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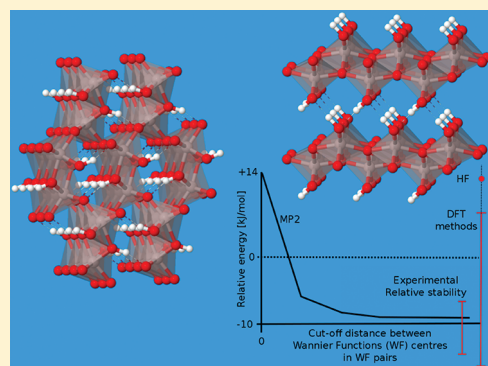
1 Relative Energy of Aluminum Hydroxides: The Role of Electron 2 Correlation

3 Silvia Casassa^{*,†} and Raffaella Demichelis[‡]

4 [†]Dipartimento Chimica IFM and Centre of Excellence NIS (Nanostructured Interfaces and Surfaces), Università degli Studi di
5 Torino, via P. Giuria 5, I-10125 Torino, Italy

6 [‡]Nanochemistry Research Institute, Department of Chemistry, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

7 **ABSTRACT:** The relative energy of aluminum mono- (boehmite and
8 diaspore) and trihydroxides (gibbsite, bayerite, doyleite, and nordstrandite)
9 was investigated with a periodic local Møller–Plesset second-order
10 perturbative approach, with the aim of providing a reliable trend of stability
11 on the basis of a proper description of both the long-range Coulomb
12 interactions and the short-range correlation effects. These components,
13 disregarded in previous studies based on the density functional theory, turn
14 out to be important for these kinds of systems, where hydrogen bonds and van
15 der Waals forces play a fundamental role in stabilizing the structure. The
16 results are in good agreement with the available experimental evidence. The
17 reasons for the monohydroxides energy difference were investigated, with
18 diaspore showing an electronic structure for oxygen atoms more favorable
19 than that for boehmite. The problem of the nordstrandite structure was re-
20 examined because of the presence of a second minimum energy structure on
21 the energy surface. Both of them are higher in energy than those of the other trihydroxide polymorphs, and the relative stability
22 of one of these structures with respect to gibbsite is in agreement with recent experimental investigations.



1. INTRODUCTION

23 Aluminum mono- and trihydroxides exhibit the general formula
24 $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, where $n = 1$ for monohydroxides (boehmite and
25 diaspore), and $n = 3$ for trihydroxides (bayerite, gibbsite,
26 nordstrandite, and doyleite). They all consist of an oxygen
27 network with Al hosted in interstices and octahedrally
28 coordinated. Hydrogen bonds (HB) are present, which ensure
29 the interlayer cohesion of layered structures (all but diaspore).
30 Gibbsite (indicated as \mathcal{G} in the following), boehmite ($\mathcal{B}h$)
31 and diaspore ($\mathcal{D}s$) are the main constituents of aluminum ores.
32 Bayerite ($\mathcal{B}y$) is less abundant, whereas doyleite ($\mathcal{D}y$) and
33 nordstrandite (\mathcal{N}) are rarely observed as natural compounds.
34 They all play an important role in the aluminum industry, as
35 hydrated precursor of transition aluminas or as raw materials
36 for the manufacture of many objects, other than being used also
37 as adsorbents, emulsifiers, ion exchangers, antacid drugs, and
38 filtering media.^{1–6}

39 Despite several experimental studies carried out during the
40 last 50 years, some of their properties are still a matter of
41 debate, due to the many problems affecting the experimental
42 measures (e.g., adsorbed water, disorder, mixed phases,
43 environment pH) and thus giving rise to different interpreta-
44 tions by the various authors.⁷

45 In the past few years some of the unresolved questions have
46 been addressed to atomistic simulation, the main outcomes
47 being the unambiguous determination of the structure and the
48 HB pattern,^{7–13} the accurate analysis of the vibrational
49 properties,^{7–9,14–17} and the study of boehmite surface and

water-surface properties.^{18,19} Less successful results were
50 obtained when trying to estimate the energetics at the density
51 functional theory level (DFT),^{7,12,20–24} the worst case being
52 the relative stability between boehmite and diaspore, shown to
53 be functional-dependent due to their major structural differ-
54 ences.^{7,24}

55 Thermodynamic properties represent a mandatory item for a
56 better insight into the physical chemistry of aluminum
57 hydroxides and a step for further investigations of the structure
58 of transition aluminas. When considering the relative stability of
59 aluminum hydroxides in a wide range of temperatures, the
60 following framework emerges from the most accredited
61 experiments and simulations: (i) the lower the temperature,
62 the higher the hydration degree; (ii) the HB pattern might be
63 one of the main responsible for the energy difference of the
64 polymorphs; for trihydroxides, the stacking sequence of the
65 layers, which can determine a more convenient HB pattern in
66 terms of $\text{H}\cdots\text{O}$ and $\text{O}-\text{H}$ distances and $\text{O}-\hat{\text{H}}\cdots\text{O}$ angles, was
67 shown to have a non-negligible effect in determining the
68 relative stability of the polymorphs;^{12,13} (iii) $\mathcal{D}s$ and \mathcal{G} are
69 considered the most stable mono- and trihydrated phases at
70 standard conditions, respectively.

71 However, many contradictions are present in the literature,
72 and quantitative values are still missing. In the case of 73

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74 trihydroxides, only data for $\mathcal{B}y$ and \mathcal{G} are available, with ΔG^{298} ,
75 i.e., the Gibbs free energy difference between the two
76 compounds, ranging from -11.8 to -4.0 kJ/mol per Al_2O_3
77 unit^{1,25–27} (with error bars between ± 1 and ± 8 kJ/mol and \mathcal{G}
78 being the most stable). Clear experimental evidence is not yet
79 available for $\mathcal{D}y$ and \mathcal{N} , and contrasting data were proposed as
80 a result of a DFT simulation⁷ and Hemingway and Sposito's
81 estimations.²⁸

82 Because of the high structural similarity of these four
83 polymorphs, their relative stability is quite well reproduced with
84 DFT simulations (i.e., roughly, they are affected by the same
85 error in estimating interlayer dispersive interactions): ΔG^{298}
86 between $\mathcal{B}y$ and \mathcal{G} ranges from -10.3 to -5.8 kJ/mol with six
87 different functionals.²⁴ ΔG^{298} between \mathcal{N} or $\mathcal{D}y$ and \mathcal{G}
88 obtained with three different levels of DFT approximation
89 ranges from -30.3 to -27.5 kJ/mol and from -10.6 to -8.8
90 kJ/mol,⁷ respectively, whereas Hemingway and Sposito²⁸
91 estimated it to be -6.8 and -8.8 kJ/mol, respectively. Recently,
92 thermochemical experiments have been carried out on \mathcal{N} ,
93 estimating its enthalpy difference with respect to \mathcal{G} , ΔH^{298} , to
94 -28.2 ± 3.6 kJ/mol.²⁹ Assuming the similarity of standard
95 entropies of the two polymorphs, this datum can be roughly
96 compared to the results of the previous DFT simulations,^{7,13}
97 showing a good agreement and thus confirming the high
98 instability of \mathcal{N} with respect to its polymorphs.

