Solid state NMR studies of layered double hydroxides

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Solid State NMR Studies of Layered Double Hydroxides

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Abstract:

Layered double hydroxides (LDH) are a versatile group of materials, which receive significant attention due to their many applications within catalysis, energy conversion and storage, drug delivery, environmental remediation, and carbon dioxide sequestration. Moreover, many LDH exists
Layered double hydroxides (LDH) are widely studied class of inorganic materials, which find application within a suite of applications ranging including catalysis[1, 2], energy materials[3, 4], drug delivery[5-7], CO₂ sequestration[8], sensors[9], cements[10], and environmental remediation[11-13]. The majority of these LDH are the so-called hydrotalcite LDH, which are named after the mineral hydrotalcite, Mg₃Al(OH)₈(CO₃)₄H₂O[14]. Several LDH minerals are also known and adsorption of heavy metal ions such as Ni(II) and Zn(II) on the surface of aluminum (hydr)oxides leads to formation of LDH in the environment[15]. Moreover, synthetic LDH can be further modified to form so-called nanohybrid materials with both organic and inorganic components as well as be exfoliated to form two dimensional (2D) materials[16-18], which consist of ultrathin nanosheets with high surface areas and reactivity, which have further expanded their applicability. The versatility of LDH relies on their flexible chemical composition and ion-exchange properties, as they are a rare example of an anion-exchange material. For example, the variable oxidation states and doping with transition metals is central for their application as energy and catalytic materials, whereas their high anion-exchange capacity is extensively used for sequestration of pollutants such as phosphate and arsenate from water[12] and for the controlled release of drugs (Fig 1). Given the versatility of the LDH, nearly 14,000 papers have been published since 2010 based on a Web of Science search, when
the term “layered double hydroxides” is used, whereas combined with “solid state NMR” leads less than 200 papers[19].

Structural characterization of LDH is demanding, as they are notorious for e.g., low crystallinity, frequent stacking faults, and small particle size (nm-µm). Moreover, the structural disorder of the metal ions in the cation layer and interlayer species (water and anions) further complicates the analyses by X-ray diffraction techniques (XRD). Thus, the most detailed crystal structures have been obtained from XRD studies of single crystals isolated from mineral specimens[20-23]. Moreover, 2D LDH and nano-hybrid materials are further challenging, as they inherently lack long-range structural order along one or more dimensions. Thus, SSNMR, which probes the local structure and does not require long range order, is a powerful technique to investigate the structure on the atomic scale, e.g., cation ordering, and the dynamic processes in the LDH interlayer in these challenging materials.

This review focusses on how SSNMR has been used to advance the understanding of atomic level structure of LDH and its application as an analytical tool to establish the structure-property-function relationship. The reported studies fall in two groups. one where advanced, time-consuming, and/or experimentally demanding SSNMR experiments in combination with detailed analyses of the NMR data have been performed on LDH to understand the structural features and dynamic processes in detail. These studies have been performed by research groups with specialized SSNMR equipment that allows for, e.g., studies low-γ nuclei, fast MAS, high-power decoupling, high magnetic field strengths, and variable temperature as well as isotope enrichment (13C, 15N, 17O, and 25Mg). For the second group of studies, SSNMR is one of a suite of characterization techniques used in studies often focused on the properties of LDH. Generally, these studies report routine SSNMR data, e.g., single pulse 6,7Li, 27Al, and 31P MAS NMR spectra as well as 13C-1H CPMAS NMR experiment recorded at a moderate field (3-500 MHz). Such SSNMR experiments can be acquired on a conventional two-channel NMR spectrometer designed for liquid-state NMR accessorized with a standard 4 or 3.2 mm double resonance MAS NMR probe, which is now becoming generally available at NMR service facilities at universities and industry, i.e., accessible to the non-SSNMR specialist. The analysis of the SSNMR data is often qualitative, e.g., visual inspection, identification of the number of resonances and their isotropic shifts, and only sometimes accompanies by quantification of the different species by simple integration or deconvolution of the SSNMR spectra. Moreover, LDH have been used as an illustrative example for NMR method development[24-26].
This review will illustrate how SSNMR can be used to obtain detailed structural information about LDH using demanding NMR experiments and illustrate how SSNMR is applied as one of several analytical techniques using drug delivery and environmental science as illustrative examples. The diamagnetic LDH especially those containing Mg(II), Zn(II), or Ca(II) and Al(III) have been widely studied in relation to these topics for several decades. In contrast, studies of LDH with paramagnetic metal ions such as Fe(II/III), Co(II), Ni(II), Cu(II), which are generally investigated in relation to catalysis and as energy materials, have only recently been investigated by SSNMR as studies of these materials often require ultrafast MAS.

2. Structure and chemical composition of LDH in relation to SSNMR studies

The following summarizes the structure and chemical composition of LDH in relation to SSNMR studies of these materials, which probes the local structure with ca 10 Å. The reader is referred to References [20-23, 27, 28] for a more detailed description of the structure and chemical composition of LDH as well as their synthesis. There are two different types of LDH structures, one derived from substitution of divalent ions with trivalent ions in divalent metal hydroxides (M(OH)₂) and the second from insertion of lithium or divalent cations into the aluminum hydroxides (Al(OH)₃) polymorphs bayerite and gibbsite. Since SSNMR provides limited insight into the long-range structure, structural aspects related to long-range disorder such as stacking faults, interstratification, and polymorphism will not be discussed.

2.1 Hydrotalcite LDH \(M(\text{II})_{1-x}M(\text{III})_x(OH)_2A \cdot nH_2O\)

The largest and most extensively studied class of LDH are structurally related to the mineral hydrotalcite (Mg₆Al₂(OH)₈(CO₃)⋅4H₂O) and they are often referred to as “hydrotalcites (LDH)”[14]. The structure of hydrotalcite is derived from brucite (Mg(OH)₂) in which one out of four Mg(II) has been substituted by Al(III). This creates a charged cation layer, and one carbonate is included per two Al for charge balance along with water in the interlayer (Fig 2). Hydrotalcite LDH have the general chemical composition \(M(\text{II})_{1-x}M(\text{III})_x(OH)_2A_{a'}nH_2O\), where \(M(\text{II}) = \text{Mg, Ca, Co(II), Fe(II), Ni(II), Cu(II), Zn(II)}\)… and \(M(\text{III}) = \text{Al, Ga, Fe(III),Co(III) Cr(III)}\) with \(1/6 \leq x \leq 1/3\), as illustrated in Fig 2. An appropriate amount of anion (A), which is needed for charge balance, as each M(III) ion creates a charge of + 1, is located in the interlayer. This expansion destroys the strong hydrogen bonding network in brucite. The interlayer water content depends on the humidity and the anion. In the following the notation \(M(\text{II})M(\text{III})\)-LDH will be used for the general type, whereas \(M(\text{II})M(\text{III})\)-A
LDH will be used for M(II)M(III)-LDH with a specific anion. The content of M(III) in an LDH is often expressed as the M(II):M(III) ratio. For example, a MgAl-LDH with 33.3% Al has a Mg:Al ratio of 2:1 and is referred to as Mg₂Al-LDH, thereby indicating the M(II):M(III) ratio.

A vast number of anions from simple inorganic halides (F⁻, Cl⁻, Br⁻, I⁻), oxyanions, e.g., carbonate, hydrogen carbonate, nitrate, phosphate, arsenate, arsenite, and sulfate to a wide range of organic anions including oxalate, carboxylic acids, amino acids, and large organic carboxylic acids such as terephthalate and dodecanoate as well as organic, anionic polymers can be intercalated. LDH are a rare example of an anion-exchange material. Given the similarity with clays, which are cation exchange materials, LDH are often referred to as anionic clays. Combined with the flexible chemical composition of the cation layer, this creates an extremely diverse class of materials. The hydrotalcite LDH have a high affinity for divalent inorganic anions such as carbonate (highest affinity), sulfate and hydrogen phosphate and a lower affinity for small inorganic anions such as chloride, nitrate, and fluoride. Thus, carbonate is a common impurity in the LDH even prepared with decarbonated water and under a nitrogen flow, although it is possible to obtain carbonate free LDH an inert atmosphere[29]. It is mainly the size and orientation of the anion that controls the interlayer spacing.

The structure of the positively charged cation layer contains a trioctahedral sheet, where the metal ions are octahedrally coordinated to six hydroxyl groups (-OH). Each hydroxyl group is coordinated three metal ions. The total charge of the cation layer is controlled by the concentration of M(III) ions, which ranges from ca. 17 to 33 %. The single crystallographic metal ion site has a mixed occupancy. One of the core strengths of SSNMR is that it can probe the atomic level structure of the LDH, e.g., ordering of metal ions in the cation layer, relative concentration of different anion sites, and dynamic processes, where X-ray diffraction provides the average structure. The structure of the calcium containing hydrotalcite LDH are slightly different, as the hepta coordinated Ca is bonded to six -OH and one water molecule, which fixes the Ca:M(III) ratio to 2:1[30]. Hydrotalcite LDH have the so-called memory effect: Calcination of an LDH at several hundred degrees destroy the LDH structure, but the hydrotalcite LDH structure is reconstructed by suspension of the LDH in water and hydroxide (OH⁻) become the default anion unless others are present.

2.2 The structure of LDH derived from aluminum hydroxide

A second, less studied class of LDH are based on insertion of lithium (Fig. 3) and selected divalent metal ions (Fig. 4) into gibbsite and bayerite, two common polymorphs of aluminum hydroxide (Al(OH)₃)[31]. Both Al(OH)₃ polymorphs contains a so-called dioctahedral sheets, where one third
of the Al positions are vacant. The two differ only in the stacking of the layers. All vacancies can be filled with lithium leading to a LiAl2-LDH, which is accompanied an expansion of the interlayer distance due to incorporation of anions and water. This is illustrated for the mineral drittsite (Li2Al4(OH)12Cl2·3H2O[23, 28] in Fig 3. Neutron diffraction of Li2Al-Cl LDH at room temperature showed large thermal ellipsoids for the chloride site and that water was disordered[32], which was confirmed by 35Cl SSNMR and MD simulations[33] as well as indirectly from 27Al MAS NMR[34]. Li and Al are located on different crystallographic positions, whereas significant structural disorder exists in the interlayer (water and anions). Only half the vacancies can be filled with a few divalent transition metal ions (Mg(II), Co(II), Ni(II), Cu(II), and Zn(II)) leading to the so-called MAl4-LDH or “nickelalumite” LDH illustrated in Fig. 4, which have been very sparingly studied [35]. The crystal structure is highly ordered both in the cation layer (M(II) and Al have different crystallographic positions) as well as in the interlayer due to a strong hydrogen bonding network for the MAl4-LDH with sulfate[20]. The reader is referred to Refs [20, 35-37] and references cited therein for a more detailed discussion of the MAl4-LDH properties and challenges in preparation of pure MAl4-LDH.

The two main differences between hydrotalcite and the Al(OH)3 derived LDH (LiAl2-LDH and MAl4-LDH), are that chemical composition of hydrotalcite-LDH is very flexible, whereas the stoichiometry of the Al(OH)3-LDH are fixed and only the anion and water content may be modified.

3. Acquisition, Analysis, and Interpretation of SSNMR spectra of LDH – Practical aspects

Table 1 summarizes the number of SSNMR resonances expected for an ideal LDH based on the crystal structure and SSNMR studies of ideal (non-defect) LDH, whereas Table 2 contains the properties of the most common NMR isotopes of relevance to SSNMR studies of LDH. The crystal structures of the LDH contain only one to four crystallographic inequivalent atoms of each kind. However, the mixed occupancy of M(II) and M(III) in the hydrotalcite LDH introduces additional local environment, which can be distinguished and quantified by SSNMR, c.f., Table 2. Frequently studied NMR nuclei are 2H, 13C, 15N, and 31P, all spin (I) ½, and the quadrupole nucleus 27Al (I = 5/2), c.f. Table 2. The high symmetry of the LDH structure results in a weak quadrupolar coupling constant (CQ) for 27Al in hydrotalcite and Li2Al-LDH (< 2 MHz), c.f., Table 3. Thus, these NMR isotopes can all be investigated at a moderate magnet field and spinning speeds, e.g., 9.4 T and 10-15 kHz, respectively, and have been extensively studied for about four decades. In contrast, the more demanding low-gamma nuclei, e.g., 25Mg and 67Zn, and 1H MAS NMR require high magnetic fields
Table 1 The number of NMR resonances expected in SSNMR spectra of a non-defect LDH from the metal ions in the cation layer, hydrogen and oxygen in the hydroxyl groups and interlayer water. In addition, the anion may contribute to these. For example, carbonate will contribute with one $^{13}\text{C}$ and one $^{17}\text{O}$.

<table>
<thead>
<tr>
<th>LDH</th>
<th>Metal ion sites</th>
<th>$^{17}\text{O}^b$</th>
<th>$^{1,2}\text{H}^c$</th>
<th>Anion(s)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(II)M(III)-LDH</td>
<td>1-4 M(II)$^a$</td>
<td>2-OH</td>
<td>1 H$_2$O</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1 M(III)</td>
<td>1 H$_2$O</td>
<td>1 M(II)$_2$M(III)-OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 M(III)$_2$-OH</td>
<td></td>
</tr>
<tr>
<td>M(II)$_2$M(III)-LDH$^e$</td>
<td>1 M(II)</td>
<td>1-OH</td>
<td>1 H$_2$O</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1 M(III)</td>
<td>1 H$_2$O</td>
<td>M(II)$_2$M(III)-OH</td>
<td></td>
</tr>
<tr>
<td>LiAl$_2$-LDH$^{[23]}$</td>
<td>1 Li, 1 Al</td>
<td>1-OH</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>MA$_4$-LDH$^{[20, 38]}$</td>
<td>1 M, 4 Al</td>
<td>12-OH</td>
<td>12-OH</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 H$_2$O</td>
<td>6 H$_2$O</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ M(II)(OM(II)$_{6-x}$ (OM(III)$_x$ with $x = 0, 1, 2,$ and 3 and the relative concentration depends on the M(III) content$^{[39]}$.

$^b$ Any oxygen in the anion will contribute as well, but this depends on the nature of the anion.

$^c$ Any hydrogen in the anion will contribute as well. The relative concentration of the -OH groups depends on the M(III) content$^{[40]}$.

$^d$ Crystallographic positions for the anion.

Table 2 Properties of nuclei of relevance to SSNMR studies of LDH including Larmor frequency at 9.4 T [41]. The quadrupole moment is only applicable for I > ½.

