Supplementary Material (ESI) for *PCCP*

Periodic DFT modeling of bulk and surface proprieties of $MgCl_2$

Raffaele Credendino[a], Vincenzo Busico[a], Mauro Causà[,b], Vincenzo Barone[b,c], Peter H. M. Budzelaar[d], Claudio Zicovich-Wilson[e]*

[a] Laboratory of Stereoselective Polymerizations (LSP), Dipartimento di Chimica "Paolo Corradini", Università di Napoli Federico II, Via Cintia, 80126 Naples, Italy.
E-mail: raffaele.credendino@unina.it; busico@unina.it.

[b] Laboratory of Structure and Dynamics of Molecules (LSDM), Dipartimento di Chimica "Paolo Corradini", Università di Napoli Federico II, Via Cintia, 80126 Naples, Italy.
E-mail: mauro.causa@unina.it; vincenzo.barone@sns.it.

[c] Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy.
E-mail: vincenzo.barone@sns.it.

[d] Department of Chemistry, University of Manitoba, Winnipeg MB R3T 2N2, Canada.
E-mail: budzelaa@cc.umanitoba.ca.

[e] Facultad de Ciencias, Universitad Autonoma del Estado de Morelos, Av. Universitad 1001, C. Chamilpa, 62210 Cuernavaca (MOR), Mexico.
E-mail: claudio@servm.fc.uaem.mx.

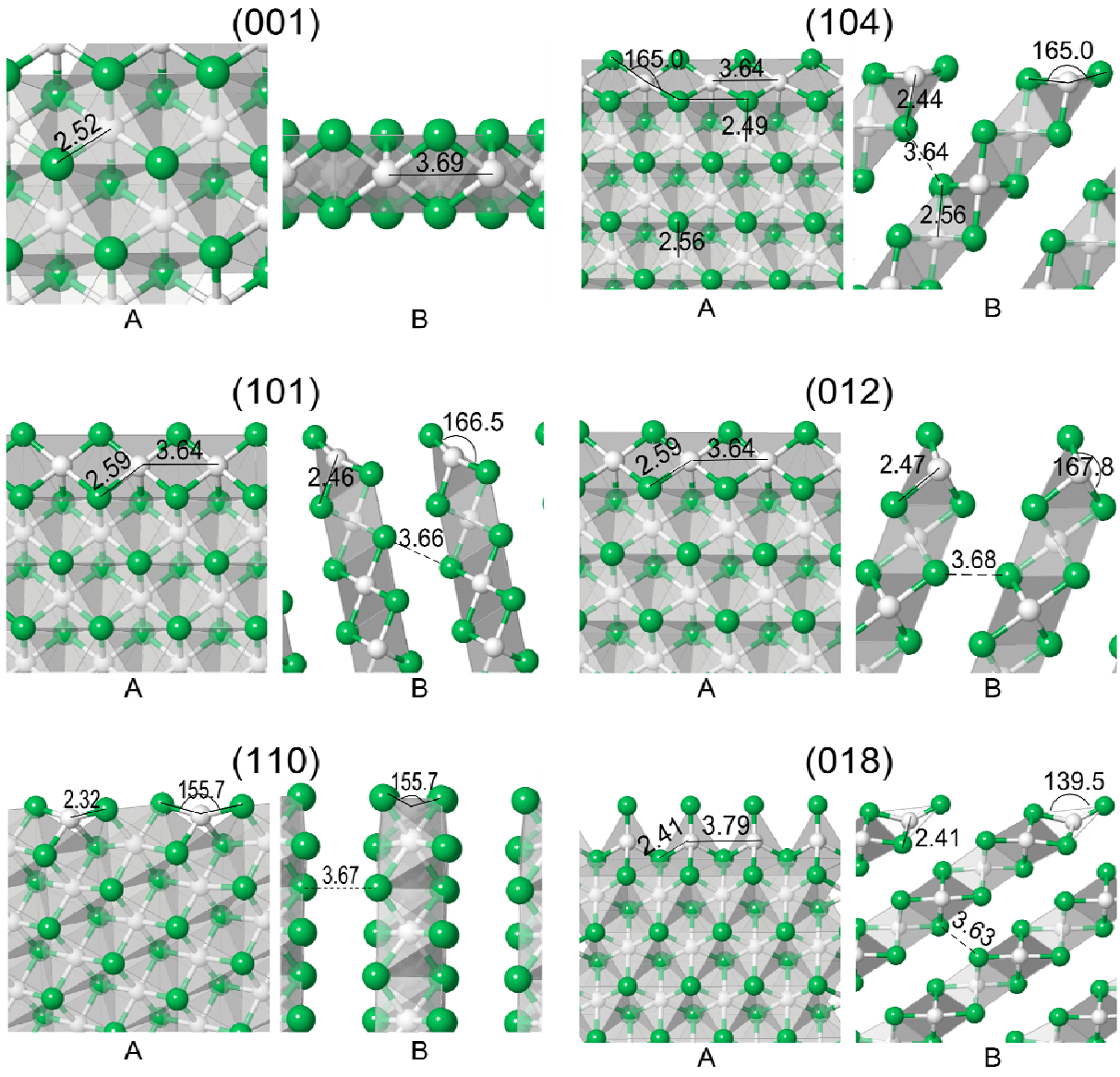
*Corresponding author. Tel.: +39081674405, Fax: +39081674090, E-mail: mauro.causa@unina.it.

