Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Unravelling the effect of paramagnetic Ni^{2+} on the ^{13}C NMR shift tensor for carbonate in $Mg_{2-x}Ni_xAl$ layered double hydroxides by quantum-chemical computations

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Contents

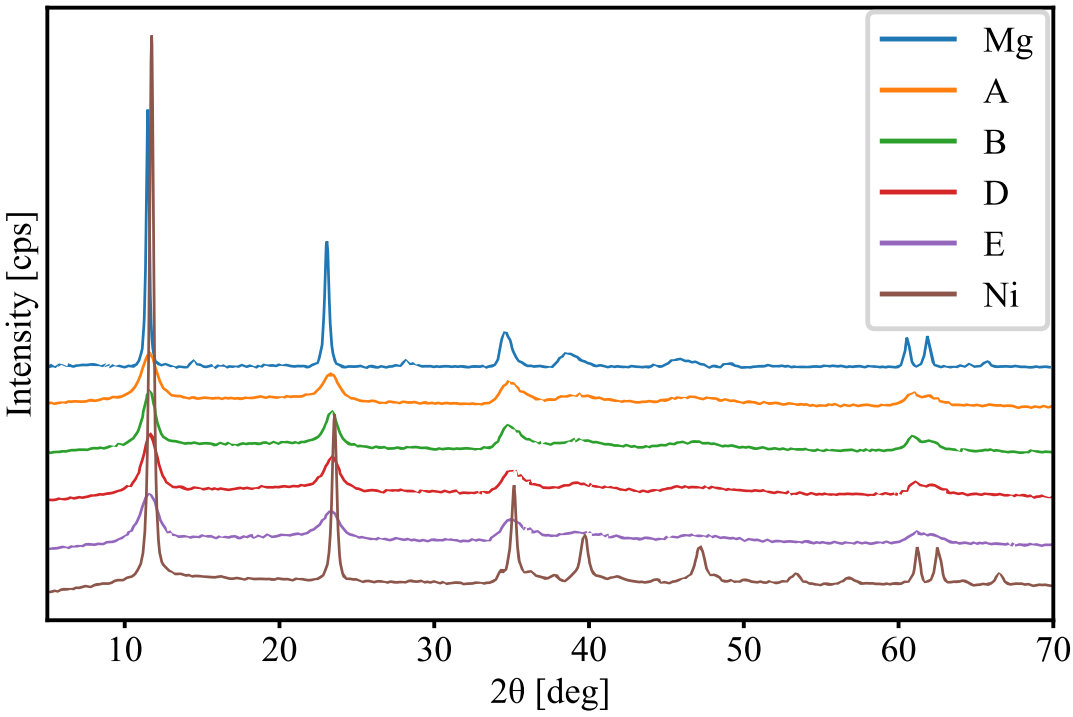

Figure S1. PXRD of the $Mg_{2-x}Ni_xAl$-LDH samples with x = 0.00 (Mg), 0.16 (A), 0.34 (B), 0.68 (D), 0.84 (E), and 2 (Ni). The diffractograms were collected on a Rigaku Miniflex600 X-ray diffractometer with Cu Kα1 radiation (1.5405 Å). The data were obtained in the 2θ range from 3 to 90° with a step size of 0.02° and a scan rate of 5 or 10°/min. The broad backgrounds for A, B, D, and E originates from the glass powder beds used due to limited sample volume.

Table S1. Optimised unit cell of the 1M structure.

```
     Real Lattice(A)                              Reciprocal Lattice(1/A)
     5.3307860    -9.1447812    -0.0114838        0.591368842  -0.342529859   0.142462751
     5.2701643     9.1067742     0.0191709        0.593838093   0.345989634   0.141440601
    -1.7762937     0.0173788     7.4152542       -0.000619428  -0.001424967   0.847187385

                   Lattice parameters(A)      Cell Angles
                   a =     10.585104          Alpha =   96.484702
                   b =     10.521803          beta  =   96.911894
                   c =      7.625058          gamma =  119.702462

                Current cell volume =           717.480159 A**3
                            density =             1.308248 amu/A**3
                                    =             2.172397 g/cm^3
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86

 H          2.6463303983        0.0873673371        1.7213664006
 H          0.5993279618        0.0646410471        5.6466532230
 H          7.8430883589       -0.4580351365        1.7550058810
 H          5.3037464457       -4.3913554052        1.7278499517
 H          5.2706016174        4.4786695651        1.7228595156
 H          5.9024764371       -0.2148877247        5.7314577528
 H          3.2634614022       -4.4109506036        5.6752655437
 H          3.2728906219        4.5184844335        5.6887683699
 H          2.4992834936        3.1179427752        1.7319553880
 H          0.8591123858        3.1201476524        5.6746318989
 H          0.8291609685       -3.1290238626        5.6627730866
 H          2.5087921175       -3.1602358545        1.7051178655
 H          7.7480469071        3.1183647772        1.7705494953
 H          5.0437595770       -1.4252799562        1.7677247738
 H          5.1608206949        7.6199607519        1.6730720450
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 H          3.3700183257       -1.4035810853        5.6901255149
 H          3.5408128988        7.6153250196        5.6680210219
 H          6.1074289411       -3.3148726919        5.7132827259
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 H          7.7566315713       -3.3099081819        1.7254081001
 H          5.2825577598       -7.5690584262        1.6892934651
 H          5.2015164602        1.3818251761        1.7683977522
 H          3.5334044667       -0.3776942149       -0.0533161688
 H          3.2180503657        1.2022223378       -0.0484993138
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 H          8.3834813815        1.2734840862        1.1456536223
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 H          5.2385771644        6.1318870774       -0.0163423766
 H          8.0556700124       -2.0527849068        0.0596680637
 H          6.6007106539       -1.5554416610        0.1066939962
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 H          5.2857941919       -5.5801380443       -0.0398874327
 H          6.6334115072        1.3410534807       -0.0068048531
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 C          4.2081082052       -2.8109567378       -0.0034042311
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 O          0.8017562189       -3.1393377604        4.6768003359
 O          2.4698052045       -3.1437458133        2.6887066431
 O          7.7234127704        3.1306562397        2.7444822105
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O	2.9258383812	-2.9131543614	-0.0296987719
O	4.7553988269	-1.5943575060	0.0242453544
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O	7.5323876546	-1.2093583018	0.1221440316
O	5.6359275294	-6.5069559564	-0.0793170944
O	5.6653949580	1.1329532365	0.0144859365
Mg	1.6293764266	1.5209239169	3.7121578244
Mg	1.6264854698	-1.5176757412	3.6642495696
Mg	6.9143432831	1.4896013585	3.7662928347
Mg	4.2900731522	-3.0479747840	3.7335473463
Mg	4.2561126677	6.0632249972	3.6805230633
Mg	6.9299089675	-1.5623590310	3.7663604843
Mg	4.3031985055	-6.0712648962	3.6843179738
Mg	4.2604843991	3.0345838524	3.7135907189
Al	-1.0091243524	-0.0136703837	3.6365397755
Al	4.2689201233	-0.0057404403	3.7302420314
Al	1.6379543088	-4.5414239620	3.6934028357
Al	1.6142256016	4.5586452230	3.7098346191

Table S2. Optimised unit cell of the 2T structure.

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     Real Lattice(A)                              Reciprocal Lattice(1/A)
     9.1830756    -5.3065451     0.0008811        0.684757970   0.000942022  -0.000061789
    -0.0145659    10.5879796     0.0001429        0.343190975   0.593898404  -0.000022911
     0.0013534    -0.0002036    14.9960022       -0.000043505  -0.000005714   0.418990693

                   Lattice parameters(A)      Cell Angles
                   a =     10.606050         Alpha =   90.000012
                   b =     10.587990         beta  =   89.990373
                   c =     14.996002         gamma =  120.100782

                Current cell volume =         1456.905439 A**3
                            density =            1.288542 amu/A**3
                                    =            2.139674 g/cm^3

172

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 H          1.5145044728        0.9094825712       13.0130529635
 H          0.2253943366        1.7201248169        5.5151233140
 H          4.6194726633       -0.8959629668        1.9566272759
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 H          3.2767266062        3.5474661472       13.0108302015
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 H          6.0722973344        1.8135107795        5.5510975448
 H          1.4504714273        9.8336030117        5.5147433680
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 H          3.2759308070        3.5477849386        9.4720270212
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C	1.5696007700	-0.6401385449	11.2413881899
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O	2.2883408910	7.3984817082	3.7431708484

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O	8.4186418723	-1.3455669132	3.7439787082
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O	7.6824222399	3.9449710667	3.7438924915
O	0.8893716081	1.7708845720	3.7430477781
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O	0.8153770285	3.3396734724	11.2415336480
Mg	1.6035949728	2.7227555213	14.9973585085
Mg	1.6028432010	2.7228003047	7.4852241039
Mg	3.1312401364	0.0719159673	7.5135136549
Mg	3.1306830949	0.0720249574	-0.0268256594
Mg	6.1814686915	5.3526031683	15.0381634714
Mg	6.1884889449	0.0606072827	14.9428296598
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Mg	3.1196099966	5.3581823719	0.0368599452
Al	0.0686264799	0.0720329335	0.0003845073
Al	0.0691538243	0.0719028913	7.4856815521
Al	4.6547669332	2.7097028835	-0.0292108829
Al	4.6592080456	-2.5845612153	0.0160625113
Al	0.0629683558	5.3644481378	-0.0352116124
Al	4.6553101772	2.7095649618	7.5163643915
Al	4.6597668461	-2.5847121184	7.4708862279
Al	0.0635183689	5.3642524239	7.5215704346

Construction and optimisation of the finite cluster models for Ni^{2+} susceptibility

The fractional nuclear charges and number of electrons for each of the pseudohydrogen were fixed so that the formal valence of all the real cluster atoms was retained, despite that the bonds to the next LDH atoms at the perimeter of the cluster were removed. The atomic structures for the three models are displayed in Figure S2, Table S3 summarises the number of atoms and electrons for each, and the coordinates for the clusters are presented in Tables S4, S5 and S6. The resulting, terminated cluster models were geometry-optimised using the Turbomole code[1] at the DFT level with the PBE0 functional,[2] empirical D3(BJ) dispersion corrections,[3,4] and the Stuttgart-Cologne quasirelativistic ECP10MDF effective core potentials[5] with corresponding valence basis sets applied to the metal sites, def2-TZVP all-electron basis set[6] to the other real atoms of the system, and def2-SV(P) for the terminating pseudohydrogens. The pseudohydrogen positions were kept fixed while the positions of the real cluster atoms were relaxed.

Figure S2. Atomic structure of the (a) small, (b) medium and (c) large cluster models of the paramagnetic Ni centre in the LDH layer. Ni in yellow, Al in cyan, Mg in grey, O in red and H in white.

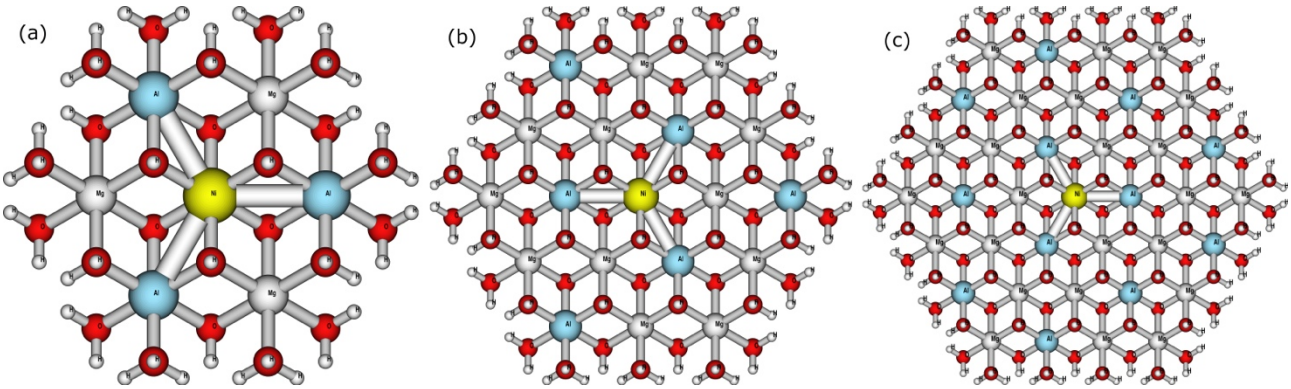

Table S3. The number of real atoms N_{at}, the number of electrons N_e, the number of each element $N_{Ni/Al/Mg/O/H}$, the number of pseudohydrogen termination atoms N_{H^*} and the total charge q in the cluster models of the paramagnetic Ni centre in the LDH layer.

Model	N_{at}	N_e	N_{Ni}	N_{Al}	N_{Mg}	N_O	N_H	N_{H^*}	q / e
small	55	326	1	3	3	24	24	30	+3
medium	175	746	1	6	12	54	54	48	+6
large	295	1346	1	12	24	96	96	66	+12

Table S4. Coordinates (.xyz format, in Å) of the small cluster model of Fig. S2(a) used in the calculation of the susceptibility of the paramagnetic Ni^{2+} site. The entries "z 0.33333" occurring after the coordinates of the pseudohydrogen centres indicate modified nuclear charge.

