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³¹P MAS NMR and DFT study of crystalline phosphate matrices

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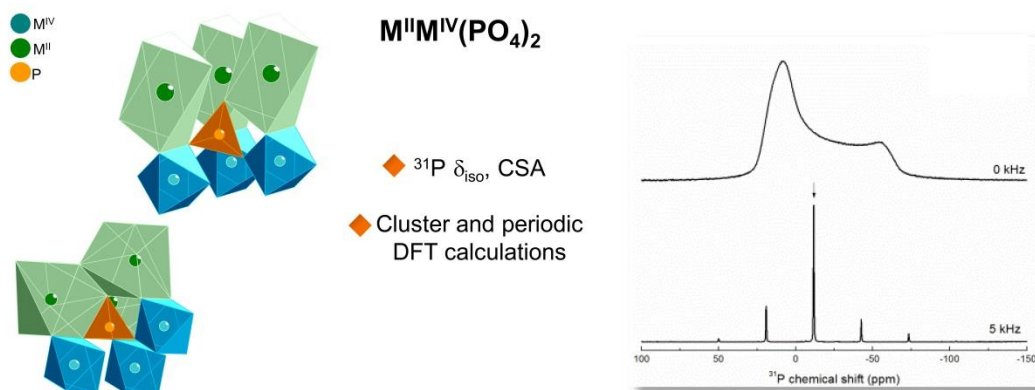
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Abstract

We present the study of the phosphorus local environment by using ³¹P MAS NMR in a series of seven double monophosphates $M^{II}M^{IV}(PO_4)_2$ (M^{II} and M^{IV} being divalent and tetravalent cations, respectively) of yavapaiite and low-yavapaiite type crystal structures. Solid-state and cluster DFT calculations were found to be efficient for predicting the ³¹P isotropic chemical shift and chemical shift anisotropy. To achieve this performance, however, a proper computational optimisation of the experimental structural data was required. From the three optimisation methods tested, the full optimisation provided the best reference structure for the calculation of the NMR parameters of the studied phosphates. Also, a better prediction of the chemical shifts was possible by using a correction to the GIPAW calculated shielding.

Keywords: Yavapaiite; phosphates; ³¹P NMR; DFT calculations; cluster model.

Graphical abstract



28 1. Introduction

29

30 Crystalline phosphates have aroused a lot of interest in the research community due to
31 their numerous useful properties as ionic conductors¹, catalysts and ion exchangers² or
32 luminescent materials and UV-emitting X-ray phosphors^{3,4,5,6,7}. Most importantly, thanks to
33 their structural and chemical stability, crystalline phosphates such as monazite, apatite or
34 double monophosphates have been considered as matrices for immobilization of nuclear
35 waste.^{8,9,10,11,12,13,14,15,16,17,18,19,20,21,22} Even though the chemistry of double monophosphates
36 has been studied in detail,^{23,24} to our knowledge, the phosphorous local environment using ³¹P
37 solid-state NMR has not yet been probed. The efficiency of NMR in characterising the local
38 environment of various nuclei has been demonstrated previously^{25,26,27} and can therefore be
39 extended to the titled systems. Our present aim is to analyse the local structure around the P
40 atom in such diamagnetic phosphates via density functional theory (DFT) calculations. This
41 knowledge can serve as basis for the understanding of the more complex NMR shifts of
42 phosphates containing actinide or rare-earth cations. Indeed, as the NMR signals,^{28,29} are
43 influenced by the paramagnetic interactions,^{30,31,32} the use of the cluster model can
44 successfully help in the prediction of the paramagnetic shifts as shown in our recent study³³
45 on the La_xEu_{1-x}PO₄ series in which an LaPO₄ cluster was make. This approach was also
46 applied by other authors in lithium batteries and is very promising.³⁴

