Slow magnetic relaxations of an *S*=1/2 copper(II) ion incorporated into the nuclear-spin-free Keggin-type tungstosilicate

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Recently, slow magnetic relaxations of *S*=1/2 systems after removal of an applied magnetic field are expected as the spin qubit for quantum information processing device.[1] In order to increase relaxation times, it is important to suppress the fast quantum tunneling relaxations which facilitated by dipolar interactions and hyperfine interactions in this system. From this point of view, large, rigid and nuclear-spin-free polyoxometalates would be useful for the ligand toward the potential spin qubits.[2] However, reported examples of slow relaxation behaviors, especially complexes with only one spin center are very limited. Here we report, slow magnetic relaxations of copper(II) ion incorporated in the large, rigid and nuclear-spin-free tungstosilicate are presented.

The tetrabutylammonium salt $[(n\text{-}C_4H_9)N_4]H_2[SiW_{11}O_{39}Cu]$ (**1**) was prepared from the potassium salt.[3] The X-band ESR spectrum of powder form of **1** showed well separated four peaks originated by the copper(II) ion. The *g*-value was decreasing and *A*-value was increased compared with the potassium salt, which would indicate decreasing coordination number from six to five by removing terminal water ligand.[4] DC magnetic susceptibility measurements indicated *S*=1/2 state of **1**. AC magnetic susceptibility measurements revealed that **1** shows slow magnetic relaxations in an applied static magnetic field (H_{DC}). The temperature- and static-field-dependences of extracted relaxation times of 5 % magnetically diluted **1** $[(n\text{-}C_4H_9)N_4]H_2[SiW_{11}O_{39}Cu_{0.05}Zn_{0.95}]$ (**dil.1**) collected in H_{dc}=3000 Oe and at 1.8 K, respectively, were successfully reproduced by simultaneously fitting of direct, Raman and quantum tunneling processes.[5] From the analyses, Raman relaxation process is dominated at all measured temperatures in H_{dc}=3000 Oe. The utilization of nuclear-spin-free polyoxometalate ligand seems to have reduced the contribution of quantum tunneling process even at low temperatures.

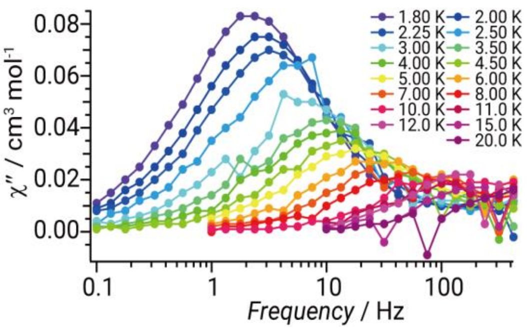

Fig.1 Frequency dependence of out-of-phase susceptibilities of **dil.1** in H_{DC}=3000 Oe at indicated temperatures.

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