```
85
Atom          x             y             z          charge
O         -3.52646       0.00000      -0.99831
O         -1.76323       3.05400       0.99832
O         -3.52646       3.05400      -0.99831
O         -3.52646      -3.05400      -0.99831
O          1.76322      -3.05400      -0.99831
H          0.88161       1.52700       1.84913
H          0.88161      -1.52700       1.84913
H         -0.88162       1.52700      -1.84913
H         -0.88162      -1.52700      -1.84913
O          1.76322       0.00000      -0.99831
O          0.88161      -4.58100       0.99832
O          0.88161      -1.52700       0.99832
O          3.52645       3.05400       0.99832
H         -1.76323       0.00000       1.84913
O          3.52645       0.00000       0.99832
O          3.52645      -3.05400       0.99832
Al         0.00000      -3.05400       0.00000
O         -1.76323       0.00000       0.99832
O         -1.76323      -3.05400       0.99832
O          1.76322       3.05400      -0.99831
O         -4.40807      -1.52700       0.99832
O         -4.40807       1.52700       0.99832
Ni         0.00000       0.00000       0.00000
O          0.88161       1.52700       0.99832
Mg         0.00000       3.05400       0.00000
H          1.76322       0.00000      -1.84913
O          4.40807      -1.52700      -0.99831
Al         2.64484       1.52700       0.00000
Mg         2.64484      -1.52700       0.00000
Mg        -2.64485      -1.52700       0.00000
Al        -2.64485       1.52700       0.00000
O         -0.88162       4.58100      -0.99831
O         -0.88162      -1.52700      -0.99831
O         -0.88162       1.52700      -0.99831
O         -0.88162      -4.58100      -0.99831
O          0.88161       4.58100       0.99832
O          4.40807       1.52700      -0.99831
H         -4.40536       0.00000      -0.50069  z  0.33333
H         -3.52646       0.00000      -2.00831
H         -1.76323       3.05400       2.00832
H         -2.20268       3.81515       0.50070  z  0.33333
H         -4.40536       3.05400      -0.50069  z  0.33333
H         -3.08701       3.81515      -0.50069  z  0.33333
H         -3.52646       3.05400      -2.0083
H          1.76322      -3.05400      -2.00831
H          2.20267      -3.81515      -0.50069  z  0.33333
H         -4.84752       0.76585       0.50070  z  0.33333
H         -4.40807       1.52700       2.00832
H         -4.84752       2.28815       0.50070  z  0.33333
H          0.44216      -5.34215       0.50069  z  0.33333
H          1.76051      -4.58100       0.50070  z  0.33333
H          0.88161      -4.58100       2.00832
H         -3.52646      -3.05400      -2.00831
H         -3.08701      -3.81515      -0.50069  z  0.33333
H         -4.40536      -3.05400      -0.50069  z  0.33333
H          3.52645       0.00000       2.00832
H          4.40535       0.00000       0.50070  z  0.33333
H         -4.84752      -0.76585       0.50070  z  0.33333
H         -4.40807      -1.52700       2.00832
H         -4.84752      -2.28815       0.50070  z  0.33333
H          1.76322       3.05400      -2.00831
H          2.20267       3.81515      -0.50069  z  0.33333
H          0.44216       5.34215       0.50069  z  0.33333
H          0.88161       4.58100       2.00832
H          1.76051       4.58100       0.50070  z  0.33333
H         -0.44217       5.34215      -0.50069  z  0.33333
```

```
H         -0.88162        4.58100       -2.00831
H         -1.76052        4.58100       -0.50069  z  0.33333
H          3.08700       -3.81515        0.50069  z  0.33333
H          3.52645       -3.05400        2.00832
H          4.40535       -3.05400        0.50070  z  0.33333
H          3.52645        3.05400        2.00832
H          4.40535        3.05400        0.50070  z  0.33333
H          3.08700        3.81515        0.50069  z  0.33333
H         -0.44217       -5.34215       -0.50069  z  0.33333
H         -1.76052       -4.58100       -0.50069  z  0.33333
H         -0.88162       -4.58100       -2.00831
H          4.84752       -2.28815       -0.50069  z  0.33333
H          4.84752       -0.76585       -0.50069  z  0.33333
H          4.40807       -1.52700       -2.00831
H         -1.76323       -3.05400        2.00832
H         -2.20268       -3.81515        0.50070  z  0.33333
H          4.84752        2.28815       -0.50069  z  0.33333
H          4.84752        0.76585       -0.50069  z  0.33333
H          4.40807        1.52700       -2.00831
```

Table S5. Coordinates (.xyz format, in Å) of the medium cluster model of Fig. S2(b) used in the calculation of the susceptibility of the paramagnetic Ni^{2+} site. The entries ”z 0.33333” occurring after the coordinates of the pseudohydrogen centres indicate modified nuclear charge.

```
175
Atom    x          y          z          charge
O    7.0529100  0.0000000 -0.9983100
H    3.5264500  0.0000000  1.8491300
H    1.7632200  0.0000000 -1.8491300
H   -1.7632300  0.0000000  1.8491300
H    3.5264500  3.0540000  1.8491300
O    3.5264500  3.0540000  0.9983200
H    3.5264500 -3.0540000  1.8491300
O    3.5264500  6.1080000  0.9983200
O   -1.7632300 -6.1080000  0.9983200
O    6.1712900  4.5810000  0.9983200
H   -0.8816200  1.5270000 -1.8491300
O   -3.5264600 -6.1080000 -0.9983100
O   -0.8816200  1.5270000 -0.9983100
O   -4.4080700  1.5270000  0.9983200
O   -0.8816200  4.5810000 -0.9983100
O   -0.8816200  7.6350000 -0.9983100
H    4.4080700 -1.5270000 -1.8491300
H   -3.5264600  3.0540000 -1.8491300
H   -3.5264600  0.0000000 -1.8491300
O    4.4080700  4.5810000 -0.9983100
H   -4.4080700 -1.5270000  1.8491300
O    4.4080700 -1.5270000 -0.9983100
O   -7.0529100 -3.0540000  0.9983200
O   -7.0529100  3.0540000  0.9983200
O    0.8816100  1.5270000  0.9983200
H   -4.4080700  1.5270000  1.8491300
O    4.4080700  1.5270000 -0.9983100
O   -3.5264600  3.0540000 -0.9983100
O    0.8816100  4.5810000  0.9983200
O    0.8816100 -1.5270000  0.9983200
O    0.8816100 -7.6350000  0.9983200
O    7.0529100  3.0540000 -0.9983100
H   -1.7632300  3.0540000  1.8491300
O    7.0529100 -3.0540000 -0.9983100
H    1.7632200  3.0540000 -1.8491300
H    1.7632200 -3.0540000 -1.8491300
O   -6.1713000 -4.5810000 -0.9983100
O   -6.1713000  1.5270000 -0.9983100
O    3.5264500 -3.0540000  0.9983200
H   -0.8816200  4.5810000 -1.8491300
H   -0.8816200 -1.5270000 -1.8491300
H   -0.8816200 -4.5810000 -1.8491300
O    3.5264500  0.0000000  0.9983200
Al   0.0000000  3.0540000  0.0000000
Ni   0.0000000  0.0000000  0.0000000
O   -1.7632300  6.1080000  0.9983200
O   -1.7632300 -3.0540000  0.9983200
Mg   0.0000000  6.1080000  0.0000000
Mg   0.0000000 -3.0540000  0.0000000
O   -4.4080700 -4.5810000  0.9983200
O   -0.8816200 -4.5810000 -0.9983100
Al   0.0000000 -6.1080000  0.0000000
O   -1.7632300  3.0540000  0.9983200
O   -1.7632300  0.0000000  0.9983200
O    6.1712900 -4.5810000  0.9983200
O    6.1712900 -1.5270000  0.9983200
H    4.4080700  1.5270000 -1.8491300
O   -6.1713000  4.5810000 -0.9983100
H   -3.5264600 -3.0540000 -1.8491300
O   -4.4080700 -1.5270000  0.9983200
O    0.8816100 -4.5810000  0.9983200
O   -4.4080700  4.5810000  0.9983200
O    3.5264500 -6.1080000  0.9983200
O   -0.8816200 -7.6350000 -0.9983100
Mg   2.6448400  4.5810000  0.0000000
Al   2.6448400 -1.5270000  0.0000000
```

```
Mg   2.6448400  1.5270000  0.0000000
Mg   2.6448400 -4.5810000  0.0000000
O   -3.5264600  6.1080000 -0.9983100
Mg   5.2896800  0.0000000  0.0000000
Mg  -2.6448500  4.5810000  0.0000000
Al  -2.6448500 -1.5270000  0.0000000
Mg  -2.6448500  1.5270000  0.0000000
O   -0.8816200 -1.5270000 -0.9983100
Mg  -2.6448500 -4.5810000  0.0000000
Mg  -5.2896900  0.0000000  0.0000000
H    0.8816100  1.5270000  1.8491300
Mg   5.2896800 -3.0540000  0.0000000
H    0.8816100 -4.5810000  1.8491300
H    0.8816100 -1.5270000  1.8491300
Al   5.2896800  3.0540000  0.0000000
H    0.8816100  4.5810000  1.8491300
Al  -5.2896900  3.0540000  0.0000000
O   -3.5264600 -3.0540000 -0.9983100
O   -3.5264600  0.0000000 -0.9983100
O   -7.0529100  0.0000000  0.9983200
Mg  -5.2896900 -3.0540000  0.0000000
H   -1.7632300 -3.0540000  1.8491300
O   -6.1713000 -1.5270000 -0.9983100
O    1.7632200 -3.0540000 -0.9983100
O    1.7632200  3.0540000 -0.9983100
O    1.7632200  0.0000000 -0.9983100
O    1.7632200  6.1080000 -0.9983100
O    1.7632200 -6.1080000 -0.9983100
O    4.4080700 -4.5810000 -0.9983100
O    0.8816100  7.6350000  0.9983200
O    6.1712900  1.5270000  0.9983200
H    4.4053527  6.1080000  0.5006957   z  0.33333
H    3.0870003  6.8691525  0.5006948   z  0.33333
H    3.5264500  6.1080000  2.0083200
H   -2.2026837 -6.8691509  0.5006958   z  0.33333
H   -1.7632300 -6.1080000  2.0083200
H    6.1712900  4.5810000  2.0083200
H    5.7318403  5.3421525  0.5006948   z  0.33333
H    7.0501927  4.5810000  0.5006957   z  0.33333
H   -4.8475237 -5.3421509  0.5006958   z  0.33333
H   -4.4080700 -4.5810000  2.0083200
H   -4.8475237  5.3421509  0.5006958   z  0.33333
H   -4.4080700  4.5810000  2.0083200
H   -0.8816200  7.6350000 -2.0083100
H   -1.7605249  7.6350000 -0.5006894   z  0.33333
H   -0.4421652  8.3961527 -0.5006896   z  0.33333
H   -1.7605249 -7.6350000 -0.5006894   z  0.33333
H   -0.4421652 -8.3961527 -0.5006896   z  0.33333
H   -0.8816200 -7.6350000 -2.0083100
H    3.5264500 -6.1080000  2.0083200
H    4.4053527 -6.1080000  0.5006957   z  0.33333
H    3.0870003 -6.8691525  0.5006948   z  0.33333
H    4.4080700  4.5810000 -2.0083100
H    4.8475207  5.3421543 -0.5006885   z  0.33333
H   -7.4923637 -0.7611509  0.5006958   z  0.33333
H   -7.0529100  0.0000000  2.0083200
H   -7.4923637  0.7611509  0.5006958   z  0.33333
H   -7.4923637 -3.8151509  0.5006958   z  0.33333
H   -7.4923637 -2.2928491  0.5006958   z  0.33333
H   -7.0529100 -3.0540000  2.0083200
H   -7.4923637  3.8151509  0.5006958   z  0.33333
H   -7.0529100  3.0540000  2.0083200
H   -7.4923637  2.2928491  0.5006958   z  0.33333
H    4.8475207 -5.3421543 -0.5006885   z  0.33333
H    4.4080700 -4.5810000 -2.0083100
H   -3.5264600 -6.1080000 -2.0083100
H   -3.0870093 -6.8691543 -0.5006885   z  0.33333
H   -4.4053649 -6.1080000 -0.5006894   z  0.33333
H   -3.5264600  6.1080000 -2.0083100
H   -4.4053649  6.1080000 -0.5006894   z  0.33333
H   -3.0870093  6.8691543 -0.5006885   z  0.33333
H    7.4923607  3.8151543 -0.5006885   z  0.33333
H    7.4923607  2.2928457 -0.5006885   z  0.33333
H    7.0529100  3.0540000 -2.0083100
H    7.0529100  0.0000000 -2.0083100
H    7.4923607 -0.7611543 -0.5006885   z  0.33333
H    7.4923607  0.7611543 -0.5006885   z  0.33333
```

```
H    7.4923607 -2.2928457 -0.5006885   z  0.33333
H    7.4923607 -3.8151543 -0.5006885   z  0.33333
H    7.0529100 -3.0540000 -2.0083100
H   -6.1713000  1.5270000 -2.0083100
H   -7.0502049  1.5270000 -0.5006894   z  0.33333
H   -6.1713000 -4.5810000 -2.0083100
H   -7.0502049 -4.5810000 -0.5006894   z  0.33333
H   -5.7318493 -5.3421543 -0.5006885   z  0.33333
H   -5.7318493  5.3421543 -0.5006885   z  0.33333
H   -6.1713000  4.5810000 -2.0083100
H   -7.0502049  4.5810000 -0.5006894   z  0.33333
H   -7.0502049 -1.5270000 -0.5006894   z  0.33333
H   -6.1713000 -1.5270000 -2.0083100
H   -2.2026837  6.8691509  0.5006958   z  0.33333
H   -1.7632300  6.1080000  2.0083200
H    2.2026748  6.8691527 -0.5006896   z  0.33333
H    1.7632200  6.1080000 -2.0083100
H    1.7632200 -6.1080000 -2.0083100
H    2.2026748 -6.8691527 -0.5006896   z  0.33333
H    6.1712900 -4.5810000  2.0083200
H    7.0501927 -4.5810000  0.5006957   z  0.33333
H    5.7318403 -5.3421525  0.5006948   z  0.33333
H    7.0501927 -1.5270000  0.5006957   z  0.33333
H    6.1712900 -1.5270000  2.0083200
H    0.8816100  7.6350000  2.0083200
H    1.7605127  7.6350000  0.5006957   z  0.33333
H    0.4421603  8.3961525  0.5006948   z  0.33333
H    0.8816100 -7.6350000  2.0083200
H    0.4421603 -8.3961525  0.5006948   z  0.33333
H    1.7605127 -7.6350000  0.5006957   z  0.33333
H    7.0501927  1.5270000  0.5006957   z  0.33333
H    6.1712900  1.5270000  2.0083200
```

Table S6. Coordinates (.xyz format, in Å) of the medium cluster model of Fig. S2(c) used in the calculation of the susceptibility of the paramagnetic Ni^{2+} site. The entries ”z 0.33333” occurring after the coordinates of the pseudohydrogen centres indicate modified nuclear charge.

```
295
Atom    x          y          z       charge
H   -0.8816100  7.6350000 -1.8491300
O    9.6977600 -4.5810000 -0.9983200
O   -3.5264500  0.0000000 -0.9983200
H   -3.5264500  6.1080000 -1.8491300
O   -3.5264500  6.1080000 -0.9983200
O   -3.5264500 -9.1620000 -0.9983200
O    1.7632300  0.0000000 -0.9983200
H   -0.8816100  1.5270000 -1.8491300
O    1.7632300  6.1080000 -0.9983200
O    4.4080700 -7.6350000 -0.9983200
O    1.7632300 -9.1620000 -0.9983200
Mg  -7.9345200 -1.5270000  0.0000000
O   -6.1712900  4.5810000 -0.9983200
O   -6.1712900 -7.6350000 -0.9983200
O   -6.1712900  7.6350000 -0.9983200
H    1.7632300  0.0000000 -1.8491300
O   -4.4080700  4.5810000  0.9983100
O   -4.4080700 -7.6350000  0.9983100
H   -3.5264500  3.0540000 -1.8491300
O   -4.4080700  1.5270000  0.9983100
O   -4.4080700 -4.5810000  0.9983100
O    4.4080700  4.5810000 -0.9983200
O    4.4080700 -1.5270000 -0.9983200
O    4.4080700 -4.5810000 -0.9983200
O   -8.8161300  6.1080000 -0.9983200
O    3.5264600 -9.1620000  0.9983100
H   -6.1712900  4.5810000 -1.8491300
O    3.5264600  6.1080000  0.9983100
O   -4.4080700  7.6350000  0.9983100
O    3.5264600 -3.0540000  0.9983100
O   -8.8161300  3.0540000 -0.9983200
O   -8.8161300 -6.1080000 -0.9983200
O   -8.8161300 -3.0540000 -0.9983200
O    3.5264600  0.0000000  0.9983100
O   -7.0529100  3.0540000  0.9983100
O    7.0529100  6.1080000 -0.9983200
O   -7.0529100  6.1080000  0.9983100
O    7.0529100 -3.0540000 -0.9983200
O    7.0529100  3.0540000 -0.9983200
O    1.7632300 -3.0540000 -0.9983200
O    6.1713000  4.5810000  0.9983100
O    6.1713000 -4.5810000  0.9983100
O    6.1713000 -7.6350000  0.9983100
H   -0.8816100 -7.6350000 -1.8491300
O    6.1713000 -1.5270000  0.9983100
O   -9.6977500  4.5810000  0.9983100
O   -9.6977500 -4.5810000  0.9983100
O   -7.0529100 -6.1080000  0.9983100
O    8.8161400  6.1080000  0.9983100
O    8.8161400 -6.1080000  0.9983100
O    8.8161400  0.0000000  0.9983100
O    8.8161400 -3.0540000  0.9983100
Al  -2.6448400  1.5270000  0.0000000
O   -1.7632200 -3.0540000  0.9983100
H   -1.7632200  6.1080000  1.8491300
Mg   5.2896900  0.0000000  0.0000000
O    0.8816200 -4.5810000  0.9983100
O    0.8816200  4.5810000  0.9983100
H    1.7632300  3.0540000 -1.8491300
Ni   0.0000000  0.0000000  0.0000000
Al   0.0000000 -3.0540000  0.0000000
O   -4.4080700 -1.5270000  0.9983100
Mg   0.0000000  3.0540000  0.0000000
O    3.5264600 -6.1080000  0.9983100
O    3.5264600  3.0540000  0.9983100
O    3.5264600  9.1620000  0.9983100
```

```
H    4.4080700  1.5270000 -1.8491300
H    4.4080700  4.5810000 -1.8491300
H    4.4080700 -4.5810000 -1.8491300
Mg   0.0000000 -9.1620000  0.0000000
H    7.0529100  0.0000000 -1.8491300
H    7.0529100 -3.0540000 -1.8491300
H    4.4080700 -1.5270000 -1.8491300
H   -0.8816100 -1.5270000 -1.8491300
O    6.1713000  7.6350000  0.9983100
O   -9.6977500 -1.5270000  0.9983100
Al  -2.6448400 -7.6350000  0.0000000
Mg  -2.6448400  4.5810000  0.0000000
O    7.0529100 -6.1080000 -0.9983200
Mg  -2.6448400 -1.5270000  0.0000000
H    0.8816200 -4.5810000  1.8491300
O    8.8161400  3.0540000  0.9983100
O   -7.0529100  0.0000000  0.9983100
H   -3.5264500  0.0000000 -1.8491300
H   -3.5264500 -3.0540000 -1.8491300
H    1.7632300 -3.0540000 -1.8491300
Mg   7.9345300  4.5810000  0.0000000
H    0.8816200  7.6350000  1.8491300
H    0.8816200  1.5270000  1.8491300
Mg   2.6448500 -1.5270000  0.0000000
H   -1.7632200 -6.1080000  1.8491300
Mg   2.6448500 -4.5810000  0.0000000
Al   2.6448500  1.5270000  0.0000000
Mg   2.6448500  7.6350000  0.0000000
H    7.0529100  3.0540000 -1.8491300
Al  -5.2896800  6.1080000  0.0000000
Al  -5.2896800 -3.0540000  0.0000000
H   -0.8816100 -4.5810000 -1.8491300
Mg  -5.2896800  3.0540000  0.0000000
Mg  -5.2896800 -6.1080000  0.0000000
Mg  -5.2896800  0.0000000  0.0000000
Mg   5.2896900 -6.1080000  0.0000000
Al   5.2896900 -3.0540000  0.0000000
Al  -7.9345200  1.5270000  0.0000000
Mg  -7.9345200 -4.5810000  0.0000000
Mg  -7.9345200  4.5810000  0.0000000
H   -3.5264500 -6.1080000 -1.8491300
H   -6.1712900  1.5270000 -1.8491300
Al   7.9345300  1.5270000  0.0000000
H   -6.1712900 -4.5810000 -1.8491300
Mg   7.9345300 -1.5270000  0.0000000
Mg   7.9345300 -4.5810000  0.0000000
O   -3.5264500  9.1620000 -0.9983200
O    4.4080700  1.5270000 -0.9983200
O   -3.5264500 -6.1080000 -0.9983200
O   -6.1712900 -4.5810000 -0.9983200
O   -0.8816100  4.5810000 -0.9983200
O   -0.8816100 10.6890000 -0.9983200
O   -0.8816100 -4.5810000 -0.9983200
O    9.6977600 -1.5270000 -0.9983200
H   -4.4080700 -1.5270000  1.8491300
Al   0.0000000  6.1080000  0.0000000
Mg  -2.6448400 -4.5810000  0.0000000
H    1.7632300  6.1080000 -1.8491300
O   -9.6977500  1.5270000  0.9983100
H   -0.8816100  4.5810000 -1.8491300
Mg   2.6448500  4.5810000  0.0000000
Al   2.6448500 -7.6350000  0.0000000
H    6.1713000  4.5810000  1.8491300
Mg   5.2896900  3.0540000  0.0000000
O   -3.5264500 -3.0540000 -0.9983200
O   -8.8161300  0.0000000 -0.9983200
O    4.4080700  7.6350000 -0.9983200
O   -3.5264500  3.0540000 -0.9983200
O    1.7632300  3.0540000 -0.9983200
O    1.7632300 -6.1080000 -0.9983200
O    1.7632300  9.1620000 -0.9983200
O   -6.1712900  1.5270000 -0.9983200
O   -6.1712900 -1.5270000 -0.9983200
O   -7.0529100 -3.0540000  0.9983100
H   -1.7632200  3.0540000  1.8491300
H   -1.7632200  0.0000000  1.8491300
O    7.0529100  0.0000000 -0.9983200
```