99 Concerning monohydroxides, the experimental ΔG^{298}
100 between $\mathcal{B}h$ and $\mathcal{D}s$ ranges from -15.5 to -6.7 kJ/mol per
101 Al_2O_3 unit^{1,25–27} (with error bars between ± 5 and ± 13 kJ/mol
102 and $\mathcal{D}s$ being the most stable). DFT simulations provide ΔG^{298}
103 data from -16.2 to $+7.5$ kJ/mol,^{22,24,30} depending on the
104 adopted method (level of approximation, basis set, and
105 pseudopotential). This is probably due to the major structural
106 differences between $\mathcal{B}h$ and $\mathcal{D}s$, in particular to the layered
107 nature of $\mathcal{B}h$, and a significant improvement in the results
108 could be obtained with a more accurate estimation of both
109 exchange and Coulomb electron correlation.

110 In this paper, we used a quantum-mechanical periodic
111 local^{31–33} Møller–Plesset perturbative approach truncated at
112 the second order (LMP2), as implemented in the CRYSCOR
113 code,^{34,35} for the study of aluminum mono- and trihydroxides.
114 The aims are to provide unambiguous data for their relative
115 energy and to demonstrate the effectiveness of this post-
116 Hartree–Fock (HF) scheme for the treatment of electron
117 correlation in large unit cell systems containing different
118 chemical bonds (covalent, semi-ionic, HB) to be described with
119 the same accuracy and non-negligible van der Waals
120 interactions.

121 The paper is structured as follows. Section 2 deals with the
122 adopted computational methods, focusing on the accurate
123 calibration of parameters and basis set for the LMP2
124 calculations. Results are reported, discussed, and compared
125 with DFT and experimental data in section 3, where the
126 analysis of the LMP2 energy contribution is also performed.
127 Finally, section 4 summarizes the main conclusions.

2. COMPUTATIONAL METHODS

128 These calculations were performed with the periodic ab initio
129 CRYSTAL09³⁶ and CRYSCOR09^{37,38} codes, using all electron
130 Gaussian-type basis sets. Because an automatic procedure for
131 the analytical geometry optimization at the LMP2 level is not
132 yet available in CRYSCOR, equilibrium geometries were
133 obtained at the DFT (SVWN,^{39,40} PBE,⁴¹ PBEsol,⁴² PBE0,⁴³

and B3LYP^{44,45}) and HF levels, with 8-621G(d) (Al), 8-
411G(d) (O), and 211G(p) (H) basis sets,¹⁷ indicated in the
following as BSA. Geometry optimization was performed using
analytical gradients with respect to atomic coordinates and unit-
cell parameters, within a quasi-Newtonian scheme combined
with Broyden–Fletcher–Goldfarb–Shanno^{46–49} Hessian up-
dating. The default convergence criteria were used for both
gradient components and nuclear displacements. The phonon
spectra were computed by diagonalizing the dynamical matrix
built by numerically differencing the analytical gradient with
respect to atomic Cartesian coordinates. Tolerances on the self
consistent field were set to 10^{-8} a.u. for geometry optimization
and to 10^{-10} a.u. for frequency calculation. The DFT exchange-
correlation contribution was evaluated by numerical integration
over the unit cell volume, using a pruned grid with 75 radial
(Gauss–Legendre radial quadrature) and 974 angular (Lebedev
two-dimensional generation) points.

To properly compare our results with experimental data, the
electronic energy obtained with the LMP2 approach should be
corrected by the zero point energy, the entropy, and the heat
capacity at 298 K. However, the fact that the phonon
calculation is not yet implemented in CRYSCOR is only a
minor limit for this study, because vibrational contributions to
the free energy of these systems are on the order of 1–2 kJ/mol
per Al_2O_3 unit with all the adopted DFT schemes, much
smaller than the experimental error bar, and were shown to be
insufficient to invert the stability between these polymorphs.²⁴

The five parameters controlling the Coulomb and HF
exchange series accuracy were set to [7,7,7,7,16] and, once the
equilibrium structure was obtained, were tightened to
[7,7,7,15,50] for the evaluation of the high-quality one-electron
HF wave functions required by the post-HF correction.³⁶ The
reciprocal space was sampled using a shrinking factor IS = 8 for
monohydroxides (i.e., 105 k points in the irreducible part of the
Brillouin zone for $\mathcal{B}h$ and 125 for $\mathcal{D}s$) and IS = 6 for
trihydroxides (80 k points for \mathcal{G} and $\mathcal{B}y$ and 112 for $\mathcal{D}y$ and
 \mathcal{N}). The same grids were adopted in the unitary transformation
of the crystalline orbitals yielding the equivalent set of well-
localized, symmetry adapted, mutually orthogonal, translation-
ally equivalent Wannier functions^{50,51} (WF) used to describe
the valence part of the occupied manifold in CRYSCOR.

Calibration of LMP2 Computational Parameters. The
size of trihydroxides (192 valence electrons for \mathcal{G} and $\mathcal{B}y$),
which currently represents an upper limit for the CRYSCOR
code in terms of memory usage and CPU time, and the
relatively small energy difference between polymorphs are such
that computational parameters must be accurately set, to
achieve a compromise between good results quality and
reasonable computational effort.

