samples were measured at ambient temperature and under vacuum to avoid spurious x-ray scattering from air.

The morphology of the VA-SWNT double layer was confirmed before and after IXS measurements by scanning electron microscopy (SEM, Hitachi S-4800 operated at 1 kV).

III. RESULTS AND DISCUSSION

In Fig. 1 we show the overall morphology of our thin-bundled SWNT forests. The micrographs taken after the IXS experiments clearly show that the majority of the sample area is indeed a uniform bilayer structure, and that the height of each forest is $\sim 50 \text{ }\mu\text{m}$.

The dispersive loss functions of highly ordered pyrolytic graphite (HOPG) and thin-bundled VA-SWNTs are shown in Fig. 2. The momentum transfer along the basal planes of the turbostratic layers in HOPG is reminiscent of the inherent spread of chiralities for q along the axis of the aligned SWNTs. The probed momentum transfers q extend from 0.5 up to 2.75 \AA^{-1} . The archetypical in-plane loss function of all sp^2 carbon comprises the mono-modal π and the structured $\pi + \sigma$ plasmons. In the present case the dispersive π plasmon is observed between energy losses of 7 and 12 eV, and the maximum of the $\pi + \sigma$ plasmon is observed in the range between 20 and 40 eV. The in-plane average of HOPG is in excellent agreement with earlier IXS studies on a graphitic

single crystal.¹³ While most of the spectral features show a dispersive behavior, there is also one localized peak resolved at $\sim 15.5 \text{ eV}$. In the earlier studies¹³ this feature, which becomes more pronounced at higher q , has been assigned to the non-dispersing c axis $\sigma \rightarrow \pi^* / \pi \rightarrow \sigma^*$ response of graphite. The non-dispersing c -axis excitation may also be discerned in the aligned VA-SWNTs at the same position.

Dispersive behavior is only observed for the in-plane π and $\pi + \sigma$ plasmons that can propagate in the graphene sheet. The dispersive plasmons are strongly affected by different densities in the graphite or thin bundled SWNT architecture. The energies of the dispersive π and $\pi + \sigma$ plasmons in thin-bundled SWNTs are, as shown in Fig. 2, noticeably lowered with respect to bulk HOPG. Noteworthy, the shift in peak positions is only well observed at small q , but not found at high q .

In bulk graphite, the same upshift of in-plane plasmon frequencies^{18,19} with respect to the inter-band transitions from optical absorption²⁰ is a long established finding. However in the present case we experimentally demonstrate that the effect of the macroscopic screening is strongly dependant

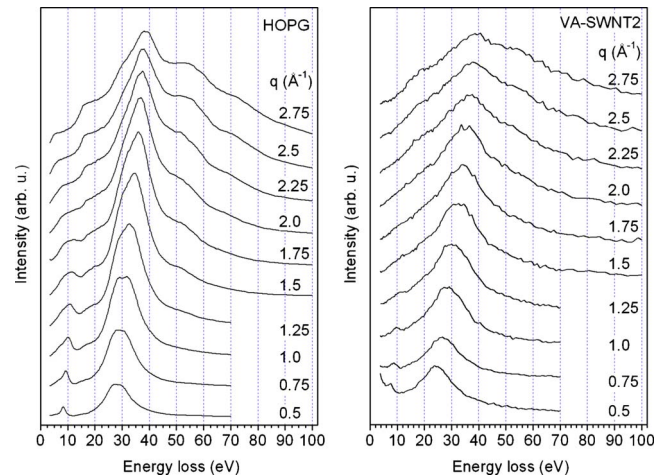


FIG. 2. (Color online) *Left panel*: IXS spectra of HOPG as recorded at 9.68 keV for increasing q in the basal plane. *Right panel*: the corresponding IXS spectra of a VA-SWNT film with q along the net alignment.

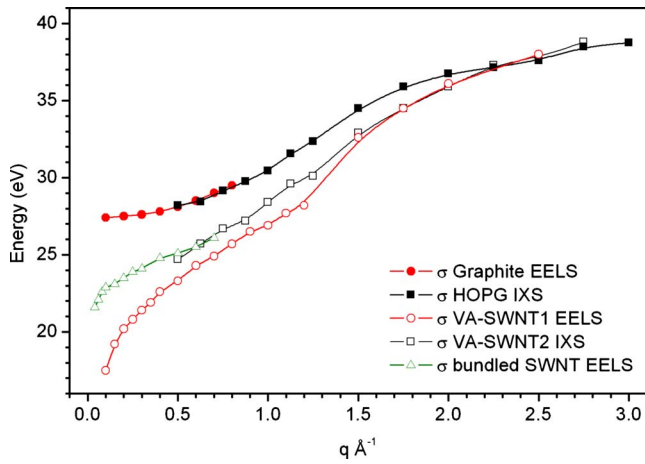


FIG. 3. (Color online) Dispersion of the $\pi+\sigma$ plasmon in Graphite, (Ref. 8) bundled bulk SWNT, (Ref. 9) VA-SWNT1 (Ref. 10), and VA-SWNT2.