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Spin</th>
<th>Natural abundance (%)</th>
<th>Quadrupole moment (fm²)</th>
<th>Frequency (MHz)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>$^1$H</td>
<td>$\frac{1}{2}$</td>
<td>99.99</td>
<td>--</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>$^2$H</td>
<td>1</td>
<td>0.01</td>
<td>0.2860</td>
<td>61.40</td>
</tr>
<tr>
<td>Carbon</td>
<td>$^{13}$C</td>
<td>$\frac{1}{2}$</td>
<td>1.07</td>
<td>--</td>
<td>100.58</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$^{15}$N</td>
<td>1/2</td>
<td>0.37</td>
<td>--</td>
<td>40.55</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$^{17}$O</td>
<td>5/2</td>
<td>0.038</td>
<td>-2.56</td>
<td>54.23</td>
</tr>
<tr>
<td>Fluorine</td>
<td>$^{19}$F</td>
<td>1/2</td>
<td>100</td>
<td>--</td>
<td>376.38</td>
</tr>
<tr>
<td>Magnesium</td>
<td>$^{25}$Mg</td>
<td>5/2</td>
<td>10</td>
<td>19.94</td>
<td>24.49</td>
</tr>
<tr>
<td>Aluminum</td>
<td>$^{27}$Al</td>
<td>5/2</td>
<td>100</td>
<td>14.66</td>
<td>104.23</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>$^{31}$P</td>
<td>1/2</td>
<td>100</td>
<td>--</td>
<td>161.92</td>
</tr>
<tr>
<td>Sulfur</td>
<td>$^{33}$S</td>
<td>3/2</td>
<td>0.76</td>
<td>-6.78</td>
<td>30.70</td>
</tr>
<tr>
<td>Chlorine</td>
<td>$^{35}$Cl</td>
<td>3/2</td>
<td>75.78</td>
<td>-8.165</td>
<td>39.19</td>
</tr>
<tr>
<td>Calcium</td>
<td>$^{43}$Ca</td>
<td>7/2</td>
<td>0.135</td>
<td>-4.08</td>
<td>26.92</td>
</tr>
<tr>
<td>Zinc</td>
<td>$^{67}$Zn</td>
<td>5/2</td>
<td>4.10</td>
<td>15.00</td>
<td>25.03</td>
</tr>
<tr>
<td>Gallium</td>
<td>$^{71}$Ga</td>
<td>3/2</td>
<td>32.892</td>
<td>10.7</td>
<td>121.99</td>
</tr>
<tr>
<td>Selenium</td>
<td>$^{77}$Se</td>
<td>1/2</td>
<td>7.63</td>
<td>--</td>
<td>72.28</td>
</tr>
<tr>
<td>Bromine</td>
<td>$^{81}$Br</td>
<td>3/2</td>
<td>49.31</td>
<td>26.2</td>
<td>108.03</td>
</tr>
<tr>
<td>Iodine</td>
<td>$^{127}$I</td>
<td>5/2</td>
<td>100</td>
<td>-71</td>
<td>80.03</td>
</tr>
</tbody>
</table>

In addition, the analyses of SSNMR spectra are often limited to visual inspection, i.e., identification of main features or simple deconvolution of the spectra for a more precise determination of the isotropic shifts and the relative concentration of the different species. Detailed analyses of the spectra require SSNMR simulation software, which preferably can model the structural disorder, e.g. DMFit[42], Quadfit[43], and ssNake[44]. Tables 3–7 summarize the NMR parameters reported from SSNMR studies of LDH, which may be used as starting parameters for the analyses of SSNMR spectra of LDH.
strengths and fast MAS (35+ kHz), respectively, i.e., state-of-the-art SSNMR equipment, as will be discussed in Section 4.

The chemical shift tensor is described by the isotropic chemical shift ($\delta_{iso}$), the chemical shift anisotropy ($\delta_\sigma$) and the asymmetry parameter ($\eta$):

$$\delta_{iso} = \frac{1}{3}(\delta_{xx} + \delta_{yy} + \delta_{zz})$$  \hspace{1cm} (1)

$$\delta_\sigma: \delta_\sigma = \delta_{zz} - \delta_{iso}$$  \hspace{1cm} (2)

$$\eta = \frac{\delta_{yy} - \delta_{xx}}{\delta_\sigma}, \quad 0 \leq \eta \leq 1$$  \hspace{1cm} (3)

The quadrupole coupling constant ($C_Q$) and asymmetry parameter ($\eta_Q$):

$$C_Q = \frac{eq_{zz}h}{4\pi}$$  \hspace{1cm} (4)

$$\eta_Q = \frac{V_{yy} - V_{xx}}{V_{zz}}$$  \hspace{1cm} (5)

Which are defined using the convention: $|\delta_{zz} - \delta_{iso}| \geq |\delta_{xx} - \delta_{iso}| \geq |\delta_{yy} - \delta_{iso}|$ and $|V_{zz}| \geq |V_{xx}| \geq |V_{yy}|$, respectively. For paramagnetic samples, is should be emphasized that the total shift tensor will contain contributions from both the chemical shift (diamagnetic) and a contribution from paramagnetic effects (Fermi contact and/or pseudocontact), that originate from the dipolar interaction between the unpaired electron(s) and the NMR nucleus[45]. Thus, total shift anisotropy contain bot a diamagnetic (chemical shift) and paramagnetic interaction, which for the isotropic shift is:

$$\delta_{iso} = \delta_{diamagnetic} + \delta_{Fermi-contact} + \delta_{pseudocontact}$$  \hspace{1cm} (6)

It is noted that for $I > \frac{1}{2}$ the spectrum will contain a contribution from both the total shift anisotropy and the quadrupole interaction as well as reflect the relative orientation of these tensors, but such detailed studies have not been reported so far for LDH.

It is highly recommended that the LDH samples are characterized in detail by other techniques in addition to SSNMR to assess the samples composition and possible presence of non-LDH phases. For example, SSNMR cannot readily tell whether, e.g., two $^{27}$Al resonances both originate from the LDH phase or one from an impurity. Powder X-ray diffraction (PXRD) is the most common characterization technique for LDH, which provides insight into the crystalline phases present, the anion and M(II):M(III) ratio via the $c$- and $a$-values, respectively[28]. Moreover,
scanning and/or transmission electron microscopy especially combined with energy dispersive spectroscopy (EDS) can give information about the sample homogeneity. Similarly, elemental analyses as well as Raman and/or Infrared spectroscopy also provides valuable insight into the bulk chemical composition and intercalated anions, respectively, see Refs [27, 28, 46-48] for a detailed discussion. It is noted that LDH samples often contain amorphous phases especially amorphous aluminum hydroxides (AOH), which are only readily identified by $^{27}$Al MAS or triple quantum (3Q) MAS NMR. These are evident as a broad resonance in the region 0-15 ppm in $^{27}$Al MAS NMR spectra, that overlap significantly with the LDH resonance especially for MgAl-LDH. Minor amounts of tetrahedral Al may also be observed. Detailed information about $^{27}$Al SSNMR of aluminum (hydr)oxides impurities commonly found in LDH are presented in Refs [49-52]. Background signals in SSNMR spectra have also been observed in $^1$H and $^{13}$C (rotor polymer parts and probe), $^{25}$Mg (MgO in rotor), and $^{27}$Al (rotor) SSNMR, which especially become important when the NMR nuclei of interest is present in low quantities or for paramagnetic samples based on the author’s experience. Moreover, it has been observed that solvent molecules in LDH-hybrid materials are expelled by moderate MAS (15 kHz) and thereby affect the $^{13}$C CPMAS NMR spectra[53], whereas the interlayer water content in ZnAl$_4$-LDH[38] may be affected by ultrafast MAS and dynamic effects such as the phase transition in Friedel’s salt can be induced by frictional heating due to MAS[34, 54, 55]. A significant temperature dependence of the $^{27}$Al NMR shift has observed for paramagnetic samples[56]. Thus, analyses of SSNMR data should consider the potential presence of impurity phases, background signals and the dynamic processes in the LDH that can affect the spectra. Moreover, possibilities for variable temperature SSNMR experiments within standard range for most narrow bore MAS probes (-50 to + 50°) to probe these dynamic effects is desirable.

Recently, DFT calculations of SSNMR parameters have been used to validate structural models for anions intercalated in LDH including calculation of $^1$H and $^{27}$Al parameters for defect MgAl-LDH (Fig 5)[57] and ZnAl$_4$-LDH[35]. A comparison experimental $\delta$iso($^{13}$C) for sulinac, a predrug, in ZnAl-LDH and with in-vacuo DFT calculations of the organic was used for assignment[58]. A similar approach used for pravastatin in MgAl-LDH[59] and coumaric in MgAl- and ZnAl-LDH[60], whereas more advanced DFT calculations of the $^{11}$B SSNMR parameters for two different orientations of a benzoxoborolate in a MgAl-LDH was used to determine the orientation in the interlayer[61]. Given the complexity of the LDH and the structural disorder, computational modelling is a non-trivial task, but is becoming more accessible. Thus, most SSNMR studies have relied on assignment and interpretation based on experimental data such as comparison with the
parent materials and earlier studies of LDH as well as to a smaller extent 1D and 2D correlation SSNMR experiments, as will be discussed in sections 4 and 5.

**4. Structural Characterization of LDH by SSNMR**

The following discusses the detailed SSNMR studies aimed to investigate the local structure of LDH especially in the cation layers as well as the dynamic disorder in the interlayer species (anions and water).

**4.1 SSNMR studies of the cation layer**

**4.1.1. $^{27}$Al SSNMR studies of M(II)Al-LDH**

The following highlights the general trends in $^{27}$Al NMR parameters determined from analyses of $^{27}$Al SSNMR spectra of well-characterized and generally phase pure LDH samples, which are summarized in Table 1. An ideal M(II)Al-LDH will contain a single $^{27}$Al resonance from an octahedrally coordinated Al resonance surrounded by 6 M(II) ions, i.e., a Al(OM(II))$_6$ due to Al-O-Al avoidance, which has been confirmed for MgAl-[39, 40, 55], ZnAl[47], CaAl-[34, 62], CoAl-LDH[63], and NiAl-LDH[56, 63]. In agreement with a quite symmetric Al octahedron, the $^{27}$Al quadrupole interaction is weak ($C_Q \approx 1.6$ MHz) for all MAl-LDH. For diamagnetic $\delta_{iso}(^{27}\text{Al})$ is in the range 8 to 16 ppm, c.f., Table 3 and Fig 6. Moreover, this local Al(OM(II))$_6$ building block has axial symmetry leading to an axial symmetric quadrupole tensor ($\eta_Q = 0$). However, at high M(II):Al ratios the dynamic processes in the interlayer (vide infra) may affect the intensity and line shape of the spinning sidebands from the satellite transitions[34, 39, 54].

It is noted that many studies report the center of gravity of the isotropic resonance, which especially at low and moderate magnetic fields are off-set by a few ppm due to the second-order quadrupolar shift. This should be taken into consideration, when $^{27}$Al SSNMR data obtained at different magnetic field strengths are compared. Especially when $\delta_{iso}(^{27}\text{Al})$ is used to identify the intercalated anion or the line shape or width is used. A precise determination of the $^{27}$Al quadrupole tensor and $\delta_{iso}(^{27}\text{Al})$ is best obtained from simulation of the central transition at low field ($\leq 9.4$ T MHz). Alternatively, from the analyses of the spinning sideband manifold of the satellite transitions (Figure 6). The central transition can be modelled with simple Gaussian line shape at high magnetic field strength for the hydrotalcite and LiAl$_2$-LDH. However, dynamics and structural disorder lead to non-ideal line shapes, which render determination of especially $\eta$ unprecise, but can be alleviated by freezing out motion at lower temperatures (highly sample dependent). Moreover, it requires the use
of at least a 500 kHz spectral window, a probe with a good Q-value and short excitation pulses. Alternatively, 3QMAS NMR spectra can be used for determination of the second-order quadrupolar product.

Numerous reported $^{27}\text{Al}$ NMR spectra of LDH contain more than the characteristic, narrow $^{27}\text{Al}$ resonance expected from the single Al site in an ideal LDH (Table 1 and Fig 6), and these non-LDH resonances may even be the major phase based on $^{27}\text{Al}$ MAS NMR [47]. Thus, these additional resonances have often been assigned to the LDH phase, as no or only minor impurities are detected by PXRD and the total chemical analyses are within the range expected for LDH, or even overlooked. For MgAl-LDH this is further hampered by the fact that the MgAl-LDH resonance overlaps with the AOH resonances in $^{27}\text{Al}$ MAS NMR spectra, whereas 3QMAS NMR improves the resolution[57, 64-66]. Quantitative determination of the AOH phase require deconvolution, which is rarely reported[47, 62, 67-69]. These additional resonances have been ascribed to variations in the local environment, e.g., hydrogen bonding to carbonate[39] or gibbsite (Al(OH)$_3$)[66, 70]. Cadars et al. prepared defect MgAl-LDH by relatively fast co-precipitation followed by aging and used a suite of 1D and 2D NMR experiments accompanies by detailed analyses of the SSNMR spectra and DFT calculations of the $^1\text{H}$ and $^{27}\text{Al}$ NMR parameters for the different local environments in the defect MgAl-LDH. This lead to the observation of additional $^1\text{H}$ and $^{27}\text{Al}$ resonances, which could be modelled by introducing Al rich defects, e.g., Al$_2$Mg-OH groups into the LDH structure[57]. Subsequently, similar defects were identified in ZnAl-LDH prepared by the same method (co-precipitation at constant pH followed by aging), whereas post-synthesis hydrothermal treatment resulted in pure ZnAl-LDH[47]. For example, the popular homogeneous precipitation by hydrolysis of urea (“urea method”), which results in $\mu$m sized LDH crystallites, leads to formation of poorly crystalline aluminum hydroxides with some similarities to Gibbsite[66, 70, 71] and hydrous M(II) hydroxide carbonates such as hydrozincite and hydromagnesite-like[71, 72]. This was established by combining $^1\text{H}$ and $^{27}\text{Al}$ SSNMR with PXRD, SEM/TEM, FT-IR, ICP-OES[71, 72]. Microwave synthesis also lead to two distinct environments, where the intensity of the LDH resonances increased with the reaction time[73]. The reader is referred to Ref. [47] for a detailed comparison of the different synthesis methods.

The effect of polymorphism (different crystal structures) on SSNMR spectra have been sparingly studied and focused on Friedel’s salt (Ca$_2$Al(OH)$_6$Cl$\cdot$2H$_2$O)[33, 34], which exists in two polymorphs $\alpha$ (monoclinic, low temperature) and $\beta$ (rhombohedral, high temperature). Detailed
analyses of the $^{27}$Al MAS NMR spectra allowed for precise determination of $\delta_{\text{iso}}$, CQ, and $\eta_Q$ from $-121$ to $109 \degree$C covering well-beyond the $\alpha$- to $\beta$-polymorph phase transition at $34 \degree$C, which was combined with point monopole calculations of the electric field gradient, provided a detailed insight into how $\delta_{\text{iso}}(^{27}\text{Al})$, CQ, and $\eta_Q$ evolved as the structure of Ca$_2$Al(OH)$_6$Cl·2H$_2$O changed[34].

$\delta_{\text{iso}}(^{27}\text{Al})$ did not vary much beyond the reported experimental uncertainty over a more than $200 \degree$C range (Table 3). In contrast, a sharp discontinuity in both CQ, and $\eta_Q$ was observed as the transition from the $\alpha$- to $\beta$-polymorph happened at $34 \degree$C. This was linked to changes in the $V_{yy}$ component of the electric field gradient tensor, where the variation in O-H bond length had a significant impact on $\eta_Q$, which changed from 0.8 to axial symmetry ($\eta_Q = 0$) [34], as illustrated in Fig. 7. Moreover, the spinning sideband manifold from the satellite transition was not observed for the $\beta$-polymorph[34]. Similar effects have been observed in MgAl-LDH and linked to dynamic processes in interlayer, c.f., Sections 4.2 and 4.3[54]. The study also highlights the fact that hydrogen positions are often poorly determined in reported X-ray structures. This may lead to incorrect bond lengths and angles, which has a significant impact on the calculated NMR parameters. It is noted that the reported phase transition temperature deviated between $^{27}$Al[34] and $^{35}$Cl SSNMR[74], which may be due to temperature off-sets in the experiments.

