

Structure-magnetic Properties of Rare-earth Metals Confined in Carbon Nano-spaces

Atoms and molecules confined in nano-sized spaces could have properties which are distinctly different from those of bulk solid or fluid. Carbon nano-space is an interesting space, which can confine atoms and molecules not only by van der Waals force but also by charge transfer interactions. Among them and of particular interest is the rare-earth metal atom confinement in carbon nano-space, namely, endohedral metallofullerenes and fullerene nano-peapods; fullerene nano-peapods are carbon nanotubes encapsulating fullerene molecules inside 1-dimensional channel (Fig. 1). These species of carbon nano-materials have attracted a wide range of researchers not only because of their specific structure and properties but also for various applications including gas sensors, optical devices, and field effect transistors [1,2]. Furthermore, in the case of nano-peapods, we expect novel transport properties correlated with the packing structure and the order-disorder of the orientated structures of encapsulated fullerene molecules. However, in the current stage, the synthetic yield of endohedral metallofullerenes (especially di- and tri-metallofullerenes) and therefore fullerene nano-peapods is very low, which presents an intrinsic difficulty for characterization of structure and properties of these novel compounds. Characterization using high brilliance synchrotron radiation is a very powerful method, which needs only a small amount of sample. Here we report the first structure-magnetic property characterization of Dy-metallofullerene (Dy@C_{82}) and the corresponding nano-peapods using synchrotron soft X-ray magnetic circular dichroism spectroscopy (SXMCD) and X-ray diffraction (XRD) [3].

Single wall carbon nanotubes (SWNTs) were synthesized using laser ablation method, in which a rotating graphite target containing Co/Ni catalyst was irradiated with Nd:YAG laser (wavelength is 532 nm) at 1200 °C. Dy@C_{82} was synthesized using arc-discharge and purified by multi-step high performance liquid chromatography. Nano-peapods were synthesized by gas-phase doping, in which SWNTs and purified Dy@C_{82} were vacuum-sealed in a Pyrex tube and heated at 500 °C for 2 days.

Figure 2 shows the X-ray diffraction pattern of nano-peapods and empty SWNTs measured at beamline BL02B2. As clearly illustrated in the figure, the XRD pattern changes drastically after the encapsulation of Dy@C_{82} molecules. Assuming SWNTs and Dy@C_{82} are represented by cylindrical and double spherical electron density, respectively, we can simulate the diffraction patterns that give the filling ratio and mean-intermolecular distance of encapsulated Dy@C_{82} ; the filling ratio is 60% and the intermolecular distance is 10.6 Å, which is much shorter than that of a bulk crystal of Dy@C_{82} . The fact that we can reproduce the observed XRD pattern of nano-peapods by a simple structure model means that the orientation of encapsulated Dy@C_{82} is random.

The temperature dependence of MCD spectra of metallofullerenes and nano-peapods clearly shows that the reciprocal magnetization of encapsulated lanthanide ions is proportional to temperature and the follows Curie-Weiss law (Fig. 1, measured at beamline BL25SU). The Weiss temperature of these ions is relatively low (11.6 and 5.2 K for nano-peapod and Dy@C_{82} , respectively), which means that magnetic interaction between encapsulated ions is weak. Curie constants are also different between nano-peapods

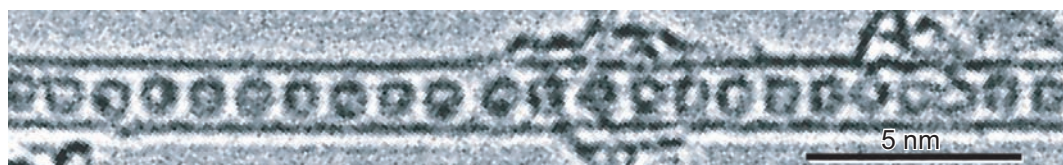


Fig. 1. High-resolution transmission electron microscope image of Dy@C_{82} encapsulating single walled carbon nanotubes. (scale bar corresponds to 5 nm).