on the actual character of a loss feature. Plasmons that occur at real zeros of $\epsilon(q, \omega)$ are strongly affected, but electronic excitations with a low oscillator strength show no noticeable shift with the charge carrier density. The direct comparison of the plasmon energies observed in the current IXS experiments with earlier AR-EELS results^{10,21} on similar films of vertically aligned SWNTs reveals that the $\sim 100 \mu\text{m}$ -thick VA-SWNT films used currently have a noticeably higher macroscopic density than the typically $5 \mu\text{m}$ thick films that were used previously. The previous VA-SWNT1 batch has been grown in a steady ethanol vapor stream²² and the current VA-SWNT2 batch has been grown in static ethanol vapor.¹⁵ The higher density and thickness of the present thin-bundled VA-SWNT forests is also an experimental necessity to perform inelastic x-ray scattering.

The dispersion of the $\pi+\sigma$ plasmon in graphite, measured by AR-EELS and IXS, is compared to the dispersion of the $\pi+\sigma$ plasmon in thin-bundled VA-SWNTs in Fig. 3. The momentum transfer q is always in the basal plane of HOPG or graphite or along the axis of the net-aligned nanotubes. The most striking observation is that the $\pi+\sigma$ dispersions along k_x (the armchair direction) in single-crystalline graphite⁸ and the uniaxial in-plane $\pi+\sigma$ dispersion in HOPG lie on the same curve. The quantitative match of the dispersions of the $\pi+\sigma$ plasmon as measured in IXS and AR-EELS demonstrates explicitly that both methods are indeed accessing the very same specific plasmon excitations, and may be combined seamlessly. However, as the scattering angle and hence the momentum transfer q is varied, there is a crucial difference in the respective electron-electron or x-ray-electron scattering cross sections involved. In AR-EELS the cross section scales as $1/q^2$, which renders it the method of choice for small q . In IXS, the cross section increases with q^2 , making it advantageous for measuring at higher momentum transfers. The combination of these equivalent techniques with complementary domains unlocks a wide range of q for the observation of the full dispersion relation of the electronic excitations.

The overall observation on the $\pi+\sigma$ plasmon dispersion in thin bundled VA-SWNT, bundled SWNT and graphite is,

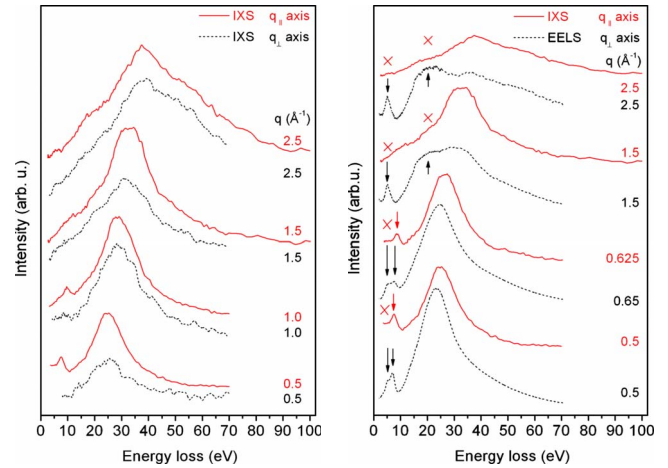


FIG. 4. (Color online) *Left panel*: Loss-functions of a VA-SWNT film as measured with IXS in transmission (q_{\perp}) and reflection (q_{\parallel}) geometry. *Right panel*: the loss function of VA-SWNT films as measured in transmissive (q_{\perp}) AR-EELS (Ref. 10) and reflective (q_{\parallel}) IXS.

that their plasmon energies differ greatly at small q on the left hand side in Fig. 3, but they have converged at high q on the right-hand side. First the $\pi+\sigma$ plasmon dispersions of the two different batches of the present thin bundled and the earlier individual VA-SWNTs converge, before only at the highest q even those of SWNT and HOPG meet. The slightly offset positions still agree well within the broadened peak widths. The nonuniform effect of the systems densities directly uncovers the evolution of the character of the loss-function with increasing q from collective plasmons to bare electronic interband excitations. Despite the very different model descriptions we observe a smooth transition from one to the other as the dielectric function evolves continuously.¹³

