Mg/Al Ordering in Layered Double Hydroxides Revealed by Multinuclear NMR Spectroscopy

NHMFL Science Highlight – Energy Storage

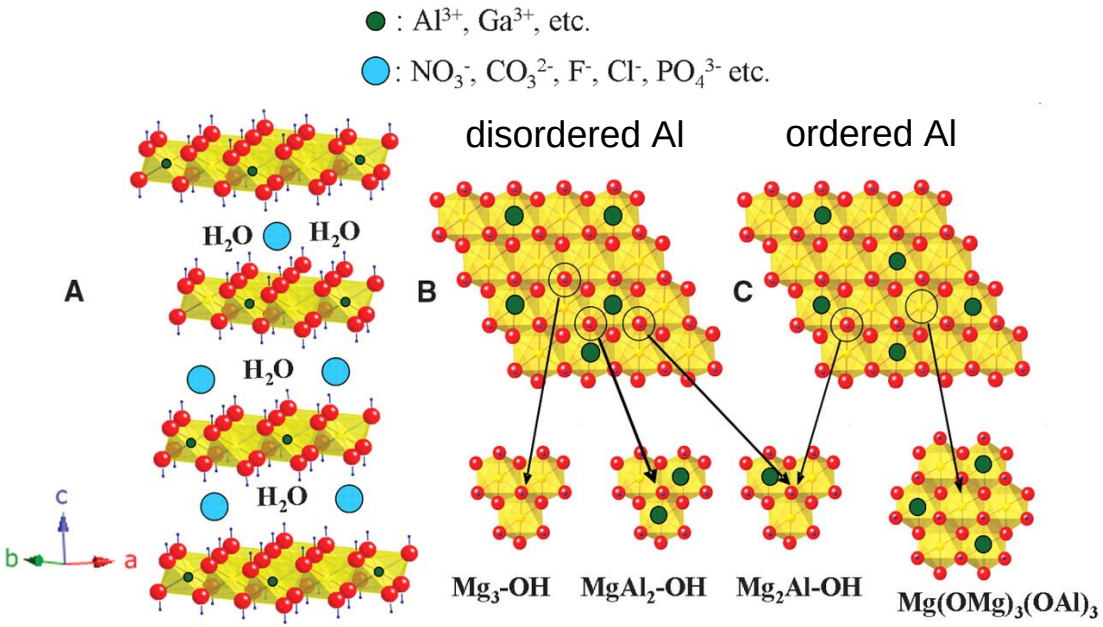
NSF DMR-Award 0654118

NMR Spectroscopy and Imaging User Program, Florida State University

Layered double hydroxides (LDHs) are among the few materials that can be engineered to have *positively* charged layers that can trap *anions*—very useful. How are the Mg and Al organized? Too bad that Al and Mg have identical X-ray cross sections!

MagLab users exploit our high magnetic fields to probe quadrupolar nuclei and study materials for applications in batteries, environmental remediation, Portland cements, anionic conductors, drug candidates, proteins.

Clare Grey and collaborators performed multinuclear quadrupolar NMR spectroscopy to determine the local environment(s) of the Mg ions as the Al concentration was varied. Disordered Al ions give rise to multiple NMR peaks corresponding to the various Mn/Al coordinations. Ordered Al ions give rise to a single Mn/Al coordination.



Structure of a layered double hydroxide (left). Magnesium NMR is sensitive to the local environment and can distinguish between a disordered distribution of Al ions (center) and an ordered distribution of Al ions (right). Ordered Al gives rise to only one Mg site, while disordered Al gives rise to multiple Mn sites and, hence, gives multiple peaks in the NMR spectrum.

This work is supported by NSF/DMR and NSF/CHE.

Paul J. Sideris, Ulla Gro Nielsen, Clare P. Grey (SUNY Stonybrook); Zhehong Gan (NHMFL)

Science 4 July 2008: Vol. 321. no. 5885, pp. 113-117

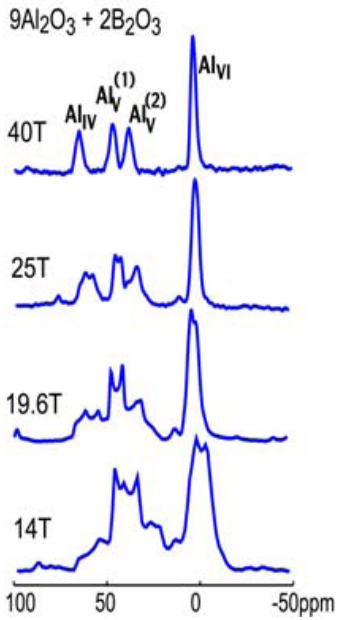
Mg/Al Ordering in Layered Double Hydroxides Revealed by Multinuclear NMR Spectroscopy

NHMFL Science Highlight – Energy Storage

NSF DMR-Award 0654118

NMR Spectroscopy and Imaging User Program, FSU

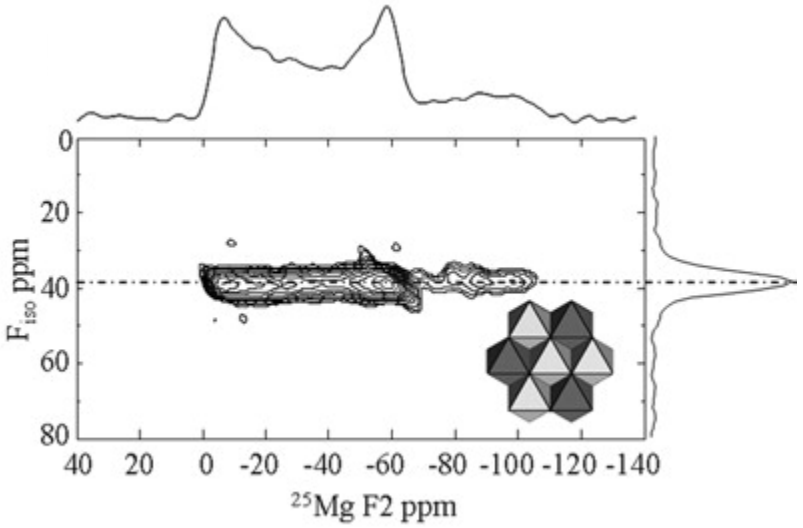
High Field MAS



Conventional Magnesium NMR, even with Magic Angle Spinning (MAS), yields broad and typically overlapping lines from the different possible Mn sites. Triple quantum NMR separates the possible overlapping resonances…but high magnetic fields (both B_0 and B_1) are required for acceptable conversion efficiency. The NHMFL can uniquely provide both in our NHMFL-engineered single resonance probe in our 19.6 T magnet.

Using MAS NMR, we have shown that the cations are fully ordered for Mg:Al ratios of 2:1, and that a non-random distribution of cations persists at lower Al content.

The NHMFL is a leader in NMR instrumentation (see Magic Angle Spinning Probe, top left) as well as methodology for NMR of low-γ quadrupolar nuclei at fields to 40 teslas (left)



2D triple-quantum ^{25}Mg (I=5/2) MAS NMR reveals that only a single Mg site is present in MgAl33. ***Data obtained with 19.6 T NHMFL magnet.***

Paul J. Sideris, Ulla Gro Nielsen, Clare P. Grey (SUNY Stonybrook); Zhehong Gan (NHMFL)

Science 4 July 2008: Vol. 321 no. 5885, pp. 113-117