

Electronic Supporting Information

The distribution of reactive Ni²⁺ in 2D Mg_{2-x}Ni_xAl-LDH nanohybrid materials determined by solid state ²⁷Al MAS NMR spectroscopy

Nicholai Daugaard Jensen¹, Claude Forano², Suraj Shiv Charan Pushparaj¹, Yusuke Nishiyama^{3,4}
Belayneh Bekele², and Ulla Gro Nielsen^{1,*}

¹ Department of Physics, Chemistry, and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark

² Université Clermont Auvergne, CNRS, ICCF, F-63000 Clermont-Ferrand, FRANCE

³ RIKEN CLST-JEOL Collaboration Center, RIKEN, Yokohama, Kanagawa 230-0045, Japan

⁴ JEOL RESONANCE Inc., Musashino, Akishima, Tokyo 186-8558, Japan

* Corresponding author: ugn@sdu.dk +45 6550 4401

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ESI-1: Binomial distribution of the divalent cation in the layers

The probability of a given number of neighbouring Ni atoms in the second coordination sphere of Al is calculated using a standard binomial distribution:

$$P(y) = \frac{N!}{y!(N-y)!} x^y (1-x)^{N-y} \quad (\text{Eq. ESI-1})$$

Where $P(y)$ is probability of y neighboring Ni in the second coordination sphere ($0 \leq y \leq 6$), N is the total number of metal ions in the second coordination sphere ($N = 6$ for LDH, c.f., Figure 1) and x is the Ni fraction of the divalent cation ($0 \leq x \leq 1$). Thus, the formula for the relative concentration of the different $\text{Al}(\text{OMg})_{2-y}(\text{ONi})_y$ environments in LDH are:

$$P(y) = \frac{6!}{y!(6-y)!} x^y (1-x)^{6-y} \quad (\text{Eq ESI-2})$$

There are several possibilities for the distribution of two to four Ni ($x = 2, 3,$ and 4) on the six positions. For example for $x = 2$, three combinations, (1, 2), (1, 3), and (1,4), are possible for the location of the two Ni^{2+} atoms on the six different positions, as the remaining two ((1, 5) and (1, 6)) are related by symmetry. However, these combinations cannot be distinguished by ^{27}Al MAS NMR based on a recent study of Ni_5Al_2 - Anderson wheels, where the metal ions in the wheel structurally resemble the first metal coordination shell in an LDH.¹

Table ESI-1: The relative concentrations of the seven different Al environments in $\text{Mg}_{2-x}\text{Ni}_x\text{Al-LDH}$ samples calculated from a binomial distribution as a function of the number (y) of Ni^{2+} in the second coordination sphere.

Relative conc. of site y [%]	0	1	2	3	4	5	6
$\text{Mg}_2\text{Al-LDH}$	100	0	0	0	0	0	0
$\text{Mg}_{1.82}\text{Ni}_{0.18}\text{Al-LDH}$	57	34	8	1	0	0	0
$\text{Mg}_{1.66}\text{Ni}_{0.34}\text{Al-LDH}$	33	40	20	6	1	0	0
$\text{Mg}_{1.32}\text{Ni}_{0.68}\text{Al-LDH}$	8	25	33	23	9	2	0
$\text{Mg}_{1.16}\text{Ni}_{0.84}\text{Al-LDH}$	4	16	30	29	16	5	0
$\text{Mg}_{0.98}\text{Ni}_{1.02}\text{Al-LDH}$	1	9	23	32	24	10	1
$\text{Mg}_{0.41}\text{Ni}_{1.59}\text{Al-LDH}$	0	0	2	8	25	39	26
$\text{Ni}_2\text{Al-LDH}$	0	0	0	0	0	0	100

ESI-2: Synthesis of the LDH samples

All $\text{Mg}_{2-x}\text{Ni}_x\text{Al-NO}_3$ LDHs were synthesized according the targeted compositions given in Table ESI-1 by the coprecipitation method in a reactor using peristaltic pumps for simultaneous addition of the metal salts and 2 M NaOH in order to keep the pH constant at a value of 10.0. For all cases, the molar ratio of divalent to trivalent cations, $\text{M}^{2+}:\text{M}^{3+}$, were two and $[\text{M}^{2+}] + [\text{M}^{3+}] = 1$ M. The syntheses were performed under a N_2 flow, with vigorous stirring and completed in 4-5 h. The resulting slurries were transferred into a Teflon lined autoclave and thermally treated for 16 h at 120 °C. The resulting solids were centrifuged and washed thoroughly with deionized water and dried at 40 °C for 24 h.