```
O   -0.8816100 -1.5270000 -0.9983200
H    1.7632300 -6.1080000 -1.8491300
Al   5.2896900  6.1080000  0.0000000
O   -0.8816100 -7.6350000 -0.9983200
O   -0.8816100  1.5270000 -0.9983200
H   -6.1712900 -1.5270000 -1.8491300
O   -0.8816100  7.6350000 -0.9983200
H    0.8816200  4.5810000  1.8491300
H    0.8816200 -7.6350000  1.8491300
O    6.1713000  1.5270000  0.9983100
H    0.8816200 -1.5270000  1.8491300
O   -0.8816100 -10.6890000 -0.9983200
O   -1.7632200  9.1620000  0.9983100
O   -1.7632200  3.0540000  0.9983100
O   -1.7632200  6.1080000  0.9983100
O   -1.7632200  0.0000000  0.9983100
O   -1.7632200 -6.1080000  0.9983100
O    9.6977600  1.5270000 -0.9983200
H    3.5264600  6.1080000  1.8491300
H   -4.4080700  4.5810000  1.8491300
H   -4.4080700  1.5270000  1.8491300
H    3.5264600  3.0540000  1.8491300
H    3.5264600 -3.0540000  1.8491300
H    3.5264600 -6.1080000  1.8491300
H    3.5264600  0.0000000  1.8491300
H   -7.0529100  3.0540000  1.8491300
H   -7.0529100  0.0000000  1.8491300
H    6.1713000 -1.5270000  1.8491300
H    6.1713000  1.5270000  1.8491300
H    6.1713000 -4.5810000  1.8491300
H   -4.4080700 -4.5810000  1.8491300
H   -7.0529100 -3.0540000  1.8491300
O   -1.7632200 -9.1620000  0.9983100
Mg   0.0000000 -6.1080000  0.0000000
O    0.8816200 -1.5270000  0.9983100
O    0.8816200 10.6890000  0.9983100
O    9.6977600  4.5810000 -0.9983200
O    0.8816200  1.5270000  0.9983100
O    0.8816200 -7.6350000  0.9983100
O    0.8816200  7.6350000  0.9983100
H   -1.7632200 -3.0540000  1.8491300
O    0.8816200 -10.6890000  0.9983100
Mg  -2.6448400  7.6350000  0.0000000
Mg   0.0000000  9.1620000  0.0000000
H   -1.7605127 -10.6890000 -0.5006957   z  0.333333333
H   -0.4421603 -11.4501525 -0.5006948   z  0.333333333
H   -0.8816100 -10.6890000 -2.0083200
H    3.0870093  9.9231543  0.5006885     z  0.333333333
H    3.5264600  9.1620000  2.0083100
H    4.4053649  9.1620000  0.5006894     z  0.333333333
H    4.8475237 -8.3961509 -0.5006958     z  0.333333333
H    4.4080700 -7.6350000 -2.0083200
H   -3.5264500 -9.1620000 -2.0083200
H   -4.4053527 -9.1620000 -0.5006957     z  0.333333333
H   -3.0870003 -9.9231525 -0.5006948    z  0.333333333
H   -10.1372007  2.2881543  0.5006885   z  0.333333333
H   -9.6977500  1.5270000  2.0083100
H   -10.1372007  0.7658457  0.5006885   z  0.333333333
H   -4.8475207 -8.3961543  0.5006885    z  0.333333333
H   -4.4080700 -7.6350000  2.0083100
H   -9.6950327 -3.0540000 -0.5006957    z  0.333333333
H   -8.8161300 -3.0540000 -2.0083200
H    9.6977600  1.5270000 -2.0083200
H   10.1372097  2.2881525 -0.5006948    z  0.333333333
H   10.1372097  0.7658475 -0.5006948    z  0.333333333
H   10.1372097 -3.8198475 -0.5006948    z  0.333333333
H   10.1372097 -5.3421525 -0.5006948    z  0.333333333
H    9.6977600 -4.5810000 -2.0083200
H    2.2026837 -9.9231509 -0.5006958    z  0.333333333
H    1.7632300 -9.1620000 -2.0083200
H   -2.2026748  9.9231527  0.5006896    z  0.333333333
H   -1.7632200  9.1620000  2.0083100
H   -5.7318403 -8.3961525 -0.5006948    z  0.333333333
H   -7.0501927 -7.6350000 -0.5006957    z  0.333333333
H   -6.1712900 -7.6350000 -2.0083200
H   -6.1712900  7.6350000 -2.0083200
H   -5.7318403  8.3961525 -0.5006948    z  0.333333333
```

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H   -7.0501927  7.6350000 -0.5006957    z  0.333333333
H    7.0502049  7.6350000  0.5006894    z  0.333333333
H    6.1713000  7.6350000  2.0083100
H    5.7318493  8.3961543  0.5006885    z  0.333333333
H   -10.1372007 -2.2881543  0.5006885   z  0.333333333
H   -9.6977500 -1.5270000  2.0083100
H   -10.1372007 -0.7658457  0.5006885   z  0.333333333
H    7.0529100  6.1080000 -2.0083200
H    7.4923637  6.8691509 -0.5006958    z  0.333333333
H    4.4080700  7.6350000 -2.0083200
H    4.8475237  8.3961509 -0.5006958    z  0.333333333
H   -3.0870003  9.9231525 -0.5006948    z  0.333333333
H   -4.4053527  9.1620000 -0.5006957    z  0.333333333
H   -3.5264500  9.1620000 -2.0083200
H   -4.8475207  8.3961543  0.5006885    z  0.333333333
H   -4.4080700  7.6350000  2.0083100
H   -9.6950327  6.1080000 -0.5006957    z  0.333333333
H   -8.8161300  6.1080000 -2.0083200
H   -8.3766803  6.8691525 -0.5006948    z  0.333333333
H    3.0870093 -9.9231543  0.5006885    z  0.333333333
H    4.4053649 -9.1620000  0.5006894    z  0.333333333
H    3.5264600 -9.1620000  2.0083100
H   10.1372097 -2.2881525 -0.5006948    z  0.333333333
H   10.1372097 -0.7658475 -0.5006948    z  0.333333333
H    9.6977600 -1.5270000 -2.0083200
H   -9.6950327  3.0540000 -0.5006957    z  0.333333333
H   -8.8161300  3.0540000 -2.0083200
H   -8.8161300 -6.1080000 -2.0083200
H   -9.6950327 -6.1080000 -0.5006957    z  0.333333333
H   -8.3766803 -6.8691525 -0.5006948    z  0.333333333
H   10.1372097  5.3421525 -0.5006948    z  0.333333333
H   10.1372097  3.8198475 -0.5006948    z  0.333333333
H    9.6977600  4.5810000 -2.0083200
H   -7.0529100 -6.1080000  2.0083100
H   -7.4923607 -6.8691543  0.5006885    z  0.333333333
H   -7.0529100  6.1080000  2.0083100
H   -7.4923607  6.8691543  0.5006885    z  0.333333333
H    7.0529100 -6.1080000 -2.0083200
H    7.4923637 -6.8691509 -0.5006958    z  0.333333333
H   -0.8816100 10.6890000 -2.0083200
H   -0.4421603 11.4501525 -0.5006948    z  0.333333333
H   -1.7605127 10.6890000 -0.5006957    z  0.333333333
H   -1.7632200 -9.1620000  2.0083100
H   -2.2026748 -9.9231527  0.5006896    z  0.333333333
H   -10.1372007  3.8198457  0.5006885   z  0.333333333
H   -10.1372007  5.3421543  0.5006885   z  0.333333333
H   -9.6977500  4.5810000  2.0083100
H   -9.6977500 -4.5810000  2.0083100
H   -10.1372007 -5.3421543  0.5006885   z  0.333333333
H   -10.1372007 -3.8198457  0.5006885   z  0.333333333
H    1.7632300  9.1620000 -2.0083200
H    2.2026837  9.9231509 -0.5006958    z  0.333333333
H    0.4421652 11.4501527  0.5006896    z  0.333333333
H    1.7605249 10.6890000  0.5006894    z  0.333333333
H    0.8816200 10.6890000  2.0083100
H    9.6950449  6.1080000  0.5006894    z  0.333333333
H    8.3766893  6.8691543  0.5006885    z  0.333333333
H    8.8161400  6.1080000  2.0083100
H    9.6950449 -6.1080000  0.5006894    z  0.333333333
H    8.8161400 -6.1080000  2.0083100
H    8.3766893 -6.8691543  0.5006885    z  0.333333333
H    8.8161400  0.0000000  2.0083100
H    9.6950449  0.0000000  0.5006894    z  0.333333333
H    9.6950449 -3.0540000  0.5006894    z  0.333333333
H    8.8161400 -3.0540000  2.0083100
H    8.8161400  3.0540000  2.0083100
H    9.6950449  3.0540000  0.5006894    z  0.333333333
H    1.7605249 -10.6890000  0.5006894   z  0.333333333
H    0.8816200 -10.6890000  2.0083100
H    0.4421652 -11.4501527  0.5006896   z  0.333333333
H   -8.8161300  0.0000000 -2.0083200
H   -9.6950327  0.0000000 -0.5006957    z  0.333333333
H    5.7318493 -8.3961543  0.5006885    z  0.333333333
H    6.1713000 -7.6350000  2.0083100
H    7.0502049 -7.6350000  0.5006894    z  0.333333333
```

Figure S3. The calculated electronic spin densities for the (a) small, (b) medium and (c) large cluster models for the single paramagnetic Ni^{2+} site in the LDH layer (see Figure S2). Positive and negative equisurfaces (at ±0.0003 a.u.) are shown in red and blue, respectively.