Paramagnetic hydrotalcite LDH such as CoAl-[63], NiAl-[56, 63, 75] and CuAl-LDH[76] have been very sparingly studied by $^{27}$Al MAS NMR. From the few $^{27}$Al MAS NMR studies [56, 63, 75] is evident that ultra-fast MAS (35-70 kHz) is needed to achieve sufficient resolution at 11.5-14.1 T for the single $^{27}$Al site in these LDH. The studies have focused on determination of $\delta_{\text{iso}}(^{27}\text{Al})$ and show that the paramagnetic shifts significantly larger $\approx$ -600 to -2800 ppm vs the ca 10 ppm diamagnetic (chemical shielding) contribution, c.f., Table 3 and Eq. 6. Static $^{27}$Al NMR spectra of NiAl-LDH using an quadrupolar echo sequence showed variation of the line shape as function of Ni content and $\delta_{\text{iso}}(^{27}\text{Al}) \approx$ -2300 ppm, but no further analyses was reported[75]. A $^{27}$Al MAS NMR study of Ni$_2$Al-LDH with different anions and Ni$_4$Al-LDH showed that both the Ni content (Ni:Al ratio) and the interlayer distances gave minor, but non-negligible contribution (< 10 %) on the paramagnetic shift[56]. Thus, the main contribution to $\delta_{\text{iso}}(^{27}\text{Al})$ in paramagnetic LDH is via the M-O-Al bonds within the cation layer. It is noted that $\delta_{\text{iso}}(^{27}\text{Al})$ for paramagnetic LDH is expected to be temperature dependent and should be considered as fast MAS leads to a significant temperature (20-50 K) increase due to frictional heating, which can be suppressed by active sample cooling. A temperature dependence of -6 ppm/K for $\delta_{\text{iso}}(^{27}\text{Al})$ in NiAl-LDH was reported[56]. Doping of a
transition metal ion into a parent LDH is often used in the preparation of catalysts as this allows for separation of the reactive centers, but these have been sparingly studied. For the diamagnetic LDH, the narrow chemical shift range, e.g., < 10 ppm for $^{27}$Al, and broad line does not provide sufficient spectral resolution in the SSNMR spectra. However, the introduction of paramagnetic ions expands the isotropic shift range difference between MgAl-LDH versus CoAl-LDH or NiAl-LDH to $\approx 600$ and 2500 ppm, respectively[63], but may also require ultra-fast MAS (40-70 kHz) and large spectral windows. It has been investigated for Mg$_{2-x}$Ni$_x$Al-[56] and CuZnAl-LDH[76]. It is noted that the $^{27}$Al resonance from AOH resonances have also incorrectly been assigned to MgCoAl- and MgNiAl-LDH[77]. The effect to Cu(II) doping into ZnAl-LDH showed formation of ZnAl-LDH as well as a very broad resonance in the region for tetrahedral Al assigned to structural changes in Al coordination upon incorporation of Cu[76]. However, the authors did not consider the possible hyperfine shifts caused by paramagnetic Cu and used only moderate spinning speeds (14 kHz). For a comparison, a single Cu-O-Al connectivities leads to a ca -100 ppm shift in CuAl$_4$-LDH[36] (Table 3). It is noted that the $^1$H-$^{27}$Al HETCOR spectrum only showed the signatures of defect ZnAl-LDH with aluminum hydroxide impurities[47]. Similarly, incorporation of paramagnetic Cu$^{2+}$ ($S = \frac{1}{2}$) and Cr$^{3+}$ ($S = \frac{3}{2}$) by reconstruction of calcinated MgAl-LDH in solutions containing the appropriate metal cation resulted in $^1$H and $^{27}$Al MAS NMR spectra of a diamagnetic phase, but more surprisingly DFT calculations of the $\delta_{\text{iso}}(^1\text{H})$ NMR shifts contained negligible paramagnetic effects[78], which contrasts experimental $^2$H NMR data for NiAl-LDH[79]. A series of Mg$_{2-y}$Ni$_y$Al-LDH with $y = 0, 1/6, 1/3, \frac{1}{2}, 5/2$ intercalated with nitrate and a small amount of carbonate showed a random distribution of Ni and Mg in the cation layer[56]. Seven different ranges of $\delta_{\text{iso}}(^{27}\text{Al})$ (Fig. 8 and Table 3), which reflects the number of paramagnetic Ni(II) in the second coordination sphere, i.e., Al(OMg)$_{6-x}$(ONi)$_x$ with $x = 0, 1, 2, 3, 4, 5, \text{and } 6$ were observed (Fig. 9). A hyperfine shift (Fermi-contact) of ca -388(17) ppm per paramagnetic Ni(II) was determined from linear regression of the experimental $\delta_{\text{iso}}(^{27}\text{Al})$ values, as illustrated in Fig. 8. Moreover, it was possible to distinguish $^{27}$Al resonances from regions with nitrate and carbonate due to their slightly different interlayer spacing. A smaller, but non negligible contribution to the hyperfine shift is the Ni content (Ni:Al) and interlayer spacing in NiAl-LDH. Reducing the Ni content from 80 % (Ni$_4$Al-LDH) to 67% (Ni$_2$Al-LDH) results in a difference of 86 ppm (-2686 vs -2600 ppm), whereas decoupling of the interlayer magnetic interactions leads to a ca 200 ppm change, c.f., Table 3[56].

$^{27}$Al SSNMR has also been used to probe structural changes in the LDH phase after calcination and reconstruction, which employ the so-called memory effect. Vyalkikh et al.
investigated MgAl-LDH prepared by the urea-method, which were calcinated and subsequently reconstructed using anionic surfactants for which both tetrahedral and octahedral Al sites were observed in $^{27}$Al MAS and 3Q MAS NMR spectra[70]. The octahedral Al region contained two sites: AlO$_6$-I and AlO$_6$-II assigned to the MgAl-LDH resonances and gibbsite (2 Al sites), respectively. The quantity of tetrahedral Al was correlated with a reduction in intensity of the LDH resonances, whereas second(AlO$_6$-II) was unchanged. Thus, exposure to the surfactant destroyed some of the LDH. AlO$_6$-II was tentatively assigned to a different LDH polymorph[66], but it was also concluded that more studies were needed. Subsequently, it has been demonstrate that the LDH synthesis by the urea method contains a gibbsite-like impurity as a result of the synthesis[71]. The gibbsite layers are neutral and held together by strong hydrogen bonding, i.e., intercalation of charged species is not likely. Formation of tetrahedral Al upon calcination is observed in $^{27}$Al SSNMR spectra[80-84] and leaching of Al from the LDH has also been observed by delamination-restacking and formation of LDH-alginate nanohybrid materials[56].

4.1.2 $^{27}$Al and $^{6,7}$Li SSNMR studies of LiAl$_2$-LDH

LiAl$_2$-LDH contains a single resonance in both $^{6,7}$Li and $^{27}$Al NMR spectra, c.f., Table 1. $^{6,7}$Li MAS NMR spectra of LiAl$_2$-LDH show a very small quadrupole interaction and a $\delta_{\text{iso}}$(Li) = -0.4 ppm with a temperature dependent line width[85-87], i.e., the NMR spectra can be deconvoluted using Gaussian and/or Lorentzian line broadening. The reported isotropic chemical shifts are all $\delta_{\text{iso}}$(Li) ≈ 0.0 ppm and only changes slightly with the anion (Table 4). Moreover, a moderate $^{27}$Al quadrupole interaction (C$_Q$ < 2 MHz) is observed for the single octahedral Al site (Table 3), which is similar to the hydrotalcite LDH and significantly smaller than those observed for the MAI$_4$-LDH, but comparable to the hydrotalcite LDH. These properties favored an in situ $^{6}$Li and $^{27}$Al MAS NMR of the formation of LiAl$_2$-LDH (Fig 10) at 20 T, which demonstrated that the importance of a solution pathway, i.e., dissolution of gibbsite followed by precipitation of the LDH, for insertion of Li$^+$ into gibbsite[86]. Moreover, a $^{7}$Li and $^{27}$Al MAS NMR ex-situ study of the Li uptake showed two Li phases, a well-defined LDH, with a strong affinity of $^{6}$Li over $^{7}$Li (isotope effect), and a broad resonance from Li in an amorphous phase[87].
Table 3 A selection of reported $^{27}$Al NMR parameters to illustrate the effect of M(II), M(II):Al ratio and anion as well as common impurities. Al values are experimental unless indicated by “DFT”, which are obtained by DFT calculation. % indicate that the parameters were not reported. It is noted that the isotropic shift for paramagnetic LDH may show a significant temperature dependence[56].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
<th>Comment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl-NO$_3$</td>
<td>11.8</td>
<td>1.55</td>
<td>0.0</td>
<td>Indication of motion for low Al content</td>
<td>[39]</td>
</tr>
<tr>
<td>Mg$_{2-y}$Ni$_y$Al-NO$_3$</td>
<td>10(2)</td>
<td>%</td>
<td>%</td>
<td>Al(OMg)$_6$</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>$\approx$ -340</td>
<td></td>
<td></td>
<td>Al(OMg)$_5$(ONi)$_1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\approx$ -720</td>
<td></td>
<td></td>
<td>Al(OMg)$_4$(ONi)$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\approx$ -1070</td>
<td></td>
<td></td>
<td>Al(OMg)$_3$(ONi)$_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\approx$ -1550</td>
<td></td>
<td></td>
<td>Al(OMg)$_2$(ONi)$_4$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\approx$ -2000</td>
<td></td>
<td></td>
<td>Al(OMg)$_1$(ONi)$_5$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\approx$ -2600</td>
<td></td>
<td></td>
<td>Al(ONi)$_6$</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Ca$_2$Al-Cl</td>
<td>9.1(0)</td>
<td>1.58(3)</td>
<td>0.80(2)</td>
<td>- 121 °C</td>
<td>[34]</td>
</tr>
<tr>
<td>$\beta$-Ca$_2$Al-Cl</td>
<td>9.4(3)</td>
<td>1.06(2)</td>
<td>0.03(4)</td>
<td>80 °C</td>
<td>[34]</td>
</tr>
<tr>
<td>MgAl-PAS$^a$</td>
<td>11.2(4)</td>
<td>1.6(2)</td>
<td>0.0(1)</td>
<td>Ca 30 % Al</td>
<td>[62]</td>
</tr>
<tr>
<td>Ca$_2$Al-PAS$^a$</td>
<td>14.8(8)</td>
<td>1.6(1)</td>
<td>0.0(1)</td>
<td>Ca 30 % Al</td>
<td>[62]</td>
</tr>
<tr>
<td>ZnAl-PAS$^a$</td>
<td>15.5(5)</td>
<td>1.6(2)</td>
<td>0.0(1)</td>
<td>Ca 24 % Al</td>
<td>[62]</td>
</tr>
<tr>
<td>Ni$_4$Al-NO$_3$</td>
<td>-2686(49)</td>
<td>%</td>
<td>%</td>
<td></td>
<td>[56]</td>
</tr>
<tr>
<td>Ni$_2$Al-CO$_3$</td>
<td>-2600 (45)</td>
<td>%</td>
<td>%</td>
<td></td>
<td>[56]</td>
</tr>
<tr>
<td>Ni$_2$Al-TPb</td>
<td>-2770(30)</td>
<td>%</td>
<td>%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoAl-NO$_3$</td>
<td>-689(30)</td>
<td>%</td>
<td>%</td>
<td></td>
<td>[63]</td>
</tr>
<tr>
<td>ZnAl-NO$_3$</td>
<td>16.4(2)</td>
<td>1.45(10)</td>
<td>0.0(1)</td>
<td>Pure Zn$_2$Al-LDH</td>
<td>[47]</td>
</tr>
<tr>
<td>ZnAl-CO$_3$</td>
<td>15.0(2)</td>
<td>1.45(10)</td>
<td>0.0(1)</td>
<td></td>
<td>[47]</td>
</tr>
<tr>
<td>ZnAl-Cl</td>
<td>15.5(2)</td>
<td>1.43(10)</td>
<td>0.0(1)</td>
<td></td>
<td>[47]</td>
</tr>
<tr>
<td>ZnAl$_4$-LDH</td>
<td>8.2(4)</td>
<td>3.0(3)</td>
<td>0.6</td>
<td>Al(1)</td>
<td>[38]</td>
</tr>
<tr>
<td>4 Al sites NMR</td>
<td>11.0(6)</td>
<td>3.1(3)</td>
<td>0.5</td>
<td>Al(2)</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>9.0(6)</td>
<td>3.5(2)</td>
<td>0.3</td>
<td>Al(3)</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>9.0(4)</td>
<td>4.9(2)</td>
<td>0.9</td>
<td>Al(4)</td>
<td>[38]</td>
</tr>
<tr>
<td>ZnAl$_4$-LDH</td>
<td>9.0</td>
<td>3.5</td>
<td>0.62</td>
<td>Al(1)</td>
<td>[35]</td>
</tr>
<tr>
<td>4 Al sites DFT</td>
<td>10.8</td>
<td>3.4</td>
<td>0.48</td>
<td>Al(2)</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>7.23</td>
<td>3.2</td>
<td>0.32</td>
<td>Al(3)</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>8.12</td>
<td>5.4</td>
<td>0.96</td>
<td>Al(4)</td>
<td>[35]</td>
</tr>
<tr>
<td>CoAl$_4$-LDH$^c$</td>
<td>$\approx$0(40),</td>
<td>%</td>
<td>%</td>
<td></td>
<td>[36]</td>
</tr>
<tr>
<td>4 Al sites</td>
<td>$\approx$-120(40)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiAl$_4$-LDH$^c$</td>
<td>$\approx$-270(30)</td>
<td>%</td>
<td>%</td>
<td></td>
<td>[36]</td>
</tr>
<tr>
<td>4 Al sites</td>
<td>$\approx$-570(50)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>CuAl$_2$-LDH</td>
<td>LiAl-Cl</td>
<td>LiAl-OH</td>
<td>Gibbsite</td>
<td>Bayerite</td>
</tr>
<tr>
<td>----------------</td>
<td>--------------</td>
<td>---------</td>
<td>---------</td>
<td>-----------</td>
<td>----------</td>
</tr>
<tr>
<td>4 Al sites</td>
<td>-77(3), -89(2), -332(5), -341(5)</td>
<td>8.6</td>
<td>9.07</td>
<td>13.6(2)</td>
<td>11.3(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>small</td>
<td>1.6</td>
<td>4.6(2)</td>
<td>2.2(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>%</td>
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<td>0.7(1)</td>
</tr>
<tr>
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<td>20 T</td>
<td>13.6(2)</td>
<td>11.3(2)</td>
</tr>
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<td></td>
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<td>1.6(1)</td>
<td>1.4(1)</td>
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<tr>
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<td></td>
<td>0.4(1)</td>
<td>0.80(5)</td>
</tr>
</tbody>
</table>

$^a$ PAS = para aminosalicylate

$^b$ terephthalate

$^c$ The structure contains four crystallographic inequivalent, but only two broad resonances can be distinguished due to significant paramagnetic broadening.
4.1.3  $^{27}$Al SSNMR studies of MAl₄-LDH

The very few $^{27}$Al SSNMR studies of MAl₄-LDH have investigated samples intercalated with sulfate and nitrate. The most detailed information has been obtained for the diamagnetic ZnAl₄-LDH, where $^{27}$Al single-pulse and 3QMAS NMR combined with DFT calculations as well as $^1$H-$^1$H NOESY (Fig. 11) and $^1$H-$^{27}$Al HMQC (Fig 12) experiments allowed for assignment and analyses of the four crystallographic inequivalent sites[35, 38]. Three $^{27}$Al sites have quite similar quadrupole interactions (3-3.5 MHz), whereas the fourth site has a significantly larger (4.9 MHz) in good agreement with the distortion of the Al octahedra in the crystal structure[20]. Similar values were also predicted from DFT calculations[35]. The remaining three MAl₄-LDH with M = Co²⁺, Ni²⁺ and Cu²⁺ are all paramagnetic and only $\delta_{\text{iso}}(^{27}\text{Al})$ has been determined due to significant paramagnetic line broadening[36]. $\delta_{\text{iso}}(^{27}\text{Al})$ falls in two groups: those with one paramagnetic and two M-O-Al connectivity, i.e., [Al(3) and Al(4)] and [Al(1) and Al(2)], respectively [36]. The hyperfine shifts are approximately proportional to the number of M-O-Al connectivities, c.f., Table 3, as also observed for Mg$_2$-Ni$_x$Al-LDH[56]. This reflects the absence of local magnetic interactions at room temperature. It is noted that ultra-fast MAS NMR (60+ kHz) is needed to obtain sufficient spectral resolution for CoAl₄- and NiAl₄-LDH, whereas more moderate speeds of 30-40 kHz sufficient for CuAl₄-LDH. Earlier $^{27}$Al MAS NMR data for MAl₄(OH)$_{12}$(NO₃)$_2$:3H₂O with M = Co²⁺, Ni²⁺ and Cu²⁺ reported $\delta_{\text{iso}}(^{27}\text{Al})$ of -12.2 ppm, 5.8 ppm, and -99.8 ppm for M = Co²⁺, Ni²⁺ and Cu²⁺, respectively[88], whereas $^{27}$Al 3QMAS NMR spectra of MAl₄(OH)$_{12}$(NO₃)$_2$:3H₂O with M = Ni²⁺ and Cu² only showed intensity in the diamagnetic region (-20 to + 20 ppm) assigned to the paramagnetic MAl₄-LDH[89]. This points to the observation of diamagnetic impurities such as unreacted gibbsite, boehmite or aluminum sulfates except for the -99.8 ppm resonance reported for CuAl₄-LDH, which may be one or two of the four $^{27}$Al resonances [36].