Exfoliated LDHs were prepared according Gordijo et al.², typically 200 mg of $\text{Mg}_{1.83}\text{Ni}_{0.17}\text{Al}$ LDH were suspended in 150 mL dimethylformamide and vigorously stirred for 2h until a clear solution was obtained. Restacking of exfoliated 2D- LDH nanoplatelets was performed by adjusting the pH of the solution to a value of 10.0 using a 1 M NaOH solution and stirred for 4h. The same LDH dispersed in a DMF solution was used to prepare the nanohybrid materials containing alginate. 200 mg of sodium alginate were dissolved in 100 mL of water and this solution was added to the LDH in DMF solution. Restacking was obtained after 12h stirring at room temperature. Both 2D- and nanohybrid materials were recovered after 3 cycles of centrifugation/washing and subsequently dried over night at 40 °C

Table ESI-2: Synthesis parameters and chemicals used (mass, m, and concentration, c, in the metal salt solution) for preparation of the $\text{Mg}_{2-x}\text{Ni}_x\text{Al-LDH}$. The actual metal ion ratio (x) determined by ICP-OES.

Sample name	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$		$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$		$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$		Mg	Ni	Al	x
	m (g)	c (mol)	m (g)	c (mol)	m (g)	c (mol)				
0.18	7.834	0.031	0.807	0.003	6.252	0.017	11/6	1/6	1	0.167
0.34	7.122	0.028	1.615	0.006	6.252	0.017	10/6	2/6	1	0.333
0.68	5.698	0.022	3.231	0.011	6.252	0.017	8/6	4/6	1	0.667
0.84	4.985	0.019	4.038	0.014	6.252	0.017	7/6	5/6	1	0.833
1.02	4.273	0.017	4.846	0.017	6.252	0.017	6/6	6/6	1	1.000
2.00	4.273	0.017	4.846	0.017	6.252	0.017	1.000	1.000	1	2.000

The following chemicals were used for the synthesis of Ni₂Al-TP and Ni₂Al-BP: Ni(NO₃)₂·6H₂O (Sigma-Aldrich), Mg(NO₃)₂·6H₂O (Sigma-Aldrich), Al(NO₃)₃·9H₂O (Sigma-Aldrich), NaOH pellets (Acros), terephthalic acid (Acros) and bi-phenyl 4-4'-carboxylic acid (Aldrich). The LDHs syntheses were carried in deionized water. Table ESI-1 summarizes the synthesis conditions. The Ni₂Al-TP and Ni₂Al-BP were prepared by direct co-precipitation using the procedure of Kooli.³ A stoichiometric amount of a metal salt solution (20 mL) was added dropwise at rate of 0.04 mL/min to a reactor containing 100 mL of a 1.332M NaOH solution with terephthalic or bi-phenyl dicarboxylic acid twice the stoichiometric ratio under vigorous stirring and aged for one hour. The pH was maintained at 10.0(3) during the reaction by simultaneous addition of a NaOH solution using a Metrohm-905 titrator.

ESI-3: Characterization of LDH samples by PXRD, FT-IR and Raman spectroscopy

Powder X-ray diffraction:

PXRD were collected using a Rigaku Miniflex 600, with Cu K α , β radiations (1.5408 Å), in a 2 Θ range of 5-70°, using a step sizes of 0.2° and with a scanning rate of 10°/min. The diffractometer was operating at 40 kV and 15 mA, the diffractograms were analysed using X'Pert HighScore Plus 3.0.0

Infrared spectroscopy (IR):

The ATR FT-IR is recorded on a Perkin Elmer spectrum 65 FT-IR spectrometer, with a spectral resolution of 1 cm⁻¹, in the range from 500 to 4000 cm⁻¹.

Elemental analysis:

The Mg, Al, and Ni content were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The sample was dissolved in concentrated nitric acid prior to analysis.

