Intrinsic Diamagnetism and Defect & Impurity Paramagnetism in Graphene and Carbon Onions

A. M. Panich1*, A. I. Shames1, V. Yu. Osipov2, N. A. Sergeev3, K. Takai4

1 Department of Physics, Ben-Gurion University of the Negev, Be'er Sheva 84105, Israel
2 Ioffe Physical-Technical Institute, St. Petersburg 194021, Russia
3 Institute of Physics, University of Szczecin, 70-451 Szczecin, Poland
4 Department of Chemical Science & Technology, Hosei University, Tokyo, 184-8584, Japan
* pan@bgu.ac.il

We report on NMR, EPR and magnetic susceptibility study of graphene, graphene oxide and carbon onions. We obtain significant deviation of 1H NMR chemical shifts of water molecules adsorbed by graphene and carbon onions compared with those of bulk water and moisture adsorbed on nanodiamond surface. This deviation is attributed to the diamagnetic screening effect of conductive graphene layers with well-developed π-electronic system. This finding is supported by our magnetic susceptibility data, which show a pronounced correlation between the proton chemical shifts and diamagnetic contribution to the magnetic susceptibility. Magnitude of this effect depending on graphene crystallite size, density of defects and possible shift of the Fermi level through the doping by metal impurities and molecular adsorbates is discussed. 1H NMR spectra and relaxation data reveal high mobility of adsorbed water molecules.

Our measurements demonstrate that carbon nanoparticles exhibit weak paramagnetism caused by uncoupled electron spins of dangling bonds. However, we show that graphene and graphene oxide samples prepared by the Hummers method also reveal isolated Mn2+ ions originating from potassium permanganate used in the process of the sample preparation. We ascertain that these ions form paramagnetic charge-transfer complexes with the graphene planes and are the main contributors to the 1H and 13C spin–lattice relaxation. Several models of manganese ion binding to the graphene planes are discussed.

References: