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Narrow gap carbon nanotubes as candidate excitonic insulators

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Summary. — Ultraclean suspended carbon nanotubes, predicted to be metallic by band theory, always exhibit a many-body transport gap at low temperature. Whereas the correlated ground state was early interpreted as a Mott insulator, it was more recently predicted that, in gapless (armchair) tubes, the gap is enforced by the permanent condensation of excitons. Here we investigate exciton instabilities in these carbon nanotubes. We show that the long range Colomb interaction remains largely unscreened even in the presence of Fermi points and stabilizes the excitonic insulator (EI) phase in all narrow-gap nanotubes. Moreover we show that the EI phase persists to observable temperatures for the large radii nanotubes commonly used in experiments.

1. – Introduction

Narrow-gap carbon nanotubes (NTs), when deposited on metals, present behaviour that are well described within independent-electrons models [1] and their gaps can be tuned up to metallic, for example, by an axial magnetic field [2]. In contrast, when suspended, all NTs are insulating, even under applied magnetic fields [3-5]. Their transport properties are believed to be determined by many-body electronic interactions and therefore a description beyond independent-electron models is required [3]. The nature of the Coulomb interactions responsible for the additional gap in suspended NTs is still under discussion. One possibility is that the short-range Coulomb interaction induces a Mott insulator phase [3, 4], while the long-wavelength contribution is cut-off by the electrostatic gates [6-8]. A competing explanation is that the NTs residual gap is actually caused by the long-range Coulomb force inducing an Excitonic Insulator (EI) phase [9, 10]. Excitons, electrons-holes bound by the Coulomb potential, behave at low temperatures as a weakly interacting bosonic gas and may condense above a critical density leading to an EI phase [11-13]. In reality, carriers recombination tends to prevent to reach the critical density, unless the long-range e-e interaction outweighs the energy cost of forming electron-hole pairs. Up to now, the EI phase has remained elusive. The prototypical systems where the EI phase is thought possible are low dimensional, indirect semiconductors and semimetals [14]. Carbon nanotubes are particularly interesting due to excitons having huge binding energies [15, 16], finite even in metallic tubes [17]. In a recent work, we proposed a new approach for the description of screening in NTs [18]. This approach gives e-e long-range interactions in good agreement with first-principles calculations. Here, we generalise to NTs with radii in the range of 4–12 Å, corresponding to narrow gaps in the order of tens of meV.

2. – Methods

The electronic structure of single-wall carbon NTs is modelled in the $\mathbf{k} \cdot \mathbf{p}$ approximation for graphene, extended to the tube geometry through zone folding [2, 15]. Near the corners of the Brillouin zone $\tau = K, K'$, the bands of NTs are truncated Dirac cones,

$$E_{c/v,\tau}(k) = s_{c/v}\gamma\sqrt{k_c^2 + k^2}, \tag{1}$$

where γ is the graphene band parameter and $s_{c/v}$ is, respectively, ± 1 for the conduction and valence bands. The direct gap $E_g^{\text{bare}} = 2\gamma k_c$ origins from curvature effects [19], and depends on the geometrical parameters of the NTs: the chiral angle θ and the radius R.

The zero momentum (direct) excitons of the NTs are determined solving the Bethe-Salpeter equation (BSE), that in the case of NTs can be written in the following form [15]:

$$E_\tau(k)\psi_{\tau\sigma}(k) - \sum_q \left(g(E_\tau(k)/2) - g(-E_\tau(k+q)/2)\right)(W^\tau_{k+q,k}$$
$$\psi_{\tau\sigma}(k+q) + V_1 \sum_{\tau'}\sum_{\sigma'} \psi_{\tau'\sigma'}(k+q) - V_2 \sum_{\tau'\neq\tau} \psi_{\tau'\sigma}(k+q)) = \mathcal{E}_u \psi_{\tau\sigma}(k),$$

where $\psi_{\tau\sigma}(k)$ is the excitonic wave function in the valley τ with spin index σ, $g(E)$ is the Fermi-Dirac distribution, $E_\tau(k) = E_{c\tau}(k) - E_{v\tau}(k) + \Sigma_\tau(k)$ is the formation energy of a free electron-hole pair. W, the long-range part of the Coulomb potential, is evaluated using the new effective mass (EM) screening model we developed in [18]. The short parts of the Coulomb potential V_1 and V_2, respectively associated to intravalley and intervalley scatterings, are written as in [9] since they are roughly constant in reciprocal space [20]. $E_\tau(k)$ includes also a self-energy Σ_τ computed in the screened Hartree-Fock approximation, and rescaled by a $\frac{1}{3}$ factor to match the quasiparticle energies predicted by first-principle calculations in the GW approximation in [5].

3. – Results

The BSE (eq. (2)) is solved at zero temperature focusing on the triplet state, the lowest-lying exciton. The triplet excitonic wave function in reciprocal space, shown in fig. 1(a)–(b) for the (18,0) zigzag and the (10,10) armchair carbon nanotubes, presents an excitonic state always localised in the region of the BZ around the K and K′ points (due to degeneracy). The picture is consistent with previous findings that show the exciton stretching for hundreds of nm along the NTs axis [9], with the excitons slightly more extended for armchair than for zigzag NTs.