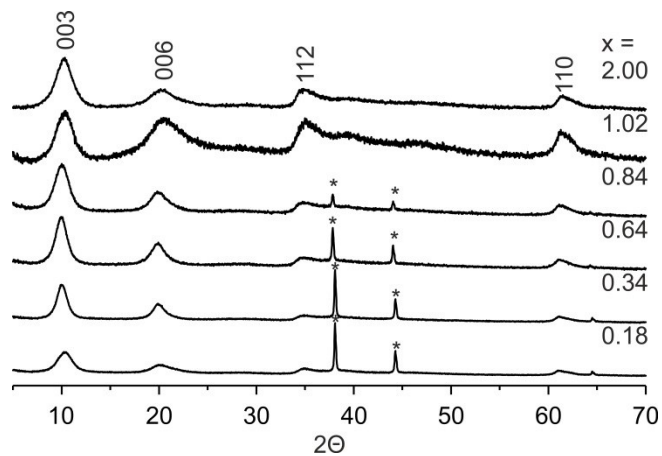


Figure ESI-1. PXRD of the $\text{Mg}_{2-x}\text{Ni}_x\text{Al-LDHs}$ with $x = 0.18, 0.34, 0.68, 0.84, 1.02, 1.59,$ and 2 . The major LDH reflections are assigned. The reflections from an aluminium background (sample holder) are marked with asterisk (*). These are mainly observed for samples of low crystallinity.

Infra-Red Spectroscopy

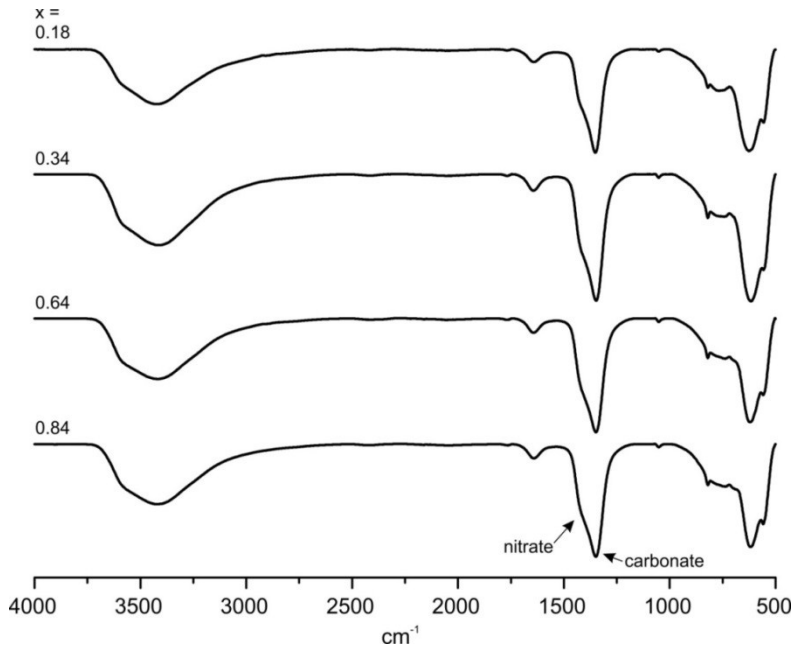
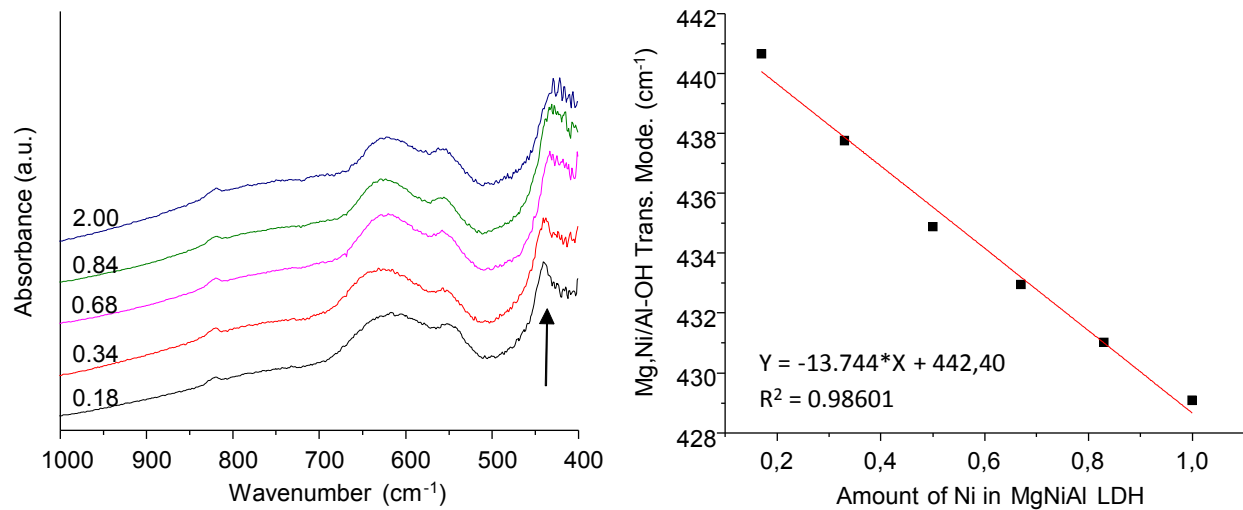


Figure ESI-2: The FT-IR spectra of the selected samples with the vibrations from nitrate and carbonate marked.