Starting from the geometry optimized at the PBE0 level
(shown in previous works^{24,52} to provide very small deviation
from experimental structures at 298 K), the LMP2 contribution
to the relative energy between $\mathcal{D}s$ and $\mathcal{B}h$ (64 and 32 valence
electrons, respectively), $\Delta E_{\text{mono}}^{(2)}$, was evaluated adopting (a)
different locality truncation tolerances and (b) different basis
sets.

a. Locality Truncation Tolerances. The complete treatment
of the periodic LMP2 approach, as implemented in the
CRYSCOR code, is reported in ref 53. Let us briefly fix the
notation and introduce the main computational parameters of
the LMP2 calculation. As already anticipated, WFs ($\{\omega\}$) play
an essential role in CRYSCOR, together with the comple-
mentary set of projected atomic orbitals (PAO, $\{\chi\}$) which

197 span the virtual space. Both these sets of functions are
 198 translationally equivalent, so that it is possible to define the
 199 reference ones (indexed i, j, \dots and a, b, \dots) settled in the reference
 200 zero cell and then concisely indicate the others according to the
 201 crystalline cell (I, J, \dots and A, B, \dots) they belong to as $\omega_{iI}, \omega_{jJ}, \dots$ and
 202 $\tilde{\chi}_{aA}, \tilde{\chi}_{bB}, \dots$, respectively. Adopting the close notation $J \equiv jJ$, $A \equiv$
 203 jA and being the first WF always in the reference cell, $I \equiv iI \equiv$
 204 $i0 \equiv i$, the LMP2 energy $E^{(2)}$ can be written as a sum of all
 205 contributions E_{ij}^{AB}

$$E^{(2)} = \sum_{i \in \text{cell}} \sum_{d_{ij} < d} E_{ij}^{(2)} \quad (1)$$

$$\begin{aligned} E_{ij}^{(2)} &= \sum_{(A,B) \in (i,j)} E_{ij}^{AB} \\ &= \sum_{(A,B) \in (i,j)} K_{AB}^{ij} (2T_{AB}^{ij} - T_{BA}^{ij}) \end{aligned} \quad (2)$$

206 each corresponding to a two-electron excitation from a pair of
 207 WFs (WW pair) to a pair of PAOs, $[(ij) \uparrow \uparrow (AB)]$. K_{AB}^{ij} are the
 208 electron repulsion integrals between the WF-PAO product
 209 distribution and T_{AB}^{ij} are the excitation amplitudes calculated via
 210 a self-consistent procedure.

211 The input parameters serve essentially to fix three kinds of
 212 tolerances, all concerning the treatment of WFs and PAOs. The
 213 first one determines the truncation of their tails: in the linear
 214 combinations defining WFs and PAOs, atomic orbitals (AOs)
 215 with coefficients lower than t (default $t = 0.0001$ was used) are
 216 disregarded.

217 The other two parameters are used to exploit the local-
 218 correlation Ansatz according to which all excitations can be
 219 ignored except those involving close-by WF and PAO pairs: a
 220 domain D_i is associated to the general WF (ω_i), consisting of a
 221 certain number of atoms close to it. Two WFs then define a
 222 pair-domain $D_{(ij)}$ which is simply the union of the
 223 corresponding domains. Only excitations $[(ij) \uparrow \uparrow (AB)]$ for
 224 which both PAOs A and B belong to atoms in $D_{(ij)}$ and the
 225 distance d_{ij} between the centers of the two WFs is within a
 226 certain value d are retained (see notations $d_{ij} < d$ in eq 1 and
 227 $(A,B) \in (i,j)$ in eq 2). The contributions due to WW pairs
 228 further than d are not explicitly evaluated but can be estimated
 229 a posteriori by means of an extrapolation technique, which
 230 exploits the fact that pair correlation energies asymptotically
 231 decrease with distance between electron according to the
 232 London $ar^{-6} \text{law}^{54}$ (LJ).

233 Figure 1 reports the difference between $\Delta E_{\text{mono}}^{(2)}(d)$ and the
 234 extrapolated limit $\Delta E_{\text{mono}}^{(2)}(\infty)$ as a function of d : the expected
 235 d^{-3} behavior of the difference is observed, and the extrapolation
 236 procedure appropriately corrects for the missing contributions.
 237 A value of $d = 12 \text{ \AA}$, combined with the systematic use of the LJ
 238 technique, was set.

239 Regarding the third local parameter, namely the PAOs
 240 selection, the Boughton–Pulay criterion with a value of 0.985
 241 was used, which corresponds for all the polymorphs to an
 242 average number of atoms $n_\alpha = 4$ for each D_i . Domains with n_α
 243 ranging from 2 to 14 were tested but, in contrast to a
 244 quadratically increase of computing time and memory usage,
 245 the difference when passing from $n_\alpha = 4$ to $n_\alpha = 14$ is on the
 246 order of $10 \mu\text{Hartree}$.

247 **b. Basis Set.** Basis set incompleteness is a principal problem
 248 for an accurate post-HF calculation, where diffuse high angular
 249 momentum functions are required to properly describe the

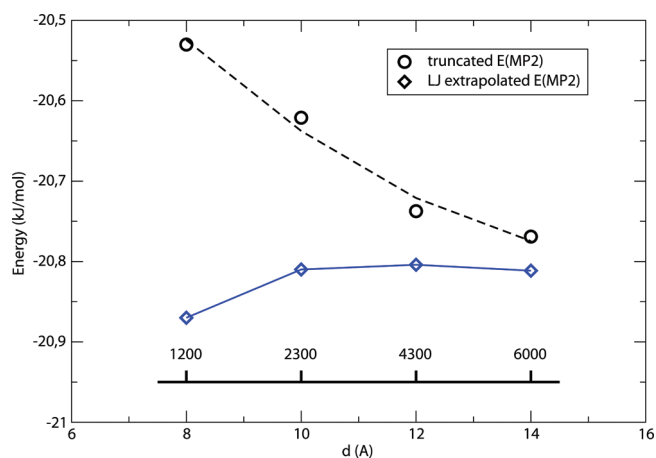


Figure 1. Correlation energy difference between \mathcal{D}_s and \mathcal{B}_h , $\Delta E_{\text{mono}}^{(2)}$ (kJ/mol per Al_2O_3), as a function of the cutoff distance d between WW pairs (the number of pairs included in eq 1 is reported on the straight line). Circles are the uncorrected values, and diamonds are the corrected ones for the London extrapolation. Geometries optimized at the PBE0 level, BSA basis set.

250 Coulomb hole. However, basis sets richer than BSA are not
 251 suitable to trihydroxides with CRYSCOR, because of the size of
 252 the systems.