Figure 1(c) shows the computed values of E_B compared with the single particle gap $E_g = E_c(0) - E_v(0) + \Sigma(0)$ in NTs of four different chiralities (labelled by the value of θ). The calculations were done considering a discretized BZ mesh of $N = 801$ k points. In the study, we consider NTs near the armchair configuration ($\theta = 29°$), where the energy gaps are relatively small, on the order of few meV —for instance, $E_g^{\theta=29°}(R = 4\ \text{Å})$ is

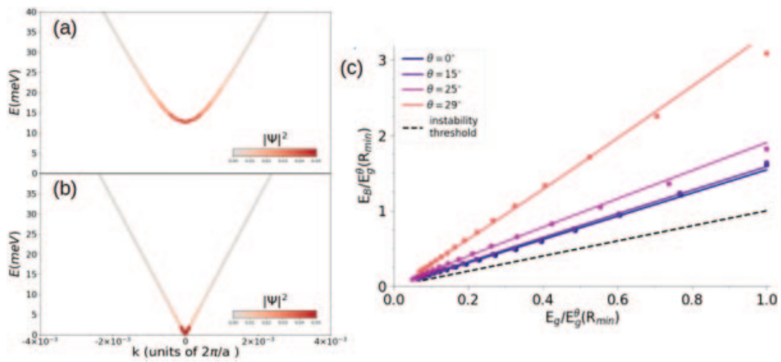

Fig. 1. – (a), (b): heat map of the triplet wave function $|\Psi|^2$ superimposed on the conduction band in the neighbourhood of the K point in the (18,0) zigzag and (10,10) armchair NTs, respectively. (c) Exciton binding energy E_B compared to the single particle gap E_g. The dashed line is the instability threshold. E_B and E_g are rescaled by $E_g^\theta(R_{min})$, a factor specific for each chirality θ equal to the value of E_g in the NT with same θ and R_{min}=4 Å.

6.8 meV. We also consider NTs with larger gaps, including the zigzag configuration ($\theta = 0°$), where the gaps can exceed 100 meV, as in the case of $E_g^{\theta=0°}(R = 4$ Å$)$ which reaches 196 meV. Despite considering NTs with gaps differing nearly by two orders of magnitude, E_B is found consistently larger than E_g (dashed line in the figure). This indicates that potentially all NTs are subject to an excitonic instability. In addition, the binding energy E_B proves to be consistently proportional to E_g in NTs of the same chirality; meaning that it acts as energy scale of the triplet state. This behaviour confirms out earlier work [18], where it was shown that the screened Coulomb potential W, responsible for the exciton binding, has a poorly screened long-range region whose extension depends on E_g. Given that the excitons are localized in reciprocal space and have E_B proportional to E_g and, consequently, to the effective mass $m^\star = E_g/2\gamma^2$, the lowest-lying triplet state can be depicted as an extremely bound Wannier-Mott exciton. A general expression for the NTs excitons' E_B cannot however be drawn as the proportionality factor depends on the chirality, ranging from 1.5 in tubes close to zigzag to 3 in tubes close to armchair.

We now study the dependence on temperature, by varying the fermionic occupation function $g(E)$ in eq. (2). The critical temperature T_c of the excitonic instability corresponds to the transition from a negative to a positive energy of the lowest-lying triplet. We neglect the temperature effect on the screened potential W, which likely, leads to a slight overestimation of the critical temperature. However, the overestimation is not significant, as the valence band should be only slightly depleted for $T < T_c$. Figure 2 shows the calculated T_c with respect to R for the NTs previously considered. The overall patterns of T_c are consistent with the dependence on E_g in fig. 1(c). The excitonic instability persists up to temperatures comparable with the formation energy of the e-h pairs. Figure 2(b) highlights a difference between the NTs: tubes with very small gaps have $T_c \approx E_g/k_B$, whereas for larger gaps $T_c \approx E_g/2k_B$. The difference is consistent with the dependence of E_B on E_g, that shows that, the smaller the narrow gap, the larger in comparison, the energy gain to form excitons (fig. 1(c)).

4. – Conclusions

In this work, we predict the presence of EI instabilities in narrow-gap carbon nanotubes independently of their chirality. We characterize the excitonic instability in terms

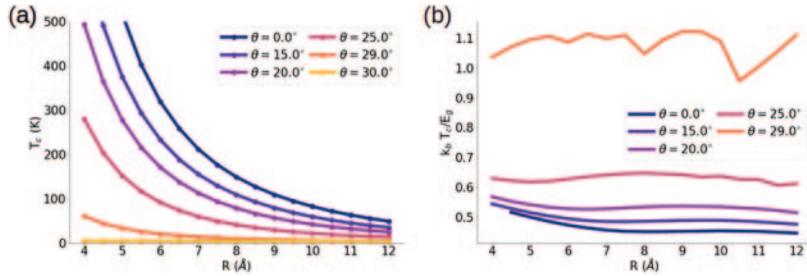

Fig. 2. – (a) Critical temperature T_c of the excitonic phase with respect to the radius in armchair and chiral NTs. (b) Critical temperature of the excitonic phase compared with the e-h formation energy in chiral NTs.

of an energy scale, which corresponds to the magnitude of the narrow-gap and is directly related to the binding energy by a factor greater than unity. This leads to the emergence of excitonic instability. The study of the temperature dependence reveals that the excitonic instability persists up to temperatures comparable to the excitation energy of free e-h pairs. The critical temperature is shown to be in the range of 50–100 K for narrow-gap tubes with $R > 1$ nm, common in transport gaps investigations. These values provide an upper bound for the critical temperatures of NTs.

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