Figure

e ESI-3. a) FT-IR spectra of the MgNiAl-LDH solid solutions and b) linear variation of Mg,Ni/Al-OH translational mode with increasing Ni content derived from the progressive evolution of the Mg,Ni/Al-OH translation mode (435 cm⁻¹) as a function of Ni²⁺ doping.

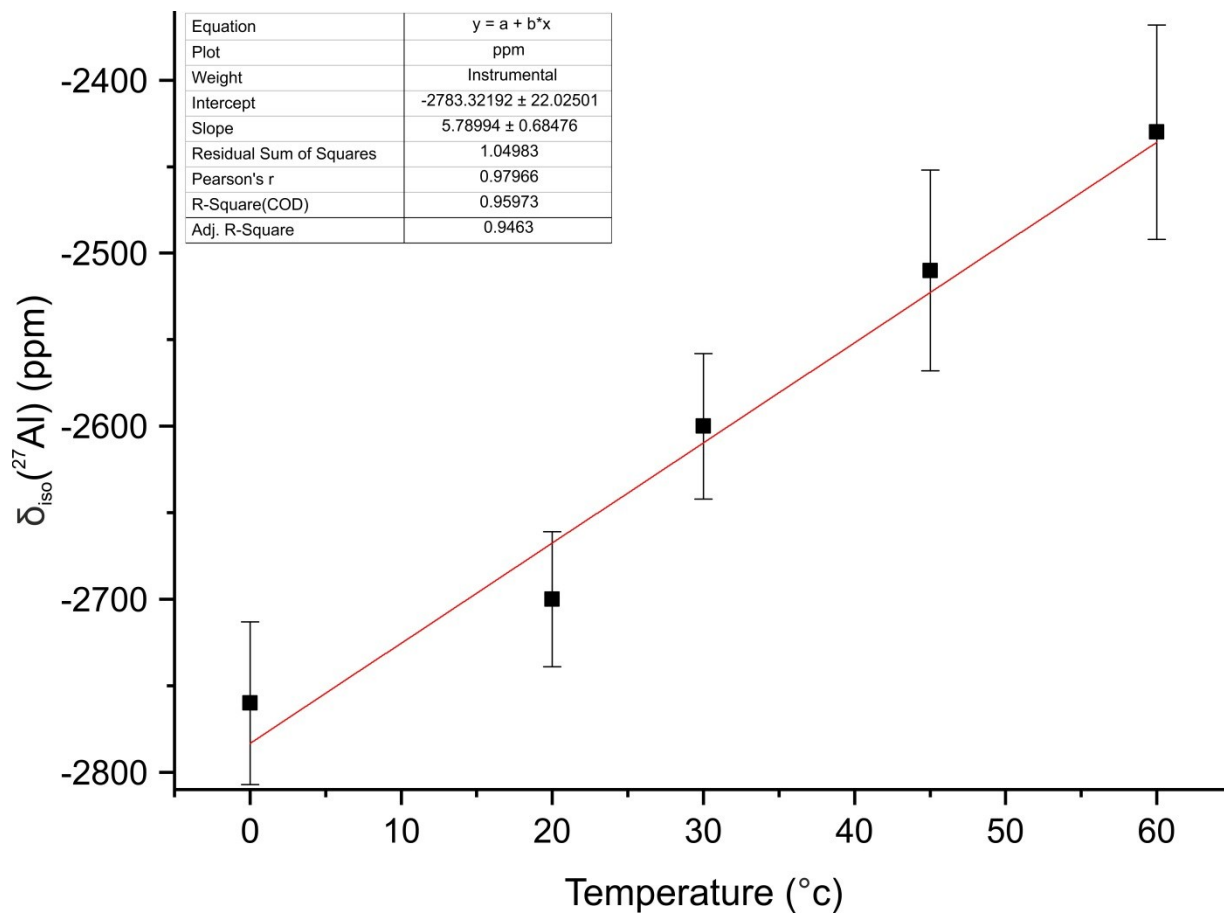


Figure ESI-4. $\delta_{\text{iso}}(^{27}\text{Al})$ for $\text{Ni}_2\text{Al-CO}_3$ as a function of the temperature (setting on temperature controller). The system was allowed to calibrate for 10 min prior to start of data acquisition.

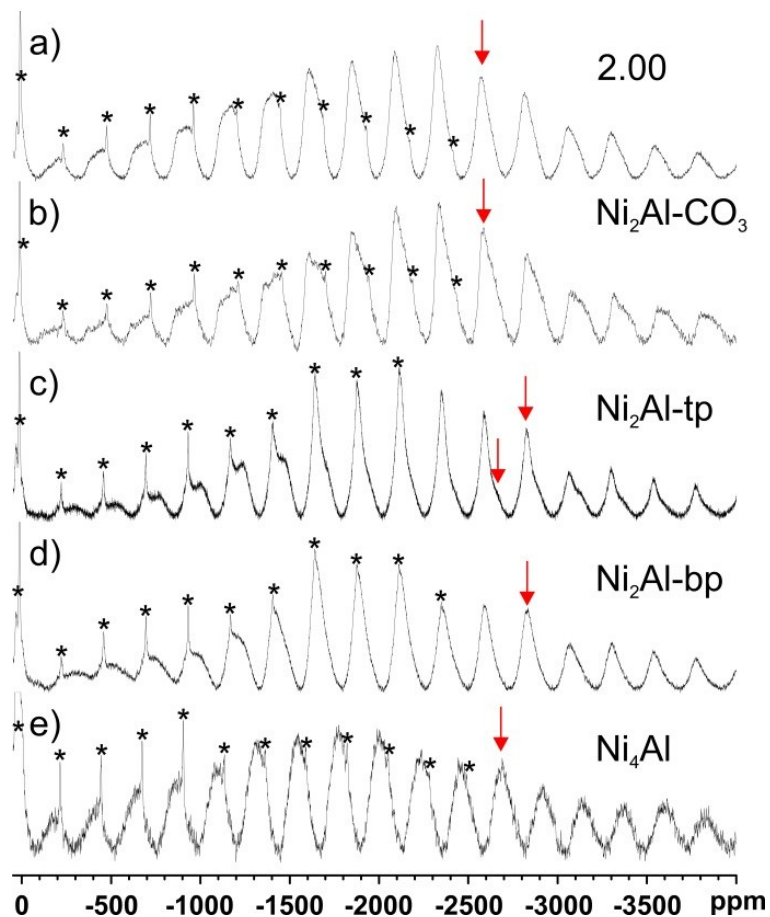


Figure ESI-5: ^{27}Al MAS NMR spectra of Ni_2Al LDH with a) nitrate, b) carbonate, c) TP and d) BP as well as e) a Ni_4Al -LDH with carbonate. The isotropic sites are marked with a red arrow, all spectra are recorded at 14.1 T with a 1.6 mm HXY probe and using 38.0 kHz, 38.3 kHz, 37.0 kHz, 37.0 kHz, and 39.0 kHz for a, b, c, d, and e respectively. An asterisk marks the spinning side bands from the rotor background, it is important to note that overlap of ssb from the sample and rotor (*) occurs.