253 To verify the accuracy of the results obtained with BSA, the
 254 effect of the basis set on $\Delta E_{\text{mono}}^{(2)}$ was tested. Two basis sets,
 255 namely BSB and BSC, were refined starting from BSA, with the
 256 exponents of the outermost shells taken from the standard cc-
 257 pVTZ set of Dunning.^{55,56} In particular, BSB was obtained
 258 from BSA by adding an f shell to the O atom ($\alpha_f = 1.428$). BSC
 259 was obtained from BSB by splitting the d shell of the O atom
 260 (from $\alpha_{d,\text{BSB}} = 0.45$ to $\alpha_{d1,\text{BSC}} = 2.31$, $\alpha_{d2,\text{BSC}} = 0.645$), adding an
 261 f shell to the Al atom ($\alpha_f = 0.244$) and modifying its d exponent
 262 (from $\alpha_{d,\text{BSB}} = 0.6$ to $\alpha_{d,\text{BSC}} = 0.33$). Results for $\Delta E_{\text{mono}}^{(2)}$ in kJ/
 263 mol per Al_2O_3 unit are -8.84 , -9.03 , and 9.46 for BSA, BSB,
 264 and BSC, respectively.

265 Despite its poor quality for a routinely LMP2 calculation,
 266 BSA allows for a sufficiently accurate comparison of the
 267 considered systems, with a difference on total energy around
 268 6% with respect to BSC. This is not totally surprising because
 269 the error affecting energies due to basis set incompleteness is
 270 approximately constant and cancel almost exactly when
 271 differences among similar systems are considered.

3. RESULTS

A. LMP2 Relative Energies. As anticipated, the full
 272 geometry relaxation scheme at the LMP2 level is not yet
 273 implemented in the adopted code, and equilibrium geometries
 274 obtained by means of HF and different DFT approaches were
 275 considered as a starting point for the HF+LMP2 calculation.
 276

277 Let us first concentrate on the monohydrated polymorphs.
 278 \mathcal{D}_s and \mathcal{B}_h are very different forms of the same compound, the
 279 former being a dense nonlayered structure (volume per formula
 280 unit 9% smaller than that of \mathcal{B}_h) and the latter being a stacking
 281 of layers kept together by HBs and dispersive forces. Both
 282 polymorphs exhibit relatively strong HBs ($\text{H}\cdots\text{O}$ 1.7 \AA), either
 283 contained in small cavities (\mathcal{D}_s), or pointing toward the
 284 adjacent layers (\mathcal{B}_h).

285 In the case of DFT methods, a general evidence of the
 286 correlation between structural predictions and relative energies
 287 was found.²⁴ In particular, functionals underestimating the

288 volume tend to overstabilize the denser structure and vice versa,
 289 the exception being GGA functionals recently reparametrized
 290 for solids (i.e., PBEsol), which turned out to provide at least the
 291 correct stability order for the considered systems. This implies
 292 that every time polymorphs with very different structures are
 293 compared, as is the case of monohydroxides, very different and
 294 conflicting results can be obtained depending on the adopted
 295 functional.

296 The main reason for such a wide range of results for Al
 297 monohydroxides (ΔE_{mono} from -18 , with SVWN, to $+4.5$, with
 298 B3LYP, kJ/mol per Al_2O_3 , see Tables 1 and 2 and ref 24) might

Table 1. Relative Energy (kJ/mol per Al_2O_3) between $\mathcal{D}s$ and $\mathcal{B}h$ Evaluated with BSA and BSC, Using Equilibrium Geometries Obtained with Different DFT Functionals and BSA Basis Set^a

geometry	$\Delta E_{\text{mono}}^{\text{HF}}$		$\Delta E_{\text{mono}}^{(2)}$		ΔE_{mono}	
	BSA	BSC	BSA	BSC	BSA	BSC
SVWN	3.3	1.8	-12.7	-13.7	-9.4	-11.9
PBE	10.1	9.1	-22.2	-21.8	-12.0	-12.7
PBEsol	7.9	6.8	-19.7	-19.6	-11.8	-12.7
PBE0	12.0	10.1	-20.8	-19.6	-8.8	-9.5
B3LYP	11.3	9.0	-16.3	-17.8	-5.0	-8.8
HF	13.1	12.2	-19.7	-20.5	-6.6	-8.3

^aHF ($\Delta E_{\text{mono}}^{\text{HF}}$) and LMP2 ($\Delta E_{\text{mono}}^{(2)}$) contributions to the total energy (ΔE_{mono}) are shown separately.

Table 2. Relative Energies (kJ/mol per Al_2O_3) for Mono- And Trihydroxides at the DFT and LMP2 Levels^a

	ΔE_{mono}	$\Delta E_{\mathcal{G}-\mathcal{B}y}$	$\Delta E_{\mathcal{G}-\mathcal{D}y}$	$\Delta E_{\mathcal{G}-\mathcal{N}}$
SVWN	-18.1	-10.6	-9.25	-28.9 (ST1)
PBE	-0.5	-7.7	-9.72	-28.8 (ST1)
PBEsol	-10.5	-11.4	-9.88	-28.8 (ST1)
B3LYP	4.5	-9.6	-8.28	-29.8 (ST1)
B3LYP	-	-	-	-17.6 (ST2)
PBE0	1.0	-7.2	-8.82	-16.6 (ST2)
LMP2(PBE)	-12.0	-4.3	-8.6	-27.5 (ST1)
LMP2(B3LYP)	-5.0	-5.9	-10.7	-29.7 (ST1)
LMP2(B3LYP)	-	-	-	-13.8 (ST2)
LMP2(PBE0)	-8.8	-5.1	-8.5	-12.8 (ST2)
$\Delta G_{298}^{\text{exp}}$	-6.7/-15.5	-4.0/-11.8	-	-
$\Delta H_{298}^{\text{exp}}$	-	-	-	-28.2

^aBSA was used. LMP2 data were obtained for PBE, B3LYP and PBE0 geometries. ST1 and ST2 refer to the structure of N, see text for details. Experimental Gibbs free energy difference, $\Delta G_{298}^{\text{exp}}$, from refs 1, 25–27, and enthalpy difference, $\Delta H_{298}^{\text{exp}}$, from ref 29.

299 be the incorrect evaluation of van der Waals and dispersive
 300 forces between $\mathcal{B}h$ layers by the various DFT functionals. This
 301 would be a minor effect if both compounds were layered
 302 structures with similar features (as in the case of trihydroxides;
 303 see later on), because the error would cancel nearly exactly
 304 when computing the energy difference.

