Emerging magnetism in boron-doped graphene nanoribbons

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Graphene nanoribbons (GNRs) are strong candidates as a platform for future nanoelectronics. On the one hand, they present a highly tunable electronic structure, that depends on the structure width and edge topology,[1] as well as on chemical functionalization[2] and doping[3]. On the other hand, they can be fabricated with atomic precision via bottom-up approaches, such as metal-catalysed on-surface synthesis,[4] and their electronic properties engineered through controlled growth.

Spin polarized states were long ago theoretically predicted on GNRs with zigzag edges[5] and more recently on the boundary of ribbons junctions and on the terminations of finite ribbons.[6] Nevertheless, unambiguous experimental observation of the magnetism in defect-free GNRs is still scarce, e.g., via spin-polarized scanning tunneling microscope (STM) or electron spin resonance (ESR) STM or Kondo fingerprints.

Here we present a joint theoretical and experimental determination of spin polarized states on 7-armchair GNRs induced by pairs of boron-substituted atoms in the ribbon backbone (2B-GNR). The presence of those states were revealed by a zero-bias Kondo resonance at electronic transport measurements, performed on a lift off configuration where the boron-doped GNR bridged the STM tip and the metallic substrate. First principles calculations via density functional theory (DFT) demonstrated that the Kondo signature can be associated to a spin 1/2 state localized in the suspended GNR when the first boron atom detaches from the metal (**Figure a**). After detaching the full boron pair segment, the magnetic state is predicted to evolve into a spin 1 state localized around the boron-group (**Figure b**). When two boron pair segments are put together, spin 1/2 states appear at the boundary between pristine and borylated segments. Therefore, depending on the concentration of the boron pair segments, different kinds of spin chains can be formed, making the 2B-GNRs attractive for spintronic devices.

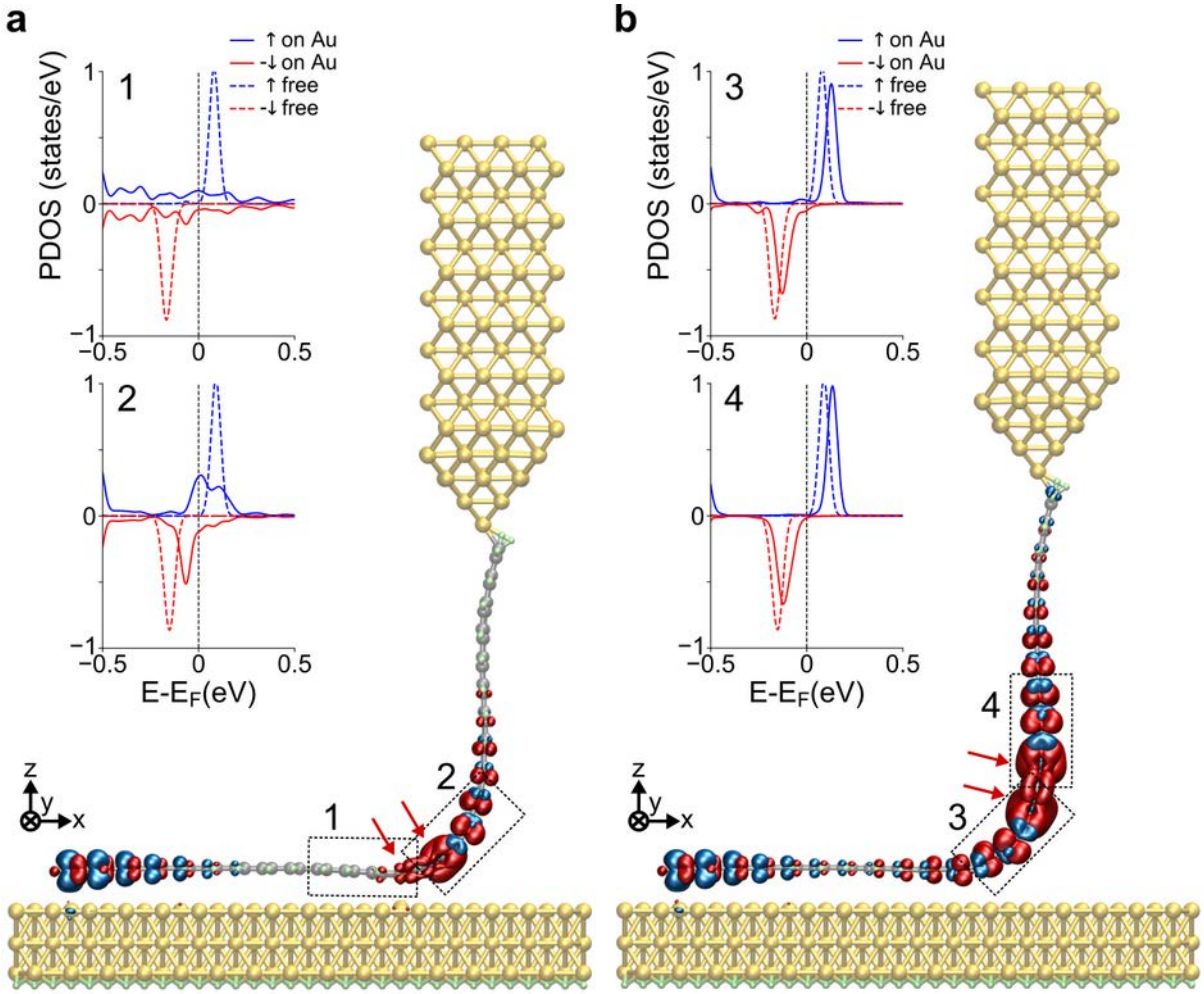

Figure: DFT optimized structures of two different configurations of a 2B-GNR contacted and lifted by a model STM tip. Red arrows indicate the position of the boron pair. Magnetization isosurfaces are shown over the atomic structure (1.7×10^{-3} e/Å^3, spin up in blue and down in red). The insets show the spin polarized density of states of a free standing ribbon (dashed lines) and of the contacted ribbons on the surface (solid lines) projected on the C and B atoms belonging to the regions marked with dashed rectangles in the atomic structures. The GNR zigzag termination holds a radical state with spin-polarization, which is quenched in the side contacted by the gold tip.

Support by the European Union FET Open project SPRING (grant 863098) and by the Spanish Ministry of Economy and Competitiveness, MINECO (grants FIS2017-83780-P and MAT2016-78293-C6).

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