MLF Experimental Report	提出日 Date of Report 2011/7/15
課題番号 Project No.2010A0044 実験課題名 Title of experiment Spin dynamics in novel Rare-earth based single-molecule magnets 実験責任者名 Name of principal investigator Maiko Kofu 所属 Affiliation Institute for Solid State Physics, University of Tokyo	装置責任者 Name of responsible person Kenji Nakajima 装置名 Name of Instrument/（BL No.） BL14:AMATERAS 実施日 Date of Experiment 2010/5/31-2010/6/1 2010/11/12-2010/11/15 2010/12/14-2010/12/18

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Complex 1 : $TbCuC_{19}D_{20}N_3O_{16}$
Complex 2 : $TbCuC_{32}D_{32}N_5O_{13}$

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Single-molecule magnets (SMMs) are a class of metal-organic compounds in which each constituent molecule, containing magnetic atoms, possesses a giant and isolated resultant spin. When the giant spin exhibits easy-axis magnetic anisotropy (D<0), the molecule has a ground state with $S_z=\pm S$, and the potential barrier between the states can be simply described as DS_z^2. The presence of barrier yields a slow relaxation of the magnetization reversal that is characteristic of SMM. To date, SMMs containing transition metal atoms such as Mn, Fe, and Ni, have been intensively studied. Recently, a new series of rare-earth based SMMs was discovered and attracts much attention. Because of large contribution of angular momenta, lanthanide complexes can become SMMs containing only one or two magnetic atoms, being simpler than the transition metal SMMs consisting of many magnetic atoms and suitable for fundamental studies. Besides, the energy scale of lanthanide SMMs is expected to be larger and they can be good candidates for magnetic devices. Now we work on dinuclear SMMs consisting Tb^{3+} and Cu^{2+} ions. Interestingly, the system switches from SMMs to non-SMMs by a slight structural modification around the Tb^{3+} ions [1]. In order to investigate their spin states and energy scheme, we have performed inelastic neutron scattering experiments on the AMATERAS spectrometer newly built at J-PARC.

To reduce the contribution from strong incoherent scattering of H atom, we have prepared deuterated samples of SMM and non-SMM complexes. The samples were loaded into the Al cans with He gas which facilitates thermal equilibration inside the can and sealed with Indium gasket. Firstly, we have performed measurements under the medium resolution condition $\Delta E/E$~3%, in order to survey magnetic excitations. The incident energies

we have chosen are 5, 8.3, 16.8, and 50meV. This multiple E_i measurement enable us to survey the excitations in the wide energy range between 0.2meV and 45meV. Then, we have investigated the temperature dependence of the excitations. Next, we have carried out the measurements under the high resolution condition $\Delta E/E$~1%. This is because the detailed structure of excitations can be investigated as described later.

Figure 1 shows the dynamical structure factor, $S(Q,E)$, as functions of energy (E) and momentum transfer (Q) for $TbCuC_{19}D_{20}N_3O_{16}$ (complex 1 : SMM) and $TbCuC_{32}D_{32}N_5O_{13}$ (complex 2 : non-SMM). The $S(Q,E)$ map of complex 1 is much different from that of complex2. Taking account of scattering intensity and the selection rule, $\Delta S = \pm 1$, we determined the energy scheme as shown in Fig. 1. In complex 1, the excitation with E = 1.7 meV corresponds to the transition from $|J_z=6, S_z=1/2\rangle$ to $|6, -1/2\rangle$, while that with E = 12.3 meV from $|6, 1/2\rangle$ to $|5, 1/2\rangle$, where J_z (S_z) is z-component of Tb^{3+} (Cu^{2+}) magnetic moment. Assuming the simple spin Hamiltonian, $H = DJ_z^2 + J_{ex}\boldsymbol{J}\cdot\boldsymbol{S}$, D and J_{ex} are estimated to be -1.1meV and -0.29 meV respectively. Note that the Tb^{3+} moment and the Cu^{2+} spin are coupled by the Heisenberg interaction. This is justified by the fact that the scattering intensity varies as $\sin(Qd)/Qd$, where d corresponds to the distance between Tb and Cu ions. It gives rise to the hybridization between $|6, -1/2\rangle$ and $|5, 1/2\rangle$ states.

