Spontaneous Electric Polarization in Graphene Polytypes

Simon Salleh Atri
Wei Cao. Bar Alon, Nirmal Roy, Maayan Vizner Stern, Vladimir Falko, Moshe Goldstein, Leeor Kronik, Michael Urbakh, Oded Hod, Nirmal Roy, Moshe Ben Shalom
School of Physics and Astronomy, Tel Aviv Univercity, Tel Aviv Israel
simons@mail.tau.ac.il

A crystalline solid is a periodic sequence of identical cells, each containing one or more atoms. If the constituting unit cell is not centrosymmetric, charge may distribute unevenly between the atoms, resulting in internal electric polarization[1]. This effect serves as the basis for numerous ferroelectric, piezoelectric, and pyroelectric phenomena[2]. In nearly all polar materials, including multilayered van der Waals stacks that were recently found to exhibit interfacial polarization, inversion symmetry is broken by having two or more atomic species within the unit cell[3]–[11]. Here, we show that even elemental crystals, consisting of one type of atom, and composed of *non-polar* centrosymmetric layers, exhibit electric polarization if arranged in an appropriate three-dimensional architecture. This concept is demonstrated here for inversion and mirror asymmetric mixed-stacking tetra-layer polytypes[12] of non-polar graphene sheets. Furthermore, we find that the room temperature out-of-plane electric polarization increases with external electrostatic doping, rather than decreases owing to screening. Using first-principles calculations, as well as tight-binding modeling, we unveil the origin of polytype-induced polarization and its dependence on doping. Extension of this idea to graphene multilayers suggests that solely by lateral shifts of constituent monolayers one can obtain multiple meta-stable interlayer stacking sequences that may allow for even larger electrical polarization.

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