and Dy@C₈₂, at 55.1 and 38.0 μ_B K for nano-peapods and Dy@C₈₂, respectively. The calculated effective magnetic moment of Dy ions based on Curie constants is 9.5 and 11.4 μ_B for the nano-peapods and Dy@C₈₂, respectively. This indicates that the encapsulation by nanotubes affects not only inter-Dy magnetic interactions but also the electronic structure of the Dy ion. Crystal field analysis of Dy³⁺ ions reveals that C_{2v} point symmetry with 10 meV energy splitting can represent the difference between nano-peapods and Dy@C₈₂. This means that the electric field acting on Dy³⁺ ions is different, which probably results from charge transfer between encapsulated Dy@C₈₂ and carbon nanotubes.

This study has shown that the interaction between SWNTs and encapsulated Dy@C₈₂ is not just a weak van der Waals interaction but a strong interaction, probably charge transfer, which means that we can expect novel properties that cannot be understood by a simple sum of contributions from SWNTs and encapsulated fullerene molecules.

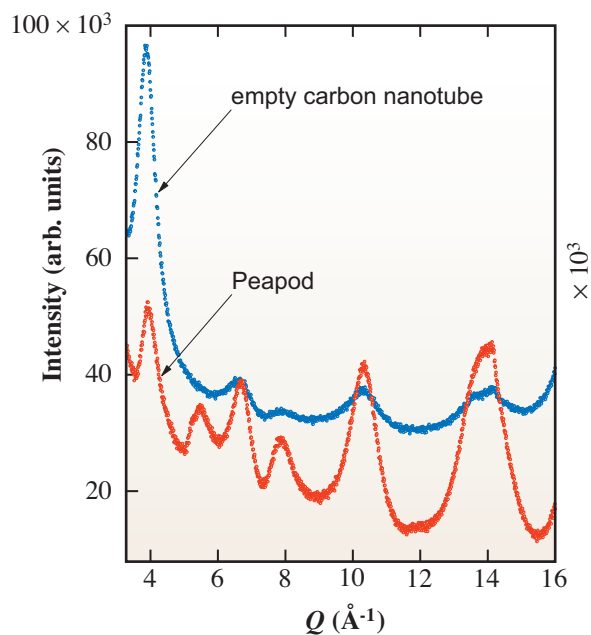


Fig. 2. XRD patterns of empty nanotubes and nano-peapods.

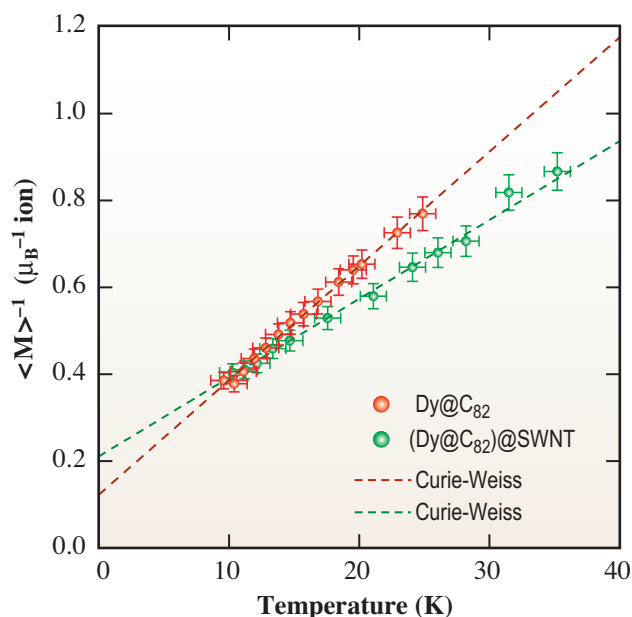


Fig. 3. Temperature dependence of reciprocal magnetization calculated from MCD measurements.

Ryo Kitaura

Department of Chemistry, Nagoya University

E-mail: kitaura@nano.chem.Nagoya-u.ac.jp

References

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