Magnetic excitation and hydrogen dynamics in goethite

Y. Nambu[A]

[A]*Institute for Integrated Radiation and Nuclear Science, Kyoto University*

Hydrogen is a structurally simple but functionally decisive constituent of many inorganic materials. Because it can participate in hydrogen bonding, proton transfer, and local structural rearrangements, even small changes in its position or mobility may substantially alter chemical reactivity and physical properties. Neutron scattering is particularly useful for studying such systems: diffraction provides direct structural sensitivity to hydrogen, whereas inelastic and quasielastic measurements can probe lattice vibrations and motion on microscopic time scales. A combined understanding of static structure and dynamics is therefore essential for clarifying how hydrogen-containing solids function.

Goethite (α-FeOOH) is one of the most common iron oxyhydroxides and a major component of iron rust. In addition to its importance in mineralogy and environmental chemistry, α-FeOOH has attracted interest as a catalyst for the photochemical reduction of CO_2 to formic acid. Its activity and selectivity are substantially higher than those of α-Fe_2O_3, indicating that hydroxyl groups play an important role in CO_2 adsorption and proton-coupled reaction processes [1]. Establishing the local hydrogen-bond environment and its dynamics is consequently relevant to microscopic models of the catalytic pathway and to the design of future in situ measurements under reaction conditions.

In our preceding study, neutron powder diffraction and first-principles calculations were combined to refine the hydrogen positions and magnetic structure of undeuterated α-FeOOH [2]. The crystal structure is described by the orthorhombic space group *Pnma*, while the Fe moments form a collinear antiferromagnetic structure with a magnetic wavevector of (0, 0, 0). The Néel temperature was estimated to be approximately 382 K. The refined O-H geometry agreed closely with the calculated structure, providing a reliable structural basis for studying the corresponding low-energy dynamics. However, diffraction alone does not determine the exchange interactions, vibrational spectrum, or possible hydrogen-related relaxation processes.

We therefore performed time-of-flight inelastic and quasielastic neutron-scattering measurements on a polycrystalline α-FeOOH sample using AGNES at JRR-3. Standard- and high-resolution configurations were employed over a temperature range from approximately 3 to 400 K, with additional measurements concentrated around the antiferromagnetic transition. The data were reduced using background subtraction and vanadium normalisation, and spectra integrated over low- and high-Q regions were compared before and after Bose-factor correction. This strategy was intended to distinguish, as far as possible in a powder sample, magnetic scattering from vibrational and hydrogen-related contributions.

The planned temperature-dependent datasets were successfully obtained, and the initial analysis confirms that the low-energy response can be followed throughout the investigated temperature regime. Detailed separation and quantitative modelling of the magnetic, phonon, and hydrogen-related components are in progress. The measurements provide a basis for determining the relevant low-energy interactions and for planning future in situ experiments under a CO_2 atmosphere.

[1] D. An *et al*., Angew. Chem. Int. Ed. **61**, e202204948 (2022).
[2] Y. Nambu *et al*., Dalton Trans. **55**, 5780 (2026).