

## Putting the Spin on Graphite: Observing the Spins of Impurity Atoms Align

The existence of magnetism in graphite is a very intriguing subject. The possibility to exploit the magnetic properties of a lightweight and robust material based on carbon that can also be produced and manipulated on the nanoscale fascinates scientists and engineers alike. Carbon-based materials can be made *e.g.* in the form of thin wires (1D), single atomic sheets called graphene (2D), or three-dimensional objects like cubes, balls etc. Researchers have also been successful in aligning such objects on the nano- and microscales in an effort to build functioning and useful devices. The concept for a device based on carbon nanotubes is depicted in Figure 1, which shows how such a tube can be used as a nanoscale x-ray detector. With the recent advance of “spintronics” – an area of science and technology which proposes to use the spin of electrons to store and process information instead of their charge as it is done conventionally – it has now become very desirable to find ways to make carbon-based nanomaterials magnetic. Hence, **introducing the spin into the carbon nanoworld**, will open the door to an entire new class of nanoscale magnetic devices.

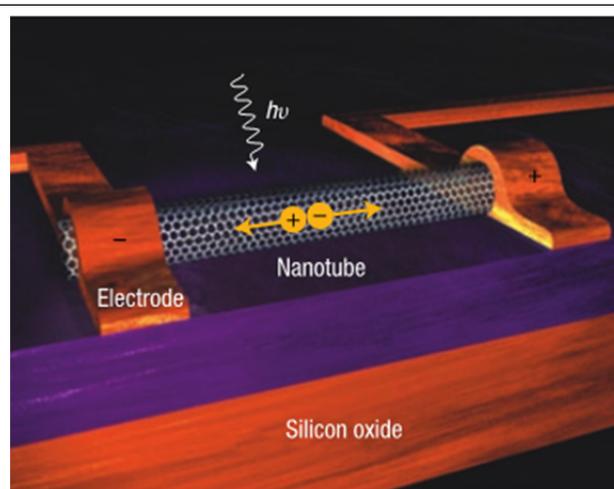


Figure 1: Schematic of a nanosized x-ray detector based on carbon nanotubes (from *Nat. Nanotechnol.* **2**, 605 (2007)).

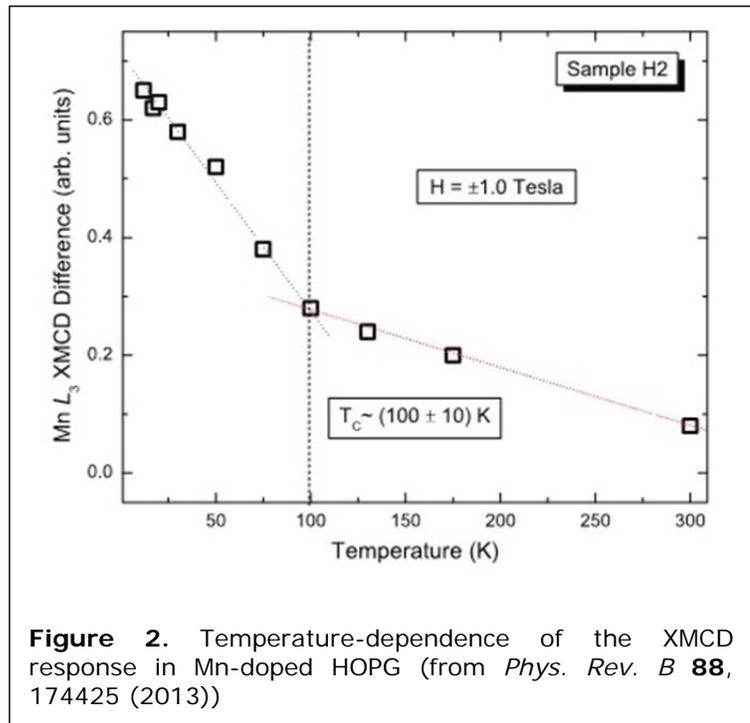
However, the potential magnetism of carbon-based materials is quite controversial from a scientific point of view. Unlike traditional magnetic materials, there are no *d*- or *f*-electrons present and it has long been discussed if long-range magnetic order is even possible in such a material. To characterize the magnetic properties of an unknown sample one often uses magnetometers like a SQUID (superconducting quantum interference device). However, a SQUID magnetometer measures the total magnetic moment of a sample, and it is not possible to pinpoint the exact microscopic origin of the magnetism and rule out the presence of other magnetic impurities as well. For this reason it is crucial to study the magnetism of carbon-based materials using element-specific magnetic probes like x-ray absorption spectroscopy. In x-ray absorption spectroscopy one uses an intense monochromatic beam of x-rays produced by a synchrotron and measures the rate of absorption as it changes with the energy of the x-ray photons. If the energy of the x-ray beam is tuned to the resonance of a particular atomic species in the sample it is possible to measure the magnetic moment of only this element in the sample (XMCD, X-ray Magnetic Circular Dichroism). Previously, SSRL researchers together with collaborators from the University of Leipzig in Germany used this approach to show that pure carbon can indeed be ferromagnetic without any additional magnetic impurities ([http://www-ssrl.slac.stanford.edu/research/c\\_ferromagnetism\\_summary.html](http://www-ssrl.slac.stanford.edu/research/c_ferromagnetism_summary.html) and <http://today.slac.stanford.edu/feature/2010/magnetic-carbon.asp>). So the question was now if it is possible to control and enhance the ferromagnetism of carbon by simply adding magnetic atoms in a controlled manner.