4.1.4 $^{71}$Ga SSNMR studies of MgGa-LDH

The only other trivalent metal ion investigated by SSNMR is Ga in MgGa-LDH. $^{71}$Ga NMR spectra of MgGa-LDH showed the presence of a single $^{71}$Ga site with well-defined quadrupolar line shape due to the significantly larger quadrupole moment and lower spin value for $^{67}$Ga as compared to $^{27}$Al. Analyses of the single-pulse NMR spectra recorded at high field (14.1 T) unambiguously showed a
single $^{67}$Ga resonance thereby confirming Ga-O-Ga avoidance[90]. The $^{71}$Ga NMR parameters matched well with the correlations reported for $^{71}$Ga and $^{27}$Al NMR parameters for isostructural compounds[91] in Eqs 7 and 8:

$$\delta_{iso}(^{71}\text{Ga}) = 2.84(8)\delta_{iso}(^{27}\text{Al}) - 1(4) \text{ [ppm]} \quad (7)$$

$$CQ(^{71}\text{Ga})/CQ(^{27}\text{Al}) = 3.11(13) \quad (8)$$

Earlier studies only reported the $^{71}$Ga MAS NMR spectra and marked the position of singularities in studies of the thermal degradation of MgGa-LDH[92, 93].

4.1.5 The M(II) ions in hydrotalcite, hydrocalumite and MAl$_x$-LDH

For the hydrotalcite LDH, the most common M(II) ions are Mg(II), Zn(II), Ni(II), Co(II), Cu(II), and Fe(II), where the first two (Mg(II) and Zn(II)) are low-gamma nuclei and the remaining are paramagnetic. Thus, the very few SSNMR studies of M(II) ions in LDH have focused on $^{25}$Mg NMR of MgAl-LDH intercalated with nitrate[39, 40, 68], carbonate[39, 82], phosphate[68, 94], and benzoxoborolate[95] as well as a single $^{67}$Zn SSNMR study[47]. Table 4 summarizes the NMR parameters determined for $^{25}$Mg in a different MgAl-LDH. It is noted that the quadrupolar line shapes deviate from the ideal, which is indicative of a distribution in NMR interaction parameters ascribed to stacking faults and/or variations in local environment[38-40, 68]. Each $^{25}$Mg has six metal-ions in the first metal ion coordination sphere of which none to three can be $^{27}$Al, this leads to the existence of up to four different local $^{25}$Mg environments. These can be described as Mg(OAl)$_x$(OMg)$_{6-x}$ with $x = 0, 1, 2, \text{ and } 3$. Their relative intensity is determined by the Al content[39]. An ideal Mg$_2$Al-LDH contains a single $^{25}$Mg NMR resonances with $C_Q \approx 4.6$ MHz and axial symmetry ($\eta_Q = 0$) irrespective of the intercalated anion[39, 40, 68, 82, 95], whereas the “brucite-like” Mg(OMg)$_6$ environment ($C_Q \approx 3.1$ MHz, $\eta = 0$) named after brucite (Mg(OH)$_2$), is present at lower Al contents, c.f., Table 4. For both these sites, the local symmetry of the crystallographic Mg site restricts the quadrupole tensor to axial symmetry, whereas this is not the case for the $x = 1$ and 2 sites. In 1D $^{25}$Mg SSNMR spectra these sites overlap extensively, which prevents quantification of their relative concentration and extraction of $^{25}$Mg NMR parameters. These can be resolved by $^{25}$Mg 3QMAS NMR of MgAl-LDH intercalated with nitrate and with different Al content [39], as illustrated in Fig. 13. This allowed for determination of the NMR parameters, which can be used to quantify the different $^{25}$Mg sites by deconvolution of the quantitative 1D $^{25}$Mg MAS NMR spectra[39, 68]. The parameters in Table 4
can be used as starting values for deconvolution of MgAl-LDH, as \( \delta_{\text{iso}}(^{25}\text{Mg}) \) is the parameters most affected by changes in the anion. Generally, only 1D NMR spectra at either ultra-high field or 8+ hrs are needed to obtain a good signal-to-noise ratio. At 14.1 T a good spectrum is obtained overnight using DFS-echo sequence[95] for sensitivity enhancement and a 5 mm MAS NMR probe, as ca. 9+ kHz spinning speed is needed to avoid too distorted quadrupolar line shapes. In contrast, a few hours at 21.1 T using a 4 mm MAS probe, 10-14 kHz pinning and a standard Hahn echo sequence gives similar quality[68, 72]. The non-ideal line shapes are generally observed in \(^{25}\text{Mg} \) SSNMR spectra due to variation of the local environments as well as non-ideal excitation for \(^{25}\text{Mg} \) 3QMAS NMR spectra render analyses more demanding. However, the effect of interlayer dynamics has not been studied, but may also influence the \(^{25}\text{Mg} \) SSNMR spectra.

Only a single \(^{67}\text{Zn} \) NMR study has been reported. A \(^{67}\text{Zn} \) resonances observed for a Zn\(_2\)Al-LDH and the \( C_Q \) value matched well with a scaling factor of approximately 2.5 for \(^{25}\text{Mg} \).\(^{67}\text{Zn}\)[47]. It is noted that static \(^{67}\text{Zn} \) SSNMR spectra of a ZnAl-LDH samples with less than 33 % Al indicated the presence of multiple environments, but the poor signal-to-noise ratio and Zn impurities even at 19.6 T prevented further analysis.

No SSNMR studies of the M(II) in MAl\(_4\)-LDH have been reported, which reflect the challenges related to preparation of phase pure samples as well as the paramagnetic nature of Co(II), Ni(II), and Cu(II)[36] and the low-gamma properties of \(^{67}\text{Zn} \) and \(^{25}\text{Mg} \), c.f. Table 2. For \(^{67}\text{Zn} \), a \( C_Q \approx 14.3 \) MHz was predicted based on DFT calculations (Table 5), where good agreement between experimental and calculated \(^{27}\text{Al} \) quadrupole parameters was observed [35], c.f. Table 3. This points to the feasibility of \(^{67}\text{Zn} \) SSNMR under static conditions at ultra-high field.
Table 4 $^{25}$Mg SSNMR parameters reported for MgAl-LDH with different intercalated anions and Mg:Al ratio for the different possible Mg(OAl)$_x$(OMg)$_{6-x}$ (x ranges from 0 (parent brucite mineral) to 3 for an ideal Mg$_2$Al-LDH. It is noted that $\eta_Q$ is restricted to zero for Mg(OMg)$_6$ and Mg(OAl)$_3$(OMg)$_3$ due to the symmetry of the Mg site. The parameters for Mg(OH)$_2$ are shown for a comparison.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Site</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
<th>Comment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$Al-CO$_3$</td>
<td>Mg(OAl)$_3$(OMg)$_3$</td>
<td>10</td>
<td>4.4</td>
<td>0</td>
<td>35 % Al, commercial LDH</td>
<td>[82]</td>
</tr>
<tr>
<td>Mg$_2$Al-CO$_3$</td>
<td>Mg(OAl)$_3$(OMg)$_3$</td>
<td>13.7(6)</td>
<td>4.5(1)</td>
<td>0.0</td>
<td>Urea method with significant AOH impurities.</td>
<td>[39]</td>
</tr>
<tr>
<td>Mg$_2$Al-NO$_3$</td>
<td>Mg(OAl)$_3$(OMg)$_3$</td>
<td>11.5(6)</td>
<td>4.6(1)</td>
<td>0.0(1)</td>
<td>33 % Al</td>
<td>[39]</td>
</tr>
<tr>
<td>Mg$_3$Al-NO$_3$</td>
<td>Mg(OAl)$_3$(OMg)$_3$</td>
<td>14.2(6)</td>
<td>4.5(2)</td>
<td>0.0(1)</td>
<td>25% Al</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>Mg(OAl)$_2$(OMg)$_4$</td>
<td>14.1(9)</td>
<td>4.8(3)</td>
<td>0.2(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg(OMg)$_6$</td>
<td>16.0(5)</td>
<td>3.0(1)</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg$_4$Al-NO$_3$</td>
<td>Mg(OAl)$_3$(OMg)$_3$</td>
<td>14(1)</td>
<td>4.6(1)</td>
<td>0.0(1)</td>
<td>19% Al</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>Mg(OAl)$_2$(OMg)$_4$</td>
<td>13.8(5)</td>
<td>4.9(1)</td>
<td>0.2(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg(OMg)$_6$</td>
<td>12.2(6)</td>
<td>3.1(1)</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgAl-NO$_3$</td>
<td>Mg(OAl)$_3$(OMg)$_3$</td>
<td>14.0(9)</td>
<td>4.6(1)</td>
<td>0(1)</td>
<td>Mg:Al = 2.6</td>
<td>[68]</td>
</tr>
<tr>
<td>Mg$_2$Al-BBzx</td>
<td>Mg(OAl)$_3$(OMg)$_3$</td>
<td>14</td>
<td>4.5</td>
<td>0.12</td>
<td>BBzx = benzo-xoborolate</td>
<td>[95]</td>
</tr>
<tr>
<td>Mg(OH)$_2$</td>
<td>Mg(OMg)$_6$</td>
<td>10.2(2)</td>
<td>3.1(1)</td>
<td>0.0</td>
<td>Brucite</td>
<td>[39]</td>
</tr>
</tbody>
</table>
Table 5 SSNMR parameters reported for $^6$Li, $^{17}$O, $^{67}$Zn, $^{71}$Ga in LDH obtained from experimental and computational NMR (DFT) studies.

<table>
<thead>
<tr>
<th>Compound</th>
<th>NMR</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>C$_Q$ (MHz)</th>
<th>$\eta_Q$</th>
<th>Comment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAl-LDH$^a$</td>
<td>$^6$Li</td>
<td>-0.08</td>
<td>Small</td>
<td>%</td>
<td>Anion = Cl</td>
<td>[86]</td>
</tr>
<tr>
<td>LiAl-LDH$^a$</td>
<td>$^6$Li</td>
<td>-0.05</td>
<td>Small</td>
<td>%</td>
<td>Anion = OH</td>
<td>[85]</td>
</tr>
<tr>
<td>MgAl-LDH</td>
<td>$^{17}$O</td>
<td>2.5(5)</td>
<td>6.6(1)</td>
<td>0.0(1)</td>
<td>Mg$_3$$^{17}$OH,</td>
<td>[96]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>experimental Mg$_3$$^{17}$OH (DFT)$^b$</td>
<td></td>
</tr>
<tr>
<td>MgAl-LDH</td>
<td>$^{17}$O</td>
<td>N/A</td>
<td>6.97-7.51</td>
<td>0.00</td>
<td>Mg$_2$$^{17}$OH</td>
<td>[96]</td>
</tr>
<tr>
<td>MgAl-LDH</td>
<td>$^{17}$O</td>
<td>18.0</td>
<td>6.2(1)</td>
<td>0.3(1)</td>
<td>Mg$_2$$^{17}$OH</td>
<td>[96]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>experimental Mg$_2$$^{17}$OH (DFT)$^b$</td>
<td></td>
</tr>
<tr>
<td>MgAl-LDH</td>
<td>$^{17}$O</td>
<td>N/A</td>
<td>6.49-6.97</td>
<td></td>
<td>Ideal Zn$_2$Al-LDH</td>
<td>[47]</td>
</tr>
<tr>
<td>Zn$_2$Al-LDH</td>
<td>$^{67}$Zn</td>
<td>10.6</td>
<td>15</td>
<td>0.02</td>
<td>Zn(OAl)$_3$(OZn)$_3$</td>
<td></td>
</tr>
<tr>
<td>ZnAl$_4$-LDH</td>
<td>$^{67}$Zn</td>
<td>%</td>
<td>14.3</td>
<td>0.24</td>
<td>DFT</td>
<td>[35, 47]</td>
</tr>
<tr>
<td>MgGa-LDH</td>
<td>$^{71}$Ga</td>
<td>40(2)</td>
<td>5.35(10)</td>
<td>0.04</td>
<td>Three samples with</td>
<td>[90]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13-20 % Ga</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The quadrupole interaction is very weak given the small quadrupole moment of $^6$Li and the local symmetry, hence this cannot be determined from analyses of the reported spectra.

$^b$ Four different basis sets were employed for the same cluster model for calculation of the quadrupole tensor. The range corresponds to the minimum and maximum values reported in Table S3 in Ref. [96].

4.1.5 $^{17}$O SSNMR studies of LDH

$^{17}$O isotope enrichment strategies are needed for $^{17}$O SSNMR studies due to the low natural abundance of this isotope (Table 2). Thus, only few studies have been reported[96-98]. LDH are generally prepared in aqueous solution often using metal salts with significant amounts of crystallographic water. Thus, the use of $^{17}$O enriched water (H$_2$$^{17}$O) in the synthesis is too expensive for routine NMR studies as 10+ mL of water is necessary for preparation of sufficient sample. The few studies have employed the so-called memory effect, where thermally treated LDH of the desired chemical composition is suspended in a small amount of $^{17}$O enriched water followed by uptake of $^{17}$O[96-98].
A high level of $^{17}$O enrichment was achieved by calcination of the LDH at 500 °C to remove interlayer water and the anion (carbonate or nitrate) followed by reconstruction of the LDH in very small amounts of $\text{H}_2^{17}$O taking advantage of the memory effect, an approach that was successfully demonstrated for four different Mg:Al ratios[96]. The reconstruction of the LDH structure was verified by PXRD and $^{27}$Al SSNMR. Simply by soaking the MgAl-NO$_3$ LDH samples in $\text{H}_2^{17}$O for a week resulted in an $^{17}$O enrichment sufficient for NMR experiments[98], whereas soaking a Mg$_2$Al-CO$_3$ in $\text{H}_2^{17}$O for six days in insufficient enrichment, as evident by a poor signal-to-noise ratio in the $^{17}$O MAS NMR spectra[96]. The reconstructed LDH contained hydroxide as anion based on the $^{17}$O MAS NMR spectra (vide infra), but also some amount of carbonate incorporated during the hydrothermal treatment [96]. It was convincingly proven that water and hydroxides exhibited a fast exchange with water in the atmosphere. Thus resonances from interlayer water was not observed and the signal from the hydroxide in the $^{17}$O SSNMR spectra decreased during storage, see supporting information in Ref [96] for a detailed discussion. Thus, $^{17}$O enrichment strategies appears to be linked to dynamic processes in the interlayer (see Section. 4.3), which affect both sample preparation and storage. It is noted that calcination at 500 °C followed by reconstruction will also destroy other organic anions, may potentially be irreversible, and the approach will need to be modified for intercalation other anions than hydroxide, which limits the $^{17}$O enrichment strategy above. Thus, $^{17}$O SSNMR is a powerful, but sparingly used tool for structural insight into the LDH as well as mobility and chemical exchange processes, but protocols for enrichment that allow for control of the interlayer anion needs to be developed as well as use a minimal amount of expensive $^{17}$O labelled chemicals are needed.