305 When performing the HF calculation starting from the
 306 various equilibrium geometries, $\mathcal{B}h$ is predicted as the lowest
 307 energy structure. As expected, also the HF approximation is
 308 unable to describe properly the long-range dispersive
 309 interactions that, on the basis of the correlated-corrected
 310 results, are responsible for the opposite observed relative
 311 energy. As a matter of fact, in all the considered cases, the
 312 LMP2 contribution inverts the relative energy of the two phases

predicting $\mathcal{D}s$ more “stable” than $\mathcal{B}h$ by 8.3–12.7 kJ/mol (see
 Table 1). For an appropriate use of the term “stability” and a
 direct comparison to the experimental data, one might include
 the thermodynamic contributions in the estimation. However,
 for these systems they were shown to contribute by about 1–2
 kJ/mol to the Gibbs energy with several DFT functional,^{7,52} so
 that we can assume that our current results are reasonable and
 in agreement with the experimental range of stability.

The extension of this approach to the study of trihydroxides
 supports our considerations. As anticipated, the large unit cell
 of $\mathcal{B}y$ and \mathcal{G} is currently a limit for the adopted code, so that
 BSA was used. LMP2 relative stabilities of $\mathcal{B}y$, $\mathcal{D}y$ and \mathcal{N} with
 respect to \mathcal{G} , starting from equilibrium geometries evaluated at
 different DFT levels, are reported in Table 2. The relative
 energy of monohydroxides calculated with the same basis set is
 also reported for the sake of comparison.

As expected, the LMP2 contribution to the total energy is
 not as crucial as for the monohydroxides in deciding the relative
 energies of trihydroxides, because of their very similar structural
 features. However, there are a few concerns regarding \mathcal{N} .
 Unfortunately, only a couple of dated experimental studies are
 available for this structure, and their accuracy is very poor.
 Moreover, no experimental data regarding the H atom
 positions and the HB pattern are available. A solution to the
 \mathcal{N} structural problem was proposed as a result of first principles
 calculations at the B3LYP level in ref 13, in good agreement
 with the experimental structure proposed by Saalfeld and
 Jarchow⁵⁷ and confirmed later by Chao and Baker.⁵⁸ The same
 structure was shown to exhibit vibrational features in good
 agreement with experimental IR and Raman spectra in ref 7.
 Also, its relative stability with respect to \mathcal{G} has been recently
 confirmed by thermochemical experiments.²⁹

When optimizing the structure with SVWN, PBEsol, and
 PBE, results similar to that with B3LYP were provided, whereas
 with PBE0 a quite different and much more stable structure was
 obtained. Phonon calculation confirmed that this is a minimum
 energy structure, and the optimizations with the other
 functionals using the new structure as an initial guess (instead
 of the experimental one) all led to a similar result.

Table 3 shows the experimental structure, those optimized
 with B3LYP and PBE0 using the experimental parameters as an
 initial guess, and that obtained with B3LYP using the PBE0
 result as an initial guess. The main differences between the less
 stable and the more stable structures (in the following ST1 and
 ST2, respectively) are related to the stacking of the layers, i.e.,
 the c and α lattice parameters (differing by 9–15% with respect
 to the experimental structure), whereas the geometry within a
 single layer is preserved. This modification also involves the
 pattern, shown in table 4. Both structures exhibit quite unusual
 $\text{O}-\text{H}\cdots\text{O}$ angles and relatively long HBs with respect to the
 other Al hydroxides, but the interlayer setting of ST2 allows the
 formation of stronger HB interactions (1.853 Å), which is
 probably one of the main responsible for the stabilization of
 this structure.

Dealing with the \mathcal{N} structure and, in general, with the
 possible arrangements of $\text{Al}(\text{OH})_3$ layers is not the purpose of
 this paper, so we do not enter into further detail. The only
 comment we add is that the available experimental evidence
 (structural, vibrational, and thermochemical) suggests ST1 as
 the best candidate for the \mathcal{N} structure. However, considering
 that a new minimum energy structure was obtained (ST2) and
 that, despite exhibiting the largest deviation from the
 experimental geometry, it turns out to be around 15 kJ/mol

Table 3. Structure of \mathcal{N} : Experimental Data, PBE0 and B3LYP Results (ST2 and ST1, respectively) Obtained Using the Experimental Structure as an Initial Guess, and B3LYP Results (ST2) Obtained Using the PBE0 Structure As Initial Guess^a

	exp ⁵⁷	B3LYP (from exp)	PBE0 (from exp)	B3LYP (from PBE0)
<i>a</i>	5.069	5.056	4.988	5.039
<i>b</i>	8.752	8.868	8.804	8.895
<i>c</i>	6.155	6.296	5.320	5.371
α	127.73	127.70	115.59	114.28
β	80.97	81.39	82.44	81.63
γ	91.66	88.98	90.24	90.44
vol	212.48	218.64	208.49	216.76
Al–O _{max}	2.041	1.955	1.923	1.935
Al–O _{min}	1.821	1.882	1.884	1.894
O–H _{max}	–	0.978	0.979	0.978
O–H _{min}	–	0.968	0.964	0.966
H···O _{max}	–	2.257	2.362	2.232
H···O _{min}	–	1.914	1.792	1.853
O–H···O _{max}	–	176.5	168.9	170.9
O–H···O _{min}	–	140.2	136.5	138.7
ΔE	–	–29.79	–16.59	–17.59

^aThe relative energy with respect to \mathcal{G} (ΔE , kJ/mol per A_2O_3) is reported. Lengths in angstroms, angles in degrees; BSA was used.

Table 4. Hydrogen Bond Pattern in ST1 and ST2 As Obtained with the B3LYP Functional and BSA^a

	ST1				ST2			
	O–H	H···O	type	O–H···O	O–H	H···O	type	O–H···O
(O–H) ₍₁₎	0.968	1.994	inter	150.9	0.966	2.157	inter	138.9
(O–H) ₍₂₎	0.978	1.914	inter	176.5	0.976	1.924	inter	170.9
(O–H) ₍₃₎	0.972	1.982	inter	166.6	0.978	1.853	inter	165.2
(O–H) ₍₄₎	0.977	2.018	intra	150.5	0.972	2.226	intra	142.7
(O–H) ₍₆₎	0.973	2.257	intra	140.2	0.973	2.232	intra	142.8
(O–H) ₍₅₎	0.968	(2.322–2.329)	1,3(intra)	(93.5, 105.1)	0.9658	(2.465–2.581)	(inter-intra)	(111.7–92.0)

^aLengths in angstroms, angles in degrees. Intra and inter refer to intralayer and interlayer HB interaction, respectively.