To address the question how magnetic impurities in carbon behave the researchers set out to study the magnetic ordering of manganese atoms (Mn) implanted into highly oriented pyrolytic graphite (HOPG). They used Mn for a particular reason. Over a decade ago many groups around the globe tried to introduce magnetism into semiconductors like gallium

arsenide (GaAs). For this reason they implanted Mn atoms into GaAs, since Mn exhibits a large magnetic moment. Unfortunately the magnetism of such samples vanished well below room temperature, with the highest Curie temperature reported around 173 K. Using both SQUID and XMCD in this present work they probed the magnetic properties of Mn-implanted HOPG and long-range magnetic order up to room temperature was observed. Since the efforts to establish ferromagnetism in this particular system are just at the beginning, the authors are optimistic that the magnetic ordering temperature can be further elevated in the not too distant future.

For our studies we doped HOPG substrates with Mn atoms by ion implantation at constant temperature. Implanted Mn atoms reacted with carbon and formed nanocrystals of three stable manganese carbides:  $Mn_7C_3$ ,  $Mn_5C_2$  and  $Mn_{23}C_6$ , as confirmed by the grazing-incident x-ray diffraction experiments performed at SSRL Beam Line 11-3. High-resolution cross-section tunneling electron microscopy (TEM) images also confirm the existence of embedded nanocrystals in HOPG. Using the element-specific XMCD probe, we were then able to observe that Mn atoms are indeed magnetically aligned inside the HOPG substrates due to the magnetic exchange mechanism between neighboring Mn atoms at 14 K. A magnetic response in the soft x-ray XMCD spectrum of Mn was found, indicating that Mn is indeed ordered ferromagnetically.

The temperature-dependence of the XMCD data revealed another interesting twist (Figure 2), by exhibiting a change of slope at around 100 K. The combination of state-of-the-art soft x-ray absorption spectroscopy performed at Beam Line 4.0.2 at the ALS and Beam Line 13-1 at SSRL as well as hard x-ray diffraction at Beam Line 11-3 at SSRL provides the answer to this riddle. X-ray diffraction data suggests the existence of small antiferromagnetic nanocrystals of  $Mn_{23}C_6$ . Because of their finite size these exhibit a small, nonzero magnetic moment originating from the surface of the nanocrystals and that moment will align along the local magnetic field inside the HOPG substrate. Above the Néel temperature of  $Mn_{23}C_6$  – which is approximately 100 K – that moment will vanish and result in a change of slope in the temperature-dependent XMCD. Above that temperature only ferromagnetically ordered Mn sites remain that are aligned by the internal magnetic exchange field between Mn sites mediated by the HOPG host.



Since the discovery of graphene, a great deal of research efforts have been geared towards carbon-based electronics materials. Today, it seems possible to imagine pure spin-logic using graphene interconnects and graphite magnetic quantum dots. The results described here present an important step in this endeavor. It began by asking the question if Mn-doping can be used to control and enhance the ferromagnetic properties of HOPG. So far it has been found that Mn-doping does indeed help to stabilize the magnetic order in HOPG at

room temperature. It will be particularly interesting to explore how the interplay of antiferromagnetic nanocrystals and ferromagnetically ordered dopant sites in the HOPG host can be exploited. The presence of antiferromagnetic nanocrystal may help stabilize the ferromagnetism in Mn-doped HOPG well above room temperature and enable the deployment of this material in future device applications. But an even more important step will be to investigate how the magnetic properties will change if Mn atoms are implanted into carbon nano-devices instead of continuous films as it was done for this study. Hence, state-of-the-art microscopes like the scanning transmission x-ray microscope for the study of magnetic materials at SSRL Beam Line 13-1 will play an important role in the future of this material.

### **Primary Citation**

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