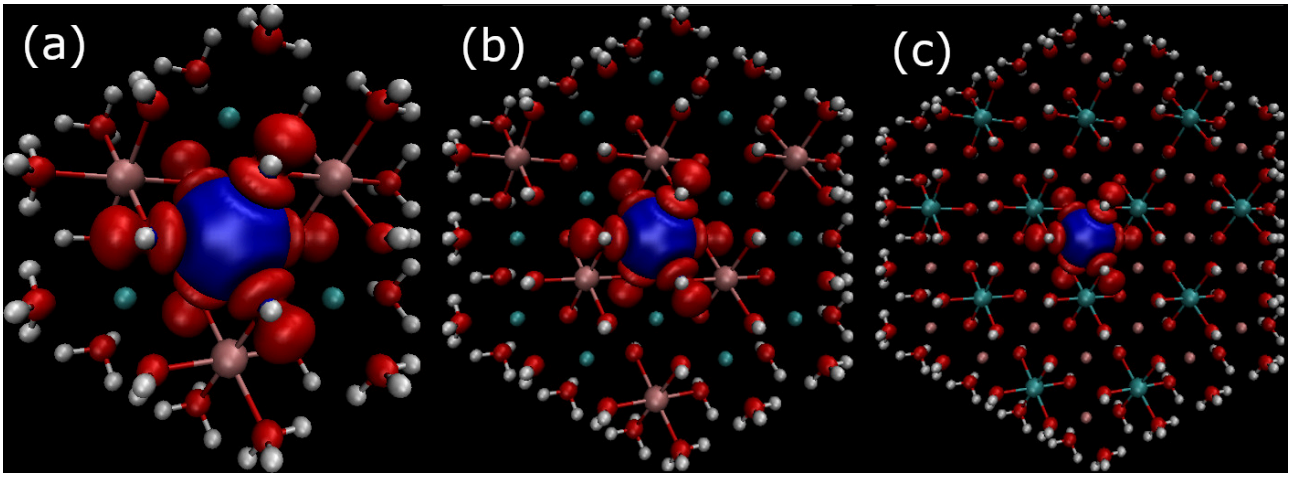

Table S7. Atomic positions (Å) of the cluster model used for the calculation of the local hyperfine contributions, σ_{con}, to the ^{13}C shielding tensor. In the calculations, only one of the eight Ni positions was occupied by a paramagnetic Ni^{2+} atom at a time, whereas the remaining seven positions were diamagnetic Mg^{2+}. The entries "z 0.33333" occurring after the coordinates of the pseudohydrogen centres indicate modified nuclear charge.

```
174
Atom       x             y             z       charge
Ni      0.075792     -6.164210      8.435539
Ni     -0.811502     -4.651290      0.950987
Ni      1.852086     -6.181589      1.020285
Ni     -2.587796     -4.633911      8.366241
Ni      2.715628     -4.678594      8.468352
Ni      0.088917     -9.187500      8.386310
Ni     -3.452039     -6.177163      0.948090
Ni     -0.808611     -1.612690      0.998895
H      -2.547331     -4.620428     -1.059361
H      -2.481067     -1.553484     -1.046386
H      -2.437799     -7.762943     -1.031962
H      -5.281909     -6.408986     -1.019302
H       2.865938     -7.520242     -1.012824
H       0.070805     -6.293850     -1.008144
H       0.062957     -0.016096     -1.007907
H       0.040797     -9.122474     -0.997548
H       0.208343     -3.046247     -0.991896
H       2.603717     -4.559161     -0.971861
H       2.765674     -1.752441     -0.970232
O      -5.101841     -3.108889     -0.081988
O      -2.631533     -4.549932     -0.076265
O      -2.631487     -1.682249     -0.055985
O       0.031818     -6.277360     -0.024556
O      -2.426613     -7.707830     -0.023529
O      -5.298606     -6.263040     -0.020042
O       2.859434     -7.691893     -0.017538
O       0.203607     -3.126146     -0.007782
O       0.000000      0.000000      0.000000
O       0.015261     -9.109732      0.012049
O       2.682336     -4.548951      0.035023
O       2.680609     -1.726591      0.035848
H      -3.032844     -0.901683      0.443745  z 0.333333
H      -5.584756     -2.399271      0.450305  z 0.333333
H      -5.584756     -3.818507      0.450305  z 0.333333
H      -2.924172     -8.437792      0.466054  z 0.333333
H       2.372624     -8.432709      0.466515  z 0.333333
H       0.911004     -9.155802      0.476399  z 0.333333
H      -5.690240     -5.487395      0.494834  z 0.333333
H      -0.374671     -9.900640      0.504511  z 0.333333
H       2.263405     -0.935291      0.504767  z 0.333333
H       3.722144     -7.706480      0.507456  z 0.333333
H      -5.719627     -7.014064      0.507978  z 0.333333
H      -0.432393      0.747999      0.523101  z 0.333333
H       0.432393      0.747999      0.523101  z 0.333333
H       3.560391     -4.620290      0.529018  z 0.333333
H       3.558714     -1.686211      0.533241  z 0.333333
Al     -3.447112     -3.147285      0.923277
Al     -0.800033     -7.675038      0.980140
Al      1.830932     -3.139355      1.016980
H      -5.307603     -7.685448      1.449660  z 0.333333
H      -1.218780      0.751846      1.462447  z 0.333333
H      -3.884307     -0.917074      1.475498  z 0.333333
H       4.110449     -7.050716      1.480642  z 0.333333
H      -3.955565     -8.431122      1.486201  z 0.333333
H      -2.541584     -0.027414      1.492380  z 0.333333
H       1.333690     -8.425871      1.498254  z 0.333333
H      -5.185800     -1.665611      1.499839  z 0.333333
H      -5.173197     -4.600243      1.507373  z 0.333333
H       1.403810     -0.932084      1.519057  z 0.333333
```

```
H      -2.492481     -9.153255      1.523568  z 0.333333
H      -1.217862     -9.901136      1.543855  z 0.333333
H       4.076368     -5.522192      1.547337  z 0.333333
H       3.966127     -2.423110      1.567860  z 0.333333
H       3.969400     -3.902727      1.572171  z 0.333333
O      -4.278211     -1.723235      1.939227
O      -1.836032     -3.134195      1.948102
O      -4.268915     -4.544465      1.953761
O      -1.636231     -6.272952      1.963538
O      -4.441768     -7.689528      1.969672
O      -1.657696      0.003852      1.980093
O       0.836812     -7.697637      1.991091
O       1.001660     -4.554737      1.997271
O       1.007467     -1.720681      2.010104
O      -1.615212     -9.104991      2.021733
O       3.676117     -6.317984      2.023376
O       3.481853     -3.162576      2.056500
H      -4.139733     -1.607626      2.932986
H      -1.838660     -3.068973      2.933391
H      -1.608827     -6.262638      2.949511
H       0.932031     -4.537195      2.976863
H      -4.435111     -7.722651      2.979107
H      -1.576841     -0.013914      2.986695
H       0.825162     -7.540356      2.988701
H       1.077223     -1.720920      3.017692
H       3.669274     -6.451752      3.024455
H      -1.635174     -9.027981      3.028595
H       3.463951     -3.354261      3.047982
O      -1.288443     -6.029390      4.672293
O       0.770226     -6.944929      4.691196
C      -0.006173     -5.927192      4.698588
O       0.541118     -4.710593      4.726237
H       1.073425    -10.680886      6.357385
H      -4.214092     -7.745564      6.383292
H       3.542747     -6.429614      6.403639
H      -1.705489     -6.276471      6.407110
H      -1.735497     -9.105095      6.417706
H       1.089465     -7.507591      6.429842
H       0.989380     -1.735062      6.445022
H       0.829478     -4.541516      6.469717
O      -4.407827     -4.532553      7.338989
O       3.722815     -3.129517      7.340954
O       0.923005    -10.809651      7.347785
O      -1.744476     -6.259981      7.390698
O      -4.202906     -7.690451      7.391726
O       1.083140     -7.674514      7.397716
O       3.526050     -6.283669      7.402899
O       3.554492     -9.127402      7.403770
O      -1.572686     -3.108767      7.407472
O      -1.761033     -9.092353      7.427303
O       0.906042     -4.531573      7.450277
O       0.904315     -1.709212      7.451102
H      -4.804234     -5.318710      7.833881  z 0.333333
H       1.796707    -10.776312      7.853388  z 0.333333
H       0.498766    -11.571675      7.857139  z 0.333333
H      -4.700136     -6.948231      7.862864  z 0.333333
H       4.585840     -3.149542      7.865250  z 0.333333
H      -4.840076     -3.789164      7.868737  z 0.333333
H       4.419807     -6.242103      7.871485  z 0.333333
H       3.239901     -2.419899      7.873247  z 0.333333
H      -4.700465     -8.420413      7.881308  z 0.333333
H       4.438887     -9.175458      7.889195  z 0.333333
H       3.158448     -9.917271      7.893012  z 0.333333
H      -2.064075     -2.374049      7.896171  z 0.333333
H      -2.150964     -9.883261      7.919765  z 0.333333
H       0.487111     -0.917912      7.920021  z 0.333333
H       1.782420     -1.668832      7.948496  z 0.333333
Al     -2.576327     -7.657659      8.395395
Al      2.730730     -7.702371      8.400343