376 more stable than ST1, the corresponding fractional coordinates
377 of the asymmetric unit are reported in Table 5. Whichever the

Table 5. Fractional Coordinates of the ST2 Structure Optimized with B3LYP and BSA

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Al	0.02066	0.33295	0.99047
Al	0.48434	0.83575	0.00615
O	0.25616	0.75290	0.23464
O	0.80608	0.23219	0.20002
O	0.32522	0.05829	0.20825
O	0.83173	0.54179	0.20295
O	0.76178	0.86739	0.22371
O	0.30546	0.36949	0.21058
H	0.19269	0.84483	0.40864
H	0.76065	0.29192	0.39809
H	0.13498	0.06442	0.19687
H	0.79473	0.58358	0.40404
H	0.70353	0.88361	0.41533
H	0.41298	0.46045	0.20937

378 structure, both the \mathcal{N} models are much higher in energy than
379 the other Al trihydroxide polymorphs with all the considered
380 functionals, also when the LMP2 correction is included. The
381 stability order of $Al(OH)_3$ polymorphs is unambiguously
382 confirmed in this study, with \mathcal{G} being the lowest energy
383 structure, followed by \mathcal{B}_y (between +4 and +6 kJ/mol), \mathcal{D}_y

(between +8 and +11 kJ/mol), and \mathcal{N} (either around +28 kJ/mol for ST1, or around +12 kJ/mol for ST2).

B. Energy Partition. Figure 2 reports the relative energy trend of the polymorphs as a function of the cutoff distance between the centers of WFs in WW pairs $d_{ij} = |C_i - C_j|$. For each pair, d_{ij} depends on the crystal cell J where the second WF is located, because the first one is always centered in the zero reference cell, and its $E_{ij}^{(2)}$ contribution decreases following the

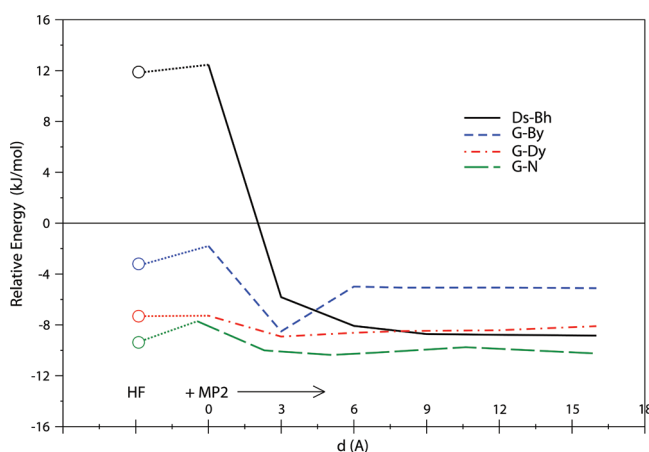


Figure 2. Relative energy trend as a function of the cutoff distance between the centers of WW pairs: \mathcal{D}_s vs \mathcal{B}_h and \mathcal{G} vs \mathcal{B}_y , \mathcal{D}_y and \mathcal{N} . Geometries optimized at the PBE0 level, BSA basis set.

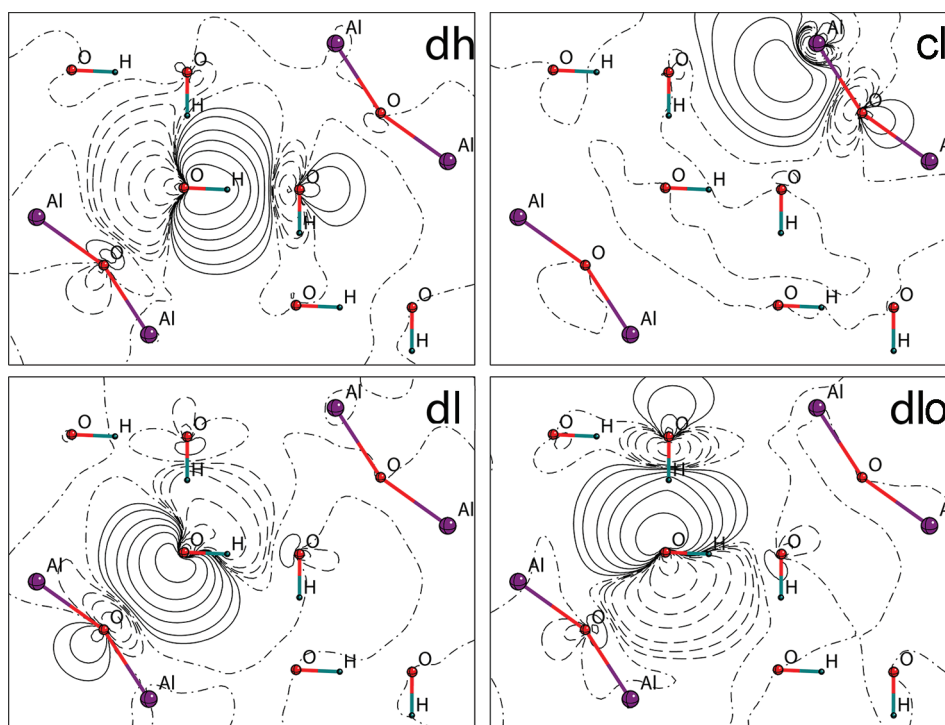


Figure 3. Projection of the four types of $\mathcal{B}h$ WFs: $\omega_b^h, \omega_c^1, \omega_b^1, \omega_a^1$. The selected plane permits appreciation of the differences between the ω_b^h, ω_b^1 and ω_a^1 WFs. Isoamplitude lines differ by 0.01 au; positive, zero, and negative amplitudes are drawn with solid, dot-dashed, and dashed lines, respectively.

