Ph. D. Thesis Project (3 years):

Unravelling the structure of paramagnetic materials by solid-state NMR

Host Institute: Very High Field NMR Center (CRMN), CNRS, ENSL, UCBL, University of Lyon

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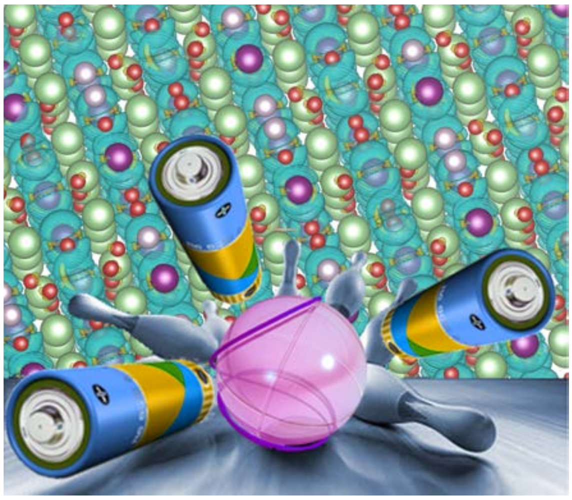
Many materials that impact strongly on industry, energy, climate change, and the environment contain paramagnetic metal ions, which lie at the heart of many macroscopic processes such as reactivity (e.g. for catalysts), charge storage and transport (e.g. for batteries), or lighting (e.g. for solid-state phosphors). To understand the function of these paramagnetic materials, and thus to tune their performance, their structural properties must be determined. This involves characterizing different length scales, from the morphology on the nano scale down to the local structure of the metal-containing active sites. In diamagnetic materials, these structural features typically escape X-ray diffraction (XRD) and electron microscopy (EM), but are readily accessible to solid-state nuclear magnetic resonance (NMR). However, the current repertoire of NMR methods is not tailored to paramagnetic systems, where metal centres produce large perturbations in the spectrum of the surrounding nuclei and hamper the critical steps of the acquisition of the NMR experiments and the subsequent spectral assignment and interpretation.



In this project, we will develop new experimental and computational paramagnetic NMR (pNMR) methods to remove the current barriers to spectral acquisition from paramagnetic nuclei and to extend the amount of information that can be extracted from them. This will enable the acquisition of both local structural information closest to a paramagnetic centre of action, and global data on a nm–μm length scale, as well as a link between these structures and the bulk properties.

Characterization of paramagnetic materials will be made possible: (i) through broadband irradiation schemes, notably, adiabatically modulated radiofrequency pulses to manipulate the broad anisotropic, fast relaxing patterns of quadrupolar nuclear spins subject to large hyperfine interactions and to provide high-dimensional correlations useful to identify the signals from nuclei close to a metal ion and to quantitatively measure long-range paramagnetic effects; (ii) through innovative sample formulations, notably by introducing suitably designed lanthanide chelate dopants, for which the electronic relaxation time matches the Larmor period of the paramagnetic centre of interest (a reduction of its electron relaxation time will reduce its deleterious effects on the relaxation properties of the nearby nuclei); (iii) through landmark computational studies, notably by testing new double-hybrid DFT methods to improve the accuracy in the structure-based calculation of the Fermi-contact terms, currently polluted by the delocalization errors, which dominate any higher-order spin-orbit coupling contributions.

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