

Toroidal State in {Fe₈Dy₈} Ring Identified by High-Frequency Electron Paramagnetic Resonance

We synthesized a new ring shaped magnet {Fe₈Dy₈} in which the toroidal magnetic state is realized by the cooperation of a strong anisotropy of Dy ion and a substantial ferromagnetic exchange coupling between Dy and Fe ions. The high-frequency electron paramagnetic resonance measurement revealed the ferromagnetic exchange, otherwise the determination is difficult.

In magnetic recording materials, small ferromagnetic particles or ferromagnetic domains with unidirectionally aligned magnetic moments have been used for decades. When the size of the recording approaches the nanoscale, such uniform domain materials show a fundamental vulnerability for weak magnetic fields in the environment. In future societies with advanced electrification, the magnetic fields around us will increase substantially. This highlights the need to develop magnetic recording materials based on a novel concept.

Magnetic molecules are promising candidates for ultra-dense information storage applications. One of the features is the diversity of structures, such as linear, zigzag, star, and ring. Among them, the ring structure shows promise for the possible realization of toroidal magnetic structures. There are two distinguished states in a toroidal structure: the left and right windings. When information is stored as these windings, such states are stable and insensitive to magnetic perturbations. This would be an ideal candidate for nanoscale molecular magnetic storage.

We synthesized a new toroidal magnet called {Fe₈Dy₈}, in which 16 magnetic metal ions can be alternately arranged into a macrocycle [1]. The possibility of the toroidal arrangement is given by the magnetization curve, which shows no spontaneous ferromagnetic moment at zero field, but a slow increase toward higher fields. The magnetization at 7 T was only 40% of the full saturated moment, which indicates two possible arrangements of magnetic moments: ferri-magnetic and toroidal. In the ferrimagnetic case, Dy³⁺ and Fe³⁺ ions were coupled antiferromagnetically, and the strong anisotropy was responsible for the slow increase in magnetization. Note that the easy axis of the anisotropy of Dy³⁺ must rotate in the ring from one Dy³⁺ site to the next, because there is no large spontaneous moment. When a strong magnetic field is applied, the change from the ferrimagnet to ferromagnet will appear in the magnetization curve because the exchange coupling between 4f and 3d ions is often weak.

In the toroidal arrangement, the magnetic moments of both Dy and Fe were aligned along the tangential

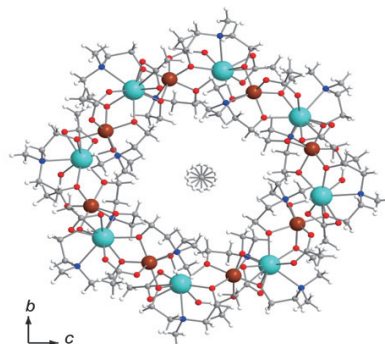


Fig. 1 Structure of {Fe₈Dy₈} molecule. Fe and Dy are represented by large red and sky blue balls. The Dy easy axis is located in the molecular plane.

direction of the ring and were confined in the ring plane owing to the strong anisotropy of Dy ions. The collaboration between ferromagnetic coupling and the strong anisotropy of Dy ions is the key to realizing a toroidal arrangement.

The key experiment distinguishing these two cases is the determination of Dy-Fe exchange coupling by high-frequency electron paramagnetic resonance (EPR) [2]. We observed the systematic frequency-dependence of the EPR spectra at frequencies between 135 GHz and 405 GHz using a THz-ESR system developed by the magnetism division of the Institute for Materials Research, Tohoku University. It shows the linear frequency-field relation with a zero field gap of approximately 110 GHz (5.3 K). The *g*-values determined by the slope of the mode shows that the signal is the transition in the Fe³⁺ multiplet, and the level is exchange-biased by the ferromagnetic coupling between Fe and Dy ions. The total magnetic coupling energy is 26.4 K for one Fe-Dy pair and over 400 K for the whole molecule. The present results provide a useful recipe to design a toroidal magnetic molecule.

References

- [1] H.-L. Zhang, Y.-Q. Zhai, L. Qin, L. Ungur, H. Nojiri, and Y.-Z. Zheng, *Matter* **2**, 1481 (2020).
- [2] H. Nojiri, Y. Ajiro, T. Asano, and J.-P. Boucher, *New J. Phys.* **8**, 218 (2006).

Keywords: high magnetic field, toroidal magnet, electron paramagnetic resonance (EPR)

Hiroyuki Nojiri (Magnetism Research Laboratory)

E-mail: nojiri@imr.tohoku.ac.jp

URL: <http://www.hfpm.imr.tohoku.ac.jp>