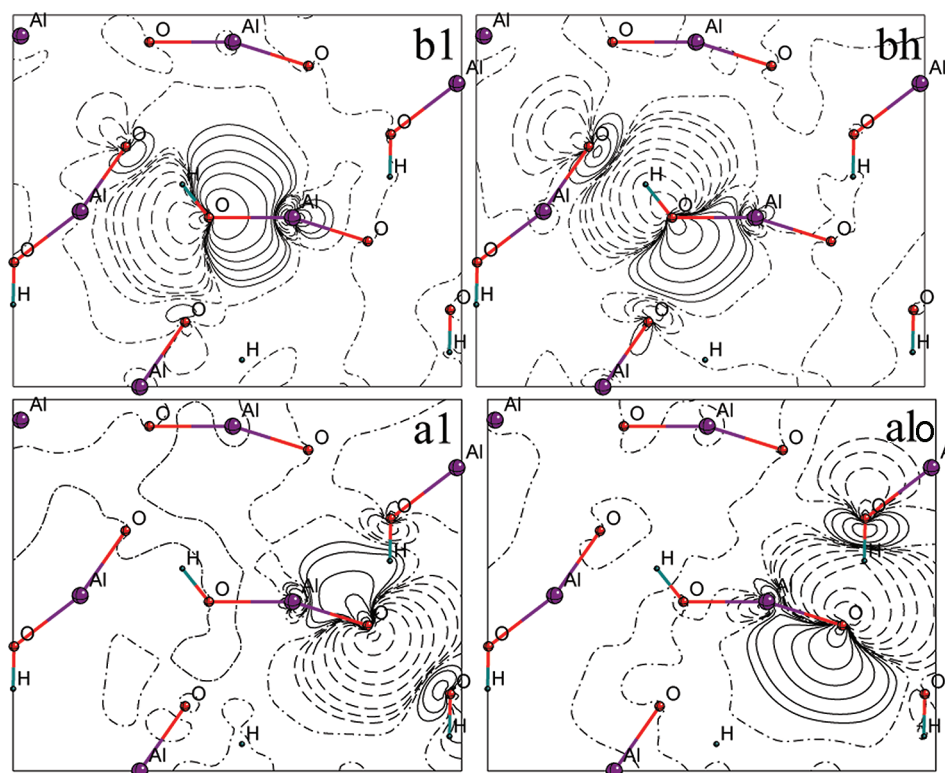


Figure 4. Projection of the four types of $\mathcal{D}s$ WFs: $\omega_b^1, \omega_b^h, \omega_a^1, \omega_a^h$. Conventions as in Figure 3.

392 r^{-6} law as d_{ij} increases. $\mathcal{D}s$ and \mathcal{G} are taken as a reference for
 393 mono- and trihydroxides, respectively. The ST2 structure was
 394 used for \mathcal{N} , because of its higher stability with respect to ST1.
 395 Good results were obtained at the HF and DFT levels for the
 396 relative energy of trihydroxides. This means on the one hand, as
 397 discussed in the previous sections, that the similarity of the

structures is such that dispersive contributions cancel nearly
 398 exactly when performing the energy difference, and on the
 399 other hand that electrostatic interactions play the fundamental
 400 role in deciding the stability of these structures, whereas
 401 dispersive forces only affect their absolute value.
 402

403 The LMP2 contribution can be partitioned as follows. First,
 404 the correlation due to the closest WW pairs, corresponding to
 405 WFs centered on the same atom ($d = 0$, usually referred as
 406 *strong* pairs), tends to stabilize $\mathcal{B}y$ and \mathcal{N} with respect to \mathcal{G} ,
 407 whereas the energy difference $\mathcal{D}y - \mathcal{G}$ remains nearly
 408 unchanged. Contributions resulting from pairs included in a
 409 sphere of 3 Å around the reference cell (called *weak* pairs)
 410 strongly favor \mathcal{G} , and this tendency is only partially
 411 compensated in $\mathcal{B}y$ by contributions between 3 and 6 Å. The
 412 long-range part of the correlation energy contributes
 413 approximately the same for all the tryhydrates, so that we can
 414 consider the same trend up to infinity.

415 Monohydroxides exhibit a rather different behavior (solid
 416 line in Figure 2). $\mathcal{B}h$ is predicted as the most stable phase by
 417 the monodeterminantal HF approach, and the opposite relative
 418 energy is due to correlation effects. As for the trihydroxides, the
 419 addition of the closest pairs energies to the HF one increases by
 420 a small amount the relative energy in favor of $\mathcal{B}h$. However, as
 421 soon as the contributions from *weak* pairs are taken into
 422 account, $\mathcal{D}s$ becomes more stable and the progressive inclusion
 423 of contributions arising from further pairs, up to infinity,
 424 reinforces the trend.

425 The analysis of the various pair energies $E_{ij}^{(2)}$ contributing to
 426 $E^{(2)}$ in terms of type of WFs (ω_p, ω_j) from which the two
 427 electrons are excited permits a better understanding of the
 428 underlying physics. Actually, WFs lend themselves to a rather
 429 simple chemical interpretation by allowing an easy and intuitive
 430 description of the electronic structure in terms of chemical
 431 concepts such as lone pairs and ionic or covalent bonds.

432 The 32 and 64 valence electrons in the unit cell are described
 433 by 16 and 32 WF in $\mathcal{B}h$ and $\mathcal{D}s$, respectively, and for both
 434 structures an irreducible set of eight symmetry-adapted WFs⁵¹
 435 can be defined associated with the two inequivalent O atoms in
 436 the asymmetric unit. These WFs, whose shape is shown in
 437 Figures 3 and 4, can be subdivided according to their chemical
 438 character as follows.

439 In $\mathcal{B}h$, the symmetry-inequivalent O atoms are O_c and O_d ,
 440 the former having four Al atoms as first neighbors, and the
 441 latter having two Al and 1 H atoms as first neighbors and being
 442 an HB acceptor. The WFs associated to O_c ($\omega_c^1, \omega_c^2, \omega_c^3, \omega_c^4$) show
 443 a highly ionic character: they are essentially *atomic* functions
 444 centered on O_c and composed by its p-type valence AOs,
 445 oriented along the O_c -Al direction, with a negligible
 446 contribution from the AOs of Al atoms. Two similar WFs are
 447 associated to the O_d (ω_d^1, ω_d^2), and lone pair (ω_d^1) and bond
 448 (ω_d^h) WFs are present as a result of the combination of the p-
 449 type AOs of O_d with the AOs of the close H atoms. The same
 450 type of WFs can be found on $\mathcal{D}s$ with a different distribution.
 451 In $\mathcal{D}s$ both symmetry-inequivalent O atoms have three Al
 452 atoms as first neighbors, so they both have three *atomic* WFs
 453 ($\omega_a^1, \omega_a^2, \omega_a^3$ and $\omega_b^1, \omega_b^2, \omega_b^3$), but O_a is the HB acceptor and O_b is
 454 directly linked to the H atom, so that the lone-pair WF is
 455 located on O_a (ω_a^{1o}) while the O-H bond WF is localized on
 456 O_b (ω_b^h).

