Rotation of complex ions with eightfold hydrogen coordination

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Solid-state materials containing rotatable polyanions constitute a peculiar class of ionic conductors because of their unique transport mechanism, where the reorientational motions induce phase transitions with several orders of magnitude enhancement in counterion conductivities. A major drawback is the high temperature required to activate rotation, and thus the poor conductivities at room temperature. In this regard, we recently proposed a novel strategy of drastically reducing the temperature by utilizing "pseudorotation" of hydride complexes with high hydrogen coordination as a new class of rotatable polyanions [1]. We performed Quasielastic neutron scattering (QENS) measurements of Li_5MoH_{11} and Li_6NbH_{11} containing hydride complexes with ninefold hydrogen coordination and successfully observed a QENS signal above 150 K due to the relaxation of H atoms with a remarkably wide relaxation time distribution implying the emergence of pseudorotation [2]. In this study, we investigated the dynamics of WH_8^{4-} with eightfold hydrogen coordination in Mg_6WH_{16} in order to systematically elucidate the relationship between the hydrogen coordination number and the rotational dynamics.

The QENS experiments were performed using a time-of-flight chopper spectrometer AGNES at the research reactor JRR-3 in Japan Atomic Energy Agency. The incident neutron energy used was 4.6 meV at AGNES, giving rise to energy resolutions of 0.12 meV. The accessible energy window and Q-range were -4 meV $< \Delta E <$ 20 meV and 0.26 $Å^{-1} < Q <$ 2.7 $Å^{-1}$, respectively. The QENS measurements were carried out at temperatures between 150 K and 350 K. The resolution data were taken at 3 K. The measurement time was 17.5 - 21 h.

Figure 1 shows the dynamic structure factor $S(Q,E)$ of Mg_6WH_{16} measured in a temperature range of 3–350 K. We observed that a QENS signal appeared at a temperature >150 K because of the relaxation of hydrogen atoms. The intermediate scattering functions derived from the QENS spectra were fitted using a stretched exponential function called the Kohlrausch–Williams–Watts function with an anomalously small stretching exponent $\beta < 0.2$, which is much smaller than those observed for Li_5MoH_{11} and Li_6NbH_{11} containing hydride complexes with ninefold hydrogen coordination, suggesting a wider relaxation time distribution. We are currently undertaking a more detailed analysis to systematically elucidate the relationship between the hydrogen coordination number and the rotational dynamics of hydride complexes.

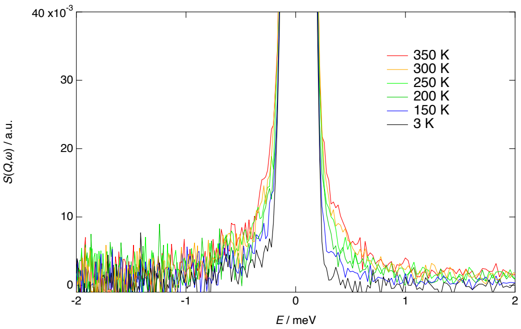

Fig. 1. Quasielastic neutron scattering (QENS) spectra of Mg_6WH_{16} measured at different temperatures.

[1] S. Takagi *et al.*, Appl. Phys Lett. **116**, 173901 (2020).

[2] Y. Ohmasa *et al.*, Phys. Rev. Res. **4**, 033215 (2022).