Contents:

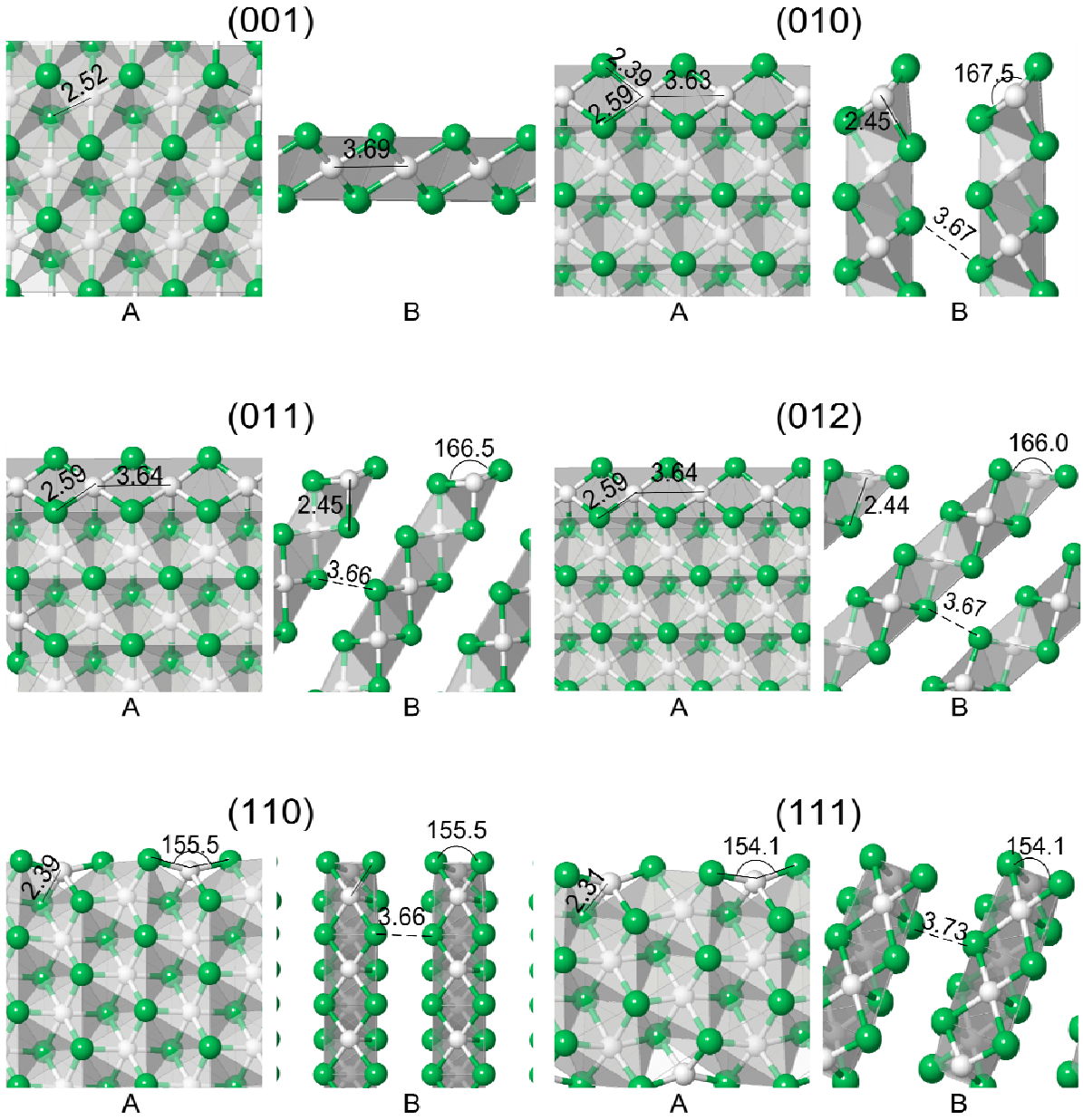
1. Pictures

Orthographic views of the structure of the optimized α- and β-$MgCl_2$ surfaces. A: perpendicular to *ab* plane; B: parallel to *ab* plane. Distances in Å, angles in ° (for optimized bulk $MgCl_2$, Mg-Cl = 2.49 Å, Mg-Mg = 3.64 Å, Cl…Cl = 3.84 Å). Drawings generated using Jmol[45] program.

