Basis set optimized and adopted for Ti and Cl atoms

Ti 7 shells

S 8		
225338.0	0.000228	
32315.0	0.001929	
6883.61	0.011100	
1802.14	0.05	
543.063	0.17010	
187.549	0.369	
73.2133	0.4033	
30.3718	0.1445	
SP 6		
554.042	-0.0059	0.0085
132.525	-0.0683	0.0603
43.6801	-0.1245	0.2124
17.2243	0.2532	0.3902
7.2248	0.6261	0.4097
2.4117	0.282	0.2181
SP 4		
24.4975	0.0175	-0.0207
11.4772	-0.2277	-0.0653
4.4653	-0.7946	0.1919
1.8904	1.0107	1.3778
SP 1		
0.8099	1.0	1.0
SP 1		
0.3242	1.0	1.0
D 3		
7.6781	0.1127	
1.8117	0.3927	
0.463	0.5206	
D 1		
1.0	0.2	

Cl 5 shells

S 8		
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	
SP 6		
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
SP 4		
4.755	-0.3740	-0.0340
1.756	-0.4754	0.1617
0.785	1.3400	0.9250
SP 1		
0.294	1.	1.
SP 1		
0.10	1.	1.
D 1		
0.75		

Phase α
FM

```
_symmetry_space_group_name_H-M    'P3'
_symmetry_Int_Tables_number       143
_symmetry_cell_setting            trigonal
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -y,x-y,z
  -x+y,-x,z
```

```
_cell_length_a                 6.2839
_cell_length_b                 6.2839
_cell_length_c                 17.1459
_cell_angle_alpha               90.0000
_cell_angle_beta                90.0000
_cell_angle_gamma                120.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
Cl1   Cl   0.35759   0.00075   0.07947   0.00000  Uiso   1.00
Cl2   Cl  -0.35755  -0.00075  -0.07949   0.00000  Uiso   1.00
Cl3   Cl  -0.33409  -0.30975   0.41284   0.00000  Uiso   1.00
Cl4   Cl   0.33260   0.02367  -0.25383   0.00000  Uiso   1.00
Cl5   Cl   0.30902   0.33256   0.25385   0.00000  Uiso   1.00
Cl6   Cl  -0.02417  -0.33408  -0.41281   0.00000  Uiso   1.00
Ti7   Ti   0.00000   0.00000   0.33366   0.00000  Uiso   1.00
Ti8   Ti   0.00000   0.00000  -0.33363   0.00000  Uiso   1.00
Ti9   Ti   0.33333  -0.33333   0.33302   0.00000  Uiso   1.00
Ti10  Ti   0.33333  -0.33333   0.00027   0.00000  Uiso   1.00
Ti11  Ti  -0.33333   0.33333  -0.33307   0.00000  Uiso   1.00
Ti12  Ti  -0.33333   0.33333  -0.00030   0.00000  Uiso   1.00
```

Phase β
AFM

```
_symmetry_space_group_name_H-M    'P-31M'
_symmetry_Int_Tables_number       162
_symmetry_cell_setting            trigonal
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -y,x-y,z
  -x+y,-x,z
  -y,-x,-z
  -x+y,y,-z
  x,x-y,-z
  -x,-y,-z
  y,-x+y,-z
  x-y,x,-z
  y,x,z
  x-y,-y,z
  -x,-x+y,z
_cell_length_a                 6.2066
_cell_length_b                 6.2066
_cell_length_c                 5.8825
_cell_angle_alpha               90.0000
_cell_angle_beta                90.0000
_cell_angle_gamma                120.0000
loop_
_atom_site_label
```

```
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
TI    Ti   0.00000  0.00000 -0.00000  0.00000 Uiso  1.00
Fe    Fe   0.00000  0.00000 -0.50000  0.00000 Uiso  1.00
CL    Cl   0.31098  0.00000  0.25000  0.00000 Uiso  1.00
```

Phase γ
FM

```
_symmetry_space_group_name_H-M    'P3112'
_symmetry_Int_Tables_number       151
_symmetry_cell_setting            trigonal
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -y,x-y,z+1/3
  -x+y,-x,z+2/3
  -y,-x,-z+2/3
  -x+y,y,-z+1/3
  x,x-y,-z
_cell_length_a                    6.2818
_cell_length_b                    6.2818
_cell_length_c                    17.2134
_cell_angle_alpha                 90.0000
_cell_angle_beta                  90.0000
_cell_angle_gamma                 120.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
Cl1   Cl   0.08725 -0.11309  0.58793  0.00000 Uiso  1.00
Cl2   Cl   0.44371 -0.47138  0.58687  0.00000 Uiso  1.00
Cl3   Cl  -0.19919  0.24404  0.58771  0.00000 Uiso  1.00
Ti4   Ti   0.11054 -0.11054  0.33333  0.00000 Uiso  1.00
Ti5   Ti  -0.22320  0.22320  0.33333  0.00000 Uiso  1.00
```

Electronic Supplementary Material for PCCP