457 In Table 6 different partitions of the correlation energy are
 458 presented. Summing the contributions $E_{ij}^{(2)}$ for WW pairs (i)
 459 with the lattice index of the second WF J running from zero up
 460 to a crystal cell closer than $d = 12$ Å to the reference cell and
 461 (ii) considering only WFs centered on the same (or symmetry-
 462 equivalent) atom, $\omega_p, \omega_j \in O_x$ (with $x = a, b, c, d$), we end with a
 463 difference between the two monohydroxides of +0.2 kJ/mol in
 464 favor of the layered compound. Despite their high absolute
 465 values, these contributions, dominated by the strong WW pairs,

Table 6. Partition of the Correlation Energy in Terms of Different WW Pair Contributions (see text for details)^a

(ij) $\mathcal{D}s$	$E_{ij}^{(2)}$	(ij) $\mathcal{B}h$	$E_{ij}^{(2)}$	$\Delta E_{ij}^{(2)}[\mathcal{D}s - \mathcal{B}h]$
O_a	-981.1	O_c	-970.3	
O_b	-961.6	O_d	-972.6	
\sum_{ij}	-1942.7	\sum_{ij}	-1942.9	+0.2
$\omega_b^2 - \omega_b^1$	-10.7	$\omega_c^1 - \omega_c^2$	-1.7	
$\omega_b^2 - \omega_a^1$	-28.4	$\omega_c^1 - \omega_d^1$	-25.1	
$\omega_b^2 - \omega_a^{1o}$	-8.7	$\omega_c^1 - \omega_d^{1o}$	-8.3	
$\omega_a^1 - \omega_a^{1o}$	-7.5	$\omega_d^{1o} - \omega_d^1$	-7.2	
$\omega_a^1 - \omega_b^h$	-6.5	$\omega_c^1 - \omega_d^h$	-4.2	
$\omega_b^2 - \omega_b^h$	-5.1	$\omega_d^{1o} - \omega_d^{1o}$	-6.2	
$\omega_a^{1o} - \omega_b^h$	-13.1	$\omega_d^{1o} - \omega_d^h$	-10.8	
\sum_{ij}	-80.0		-63.5	-16.5

^aEnergies are in kJ/mol per Al_2O_3 .

466 are not the main responsible for the relative energy between the
 467 monohydroxides because they cancel nearly exactly when the
 468 energy difference is computed.

469 On the contrary, the other contributions listed in Table 6,
 470 referring to pairs for which (i) the J lattice vector index can run
 471 up to $d = 12$ Å and (ii) the two WFs are centered on different
 472 atoms, $\omega_i \in O_x, \omega_j \in O_y$, regardless of their lower absolute
 473 value, favor the $\mathcal{D}s$ phase and are responsible for its higher
 474 stability with respect to the layered structure. In particular, the
 475 HB correlation energy, pairs $\omega_a^{1o} - \omega_b^h$ and $\omega_d^{1o} - \omega_d^h$ is stronger for
 476 $\mathcal{D}s$, and also the dispersion contributions due to atomic WFs,
 477 $\omega_b^2 - \omega_b^1, \omega_b^2 - \omega_b^h$ and $\omega_c^1 - \omega_d^1, \omega_c^1 - \omega_c^2$, tend to stabilize $\mathcal{D}s$. The
 478 overall effect is around -16.5 kJ/mol which is almost the
 479 energy gained when WW pairs in a sphere of 3.0 Å around the
 480 reference cell are considered.

481 In summary, the gain in energy due to the correlation of
 482 electron on the same atom (*strong* pairs) is sensitive but almost
 483 equivalent in the two structures. Short-range correlation effects
 484 between first-neighbor O atoms are responsible for the lower
 485 $\mathcal{D}s$ energy, and the presence of a lone pair and an O-H bond
 486 on the same atom ($\mathcal{B}h$) appears a less favorable configuration.

4. CONCLUSIONS

487 The relative energy of Al mono- and trihydroxides was
 488 investigated by means of the post-HF approaches as
 489 implemented in the CRYSCOR code. These systems are at
 490 the limit of the current capability of the code in terms of size,
 491 and consequently an accurate calibration of the computational
 492 setting was necessary to achieve reliable results.

493 LMP2 is capable of predicting relative energies in agreement
 494 with experimental data, and it is able to quantitatively
 495 determine the contribution of electron correlation. Minor
 496 structural differences obtained when optimizing with different
 497 DFT functionals turn out to be negligible when both the short-
 498 and long-range correlation effects are correctly taken into
 499 account. Actually, a more accurate description of dispersive
 500 forces seems to be the key to allow for a more accurate set of
 501 relative energies.

502 A tentative interpretation of the relative energy of
 503 monohydrates is given in terms of short-range correlation
 504 effects between oxygen atoms, whose electronic structure is
 505 more favorable for $\mathcal{D}s$ than for $\mathcal{B}h$. In particular, the partition
 506 of the correlation contribution in terms of distance and type of
 507 occupied orbitals shows the importance of an accurate
 508 description of the correlation between electrons belonging to 508

509 first-neighbor O atoms in deciding the stability between
510 monohydroxides.

511 A new minimum energy structure (ST2) was obtained when
512 optimizing \mathcal{N} with the PBE0 functional. The c and α lattice
513 parameters are 9–15% smaller than those proposed as a result
514 of experimental and previous computational studies (ST1).
515 Although ST1 geometry and energy are in better agreement
516 with the few available experiments, we cannot exclude ST2
517 from being a candidate to describe the \mathcal{N} structure, because it
518 is ≈ 15 kJ/mol per Al_2O_3 unit more stable than ST1. However,
519 this shows also that $\text{Al}(\text{OH})_3$ polymorphs have versatile
520 structures, exhibiting various possible arrangements of the HB
521 pattern and of the structural parameters related to the stacking
522 of the layers and thus leading to the presence of additional
523 minima on the energy hypersurface.

524 ■ AUTHOR INFORMATION

525 Corresponding Author

526 *E-mail: silvia.casassa@unito.it.

527 Notes

528 The authors declare no competing financial interest.

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