Al      0.054639     -3.121976      8.432234
H      -0.290295    -11.593288      8.813173  z 0.333333
H      -1.157142    -11.593288      8.813173  z 0.333333
H      -4.464502     -3.123740      8.821278  z 0.333333
H       4.987870     -3.830414      8.834843  z 0.333333
H      -4.293114     -6.209120      8.886344  z 0.333333
H       4.951577     -5.356253      8.889382  z 0.333333
H      -3.110242     -2.373282      8.899494  z 0.333333
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H	2.310505	-9.911195	8.905784	z 0.333333
H	4.869092	-8.451750	8.909142	z 0.333333
H	4.869092	-6.968562	8.909142	z 0.333333
H	-0.372484	-0.914705	8.934311	z 0.333333
H	-1.650068	-1.650901	8.934675	z 0.333333
H	-4.268775	-9.135876	8.938822	z 0.333333
H	-2.994156	-9.883757	8.959109	z 0.333333
H	2.189833	-2.405731	8.983114	z 0.333333
O	-0.723718	-10.850637	9.342997	
O	-3.612326	-3.116816	9.363356	
O	4.555741	-4.565093	9.376702	
O	-3.412525	-6.255573	9.378792	
O	1.896796	-9.123550	9.383863	
O	4.382888	-7.710156	9.392613	
O	-0.939482	-7.680258	9.406345	
O	-0.774633	-4.537358	9.412525	
O	-0.768827	-1.703303	9.425358	
O	-3.391505	-9.087612	9.436987	
O	1.899823	-6.300606	9.438630	
O	1.705559	-3.145197	9.471754	
H	-0.585241	-10.735028	10.336757	
H	-3.615013	-3.050105	10.371147	
H	-0.950820	-7.527186	10.377257	
H	4.659333	-4.647291	10.378007	
H	-3.384465	-6.245013	10.388347	
H	1.977651	-9.141316	10.390465	
H	4.389545	-7.743279	10.402048	
H	-0.844263	-4.519817	10.392117	
H	-0.699071	-1.703541	10.432946	
H	1.893148	-6.431108	10.415275	
H	-3.411467	-9.010603	10.443849	
H	1.687657	-3.336882	10.463237	
H	-1.572686	-3.108767	6.397472	
H	-4.268915	-4.544465	2.963761	
H	3.554492	-9.127402	6.393770	
H	3.722815	-3.129517	6.330953	
H	-4.407827	-4.532553	6.328989	
H	-5.101841	-3.108889	-1.091988	

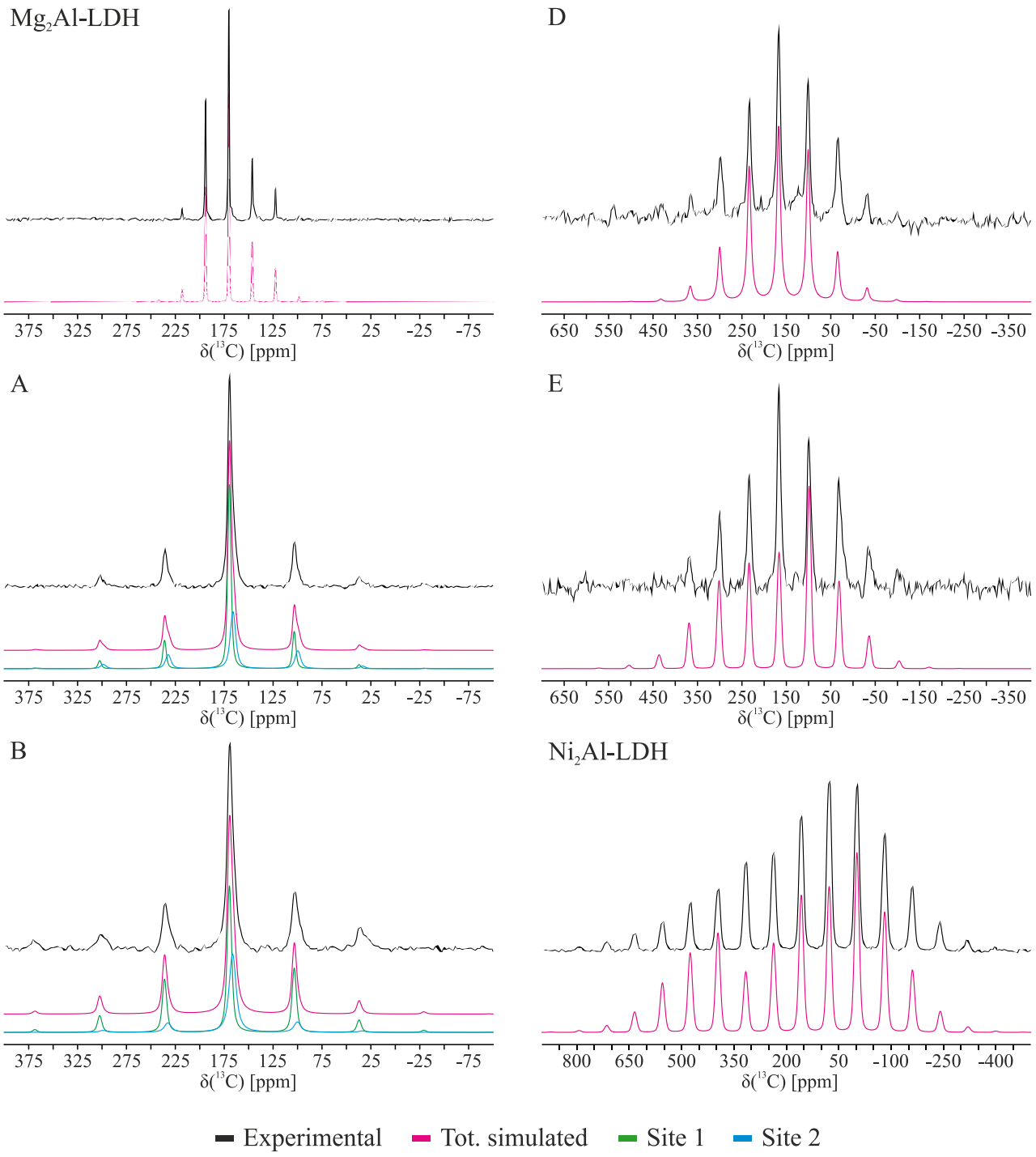

Figure S4. Experimental and simulated ^{13}C MAS NMR spectra of the $Mg_{2-x}Ni_xAl$-LDH samples with x = 0 (Mg), 0.16 (A), 0.34 (B), 0.68 (D), 0.84 (E), and 2 (Ni), the parameters given in Table 2 were used for the simulations. Notice that different scales (ppm) are used in the left and right columns. For A and B, a second site that accounts for 35% of the total intensity, was needed.

Table S8. ^{13}C MAS NMR parameters reported in the Haeberlen convention.[a]

Sample	$\delta_{iso}(^{13}C)$ (ppm)	Δ (ppm)	η
Na_2CO_3(s)	170.4(3)	-51(1)	0.30(5)
$NaHCO_3$(s)	164.3(4)	62(2)	0.40(10)
Mg_2Al-LDH	170.3(3)	-53(3)	0.25(10)
A[b]	169.7	97	0.56
	166.0	116	0.67
B[b]	169.2	114	0.57
	166.2	116	0.67
D	167.3	174	0.91
E	166.4	250	0.70
Ni_2Al-LDH	157.1	480	0.56

[a]The Haeberlen convention entails for the isotropic value $\delta_{iso} = \frac{1}{3}(\delta_{xx} + \delta_{yy} + \delta_{zz})$, with the principal values arranged adhering to $|\delta_{zz} - \delta_{iso}| \geq |\delta_{xx} - \delta_{iso}| \geq |\delta_{yy} - \delta_{iso}|$, the reduced anisotropy $\Delta = \delta_{zz} - \delta_{iso}$, and the asymmetry parameter $\eta = (\delta_{yy} - \delta_{xx})/\Delta$, where $0 \leq \eta \leq 1$. [b]The site at 169 ppm has approximately twice the intensity of the 166 ppm site.

Table S9. Calculated orbital shielding tensors, eigenvalues and the corresponding eigenvectors, as well as isotropic shielding constants (σ), shielding anisotropy (Δσ), and asymmetry parameter η, for local environments of the interlayer CO_3^{2-} in the optimised unit cells of the Mg_2Al-LDH material. The LDH layer normal is in the *z* coordinate direction.

					Eigenvectors					
Site	Shielding tensor (ppm)			Eigenvalues (ppm)	*x*	*y*	*z*	σ (ppm)	Δσ (ppm)[a]	η[b]
1M/C1	-19.01	-6.41	0.23	48.26	0.01	-0.02	1.00	-1.98	75.36	0.47
	-9.97	-35.17	-1.62	-15.73	-0.89	0.46	0.02			
	0.57	-1.04	48.23	-38.46	-0.31	-0.95	-0.01			
1M/C2	-4.95	-14.42	-1.11	46.54	-0.02	-0.01	1.00	1.96	66.86	1.02
	-22.52	-35.65	-1.57	3.37	-0.87	0.50	-0.01			
	-1.84	-1.91	46.48	-44.02	-0.35	-0.94	-0.03			
2T/C1	-33.07	-6.04	0.00	50.83	0.00	0.00	1.00	-2.63	80.20	0.32
	-8.59	-25.65	-0.01	-21.26	0.46	-0.89	0.00			
	0.00	-0.01	50.83	-37.47	0.81	0.59	0.00			
2T/C2	-9.68	7.06	-0.02	50.22	0.00	0.00	1.00	0.12	75.15	0.65
	5.20	-40.18	0.01	-8.52	-0.99	-0.16	0.00			
	-0.02	0.01	50.22	-41.34	-0.22	0.98	0.00			
2T/C3	-33.74	11.79	-0.01	51.35	0.00	0.00	1.00	-1.91	79.89	0.26
	1.42	-23.33	0.00	-21.91	-0.71	-0.71	0.00			
	-0.01	0.00	51.35	-35.15	0.99	-0.12	0.00			
2T/C4	-38.97	-0.89	-0.03	49.88	0.00	0.00	1.00	-2.04	77.89	0.44
	1.58	-17.04	0.00	-17.10	-0.04	1.00	0.00			
	-0.03	0.00	49.88	-38.91	-1.00	0.07	0.00			

[a] Defined from the shielding eigenvalues as $\Delta\sigma = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2$, where σ_{33} is in the present case the most shielded eigenvalue in the direction of the LDH layer normal. The eigenvalues σ_{11} and σ_{22} are located in the plane parallel to the LDH layers. [b] Defined from the shielding eigenvalues as $\eta = \frac{\sigma_{22}-\sigma_{11}}{\sigma_{33}}$.

Table S10. Calculated hyperfine contributions to the paramagnetic ^{13}C NMR shielding tensor $\boldsymbol{\sigma}$ (in ppm) from the different Ni^{2+} sites using the cluster model depicted in Figure 4.

Ni^{2+} site number	$\boldsymbol{\sigma}_{hf}$			$\boldsymbol{\sigma}_{pc}^{(1)}$			$\boldsymbol{\sigma}_{con}$		
1	129.6	-0.5	-7.6	126.6	0.5	-8.2	3.1	-1.0	0.7
	-0.4	129.2	21.4	0.5	125.2	23.8	-1.0	3.9	-2.4
	-8.1	21.9	-207.5	-8.7	25.1	-262.1	0.6	-3.2	54.6
2	89.2	13.7	-51.1	89.0	19.1	-55.7	0.3	-5.4	4.5
	13.8	76.1	81.0	19.1	70.8	88.2	-5.3	5.3	-7.2
	-52.8	-52.8	-138.2	-58.7	93.0	-166.2	5.9	-145.8	28.1
3	44.0	6.8	104.4	37.1	7.9	113.0	6.9	-1.1	-8.7
	6.7	89.4	-15.5	7.9	93.5	-15.5	-1.2	-4.2	-0.1
	107.6	-15.8	-113.1	119.2	-16.3	-136.0	-11.6	0.5	22.9
4	9.1	26.3	81.2	5.4	30.1	84.8	3.7	-3.8	-3.6
	26.6	51.2	-38.5	30.1	50.4	-42.5	-3.5	0.8	4.0
	83.5	-39.3	-51.1	89.4	-44.8	-58.1	-5.9	5.5	6.9
5	9.1	-25.1	-74.5	2.5	-26.2	-78.7	6.7	1.2	4.2
	-24.9	48.3	-36.1	-26.2	47.6	-36.1	1.3	0.6	0.0
	-76.3	-37.2	-45.8	-83.0	-38.1	-52.1	6.7	0.9	6.3
6	55.5	3.3	-3.2	55.7	2.1	-2.4	-0.2	1.2	-0.8
	3.6	-11.8	78.1	2.1	-17.6	82.5	1.4	5.8	-4.4
	-3.5	80.2	-34.4	-2.5	87.0	-39.7	-0.9	-6.8	5.3
7	-15.1	-5.3	-73.4	-18.6	-5.0	-74.4	3.4	-0.3	0.9
	-5.3	50.4	-6.5	-5.0	49.9	-5.4	-0.3	0.5	-1.1
	-75.2	-6.7	-34.4	-78.4	-5.7	-32.6	3.2	-1.0	-1.8
8	31.1	10.5	-9.3	33.1	11.1	-9.5	-2.1	-0.6	0.2
	10.7	-22.2	48.5	11.1	-24.5	50.8	-0.4	2.3	-2.3
	-9.7	49.9	-7.9	-10.0	53.6	-9.0	0.3	-3.7	1.2
Sum of 1…8	352.6	29.7	-33.6	330.8	39.6	-31.0	21.8	-9.9	-2.6
	30.5	410.5	132.4	39.6	395.3	145.9	-9.0	15.2	-13.5
	-34.5	0.2	-632.4	-32.7	153.8	-755.7	-1.8	-153.7	123.4

Anisotropic shift results from individual carbon sites using method 2