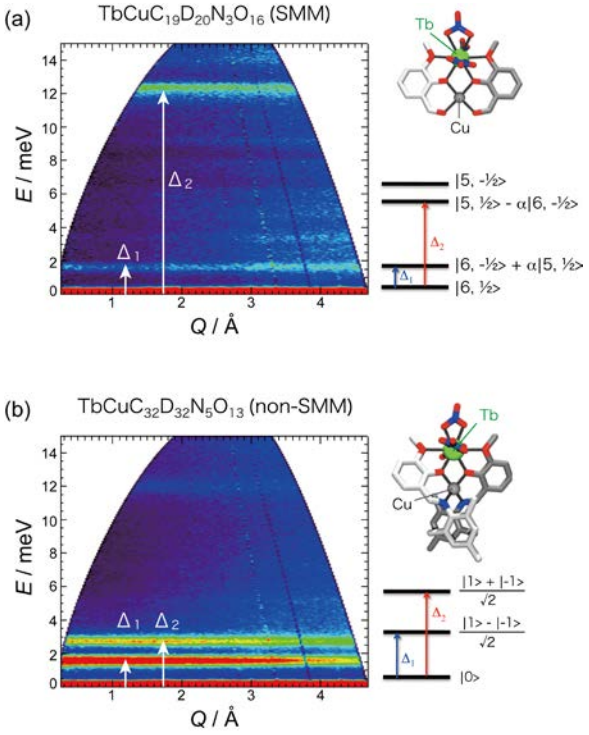

Fig. 1. Dynamical structure factors as functions of energy and momentum transfer for (a) complex 1 and (b) complex 2 taken at T = 6 K. Redder color denotes higher intensity. Molecular structures and energy scheme are also shown.

On the other hand, for complex 2, it is the most plausible scheme that the ground state is $|J_z=0\rangle$ and the observed excitations around 2 meV corresponds to the excitations from $|J_z=0\rangle$ to $(|J_z=1\rangle \pm |J_z=-1\rangle)/\sqrt{2}$. Here, we neglect the contribution from the Cu^{2+} spin because the term, $\boldsymbol{J}\cdot\boldsymbol{S}$, must be small in this case. Assuming $H = DJ_z^2 + E(J_x^2 - J_y^2)$, we obtained D = 2.2 meV and E = 0.03 meV. Therefore, the magnetic anisotropy of Tb^{3+} in complex 1 (SMM) is easy-axis type ($D < 0$), while that in complex 2 (non-SMM) easy-plane one ($D > 0$).

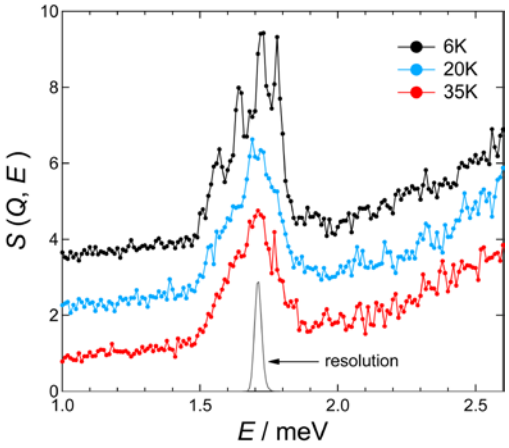

Fig. 2. Energy dependence of dynamical structure factors at T = 6, 20, and 35 K. Solid line represents the instrumental resolution.

Now let us discuss the mechanism of magnetization reversal in complex 1. The activation energy estimated by the ac-magnetic susceptibility measurements is ca. 1.5meV [1] which is close to the energy difference between $|6, 1/2\rangle$ and $|6, -1/2\rangle$. We speculate the magnetization reversal occurs through the quantum tunneling between $|6, -1/2\rangle$ and $|-6, 1/2\rangle$ states. However, the Hamiltonian mentioned above cannot cause the hybridization between these states. Our neutron scattering experiments under the high-resolution condition revealed that the peak at 1.7meV splits as shown in Fig. 2. This peak-splitting may result from the hyperfine interaction between the nuclear spin and electron spin and orbital magnetic moments. We predict that the hyperfine interaction plays an important role in the hybridization states that yield the tunneling process of magnetization reversal.