Two different $^{17}$O environments, whose relative intensity depended on the Mg:Al ratio was observed (Fig 14). These were unambiguously assigned to Mg$_3$$^{17}$OH and Mg$_2$Al-$^{17}$OH groups based on their relative intensity, computational modelling of the quadrupole interaction parameters, and $^{17}$O NMR data for brucite, which contain the Mg$_3$$^{17}$OH environment (Table 5). The sites overlapped in the $^{17}$O MAS NMR spectra, but slices of the 3QMAS NMR spectra allowed for precise determination of the NMR interaction parameters by simulations of the quadrupolar line shape. These confirmed the Al ordering in the cation layer, as earlier determined by $^1$H and $^{25}$Mg NMR [39, 40, 57]. Sahoo et al. identified two different types of oxygen environments in a Mg$_3$Al-CO$_3$ assigned to water forming strong hydrogen bonds in the interlayer (“ice like”) at -80 ppm (at least two signals based on 3QMAS NMR spectra) and from carbonate in the 100 to 200 pm chemical shift range[97]. The observation of $^{17}$O in carbonate proved chemical exchange between interlayer water and
carbonate in a dynamic process, but no detailed analyses is reported. The authors assumed labelling of only the interlayer water and carbonate, but not the Mg3-OH and Mg2Al-OH groups in the cation layer[97, 98]. However, the position of these resonances and spectral features are similar to those unambiguously assigned to Mg3.17OH and Mg2Al.17OH by Zhao et al.[96]. Moreover, it should be highlighted that carbonate, which lead to a very ordered hydrogen bonding network, was present. Thus, the second resonance (not observed by Zhao et al. [96]) may possible be from the strongly hydrogen bonded water molecules. Unfortunately, the limited analyses of the experimental 17O MAS and 3QMAS NMR data prevents further comparison of the two studies. MgAl-Cl LDH contained an addition signal at δ(17O) = 0 ppm assigned to mobile water species. However, no detailed analyses aimed at extracting the isotropic chemical shift or quadrupole interactions parameters were reported or the results discussed in relation to earlier 35Cl[33] and 13C NMR[55, 99]. This renders comparison of data with those of Zhao et al.[96] (9.4 and 16.4 T) difficult due to the significant second order quadrupole interaction, which affects both the center of gravity and the line shape of the central transition.

4.2 1H and 2H SSNMR studies of the hydrogen species in LDH

LDH contains an extensive hydrogen network and thereby strong homo-nuclear 1H-1H dipolar interactions, which require high magnetic fields and ultra-fast MAS to ensure sufficient resolution of the different species. Alternatively homonuclear dipolar decoupling sequences in order to resolve the different local hydrogen environments[40] or deuteration[100]. The hydrotalcite LDH, which have been studied for decades, contain up to three different hydrogen environments. Interlayer water, which give one resonance due to rapid motion, and two hydroxyl groups except an ideal LDH with a M(II):M(III) ratio of 2:1 (Table 1).

Thus, earlier 1H NMR studies focused on static samples both powders and oriented samples, where the plate-like LDH particle morphology allowed for preparation of highly oriented samples at moderate magnetic fields (7.1 T, 300 MHz) [99, 101]. Oriented samples of LDH, clays and other plate-like samples can be prepared by suspension of the sample in water followed by dropwise deposition of the sample on a glass slide and drying due to the plate like morphology. Subsequently, the glass slit is cut into pieces and stacked. This will facilitate determination of the mobility of the hydrogen species based on the dipolar interaction (“Pake doublet”) and T1.
measurements, which allow for discrimination between the interlayer and hydroxyl species, but not between the two possible hydroxyl groups (Table 1). For example, a static $^1$H SSNMR study of hydrotalcite powders (Mg$_3$Al-CO$_3$ LDH) and oriented samples provided insight into the orientation of the water molecules. The water molecules were shown to perform rotation parallel the crystallographic $c$-axis based on detailed simulations of the static NMR spectra taking motion and sample orientation in consideration in the analysis[99]. Static$^1$H SSNMR of MgAl-NO$_3$ LDH showed that the mobility of water was closely linked to the water content and sample temperature[101]. At low temperature, i.e., before the onset of motion on the NMR time scale, a 20-22 kHz dipolar splitting was observed. The authors considered two different motions, rotation or wobbling around the C$_2$ axis as well as an suggested diffusion[101]. T$_1$ measurements result in a low activation energy of only 4 kJ/mol. Subsequently, a similar approach was used to perform $^1$H and $^{13}$C NMR studies of $^{13}$C labelled MgAl-CO$_3$ LDH. The $^1$H NMR spectra were carefully analyzed by simulations taking both the $^1$H-$^1$H dipolar interaction and chemical shift into account. This revealed three different hydrogen environments assigned to oriented, non-oriented and physisorbed species. Studies of oriented samples, which allowed for determination of both the dipolar interaction and the chemical shift, showed that the oriented water molecules performed C$_2$ motion around an axis perpendicular to the layers. Large amounts of physisorbed water, i.e., on the surface of the particles, was more mobile. The two early $^1$H NMR studies proposed different orientation of the water molecules, but they were performed on nitrate[101] and carbonate[99], which subsequent NMR studies of the anion have shown quite different hydrogen bonding networks and water mobility. The effect of anions and relative humidity was investigated by static $^1$H SSNMR, which could be modelled by two distinct T$_1$ assigned to interlayer (T$_1$ $\approx$ 1 s) and hydroxyl groups (T$_1$ $\approx$ 1 ms) [102]. In sharp contrast, the water molecules are highly ordered in the MAI$_4$-LDH and at least three different water resonances are observed in ZnAl$_4$-LDH intercalated with sulfate[38], reflecting a strong hydrogen network[20] (vide infra).

The focus in recent $^1$H MAS NMR studies, which have generally employed fast (>30 kHz) MAS) and high magnetic fields (500 to 950 MHz)[39, 40, 47, 62, 64, 66, 71] to ensure high-resolution $^1$H MAS NMR spectra, has been identification and quantification of the different local $^1$H environments using a suite of 1D and 2D NMR spectra. It is noted that the high mobility of water can affect the intensities in $^1$H MAS NMR spectra especially for echo- and more advanced NMR sequences leading to signal loss. This effect can be used for identification of the water resonances [38, 40]. However, echo sequences are also routinely used to filter $^1$H background signals and it can
lead to incorrect assignment. For example, the resonances assigned to the ZnAl-LDH in a T₂ filtered 
¹H MAS NMR recorded with 14 kHz spinning [103] originates from background signals, when 
compared to reported 
¹H MAS NMR spectra of ZnAl-LDH[47]. Alternatively, 
¹H homonuclear decouping sequences or deuteration can be used to suppress the strong 
¹H-¹H homonuclear dipolar interaction. Vyalikh et al. acquired 2D 
¹H RFDR spectra, which allowed for assignment of the 
hydrogen species in organo LDH as well as correlate different 
¹H environments (δiso(¹H)) and T₁p 
(spin lattice relaxation in the rotation frame) using inverse Laplace transform[64]. The moderate 
spinning speeds can be achieved with a standard 3.2 mm MAS probe. Similarly, deuteration is needed 
paramagnetic for studies of paramagnetic LDH, which have only been reported for NiAl-LDH[79]. Alternatively, post-synthesis deuteration of the sample by suspension in D₂O combined with 
moderate MAS (20 kHz) and field (9.4 T) results in similar resolution of the 
¹H MAS NMR spectra[100, 104], as deuteration dilutes the 
¹H spins and thereby suppress the strong 
¹H-¹H homonuclear dipolar interaction.

A single pulse 
¹H MAS NMR spectrum of a hydrotalcite LDH will contain one 
resonance from the interlayer water located at ≈4-5 ppm, and one or two resonances from the hydroxyl 
groups, which are coordinated to three different metal ions in the interlayer (Fig 15). The ordering of 
the metal ions in the cation layer in hydrotalcite LDH (Fig 2) is very difficult to detect by diffraction 
techniques, as LDH are notorious for low crystallinity, Mg²⁺ and Al³⁺ are isoelectronic, and hydrogen 
has very low scattering power and therefore potential superstructure reflections will be weak.
Table 6 δ_{iso}(^1H) reported for the hydrogen species present in pure hydrotalcite and hydrocalumite type LDH, where M and M’ indicate the di (M(II)) and trivalent cation (M(III), respectively. An LDH with M:M’ ratio of 2:1 and ideal ordering of M’ will only contain M2M’-OH and H2O, whereas for high ratios (less Al), the M3-OH site is observed[40]. For a comparison, data are also reported for two defect LDH.

<table>
<thead>
<tr>
<th>LDH</th>
<th>M3-OH (ppm)</th>
<th>M2M’-OH (ppm)</th>
<th>H2O (ppm)</th>
<th>M’ content &amp; comments</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg₄Al-NO₃</td>
<td>0.8</td>
<td>2.4</td>
<td>4.7</td>
<td>19% Al</td>
<td>[40]</td>
</tr>
<tr>
<td>Mg₃Al-NO₃</td>
<td>0.8</td>
<td>2.9</td>
<td>4.6</td>
<td>25% Al</td>
<td>[40]</td>
</tr>
<tr>
<td>Mg₂Al-NO₃</td>
<td>%</td>
<td>3.8</td>
<td>4.7</td>
<td>33% Al (ideal)</td>
<td>[40]</td>
</tr>
<tr>
<td>Mg₂Al-NO₃ᵃ</td>
<td>1.6</td>
<td>3.8</td>
<td>4.6</td>
<td>33%Al, MgAl₂-OH at 5.3 ppm</td>
<td>[57]</td>
</tr>
<tr>
<td>MgAl-PASᵇ</td>
<td>1.1(7)</td>
<td>3.1(5)</td>
<td>4.3(5)</td>
<td>Ca. 30% Al</td>
<td>[62]</td>
</tr>
<tr>
<td>MgGa-NO₃</td>
<td>0.5(1)</td>
<td>2.4(1)</td>
<td>4.6(1)</td>
<td>16% Ga</td>
<td>[90]</td>
</tr>
<tr>
<td>MgGa-NO₃</td>
<td>0.6(1)</td>
<td>2.6(1)</td>
<td>4.7(1)</td>
<td>20 % Ga</td>
<td>[90]</td>
</tr>
<tr>
<td>Ca₂Al-PASᵇ</td>
<td>1.3(5)</td>
<td>2.9(6)</td>
<td>4.2(1)</td>
<td>Ideal Ca₂Al,</td>
<td>[62]</td>
</tr>
<tr>
<td>NiAl-NO₃ᶜ</td>
<td>%</td>
<td>-77(5)</td>
<td>10(5)</td>
<td>32.3% Al</td>
<td>[104]</td>
</tr>
<tr>
<td>NiAl-NO₃ᶜ</td>
<td>-27(10)</td>
<td>-89(5)</td>
<td>7(5)</td>
<td>25.6 % Al</td>
<td>[104]</td>
</tr>
<tr>
<td>NiAl-NO₃ᶜ</td>
<td>-24(10)</td>
<td>-101(5)</td>
<td>10(5)</td>
<td>21.3 % Al</td>
<td>[104]</td>
</tr>
<tr>
<td>ZnAl-NO₃</td>
<td>%</td>
<td>4.4(1)</td>
<td>4.6(1)</td>
<td>33% Al (ideal)</td>
<td>[47]</td>
</tr>
<tr>
<td>ZnAl-NO₃ᵃ</td>
<td>3.3(1)</td>
<td>4.4(1)</td>
<td>4.8(1)</td>
<td>Defects at 3.3 &amp; 5.3 ppm</td>
<td>[47]</td>
</tr>
<tr>
<td>ZnAl-PASᵃ</td>
<td>1.0(1)</td>
<td>3.0(1)</td>
<td>4.2(1)</td>
<td>Ca. 24 % Al</td>
<td>[62]</td>
</tr>
</tbody>
</table>

ᵃ LDH with defects prepared by co-precipitation at constant pH followed by aging.ᵇ PAS = para-amino salicylate.ᶜ This is a paramagnetic sample samples and the reported values are from ^2H MAS NMR of deuterated samples.
Deconvolution of $^1$H MAS NMR spectra allow for determination of concentration of M(III) using the normalized intensity of the M(II)$_2$(III)-OH resonance as a total of the concentration of the -OH groups[40], which for an ordered model, i.e., Al-O-Al avoidance is:

$$\% (M(III)) = \frac{I(M(II)_{2}M(III)-OH)}{3}$$ \hspace{1cm} (9)$$

A random distribution of M(III) ions for an ideal (non-defect) LDH can be modelled by a binomial distribution (see Ref [40] for further details). All SSNMR studies of pure LDH samples have so far supported Al-O-Al avoidance for MgAl, ZnAl, NiAl, CaAl, and MgGa-LDH [39, 40, 47, 57, 62, 79, 90, 100, 104]. Table 6 summarizes the $\delta_{iso}(^1H)$ reported for defect-free LDH, which were generally prepared by co-precipitation at constant pH followed by hydrothermal treatment, see Refs. [47, 71] for a detailed discussion. The general trend observed for $\delta_{iso}(^1H)$ for the hydroxyl groups is that the value shifts to higher ppm with an increasing M(III) content in the LDH, as observed for both MgAl- and GaAl-LDH[39, 40, 47, 57, 68, 90, 105], c.f., Table 6.

The presence of defects (Al-O-Al connectivities) in the LDH has been a matter of debate. The first reported high resolution $^1$H MAS NMR data for MgAl-LDH by Sideris et al. were assigned using the relative intensities of the hydrogen resonances, $^1$H-$^{27}$Al TRAPDOR, and comparison with model compounds[40] and subsequently confirmed by $^1$H-$^1$H DQ NMR experiments[39]. These studies confirmed the absence of Al-O-Al connectivities (defects). However, Cadars et al. combined both 1D and 2D SSNMR experiments with DFT calculations to assign the different $^1$H NMR shifts observed in defect MgAl-LDH[57], where an additional resonance at 5.3 ppm were assigned to MgAl$_2$-OH based on DFT calculations and 2D SSNMR correlations experiments. Both studies were performed on MgAl-LDH prepared by co-precipitation, but with[39] and without post synthesis hydrothermal treatment[57]. A later study by Sideris et al. showed a $^1$H MAS NMR spectrum with lower resolutions and an additional resonance in the $^{27}$Al MAS NMR spectra of a Mg$_2$Al-LDH-CO$_3$ prepared by the so-called urea method[39]. This was ascribed to the presence of a stronger hydrogen bonding network, as the sample did not contain significant impurities according to PXRD[57]. However, subsequent studies have shown that these samples are actually a mixture of LDH, AOH, and hydromagnesite[71, 72]. These assignments were all based on SSNMR data, which for one study was supported by DFT calculations, and assumed that MgAl-LDH was the
only phase present in the sample. However, it was later shown that the purity of and defect concentrations in the LDH is closely linked to the method of synthesis in a study comparing the purity of ZnAl-LDH prepared by different methods[47]. SSNMR, PXRD, SEM, FT-IR and chemical analyses as well as both ZnAl-LDH and “Al rich” particles existing pointing to multiple phases[47]. Thus, the purity of the LDH phase is closely linked to the method of preparation and X-ray amorphous impurities are common.

In contrast, the $^1$H SSNMR spectra of the only known diamagnetic MAl$_4$-LDH, ZnAl$_4$-LDH, contains 12 and 6 crystallographic inequivalent hydrogen from hydroxyl group and water molecules based on the crystal structure [20, 106]. The $\delta_{\text{iso}}$($^1$H) values vary more than 6 ppm from basic -OH to acidic -OH groups as well as overlap with the water molecules. The use of ultra-high magnetic field (900 MHz) and ultra-fast MAS (80 kHz) allowed for assignment of all 4 $^{27}$Al and nearly all of the 18 resonances using a combination of correlations observed in $^1$H-$^1$H NOESY (Fig 11) and $^1$H-$^{27}$Al D-HMQC (Fig. 12) spectra with DFT calculations[38]. The reader is referred to a detailed discussion of the assignment in Ref [38] and DFT calculations[35].

Only few $^1$H SSNMR studies of paramagnetic NiAl-LDH has been reported. A $^1$H MAS NMR study of a Ni$_2$Al-LDH which contain only the Ni$_2$Al-OH resonance, showed a single hydroxyl groups was reported at -50 ppm by $^1$H MAS NMR at moderate spinning speeds[107]. Much higher resolution can be obtained from deuterated samples due to suppression of the strong electron nuclei dipolar interaction by a factor of six. Thus, $^2$H MAS NMR of deuterated NiAl-LDH allowed for quantification of the D$_2$O, Ni$_3$-OD and Ni$_2$Al-OD resonances and confirmed the Al-O-Al avoidance[79], as illustrated in Fig 16. The $\delta_{\text{iso}}$($^2$H) for Ni$_2$Al-OD showed a nearly 25 ppm variation as the Ni content changed from 20 to 33 mol%, whereas the water and Ni$_3$-OD showed little variation, c.f., Table 6.