Recent *ab initio* calculations on $\phi(q, \omega)$ of single and bilayer graphene,¹⁰ in the framework of time-dependent density-functional theory with the inclusion of local field effects, provide quantitative insight into this interpretation. The long-reaching Coulomb interaction diminishes with decreasing wavelengths $\lambda=1/q$ as λ^2 . At small q and long λ , plasmons respond to the macroscopic screening from a large volume, but as q increases only the local density in a decreasing volume is probed. The momentum transfer q drives the transition from an unfocused probe of the density in the superstructure to a focused probe of the internal density. With the focused probe, there is no longer a distinction between sparse forests of thin-bundled VA-SWNTs and bulk HOPG.

The loss-functions of thin bundled VA-SWNTs as measured in transmission and reflection geometry are shown in Fig. 4 next to the comparison of the two VA-SWNT batches loss-functions as measured in IXS and AR-EELS. In IXS we find that q_{\perp} gives only a faint loss-function as compared to q_{\parallel} . This is a direct consequence of the alignment of the VA-SWNTs perpendicular to the surface of the film. Plasmons with a certain q can in thin bundled VA-SWNT only propagate along the bundles, so only the fraction of VA-SWNT with suitable orientations for a given q vector can contribute to $\phi(q, \omega)$. The challenging low count rate and inferior statistics for q_{\perp} stem from the very diminutive fraction of tubes

that are actually parallel to the films surface. Within the given statistics there is no substantial difference between q_{\perp} and q_{\parallel} for the same absolute value of q , other than the number of scattering tubes. AR-EELS is for technical reasons only possible in transmission geometry and is best suited for q_{\perp} . The same isotropy disregarding relative countrates for different scattering geometries around q_{\perp} is observed in AR-EELS.²¹ If a given SWNT, due to its actual orientation, contributes to q_{\perp} scattering events then it does it in the very same way as those SWNTs that show up in q_{\parallel} .

The direct comparison of the loss functions of thin bundled SWNT as measured in IXS and AR-EELS in Fig. 4 reveals a clear difference. While AR-EELS observes for the π as well as the $\pi+\sigma$ excitations always a pair of a dispersive and a localized loss-feature. There are always only the dispersive loss features visible in IXS in either scattering geometry. While the two experiments are evidently a perfect match for propagating plasmons, there is a striking contrast for localized excitations. The internal morphology may not only continually alter plasmons, but it may also give rise to novel excitations. A SWNT or thin bundle of the latter is, in one direction, a wire, that supports propagating excitations with a defined momentum state. In the perpendicular plane it is an isolated quantum dot, where there may be localized excitations with discrete angular momenta. While interband transitions will definitely require more elaborate theoretical methods⁶ it can be calculated directly²³ that all free charge-carrier ring modes on a metallic rod are degenerate. At sufficiently low bulk filling ratios the individual rods are isolated and a localized surface plasmon emerges for perpendicular q_{\perp} . For interacting metallic tubes²⁴ several perpendicular plasmon branches are predicted. However, they are not accessible in the present bulk average of varying bundles. The results in Fig. 4 are also unexpected within an alternative interpretation,²⁵ that associates the π plasmon structure in AR-EELS with the distribution of chiralities in SWNT. Alternatively, the difference in the emergence of localized plasmons in the right panel of Fig. 4 may have two plausible causes. First, the differences might originate from different local nanotube density distributions in the two batches of material. Second, although Fig. 3 demonstrates the equivalency of IXS and EELS in bulk materials, there might arise fundamental differences in the selection rules for electron and x-ray scattering in the realm of isolated nanostructures, where the dielectric response is governed by local field effects. In the latter context it is an entirely open issue if IXS experiments analogous to microscopic and angle integrated EELS experiments on nanotubes^{11,12} could, in principle, retrieve the very same spatial distribution of plasmon modes.