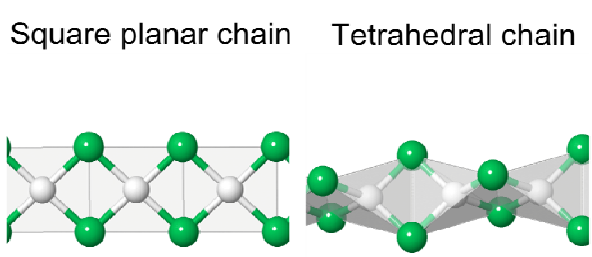
1.1 α-$MgCl_2$ crystal surfaces



1.2 β-$MgCl_2$ crystal surfaces



1.3 Ribbons



2. Basis sets

2.1 Basis set B1

Mg

```
12  5
0  0  8  2.  1.
 68371.875      0.0002226
  9699.34009    0.0018982
  2041.176786   0.0110451
   529.862906   0.0500627
   159.186000   0.169123
    54.6848     0.367031
    21.2357     0.400410
     8.74604    0.14987
0  1  5  8.  1.
   156.795     -0.00624    0.00772
    31.0339    -0.07882    0.06427
     9.6453    -0.07992    0.2104
     3.7109     0.29063    0.34314
     1.61164    0.57164    0.3735
0 1 1 0. 1.
    0.68     1.         1.
0 1 1 0. 1.
    0.23     1.         1.
0  3  1  0.  1
0.325             1.
```

Cl

```
17 6
0  0  8  2.  1.
135320.     0.000225
 19440.     0.00191
  4130.     0.01110
  1074.     0.04989
   323.4    0.1703
   111.1    0.3683
    43.4    0.4036
    18.18   0.1459
0 1 6 8. 1.
   324.8   -0.00763  0.00820
    73.00  -0.0829   0.0605
    23.71  -0.1046   0.2115
     9.138  0.2540   0.3765
     3.930  0.695    0.3967
     1.329  0.399    0.186
0 1 3 8. 1.
     4.755 -0.3740  -0.0340
     1.756 -0.4754   0.1617
     0.785  1.3400   0.9250
0 1 1 0. 1.
     0.294  1.       1.
0 1 1 0. 1.
     0.100  1.       1.
0 3 1 0. 1.0
0.75 1.0
```

2.2 Basis Set B2

Mg

```
12  8
0  0  8  2.  1.
 68371.875      0.0002226
  9699.34009    0.0018982
  2041.176786   0.0110451
   529.862906   0.0500627
   159.186000   0.169123
    54.6848     0.367031
    21.2357     0.400410
     8.74604    0.14987
0  1  5  8.  1.
   156.795     -0.00624    0.00772
    31.0339    -0.07882    0.06427
     9.6453    -0.07992    0.2104
     3.7109     0.29063    0.34314
     1.61164    0.57164    0.3735
0  1  1  0.  1.
    0.68     1.         1.
0  1  1  0.  1.
    0.23     1.         1.
0  3  1  0.  1.
    0.925          1.
0  3  1  0.  1.
    0.625          1.
0  3  1  0.  1.
    0.325          1.
0  4  1  0.  1.
    0.325          1.
```

Cl

```
17 10
0  0  8  2.  1.
  135320.     0.000225
   19440.     0.00191
    4130.     0.01110
    1074.     0.04989
     323.4    0.1703
     111.1    0.3683
      43.4    0.4036
      18.18   0.1459
0 1 6 8. 1.
     324.8   -0.00763  0.00820
      73.00  -0.0829   0.0605
      23.71  -0.1046   0.2115
       9.138  0.2540   0.3765
       3.930  0.695    0.3967
       1.329  0.399    0.186
0 1 2 8. 1.
     4.755 -0.3740  -0.0340
     1.756 -0.4754   0.1617
0 1 1 0. 1.
     0.785  1.3400   0.9250
0 1 1 0. 1.
     0.294  1.       1.
0 1 1 0. 1.
     0.100  1.       1.
0 3 1 0. 1.0
     1.5 1.0
0 3 1 0. 1.0
     0.75 1.0
0 3 1 0. 1.0
     0.38 1.0
0 4 1 0. 1.0
     0.38 1.0
```