Thus, $^1$H SSNMR especially using ultrafast MAS and magnetic field is a powerful probe of the local hydrogen environment providing insight into. e.g., M(II):M(III) ratio of the LDH phase, impurities, and also dynamics. For paramagnetic samples $^2$H MAS NMR of deuterated LDH provides better resolution.

4.3 SSNMR studies of anions in the LDH interlayer

Carbonate is the most common anion found in natural hydrotalcites specimens due to the very high carbonate affinity of these LDH. In synthetic samples with other anions, carbonate is an inherent
impurity or even the primary anion unless careful control of the atmosphere (dry nitrogen or argon) and carbonate free water is used[29]. Similarly, carbonate is also a major anion during the urea synthesis as degradation of urea leads to carbonate formation[47]. If two chemically distinct anions, e.g., carbonate and chloride, are present in significant quantities, PXRD reveals the formation of two phases with different interlayer separation, i.e., different values of the $c$-axis [108]. This is evident as a splitting of the (003) reflections. Similarly, LDH intercalated by phosphate have received increased interested due to the environmental importance of phosphate as a fertilizer is an essential nutrient and pollutant. Table 7 summarizes the SSNMR parameters for a series of different inorganic anions intercalated in LDH. The reader is referred to the original literature cited for organic anions, as $\delta_{iso}(^{13}\text{C})$ is not tabulated or assigned (vide infra).

Kirkpatrick, Kalinichev, and their co-workers have extensively combined SSNMR and MD simulations to gain insight into anion and (indirectly) water dynamics in the interlayer as a function of water content, i.e., relative humidity, and temperature in systematic studies of a wide range of different LDH. These studies require careful control of the water content, which can be achieved by exposing the sample to constant humidity in a sealed desiccator for several days followed by sample preparation e.g., in a glovebox or -bag prior to NMR and diffraction studies as well as detailed chemical analyses of the samples[29, 109]. An excellent comparison of the mobility of anions and the effect of relative humidity on a LiAl$_2$- and Mg$_3$Al-LDH samples divides the LDH into three types: Type 1 have significantly expandable interlayers (1.5 -3.0 Å) as both one and two layers of water can be present, whereas Type 2 is slightly expandable (0.5 Å) as the interlayer spacing is determined by the large anion often an oxyanion such as phosphate or selenate, where water fills the voids and the anion is mobile at high water contents. In contrast type 3, which is non-expandable and the interlayer has a rigid structure[109]. A clear correlation was seen between the PXRD and water vapor sorption isotherms with SSNMR information (speciation and anion dynamics) and MD simulation[109], where the authors combine the information of their previous NMR studies[33, 85, 108, 110, 111]. Both the direct observation of NMR active nuclei in the anion[33, 85, 108, 110-112] and indirectly via $^{27}$Al MAS NMR spectra[34, 39, 54] as a function of temperature gives insight into this motion.$_2$

For the MAI$_x$-LDH no SSNMR studies have been performed so far of the anions, as the NMR properties of $^{33}$S and $^{15}$N require extensive labelling, an extremely costly task given that often a five to tenfold excess of metal salts are needed in the synthesis[36, 38].
Table 7. NMR parameters reported for $^{13}$C, $^{17}$O, $^{31}$P, $^{35}$Cl, and $^{77}$Se for common inorganic anions in LDH. For the most studied anions such as carbonate, selected examples have been chosen to illustrate the variation. The relative humidity (RH) and temperature is indicated when actively controlled. Otherwise, ambient conditions (humidity and temperature), which can differ significantly between the studies due sample preparation and storage. % and N/A indicates not reported and not applicable, respectively.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Anion</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$\delta_{\sigma}$ (ppm) $\eta_{\sigma}$</th>
<th>$\eta_{Q}$ (MHz)</th>
<th>Comments</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$Al-LDH</td>
<td>$^{13}$CO$_3$</td>
<td>170</td>
<td>-50</td>
<td>0</td>
<td>N/A</td>
<td>Static NMR</td>
</tr>
<tr>
<td>MgAl-LDH</td>
<td>$^{13}$CO$_3^{2-}$</td>
<td>170</td>
<td>%</td>
<td>%</td>
<td>N/A</td>
<td>CSA resembles Na$_2$CO$_3$</td>
</tr>
<tr>
<td>MgAl-LDH</td>
<td>H$^{13}$CO$_3^-$</td>
<td>167</td>
<td>%</td>
<td>%</td>
<td>N/A</td>
<td>CSA resembles NaHCO$_3$</td>
</tr>
<tr>
<td>NiAl-LDH</td>
<td>$^{13}$CO$_3^{2-}$</td>
<td>160</td>
<td>-150(5)</td>
<td>%</td>
<td>N/A</td>
<td>Two shifts, not assigned</td>
</tr>
<tr>
<td>Mg$_2$-Ni$_x$Al-LDH</td>
<td>$^{13}$CO$_3^{2-}$</td>
<td>170(1), 169(1)</td>
<td>-150(5), -165(5)</td>
<td>%</td>
<td>x = 0, x = 1/6</td>
<td>[113]</td>
</tr>
<tr>
<td>Mg$_3$Al-LDH</td>
<td>$^{31}$PO$_4^{3-}$</td>
<td>374</td>
<td>-148</td>
<td>0</td>
<td>N/A</td>
<td>Rapid motion</td>
</tr>
<tr>
<td>MgAl-LDH</td>
<td>$^{17}$OH$^-$</td>
<td>40</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>Samples with four different Mg:Al ratios</td>
</tr>
<tr>
<td>Mg$_3$Al-LDH</td>
<td>$^{31}$PO$_4^{3-}$</td>
<td>6.2</td>
<td>%</td>
<td>%</td>
<td>N/A</td>
<td>Visual inspections</td>
</tr>
<tr>
<td>Mg$_3$Al-LDH</td>
<td>$^{31}$HPO$_4^{2-}$</td>
<td>2-3</td>
<td>%</td>
<td>%</td>
<td>N/A</td>
<td>Deconvolution, position deped on Mg:Al ratio</td>
</tr>
<tr>
<td>Mg$_3$Al-LDH</td>
<td>$^{31}$PO$_4^{3-}$</td>
<td>$\approx$ 7</td>
<td>%</td>
<td>%</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Mg$_3$Al-LDH</td>
<td>$^{31}$HPO$_4^{2-}$</td>
<td>$\approx$ 3</td>
<td>%</td>
<td>%</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Mg$_3$Al-LDH</td>
<td>$^{35}$ClO$_4^-$</td>
<td>1001.2</td>
<td>10</td>
<td>$\approx$ 0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>LiAl$_2$-LDH</td>
<td>$^{31}$PO$_4^{3-}$</td>
<td>6.2</td>
<td>%</td>
<td>%</td>
<td>N/A</td>
<td>Visual inspections</td>
</tr>
<tr>
<td>LiAl$_2$-LDH</td>
<td>$^{31}$HPO$_4^{2-}$</td>
<td>3.2</td>
<td>%</td>
<td>%</td>
<td>N/A</td>
<td>Heated to 150 °C, 0 % RH</td>
</tr>
<tr>
<td>LiAl$_2$-LDH</td>
<td>$^{35}$ClO$_4^-$</td>
<td>997</td>
<td>22</td>
<td>$\approx$ 0</td>
<td>0.1</td>
<td>RH &gt; 11 %, ClO$_4^-$</td>
</tr>
<tr>
<td>LiAl$_2$-LDH</td>
<td>$^{35}$ClO$_4^-$</td>
<td>998</td>
<td>10</td>
<td>$\approx$ 0</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Isotope</td>
<td>Quadrupole Interaction (MHz)</td>
<td>% NMR</td>
<td>% MAS</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>---------</td>
<td>-----------------------------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td></td>
</tr>
</tbody>
</table>
| LiAl$_2$-LDH | $^{35}$Cl$^-$ | 9.0(2) | -69 | 0 | % | % | tetrahedral symmetry
| LiAl$_2$-LDH | $^{35}$Cl$^-$ | 4.97 | -107.3 | 0 | %$^a$ | % | Mobile, dominant in hydrated samples. Static NMR [33] |
| LiAl$_2$-LDH | $^{35}$Cl$^-$ | 11 | 0.0 | 0 | Mobile, dominant in hydrated samples. From MAS [33] |
| Mg$_3$Al-LDH | $^{77}$SeO$_4$$^-$ | 1053 | 4 | 0 | N/A | N/A | 11 and 33 % RH [108] |
| Mg$_3$Al-LDH | $^{77}$SeO$_4$$^-$ | 1049 | 8 | 0 | N/A | N/A | 0% RH |
| Mg$_3$Al-LDH | $^{77}$SeO$_4$$^-$ | 1046 | 15 | 0 | N/A | N/A | -40 °C |
| Mg$_3$Al-LDH | $^{77}$SeO$_3$$^-$ | 1276 | 30 | 0 | N/A | N/A | Low RH |
| Mg$_3$Al-LDH | $^{77}$SeO$_3$$^-$ | 1279 | 9 | 0 | N/A | N/A | Above 75 % RH |

$^a$ The size of the quadrupole interaction is small, but non-zero due rapid rotation of the anion and/or local symmetry and not reported.
4.3.1 Carbonate

Single pulse and $^{13}$C CPMAS NMR spectra are readily obtained at natural abundance, whereas $^{13}$C enrichment is necessary for 2D $^{13}$C-$^{13}$C correlation NMR experiments. Moreover, the $^{13}$C background in the NMR rotor and probe may also interfere with studies of samples with natural abundance and should be checked. $^{13}$C labeling can readily be achieved by synthesis using $^{13}$C enriched sodium carbonates or by post-synthesis chemical exchange with $^{13}$C enriched salts (e.g., sodium carbonate) as well as is an affordable approach for the sample amount needed for NMR studies (10-200 mg)[55, 97].

Static $^{13}$C MAS NMR of powders and oriented samples showed that the carbonate ion was oriented parallel to the hydroxide layers, i.e., flat[99]. This allowed for precise determination of the axial symmetric CSA tensor for the carbonate anion in Mg$_2$Al-CO$_3$ on $^{13}$C labelled samples[99], as summarized in Table 7. The use of oriented samples showed the carbonate to be strongly hydrogen bonded in the interlayer with the C$_{3}$-axis perpendicular to the metal hydroxide layers in agreement with the hydrotalcite crystal structure. Subsequent studies have generally used $^{13}$C CPMAS NMR spectroscopy focused on determination of $\delta_{iso}(^{13}$C), which revealed the presence of both carbonate and hydrogen carbonate in a ratio correlated with the Mg:Al ratio in the interlayer and have showed that LDH “breathe”(exchange) CO$_2$ with the atmosphere[55, 75, 97, 114]. $^{13}$C MAS NMR allowed for precise determination of the isotropic shifts, whereas the fairly small CSA is averaged out unless slow MAS (2-10 kHz) is used[55]. $^{13}$C MAS NMR studies by Di Bitetto et al. later showed that it is the presence of hydrogen carbonate that control the CO$_2$ uptake and chemical exchange of LDH, i.e., chemical exchange is favored by high Mg concentration (lower Mg:Al ratios) due to the lower interlayer charge that favors hydrogen carbonate[55], as also reported earlier[97, 107]. The dynamic exchange between carbonate and hydrogen carbonate was proven by $^{13}$C exchange spectroscopy (EXSY) experiments at variable temperature (Fig. 17). Moreover, visual comparison of the $^{13}$C spinning sideband manifold, which reflects the CSA, of carbonate and hydrogen carbonate in the interlayer were very similar to that of the corresponding sodium (hydrogen)carbonate salt, but no detailed analyses reported[55].

For paramagnetic LDH, $^{13}$C MAS NMR of NiAl-CO$_3$ LDH showed two resonance at 160 and 150 ppm, i.e., shifted ca 10 ppm lower as compared to diamagnetic MgAl-LDH[107], c.f. Tabel 7. A study of a series of Mg$_{2-x}$Ni$_x$Al-LDH, i.e. a series samples with varying Ni content, showed
a small (ca 10 ppm) negative change in the $\delta^{(13)C}$ as at the Ni content increased, whereas a much larger effect was observed for the shift anisotropy and the relaxation time[113].

4.3.2 Halides

$^{79}$Br, and $^{129}$I SSNMR of LDH intercalated with halogenides and the corresponding oxyanions containing iodide ($I^-/IO_x^-$) or bromine ($Br^-/BrO_x^-$) have not been reported most likely due to the very large quadrupole moment of these NMR isotopes (Table 2). It is noted that no $^{19}$F SSNMR studies have been reported for fluoride intercalated in LDH. Studies of hydroxide (OH$^-$) and water is primarily by $^1$H SSNMR, but a few $^{17}$O SSNMR studies have been reported of the parent LDH (Sec. 4.1.5)[96-98]. Di Bitetto et al indirectly confirmed that chloride, a small anion of low charge, is much more mobile than carbonate, and that the dynamic processes increase as the average layer charge is reduced (lower M(III) content) from changes in the line width of the $^{27}$Al spinning sidebands as a function of temperature[54], c.f. Figure 17. A combination of $^{35}$Cl static and MAS NMR studies of chloride in Li$_2$Al-LDH show the presence of two chloride sites in the interlayer and a narrow signal, i.e., absence of quadrupole interaction and CSA, assigned to chloride on the surface[33], c.f., section 4.1.5. Two chloride sites, a rigid chloride in anhydrous samples due to halogen bonding (Cl---H-O-Li) and a more mobile chloride species was observed, which could be reversibly converted by control of the relative humidity[33]. The studies were performed at high magnetic field (17.1 T), where analyses of the static and MAS spectra provided the size of the chemical shift tensor and quadrupole interaction, respectively (Table 7). Moreover, variable temperature SSNMR in the range -90 to 100 °C showed an onset of motion for the chloride ions on the particle surface at -60 °C, motion of the interlayer chloride started at -30 °C, and above 70 °C all interlayer chloride were fully mobile on the NMR time scale (> $10^5$ Hz). The initial motion was assigned to mobility of the interlayer water molecules, whereas onset of the chloride hopping was seen above 70 °C. The dynamics of the interlayer anions and water is also indirectly detected by $^{27}$Al MAS NMR as reduced intensity of the satellite transition at the onset of motion in MgAl$_{1-y}$Ga$_y$-LDH with variable Mg:M(III) ratio[54], MgAl-LDH with 19% Al[39], and Friedel’s salt (Ca$_2$Al(OH)$_6$Cl$_2$H$_2$O)[34], c.f, Sec. 4.1.1.

4.3.3 Other oxyanions including nitrate, phosphate, chlorate, and selenate

$^{11}$B single-pulse and 3QMAS NMR probed the changes in speciation of inorganic borates in ZnAl-LDH as a function of time based on the characteristic $\delta_{iso}(^{11}B)$ line shapes for the different species,
as variable temperature $^{11}$B MAS NMR spectra showed a dynamic exchange between trigonal and tetrahedral boron species[103]. Similarly, $^{11}$B MAS NMR gave insight into the structure of carboranes intercalated in ZnAl-LDH[115].

The activation energy for nitrate rotation in the LDH interlayer is 12.6 kJ/mol based on variable temperature $^{15}$N SSNMR studies[110], which clearly showed that the mobility of the nitrate ion depends on both temperature and water content in the LDH interlayer (relative humidity). However, the authors could not conclude whether the nitrate ion was rotating around the C$_3$ axis or rigid in the interlayer, whereas a more mobile species was assigned to surface sorbed nitrate[110]. This motion was also indirectly detected in $^{27}$Al MAS NMR spectra recorded at different temperatures[39], c.f., Figure 18. Phosphate can be intercalated in LiAl$_2$-LDH[109], MgAl-LDH[68, 94, 109, 116] and ZnAl-LDH[69], whereas MgFe-LDH[67, 116, 117] and CaAl-LDH[118] are unstable at high phosphate concentrations based on SSNMR. The speciation of phosphate in the interlayer depends on the pH. At high pH (10-12) mainly phosphate (PO$_4^{3-}$) is intercalated, whereas under environmental pH conditions (5-9) hydrogen phosphate is the predominant species in the LDH interlayer albeit some dihydrogen phosphate is also observed[94, 109]. The reported $\delta_{iso}(^{31}$P) for the two species are separated by a few ppm, c.f. Table 7. Further details are provided in Section 5.2.