The dispersion relations of the π plasmon for q in the basal plane of a graphite single crystal and turbostratic graphite, and q along net-aligned bulk and thin-bundled SWNTs are displayed in Fig. 5. The π plasmon can be traced beyond 1 \AA^{-1} in HOPG and VA-SWNTs before it can no longer be discerned from the onset of the structured $\pi+\sigma$ response. The anisotropy of the π plasmon in the plane of the graphene sheets is displayed in the mismatch of the in-plane averaged dispersion in HOPG and the dispersion along k_x (armchair direction) in the graphite single crystal. Note,

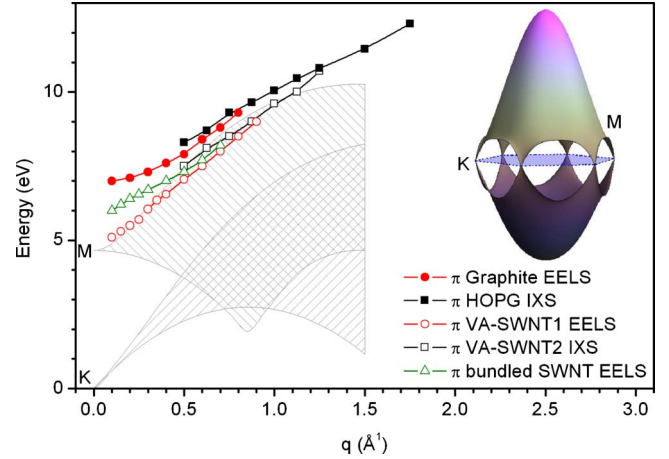


FIG. 5. (Color online) Dispersion of the π plasmon in Graphite, (Ref. 8) bulk bundled SWNT, (Ref. 9) VA-SWNT1 (Ref. 10), and VA-SWNT2. The shaded areas mark the domain of bare single-electron excitations rooting from either the K or the M point in the band structure of graphene, as shown in the inset.

that the $\pi+\sigma$ dispersions in Fig. 3 are the same experimental data as in Fig. 2. The π plasmon is just like the $\pi+\sigma$ plasmon also evolving due to the changes in the effective electronic densities with increasing q . First, the π dispersions of the two batches of VA-SWNTs with different densities meet before they branch into the dispersion of the HOPG. Since the optical limit at $q=0$ of the π dispersion in the thinner batch of VA-SWNTs quantitatively matches optical absorption measurements^{10,26} it is right from the beginning characterized as an interband transition. The two-dimensional band structure of graphene is plotted in the inset of Fig. 5. We used a parameterized tight binding scheme that was fitted to *ab initio* GW calculations as well as angle-resolved photoemission experiments²⁷ on graphite. The shaded areas plotted together with the experimentally observed π plasmon dispersions show the range of energies accessible from the K point at the Fermi level as well as from the dominant van Hove singularity at the M point. Neither of these regions can directly corroborate the observed dispersion relation alone, which points at local field effects beyond the independent electron picture. The relevance of local field effects in isolated or bilayer graphene was exemplified by clear deviations from the framework of independent particle transitions in the quantitative description of the linear π plasmon dispersion¹⁰ as well as the optical absorption.²⁸ The present nonlinear dispersion relations are proposed to be the result of a finite wavelength dependency of the local field effects in the different superstructures of sp^2 carbon. While such generalized local field effects offer a footing for a quantitative description of the observed dispersion relations, the mere complexity of these superstructures are to date beyond the reach of *ab initio* calculations.

IV. SUMMARY

We employ superstructures of sp^2 carbon sheets with different densities and effective dimensionalities to experimen-

tally address the influence of the latter on the dynamics of archetypical π and $\pi+\sigma$ plasmons. The seamless joining of the $\pi+\sigma$ plasmon dispersions from IXS and AR-EELS demonstrates that electrons and x-rays are equivalent probes of inelastic scattering events, but they are accessing complementary domains in q . We observe that the itinerant π as well as the $\pi+\sigma$ plasmons are affected by the macroscopic density, while the localized $\sigma\rightarrow\sigma^*$ plasmon is not. At low q , the energy of itinerant plasmons scales with the respective density before they turn only at high q into interband transitions. The crossover from plasmons to excitonic interband transitions is concomitant to the weakening of the Coulomb interaction with $1/q^2$, which tunes the plasmon response from a macroscopic probe of the density in the superstructure to a local probe of the internal density. We propose this in-

terpretation can be quantified in terms of wavelength dependent local field effects in the dielectric response of carbon nanostructures. The quantitative knowledge on the realms of collective excitations and inter-band excitations in hierarchical materials is a crucial step toward engineered electronic properties in man-made nano-structured materials.

ACKNOWLEDGMENTS

E.E. acknowledges support from the ‘‘Global Center of Excellence for Mechanical Systems Innovation’’ by the Japanese Ministry of Education, Culture, Sports, Science and Technology. T.P. acknowledges the DFG under Grant No. 440/3/5 and the FWF under Grant No. P21333-N20.