Method 2 described below is a variation of method 1: The shielding tensors are first diagonalised to obtain the eigenvalues, which are subsequently averaged over the different impurity distributions. In contrast to method 1, the results are reported individually for the various carbon sites (1M/C1-2 and 2T/C1-4), in method 2. Figure S5 and Table S11 present the obtained average eigenvalue data. A linear relation is observed between the eigenvalues of the shift tensor and x (Ni^{2+} content). Across the different sites and stacking models (1M or 2T) for both the X-ray and optimised geometries, each of the computed eigenvalues show significant variation for a fixed Ni^{2+} content, x. For example, this range is close to 250 ppm for the top eigenvalue δ_{11} (in the perpendicular direction with respect to the LDH layers) for the Ni end member ($x = 1$) and close to 150 ppm for the two in-plane eigenvalues (δ_{22} and δ_{33}). For the eigenvalue δ_{11}, which is in the direction of the layer normal, the differences among the individual carbon sites (C1 and C2 for 1M, C1-4 for 2T) is reduced when the geometry-optimised 1M and 2T structures are used instead of their X-ray counterparts. Some of the sites, such as that of the 2T/C3 site, change very dramatically upon relaxing the geometry, although the average over the different sites, in method 1 above, only changes a bit. Most likely the geometry optimisation is a necessary step in the present kind of modelling of the interlayer space, due to the poorly defined hydrogen positions of the X-ray structures and highly disordered interlayer, as also noted in the reported X-ray structures.[7,8]

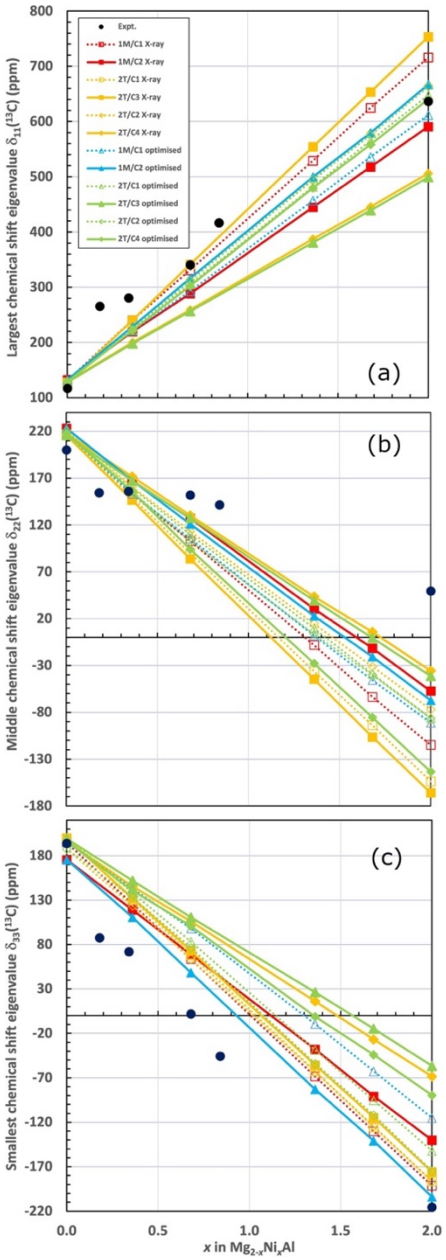

Figure S5. The experimental and computed total ^{13}C chemical shift tensor eigenvalues (δ_{11}, δ_{22}, and δ_{33}, in ppm) for CO_3^{2-} in $Mg_{2-x}Ni_xAl$-LDH as functions of x. The sum of the orbital, pseudocontact and local hyperfine contributions obtained from method 2 described in the preceding chapter of this ESI document: total shielding tensors diagonalised individually for the different carbon sites of the 1M (sites C1 and C2) and 2T (sites C1-C4) models and the obtained eigenvalues then averaged over the Ni^{2+} distributions. The results are shown separately for the experimental X-ray and computationally optimised structures. (a) Largest, (b) middle, and (c) lowest eigenvalue, which correspond to δ_{11}, δ_{22} and δ_{33}, respectively.

Table S11. Calculated ^{13}C NMR chemical shift data (ppm), $\delta(^{13}C)$, for CO_3^{2-} in $Mg_{2-x}Ni_xAl$-LDH as a function of *x*. The data includes the contributions from the orbital, pseudocontact and local hyperfine interactions and the calculations have been carried out using method 2 described in the text.

Structure	Eigenvalue	$x = 0$	$x = 0.36$	$x = 0.68$	$x = 1.36$	$x = 1.68$	$x = 2$
1M/C1 X-ray	δ_{11}	131	240	331	529	625	716
	δ_{22}	218	153	103	-8	-64	-115
	δ_{33}	195	125	64	-69	-130	-191
1M/C2 X-ray	δ_{11}	132	219	288	445	517	591
	δ_{22}	223	168	127	30	-12	-57
	δ_{33}	175	119	69	-38	-91	-140
2T/C1 X-ray	δ_{11}	128	240	342	554	654	754
	δ_{22}	217	150	90	-36	-94	-154
	δ_{33}	200	131	69	-63	-126	-186
2T/C3 X-ray	δ_{11}	128	240	341	554	653	753
	δ_{22}	216	147	84	-45	-106	-166
	δ_{33}	199	132	73	-56	-115	-176
2T/C2 X-ray	δ_{11}	129	228	314	493	579	665
	δ_{22}	220	161	113	15	-31	-77
	δ_{33}	187	123	64	-63	-125	-186
2T/C4 X-ray	δ_{11}	129	200	259	387	445	506
	δ_{22}	218	172	130	44	6	-36
	δ_{33}	196	146	106	16	-27	-68
1M/C1 optimised	δ_{11}	131	221	292	457	536	612
	δ_{22}	218	153	106	2	-46	-91
	δ_{33}	195	143	98	-9	-63	-115
1M/C2 optimised	δ_{11}	132	228	316	499	579	667
	δ_{22}	223	168	121	23	-21	-67
	δ_{33}	175	111	48	-83	-141	-204
2T/C1 optimised	δ_{11}	128	222	306	482	565	648
	δ_{22}	217	160	110	10	-39	-86
	δ_{33}	200	138	83	-39	-95	-152
2T/C3 optimised	δ_{11}	128	198	256	381	439	499
	δ_{22}	216	167	127	39	-1	-41
	δ_{33}	199	152	111	26	-15	-57
2T/C2 optimised	δ_{11}	129	224	312	495	575	663
	δ_{22}	220	156	103	4	-40	-86
	δ_{33}	187	133	76	-54	-112	-175
2T/C4 optimised	δ_{11}	129	222	302	479	558	640
	δ_{22}	218	156	94	-28	-85	-143
	δ_{33}	196	141	101	-1	-44	-90

Anisotropic shift results from diagonalised average tensors (method 3)

In method 3, the full ^{13}C shift tensors are averaged over the various impurity distributions before diagonalisation of the average tensors, at each value of *x*. Figure S6 shows such eigenvalues averaged over the two (for the 1M structure) and four (2T) carbon sites. The corresponding numerical data are presented in Table S12. The general findings are similar to those obtained from method 1 in the main text: there is a linear dependence of the shift eigenvalues on *x*. The largest (perpendicular to the LDH planes) eigenvalue, δ_{11}, is reproduced in a very good agreement with the experiment, when the local hyperfine correction δ_{con} is taken into account. Also, the furthest in-plane eigenvalue, δ_{33}, agrees in an overall satisfactory way with the SSNMR data, Finally, δ_{22} remains relative poorly reproduced by the computations. No large qualitative difference between the X-ray and optimised structures can be found. In the light of the findings of method 2, this follows from averaging over the sites. A distinct feature of method 3 as compared to both methods 1 and 2 is that averaging the tensors before diagonalisation tends to render the asymmetry, *i.e.*, difference between the in-plane eigenvalues δ_{22} and δ_{33}, small. Experimentally the two are clearly distinct.

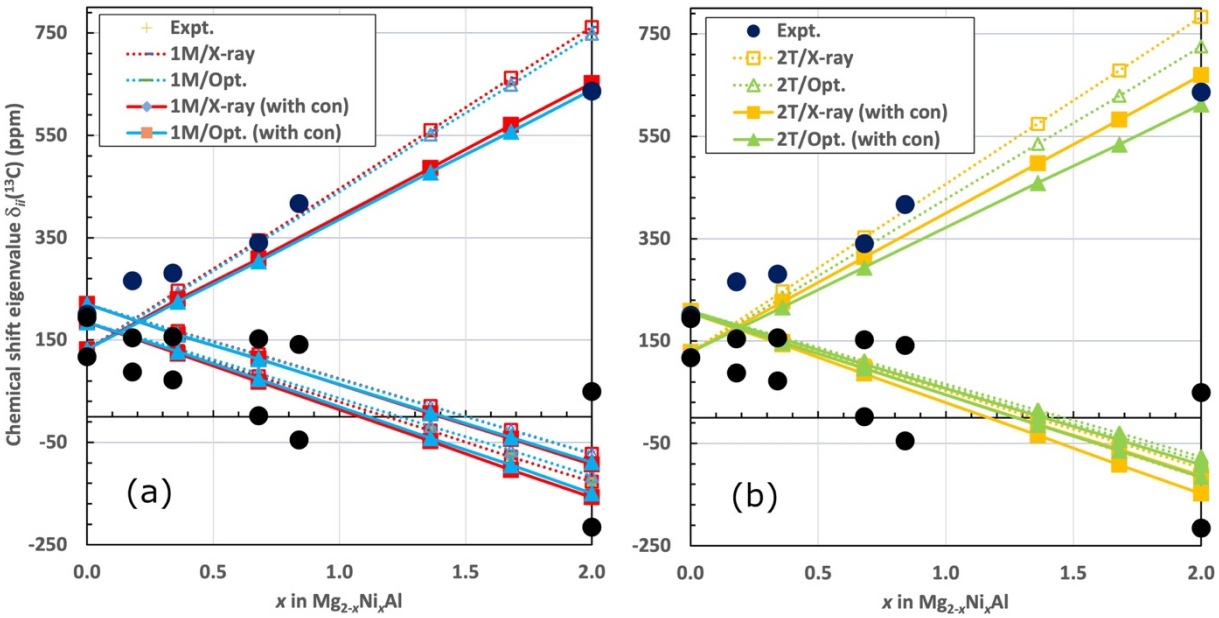

Figure S6. The experimental and computed total ^{13}C chemical shift tensor eigenvalues (δ_{11}, δ_{22}, and δ_{33}, in ppm) for CO_3^{2-} in $Mg_{2-x}Ni_xAl$-LDH as functions of x. The computational results are shown both for the sum of the orbital and pseudocontact contributions (dashed lines and open symbols) and added with local hyperfine contribution δ_{con} (full lines and symbols). Computations following method 3 are described in the text: The total shielding tensors for the different carbon sites of the 1M (sites C1 and C2) and 2T (sites C1-C4) models were first averaged and then the average tensors were diagonalised. The results are shown separately for experimental X-ray and computationally optimised structures of (a) 1M and (b) 2T type.

Table S12. The eigenvalues of averaged computational chemical shift tensors (in ppm) following method 3 described in the text for $Mg_{2-x}Ni_xAl$-LDH as functions of x. Data include the orbital, pseudocontact and local hyperfine contributions.

Structure	Eigenvalue	$x = 0$	$x = 0.36$	$x = 0.68$	$x = 1.36$	$x = 1.68$	$x = 2$
1M X-ray	δ_{11}	132	229	309	486	570	652
	δ_{22}	220	160	113	7	-43	-93
	δ_{33}	185	123	68	-48	-104	-158
1M optimised	δ_{11}	132	225	304	478	557	639
	δ_{22}	220	160	113	8	-40	-88
	δ_{33}	185	127	74	-41	-94	-150
2T X-ray	δ_{11}	128	227	314	497	583	669
	δ_{22}	209	147	96	-13	-62	-114
	δ_{33}	205	143	86	-34	-92	-148
2T optimised	δ_{11}	128	216	294	459	534	612
	δ_{22}	209	154	105	3	-43	-92
	δ_{33}	205	147	97	-14	-64	-116

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