A combination of static and $^{35,37}$Cl NMR MAS NMR combined with molecular dynamics (MD) simulations probed chlorate mobility in the interlayer of LDH at variable temperature and humidity in MgAl-LDH and LiAl$_2$-LDH.

Static $^{77}$Se NMR showed an increased mobility of the selenate ion as a function of temperature but only a 6 ppm change in $\delta_{iso}(^{77}$Se) over nearly 180 °C[108]. An activation energy of 11.8 kJ/mol for orientation for selenate in Mg$_3$Al-LDH[108], whereas the selenite ion was found to be rigid in the same temperature unlike nitrate, and it was difficult to avoid oxidation to selenate[108], as illustrated in Fig. 19. Selenate and selenite were used as a proxy for sulfate and sulfite, respectively due to the low abundance of $^{33}$S(Table 2).

An older study reported $^{11}$B, $^{27}$Al, and $^{31}$P SSNMR spectra of ZnAl-LDH intercalated with boron and phosphorus containing tungsten polyoxometalates, but no detailed analyses of the spectra[119]. The interaction of silicates with ZnAl-LDH was studied by $^1$H, $^{27}$Al and $^{29}$Si MAS NMR at moderate field using slow MAS (8 kHz), which showed condensation of silicates with different degree of condensation of the silicate tetrahedra, i.e., observation of Q$_2$, Q$_3$, and Q$_4$ sites in $^{29}$Si MAS
NMR spectra) as the presence of both tetrahedral and octahedral Al[120], which was ascribed to interstratification based on SSNMR combined with PXRD and IR.

4.3.4. Organic anions

Generally, only a small deviation (few ppm) is observed for $\delta_{\text{iso}}(^{13}\text{C})$ for organic anions intercalated in the LDH as compared to the shift in simple, diamagnetic salt or parent acid based on a visual comparison of their $^{13}$C CPMAS NMR spectra. Moreover, $\delta_{\text{iso}}(^{13}\text{C})$ is not necessarily reported nor are the $^{13}$C NMR resonances fully assigned. $^{13}$C CPMAS SSNMR is performed at natural abundance for most LDH-organic systems.

$^{13}$C MAS NMR of glutamate (Glu) intercalated in Mg$_3$Al-LDH at different pH values revealed that the low charge Glu$^-$ (1 carboxylic acid deprotonated and one not, uncharged amine) was favored over Glu$^{2-}$ (both carboxylic acids deprotonated) by a factor of 1-10 depending on pH based on pKa values[121]. Surprisingly, the effect was most pronounced at high pH. This observation contrasts inorganic anion such as carbonate and phosphate (vide supra) and was ascribed to a combination of favorable hydrogen bonding and possibly pH effect in the nanoconfined interlayer[121, 122]. Studies of citrate, a trivalent anion derived from citric acid, showed that the orientation of citrate changed from parallel to perpendicular to the layers and the mobility increased as the relative humidity increased from 0 to 100 %[112], which was supported by MD simulations[122]. This increased mobility resulted in narrow NMR resonances, but also less efficient CP transfer. A similar effect was observed for para-amino salicylate in LDH[62]. Moreover, the interaction of organic anions with the metal hydroxide layer was much weaker, is a key aspect in the ability of exfoliation of LDH to form 2D nanosheets.

Static $^2$H NMR of deuterated terephthalate (‘OCC-C$_6$D$_4$-COO$^-$, TP) intercalated in MgAl-LDH provided insight into the mobility of the anion in the interlayer[123]. Two different orientations of the anion, parallel and perpendicular to the metal hydroxide layer, were proposed based on the observed interlayer spacings of 7.3 and 14.2 Å, respectively based on PXRD. From $^2$H SSNMR, the TP oriented perpendicular to the layer with free rotation along the molecular C$_2$ axis based on simulation of the $^2$H NMR spectra with different time scales for motion and was closely associated with the signature of TP intercalated in the LDH (d-spacing of 14.1 Å). It is noted that the 7.3 Å spacing match that of MgAl-LDH intercalated with carbonate and significant quantities of
carbonates were reported[123]. Moreover, the two proposed models for motion of the flat TP molecule did not match the experimental spectra, as the $^2$H NMR spectrum showed a quadrupole splitting matching a static deuteron in a phenyl group[123]. The d-spacing was 8.9 Å for citrate, a smaller organic anion, with a flat orientation.[112] Thus, it may be that the TP was not intercalated in the LDH, but rather a separate phase. This would require high resolution electron microscopy, which was not a routine characterization technique, as the study was performed more than 20 years ago. $^{13}$C-$^1$H CPMAS and $^1$H MAS NMR experiments and T$_1$ measurements at variable temperature was used to probe the mobility (activation energy and correlation time) of the structural moieties of Ibuprofen intercalated in MgAl-LDH using detailed fitting of the relaxation data[124]. The results were interpreted as a strong interaction of the carboxylate group with the cation layer combined with rotation of the phenyl group along the C2 axis. Other studies include using a suite of $^{13}$C SSNMR experiments to probe C$_{60}$ intercalation in MgAl-LDH[125], dynamics of dodecyl sulfate in MgAl-LDH combined with molecular dynamics simulations[126]. The interaction between co-polymers and MgAl-LDH was studied by ultrafast $^1$H MAS NMR $^{13}$C-$^1$H CP-MAS and echo experiments with $^1$H-$^{27}$Al and $^1$H-$^{13}$C HETCOR using different contact times, which probed the interaction and dynamics of the co-polymers in the LDH interlayer[127], as illustrated in Fig 20. $^{13}$C-$^1$H and $^{29}$Si-$^1$H CPMAS combined with $^{27}$Al MAS NMR showed the formation of Si-O-Al bonds upon surface modification of ZnAl-LDH of organo silanes[128].

Phosphate and phenylphosphate intercalated in paramagnetic MgFe-LDH and Cu$_2$Cr-LDH have a negligible paramagnetic contribution to the isotropic shift, whereas significant line broadening and many spinning sidebands appear due to the anisotropic paramagnetic dipolar interaction[67, 129]. $^{31}$P MAS NMR probed the protonation of simple organophosphonate intercalated in Li$_2$Al-, Ca$_2$Al-, and Cu$_2$Cr-LDH based on the observed shift with the pristine materials, which showed a dynamic exchange for the methylphosphoric acid and methylphosphonate, as single resonance was observed albeit no variable temperature experiments were performed[129-131]. Moreover, both neutral and deprotonated phenylphosphonic acid was proposed to be present in the Cu$_2$Cr-LDH[129] interlayer, whereas the neutral species was assigned to unreacted acid in a study of MgAl-LDH[132]. Leaching of Ca$^{2+}$ and Li$^+$ from the Ca$_2$Al and Li$_2$Al-LDH, i.e., destruction of the LDH, upon exposure to organophosphate was observed[130, 131]. Similarly, $^{11}$B-$^{11}$B NOESY of benzoxyboralate intercalated in MgAl-LDH clearly showed the presence of two species in the interlayer and proved their close structural proximity[95].
SSNMR is generally used as one of several techniques for structural characterization of LDH intercalated with organic molecules, where $\delta_{\text{iso}}^{(13}\text{C})$ obtained from $\delta_{\text{iso}}^{(13}\text{C})$ CP MAS NMR is used to fingerprint studies including UV-filters[48], surfactants[133], small dicarboxylic acids[134], bi- and tricycling carboxylates[135], metalorganic molybdenum [136] and Pd(II) complexes[137], cinnemate[138]. Generally, the $\delta_{\text{iso}}^{(13}\text{C})$ for the free anion and intercalated in LDH are quite similar, but the degree of protonation does affect especially carbon in near the charged site, e.g., for $^{13}\text{COO}^-$. 

5. LDH properties investigated by SSNMR

SSNMR studies of LDH were in the early days mainly focused on structural characterization of the LDH, i.e., to identify the different local environments and dynamic processes often with detailed analyses of the NMR spectra, as discussed in Section 4. Non-expert use has increased especially recently, as standard SSNMR experiments can now be performed on NMR spectrometers designed for routine liquid state NMR equipped with a MAS NMR probe and spinning speed controller, an affordable accessory as compared to the price of a dedicated SSNMR system. The transition of SSNMR from a specialized method to general user resembles the transition of single crystal XRD to powder XRD. It is emphasized that SSNMR is one of several analytical tools used to understand how the structure and chemical composition of the functional material is related to the properties. This section illustrates the application of LDH in relation to drug delivery (release) and ion-exchange (environmental remediation), where SSNMR has been a core characterization technique to investigate the structure and properties of the LDH.

5.1 Drug Delivery

The properties of MgAl- and ZnAl-LDH intercalated with drug molecules have been extensively studied, where generally routine $^{13}\text{C}-^{1}\text{H}$ CP-MAS NMR spectra are reported to verify the presence of the organic drug molecule by a simple visual comparison of the corresponding acid or its salt (Fig 21), where SSNMR is one of several characterization techniques. For example, $^{13}\text{C}$ CP-MAS NMR spectra confirmed the intercalation of benzoxyborolates[61, 139], ibuprofen[124], indomethacin[140], p-coumaric acid[60], para-aminosalicylate[62], pravastatin[59], sulindac [58], in LDH. Only a few studies employed correlations experiments and/or DFT calculations for interpretation of the NMR data[58, 61, 62, 139].
An excellent example of how a suite of SSNMR experiments can provide detailed insight into the stability of drug formulations and anions present in the interlayer was reported by Sene et al, who studied the intercalation of benzoxoborolate (BBxz) in MgAl-LDH[95]. A comparison of $^{11}$B NMR parameters for different drug configurations in the interlayer gave insight into the orientation of BBxz [95]. $^{25}$Mg static QCPMG and MAS NMR, $^{13}$C CPMAS, $^{13}$C-$^{19}$F REDOR, $^1$H-$^{27}$Al CP, $^{11}$B MAS and 3QMAS NMR as well as $^{11}$B-$^{11}$B NOESY experiments confirmed the presence of BBxz in the LDH, a very detailed description of the SSNMR experiments are given in the main article and the supporting information[95]. Moreover, $^{11}$B SSNMR experiments proved the presence of both tetrahedral and trigonal boron species in close proximity in the interlayer. The corresponding NMR data for calcium and magnesium salts of BBxz were used as model compounds combined with DFT calculation. A subsequent study compared the release properties of the BBxz drug and its fluorine analogue intercalated in LDH with organic polymers, where $^{11}$B and $^{19}$F MAS NMR were used for characterization[139]. Rocha et al combined advanced analyses of PXRD data, $^{13}$C SSNMR and vibrational spectroscopy with DFT calculations to gain detailed insight into the structure of sulinac, a precursor for a non-steroidal anti-inflammatory drug, in ZnAl, using the correlation between experimental and DFT calculated $\delta_{iso}(^{13}$C)[58].

5.2 Environmental Science and remediation

Phosphate is a pollutant in the environment and an essential nutrient as well a limited resource, which has created a demand for a circular phosphorus economy[141]. LDH are promising sorbents for recovery of phosphate from wastewater and remediation of polluted water[11]. SSNMR is a powerful characterization for studies of LDH in relation to environmental processes. Mainly $^{27}$Al and $^{31}$P SSNMR data are reported due to their very favorable NMR properties, whereas $^1$H and $^{25}$Mg NMR are less common (Table 2). SSNMR has been used to probe the ion-exchange properties of LDH with emphasis on phosphate and the formation of LDH phases due to the reaction of Zn(II), a toxic heavy metal, and aluminum hydroxides. SSNMR in combination with other characterization techniques such as X-ray absorption spectroscopy (EXAFS and XANES), electron microscopy, and PXRD allow for a detailed understanding of environmental process at the atomic level. Especially EXAFS and SSNMR are complimentary techniques, as NMR accessible nuclei such as light elements ($^1$H, $^{13}$C, $^{27}$Al) are not poised for EXAFS. Similarly, many low-$\gamma$ and/or paramagnetic nuclei can be accessed by EXAFS, as discussed in detail in Ref. [142]. Generally, 1D MAS NMR spectra are reported, and the data analyses is limited to identification of distinct spectral features and in some cases simple
deconvolution for identification of the number of sites and their relative concentration. Very few studies perform detailed analyses aimed at extraction NMR parameters and/or report 2D NMR data, e.g., $^{27}$Al 3QMAS and $^{31}$P-$^{31}$P correlation experiments[68, 94, 118].

Aluminum hydroxides and oxides are one of the most important adsorption sites for toxic metal ions such as Ni(II), Zn(II), Cu(II)[15]. $^{27}$Al MAS NMR successfully probe the reaction between Zn$^{2+}$[143] and nanosized zinc oxide[144] with γ-alumina ($\gamma$-Al$_2$O$_3$) leading to the formation of ZnAl-LDH on the surface of the γ-alumina particles and a reaction to forming ZnAl-LDH, respectively. Moreover, the presence of phosphate on the alumina prevented ZnAl-LDH formation[145, 146]. Fig 22 illustrates how $^{27}$Al MAS NMR spectroscopy qualitatively can monitor the formation of ZnAl-LDH due to a reaction of ZnO and $\gamma$-Al$_2$O$_3$ under environmental conditions. The appearance of a resonance at $\delta^{(27)\text{Al}} = 13.91$ ppm revealed the formation of ZnAl-LDH[143, 144].

LDH have been extensively investigated as potential phosphate sorbents due to their high affinity for phosphate and phosphate adsorption capacity[11]. The research has focused on MgAl-, MgFe-, CaAl-, ZnAl-, and CaFe-LDH tested in mainly simulated phosphate solution[67, 68, 116-118, 147-151], while limited studies have used wastewater[69, 94]. $^{27}$Al MAS NMR is routinely used to identify diamagnetic LDH, i.e., MgAl, CaAl, and ZnAl-LDH as well as possible amorphous Al hydroxides and aluminum phosphate phases both in the pristine materials and after phosphate adsorption[68, 69, 116, 118, 148, 149, 151]. $^{31}$P MAS NMR probes the speciation of the phosphate species including intercalated phosphate and phosphate minerals formed by the dissolution of the LDH[68, 69, 116, 118, 148, 149] as well as the release of phosphate from MgAl-LDH fertilizers[147, 152]. Fig 23 illustrates how $^{27}$Al and $^{31}$P MAS NMR was used to probe the degradation of CaAl-LDH upon exposure to phosphate. $^1$H and $^{25}$Mg MAS NMR spectra allowed for quantification of the Mg:Al ratio in the LDH and confirmed preservation of the MgAl-LDH after phosphate adsorption, respectively. This information could not be unambiguously determined by PXRD and bulk chemical analyses due to the low crystallinity and presence of amorphous phases[118]. Similarly, the phosphate speciation and LDH stability was studied for ZnAl-LDH used in acidified sludge at different pH[72]. PXRD and SEM showed no sign of intercalation of phosphate in MgFe-LDH, loss of intensity of the LDH reflections in PXRD, and formation of a surface precipitate on the LDH particles, which combined with the observation of no paramagnetic shifts for the species in $^{31}$P NMR was interpreted as formation of a surface precipitate and/or weakly bound phosphate possible in the interlayer[94,
This was supported by modelling of the chemical speciation showed MgFe-LDH towards phosphate except at low phosphate concentration and around neutral pH [116]. However, combined with the observation of very small paramagnetic shifts observed in the $^{13}$C MAS NMR spectra of carbonate in NiAl-LDH (Table 7), part of the $^{31}$P signal may originate from phosphate intercalated in the MgFe-LDH.