-
- ¹S. Das Sarma and E. H. Hwang, *Phys. Rev. B* **54**, 1936 (1996).
²M. F. Lin, *Phys. Rev. B* **62**, 13153 (2000).
³F. Wang, G. Dukovic, L. E. Brus, and T. F. Heinz, *Science* **308**, 838 (2005).
⁴C. D. Spataru, S. Ismail-Beigi, R. B. Capaz, and S. G. Louie, *Quasiparticle and Excitonic Effects in the Optical Response of Nanotubes and Nanoribbons* (Springer Verlag, Berlin, 2008), Vol. 111.
⁵P. Nozières and D. Pines, *Phys. Rev.* **113**, 1254 (1959).
⁶G. Onida, L. Reining, and A. Rubio, *Rev. Mod. Phys.* **74**, 601 (2002).
⁷H. Raether, *Excitation of Plasmons and Interband Transitions by Electrons* (Springer Verlag, Berlin, 1980), Vol. 88.
⁸A. G. Marinopoulos, L. Reining, V. Olevano, A. Rubio, T. Pichler, X. Liu, M. Knupfer, and J. Fink, *Phys. Rev. Lett.* **89**, 076402 (2002).
⁹X. Liu, T. Pichler, M. Knupfer, M. S. Golden, J. Fink, D. A. Walters, M. J. Casavant, J. Schmidt, and R. E. Smalley, *Synth. Met.* **121**, 1183 (2001).
¹⁰C. Kramberger *et al.*, *Phys. Rev. Lett.* **100**, 196803 (2008).
¹¹M. Kociak, L. Henrard, O. Stephan, K. Suenaga, and C. Colliex, *Phys. Rev. B* **61**, 13936 (2000).
¹²M. H. Upton *et al.*, *Carbon* **47**, 162 (2009).
¹³N. Hiraoka, H. Ishii, I. Jarrige, and Y. Q. Cai, *Phys. Rev. B* **72**, 075103 (2005).
¹⁴E. Einarsson, H. Shiozawa, C. Kramberger, M. H. Rummeli, A. Gruneis, T. Pichler, and S. Maruyama, *J. Phys. Chem. C* **111**, 17861 (2007).
¹⁵H. Oshima, Y. Suzuki, T. Shimazu, and S. Maruyama, *Jpn. J. Appl. Phys.* **47**, 1982 (2008).
¹⁶Y. Murakami and S. Maruyama, *Chem. Phys. Lett.* **422**, 575 (2006).
¹⁷R. Verbeni, T. Pykkänen, S. Huotari, L. Simonelli, G. Vankó, K. Martel, C. Henriquet, and G. Monaco, *J. Synchrotron Radiat.* **16**, 469 (2009).
¹⁸K. Zeppenfeld, *Z. Phys.* **211**, 391 (1968).
¹⁹E. Tosatti and F. Bassani, *Nuov. Cim. Fis. B* **65**, 161 (1970).
²⁰E. A. Taft and H. R. Philipp, *Phys. Rev.* **138**, A197 (1965).
²¹C. Kramberger, M. Rummeli, M. Knupfer, J. Fink, B. Buchner, E. Einarsson, S. Maruyama, and T. Pichler, *Phys. Status Solidi B* **245**, 2284 (2008).
²²S. Maruyama, E. Einarsson, Y. Murakami, and T. Edamura, *Chem. Phys. Lett.* **403**, 320 (2005).
²³J. M. Pitarke, J. E. Inglesfield, and N. Giannakis, *Phys. Rev. B* **75**, 165415 (2007).
²⁴T. McNeish, G. Gumbs, and A. Balassis, *Phys. Rev. B* **77**, 235440 (2008).
²⁵S. Dmitrović, T. Vukovic, B. Nikolic, M. Damjanovic, and I. Milosevic, *Phys. Rev. B* **77**, 245415 (2008).
²⁶Y. Murakami, E. Einarsson, T. Edamura, and S. Maruyama, *Phys. Rev. Lett.* **94**, 087402 (2005).
²⁷A. Grüneis, C. Attacalite, L. Wirtz, H. Shiozawa, R. Saito, T. Pichler, and A. Rubio, *Phys. Rev. B* **78**, 205425 (2008).
²⁸L. Yang, J. Deslippe, C. H. Park, M. L. Cohen, and S. G. Louie, *Phys. Rev. Lett.* **103**, 186802 (2009).