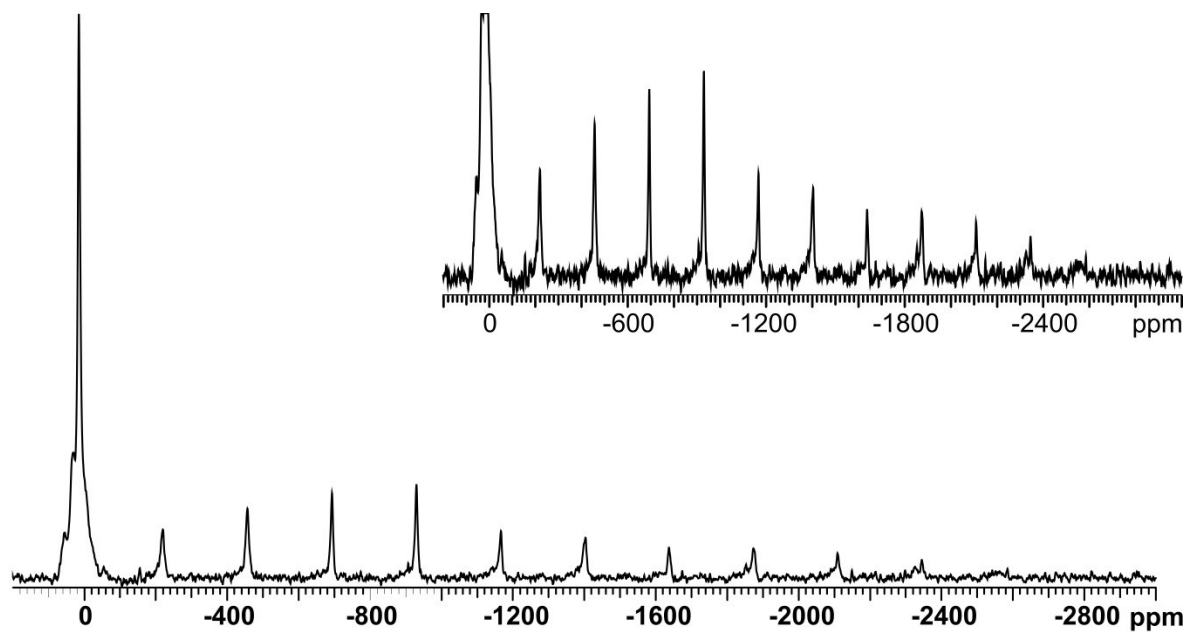


Figure ESI-6: ^{27}Al MAS NMR spectrum of a 1.6 mm Agilent rotor containing glutamate (aluminum free sample) spinning at 37 kHz illustrating the large Al background in the 1.6 mm rotor.

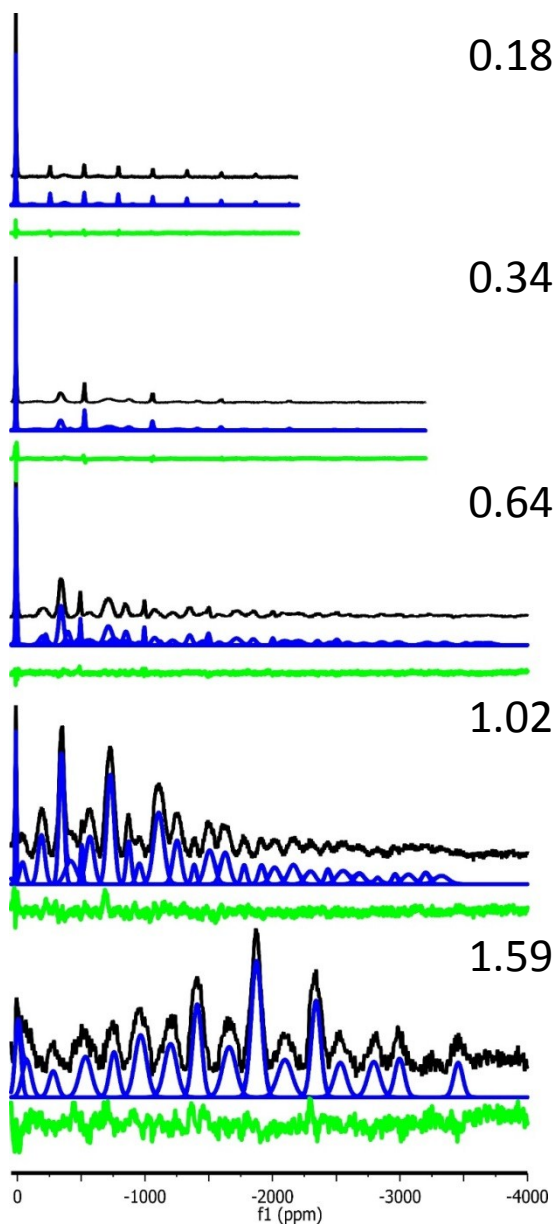


Figure ESI-7: Deconvolution of the selected ^{27}Al MAS NMR spectra for the $\text{Mg}_{2-x}\text{Ni}_x\text{Al-LDH}$ with x indicated in the figure. The results are summarized in Table 3.

References:

1. H. Fraser, G. S. Nichol, D. Uhrin, U. G. Nielsen, M. Evangelisti, J. Schnack and E. K. Brechin, *Dalton Transactions*, 2018, **7**, 11834-11842
2. C. R. Gordijo, V. R. Leopoldo Constantino and D. de Oliveira Silva, *J.Solid State Chem.*, 2007, **180**, 1967-1976.
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