6 Conclusions

This review has illustrated how SSNMR spectroscopy has advanced our understanding of the atomic level structure of LDH with respect to, e.g., cation ordering, defects, impurities, reaction pathways and synthesis optimization and chemical structure as well as revealed that the LDH interlayer is a dynamic environment with chemical exchanges processes (within the interlayer or the atmosphere) and molecular rotation and diffusion, that can be directly and indirectly observed by SSNMR. The unique ability of SSNMR to study these core aspects of the LDH structure render it a very powerful tool to investigate and thereby understand the fascinating properties of LDH. However, it is also apparent that the complexity of and dynamics processes in the LDH, which is not fully understood, can complicate the interpretation of SSNMR data. Thus, further development of SSNMR software and computational modelling is needed to fully exploit the information contained in the experimental SSNMR spectra especially related to molecular dynamic (chemical exchange and/or motion) and paramagnetic LDH. Moreover, the combination of SSNMR and computational chemistry has the potential to become a core method for characterization and understanding the properties of the rapidly growing class of 2D LDH and complex LDH-nanohybrid materials. The recent advances in fast MAS and in situ MAS NMR probes provides possibilities for investigation of paramagnetic LDH and in operando studies of LDH properties, e.g., energy storage and conversion, catalytic reaction as well as studies of LDH formation and ion-exchange. Similarly, accessibility to ultra-high field NMR especially combined with e.g., pulse sequences for sensitivity enhancement may open for further studies of the low-gamma nuclei (e.g., $^{25}$Mg, $^{67}$Zn) and $^{14}$N, whereas combined with fast MAS more advanced correlation experiments between, e.g., $^1$H-$^{25}$Mg, $^1$H-$^{13}$C and even triple resonance experiments, e.g., $^1$H-$^{13}$C-$^{27}$Al SSNMR aiming at probe the interaction of organic anions with the LDH. Moreover, it has been illustrated how routine SSNMR experiments such as $^{6,7}$Li, $^{27}$Al, $^{31}$P MAS, and $^{13}$C CPMAS have become an accessible and valuable characterization tool for non-NMR experts to study diamagnetic LDH in relation to e.g., drug delivery, environmental science and
remediation, although often only with limited data analyses. Here SSNMR can provide insight into the sample composition and quality as well as structural changes.

To understand and ultimately control the fascinating properties and complex chemistry of LDH, SSNMR is an important technique, when used in combination with other characterization techniques, e.g., PXRD, electron microscopy, vibrational spectroscopy and chemical analyses as well as computational methods.

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Fig. 1 a) The structure of an LDH, which consists of positively charged layers of metal hydroxide sheets separated by the interlayer, which contains an appropriate amount of anions for charge balance and a variable amount of interlayer water. The distance is mainly controlled by the size of the anion, which can be replaced by ion-exchange. b) The cation sheets in the structure for a hydrotalcite (Mg(OH)₂), where the metal ion composition can be tuned the relative concentration of M(III) ions and doping of metals ions, and an Al(OH)₃ derived LDH (MA₄-LDH), which has a fixed chemical composition. c) A single sheet (2D) LDH, illustrating how the high surface area can be used for catalytic reactions and adsorption.
**Fig. 2** The crystal structure of hydrotalcite ideally Mg₆Al₂(OH)₁₆(CO₃)₄H₂O (left) determined by X-ray diffraction of a single crystal mineral specimen[22]. Notice that PXRD cannot distinguish Mg(II) and Al(III), as they are isoelectronic. The unit cell contains three metal ion layers leading to an $abcabc$ stacking sequence (3R model), the 2H polymorph (not show) contains only two metal ions layers. The carbonate ions are parallel with the metal hydroxide layers and disordered. Moreover, the interlayer water molecules (not show) are located on the same plane as the carbonate ions. The metal ion layer (right) illustrating the unique Al(OMg)₆ environment and examples of the possible Mg environments, Mg(OAl)ₙ(OMg)₆₋ₙ with $n = 0, 1, 2,$ and $3$, which can be distinguished by SSNMR[39, 40].
Fig 3 Crystal structure of dritsite (ideally LiAl₄(OH)₈Cl₂ 2H₂O) based on single crystal X-ray diffraction data for a mineral specimen[23] (left), an example of a LiAl₂-LDH. Lithium is inserted in all the vacancies in the parent aluminum hydroxide layer (right) leading to one crystallographic inequivalent position for both Li and Al. The interlayer contains three different chloride positions, which are disordered and three water molecules (not shown). However, the position of the interlayer water has not been determined. Each disordered crystallographic chloride site has two or three positions related by symmetry of which only one is occupied. The reader is referred to Reference [23] for a detailed description of the crystal structure.
The crystal structure of MAl₄-LDH, MAl₄(OH)₁₂(SO₄)⋅₃H₂O with M = Co(II), Ni(II), Cu(II), and Zn(II), based on the crystal structure of M = Ni(II)[20], the so-called MAl₄-LDH. The unit cell contains two metal hydroxide layers (stacking ababa…), where the M(II) ions fill half of the vacancies in the aluminum hydroxide layer leading to the formation 1D chain of M(II) ions MAl₄-LDH based on. A more detailed description of the crystal structure can be found in Refs [20, 38]. The interlayer contains three crystallographic inequivalent water molecules and one sulfate group, which form an extensive hydrogen network[20]. Thus, the positions of all atoms including hydrogen were determined by X-ray diffraction of a mineral specimen. This is in sharp contrast to the hydrotalcite and LiAl-LDH, where high disorder is often observed for water and anions on the interlayer.
Fig 5. CA comparison of A) Calculated δiso(1H) shifts as a function of hydrogen bond length and B the correlation between the calculated and experimental δiso(1H) for defect MgAl-LDH[57]. Reprinted with permission from S. Cadars, G.R. Layrac, C. Gérardin, M.L. Deschamps, J.R. Yates, D. Tichit, D. Massiot, Identification and Quantification of Defects in the Cation Ordering in Mg/Al Layered Double Hydroxides, Chemistry of Materials, 23 (2011) 2821-2831. Copyright 2011 American Chemical Society.
Fig. 6 $^{27}\text{Al}$ MAS NMR spectrum of the central and satellite transitions for a Mg$_2$Al-LDH recorded at 14.1 T using 15 kHz spinning speed. Notice that the vertical scale is expanded by a factor of ten. The inset shows the region for the central transition.
Fig. 7. $^{27}\text{Al}$ MAS NMR spectrum of the central transition for the a) $\alpha$ (-121 °C) and b) $\beta$ (41 °C) phase of Friedels salt and b) and c) the corresponding simulations of the spectra using the parameters in Table 3. The spectra were recorded at 7.1 T to enhance the second order quadrupole line shape[34]. Reprinted with permission from M.D. Andersen, H.J. Jakobsen, J. Skibsted, Characterization of the $\alpha$–$\beta$ Phase Transition in Friedels Salt (Ca$_2$Al(OH)$_6$Cl·2H$_2$O) by Variable-Temperature $^{27}\text{Al}$ MAS NMR Spectroscopy, The Journal of Physical Chemistry A, 106 (2002) 6676-6682. Copyright 2002 American Chemical Society.
Fig. 8 a) The linear relationship between $\delta_{\text{iso}}^{(27)}$Al and the number of Ni in the first metal ion coordinations sphere (Al(OMg)$_{6-x}$(ONi)$_x$) for the different sites (Fig. 8) in a Mg$_{2-x}$Ni$_x$Al-LDH[56]. For x = 1, 2 and 3 the presence carbonate and nitrate as anion can be distinguished due to a ca 30 ppm difference in $\delta_{\text{iso}}^{(27)}$Al[56]. b) Five of the seven possible $^{27}$Al resonances observed for a sample with Mg$_{1.32}$Ni$_{0.68}$Al-LDH $^{27}$Al MAS NMR spectrum (70 kHz). Republished with permission of The Royal Chemistry Society from N.D. Jensen, C. Forano, S.S.C. Pushparaj, Y. Nishiyama, B. Bekele, U.G. Nielsen, The distribution of reactive Ni$^{2+}$ in 2D Mg$_{2-x}$Ni$_x$Al-LDH nanohybrid materials determined by solid state $^{27}$Al MAS NMR spectroscopy, Physical Chemistry Chemical Physics, 20 (2018) 25335-25342 with permission from the Royal Chemical Society permission conveyed through Copyright Clearance Center, Inc.
**Fig. 9** The seven different $^{27}$Al NMR environments observed in trimetallic Mg$_{2-y}$Ni$_y$Al-LDH. The Al environments indicated with 2, 3, 4, and 6 correspond to Al(OMg)$_{6-x}$(ONi)$_x$ with 2, 3, 4 and 6 Ni in the second coordination sphere.
Fig. 10: A) in situ $^{27}$Al MAS NMR spectra (7 T, 3 kHz MAS) of the formation of LiAl$_2$-LDH by insertion of Li$^+$ in gibbsite. The O$_h$ resonance includes both solid gibbsite and LiAl$_2$-LDH, where the LDH resonance is emphasized due to a weaker $^{27}$Al quadrupole interaction, c.f., Table 3. B) the relative concentration of the liquid Al species (T$_d$), C) their chemical shift and D) line width as a function of reaction time[86]. Reprinted with permission from T.R. Graham, J.Z. Hu, X. Zhang, M. Dembowski, N.R. Jaegers, C. Wan, M. Bowden, A.S. Lipton, A.R. Felmy, S.B. Clark, K.M. Rosso, C.I. Pearce, Unraveling Gibbsite Transformation Pathways into LiAl-LDH in Concentrated Lithium Hydroxide Inorganic Chemistry 58(18) (2019) 12385-12394. Copyright (2019) American Chemical Society.
Fig. 11. \(^1\)H,\(^1\)H NOESY NMR spectrum of a ZnAl\(_4\)-LDH (21.1 T, 80 kHz MAS) for which 12 different \(^1\)H resonances were observed from the 18 crystallographic inequivalent hydrogen. The mixing time was set to 1 ms to only probe \(^1\)H in close spatial proximity. Reprinted with permission from N.D. Jensen, N.T. Duong, R. Bolanz, Y. Nishiyama, C.A. Rasmussen, J. Gottlicher, R. Steininger, V. Prevot, U.G. Nielsen, Synthesis and Structural Characterization of a Pure ZnAl\(_4\)(OH)\(_{12}\)(SO\(_4\))·2.6H\(_2\)O Layered Double Hydroxide, Inorganic Chemistry, 58 (2019) 6114-6122. Copyright (2019) American Chemical Society
Fig. 12. $^{27}\text{Al}, ^{1}\text{H}$ HMQC with rotor synchronization illustrating the separation of the satellite transitions from the Al4 resonances due to a significantly larger $C_Q$ (Table 3) using a spectral window matching the spinning speed. This allowed for unambiguous assignment of the six -OH groups coordinated to Al4. The spectrum was recorded at 14.1 T using 80 kHz spinning[38]. Reprinted with permission from N.D. Jensen, N.T. Duong, R. Bolanz, Y. Nishiyama, C.A. Rasmussen, J. Gottlicher, R. Steininger, V. Prevot, U.G. Nielsen, Synthesis and Structural Characterization of a Pure ZnAl$_4$(OH)$_{12}$(SO$_4$)$_2$·2.6H$_2$O Layered Double Hydroxide, Inorganic Chemistry, 58 (2019) 6114-6122. Copyright (2019) American Chemical Society
Fig. 13 Natural abundance $^{25}\text{Mg}$ SPAM-3QMAS NMR spectrum of a MgAl-LDH with 19 % Al at 19.6 T[39]. The slices illustrate the different $^{25}\text{Mg}$ NMR environments in the sample and a simulation using the $^{25}\text{Mg}$ NMR parameters obtained from analyses of the spectra, c.f. Table 4. Reprinted with permission from P.J. Sideris, F. Blanc, Z. Gan, C.P. Grey, Identification of Cation Clustering in Mg–Al Layered Double Hydroxides Using Multinuclear Solid State Nuclear Magnetic Resonance Spectroscopy Chemistry of Materials, 24 (2012) 2449-2461. Copyright 2012 American Chemical Society.
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Fig. 16. $^2$H MAS NMR spectra of deuterated a) Ni(OD)$_2$ as well as NiAl-LDH with b) 32.3, b) 25.6 and d) 21.3 % Al as well B) an expansion of the isotropic resonance and the relevant two possible $^2$H environments (Ni$_3$-OD and Ni$_2$AlOD) [79]. Reprinted from G. Yu, M. Shen, M. Wang, L. Shen, W. Dong, S. Tang, L. Zhao, Z. Qi, N. Xue, X. Guo, W. Ding, B. Hu, L. Peng, Probing Local Structure of Layered Double Hydroxides with $^1$H Solid-State NMR Spectroscopy on Deuterated Samples, The Journal of Physical Chemistry Letters, 5 (2014) 363-369 with permission from Elsevier.
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Fig. 20. $^{77}$Se SSNMR spectra recorded under static (left) and MAS conditions (right) of a MgAl-LDH intercalated with selenate ($\text{SeO}_4^{2-}$) as a function of relative humidity (RH), which is indicated on the figure. The static spectra allow for determination of the full chemical shift tensor, whereas MAS results in increased spectra resolution and precise determination of $\delta_{\text{iso}}$(${}^{77}\text{Se}$). Reprinted with permission from X. Hou, R.J. Kirkpatrick, Solid-State $^{77}\text{Se}$ NMR and XRD Study of the Structure and Dynamics of Seleno-Oxyanions in Hydrotalcite-like Compounds, Chem. Mater., 12 (2000) 1890-1897. Copyright (2000) American Chemical Society.
Fig 21. $^{13}$C-$^1$H HETCOR MAS NMR spectra of an MgAl-LDH intercalated with an organic copolymer (see inset) at a) 0.25 ms and b) 5 ms contact time to probe C-H interactions within the polymer and also with -OH groups in the LDH, respectively. The Mg2Al-OH was identified by $^1$H-$^{27}$Al CP (red spectrum), respectively[127]. The spectra were recorded with 60 kHz MAS. Reprinted without changes from Intercalation and structural aspects of macroRAFT agents into MgAl layered double hydroxides D. Kostadinova, A.C. Pereira, M. Lansalot, F. D’Agosto, E. Bourgeat-Lami, F. Leroux, C. Taviot-Gueho, S. Cadars, V. Prevot, Intercalation and structural aspects of macroRAFT agents into MgAl layered double hydroxides, Beilstein Journal of Nanotechnology, 7 (2016) 200-212, doi:10.3762/bjnano.7.191.
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Fig. 23. $^{27}$Al MAS NMR spectra of a) unreacted $\gamma$-Al$_2$O$_3$ (parent material) as well as the product obtained in the reaction of ZnO nanoparticles and $\gamma$-Al$_2$O$_3$ at different pH in the range to 6.5 to 9.5; A zoom of the region for b) tetrahedral and c) octahedral Al with the center of gravity of ZnAl-LDH (13.91 ppm) indicated illustrating the formation of ZnAl-LDH. Reprinted from B. Wan, Y. Yan, R. Huang, D.B. Abdala, F. Liu, Y. Tang, W. Tan, X. Feng, Formation of Zn-Al layered double hydroxides (LDH) during the interaction of ZnO nanoparticles (NPs) with $\gamma$-Al$_2$O$_3$, Science of The Total Environment 650 (2019) 1980-1987 with permisison from Elsevier.
Fig. 24 (left) $^{27}$Al MAS NMR spectra of CaAl-LDH ($0P =$ pristine) exposed to a phosphate concentration ranging from 30 % (0.3) to 90 % (0.9) of the theoretical phosphate ion-exchange capacity. The center of gravity and the linewidth broaden as the CaAl-LDH is converted to amorphous aluminum hydroxide. (right) The $^{31}$P MAS NMR spectrum of CaAl-LDH exposed to 30 to 90 % of the theoretical phosphate capacity as well as h) hydroxyapatite and j) brushite. Thus, CaAl-LDH is destroyed leading to the formation of amorphous aluminum hydroxide and hydroxyapatite based on SSNMR[118]. Reprinted from B. Bekele, L. Lundehøj, N.D. Jensen, U.G. Nielsen, C. Forano, Sequestration of orthophosphate by Ca2Al-NO3 layered double hydroxide – Insight into reactivity and mechanism, Applied Clay Science 176 (2019) 49-57 with permisison from Elsevier.