47 Here, we present the ³¹P NMR spectra of selected crystalline structures of the type
48 yavapaiite (*C2/m*)^{35,36} (BaHf(PO₄)₂, BaSn(PO₄)₂, BaGe(PO₄)₂, BaZr(PO₄)₂, BaTi(PO₄)₂ and
49 β -SrGe(PO₄)₂) and low-yavapaiite (*C2/c*) (CaGe(PO₄)₂)³⁷). The computational work was
50 extended to other monophosphates for which experimental data are available in the literature:
51 LaPO₄,^{38,39} AlPO₄^{40,41,42}, Si₅O(PO₄)₆⁴³ and Ge₅O(PO₄)₆⁴⁴. We probe several structure models
52 used as basis for the NMR calculations. Beyond the experimental structure three
53 computationally relaxed solid-state structures and two (molecular) cluster models were
54 tested. We show the optimisation effects on the experimental crystalline structures and how
55 the NMR parameters can be predicted by means of solid-state and molecular quantum
56 chemical codes utilizing density functional theory (DFT).

57

58

59 2. Methods

60 2.1. Synthesis

61 The investigated $M^{II}M^{IV}(PO_4)_2$ compounds were obtained by solid-state reactions by
62 mixing stoichiometric amounts of M^{II} - oxides or carbonates (Prolabo, Aldrich or Johnson
63 Matthey) with $M^{IV}O_2$ and $NH_4H_2PO_4/(NH_4)_2HPO_4$. The powders were grounded and fired
64 slowly. More details about the process are presented in Refs. 18, 23, 37, 45, 46, 47. All these
65 crystalline phases²³ were checked by powder XRD and determined to be single-phased except
66 for $CaGe(PO_4)_2$ in which the presence of $CaGe_4(PO_4)_6$ and $Ca_2P_2O_7$ were revealed by X-ray
67 diffraction as small impurities (~4%).

68

69 2.2. NMR measurements

70 All ^{31}P NMR spectra (MAS and static) were collected at a Larmor frequency of 162.06
71 MHz (magnetic field 9.4 T) on a Bruker Avance III WB spectrometer using a Bruker 4mm
72 MAS probe. Powder samples were spun at slow spinning rates of 2, 3 and 5 kHz in order to
73 obtain the spinning sidebands pattern to extract the chemical shift anisotropy (CSA)
74 parameters. Spectra were acquired using a 90° pulse of 7.8 μs in length (radiofrequency field
75 of 32 kHz). The recycle delays used to have the full recovery of the magnetization were: 200
76 s for $BaHf(PO_4)_2$ and $BaSn(PO_4)_2$, 1000 s for $BaZr(PO_4)_2$, 1500 s for $BaTi(PO_4)_2$, 2200 s
77 $CaGe(PO_4)_2$, 3000 s for $BaGe(PO_4)_2$ and β - $SrGe(PO_4)_2$. The spectra were referenced with
78 respect to an external sample of liquid H_3PO_4 (0 ppm). The data were fitted using the DMfit
79 software⁴⁸ and the CSA parameters were extracted using the "*CSA MAS model*".

80

81 2.3. Solid-state DFT calculations

82 Solid-state first-principles calculations of the NMR parameters were performed using the
83 Quantum Espresso (QE)⁴⁹ package which relies on a pseudopotential plane-wave expansion
84 formalism of DFT. The ^{31}P NMR parameters were computed using the gauge including
85 projector augmented wave approach (GIPAW)^{50,51} formalisms and the generalized gradient
86 approximation (GGA) PBE functional⁵². Core electrons were described by norm-conserving
87 Trouiller–Martins pseudopotentials⁵³ available in the QE library (Al, Ba, Ge, Hf, La, O, P, Si,
88 Sn, Sr, Zr)⁵⁴, or downloaded from Davide Ceresoli's website⁵⁵(Ca) or generated with the
89 *atomic* code⁵⁶ (Hf, Ti, Zr) (Table S1). For all calculations with QE, an optimized kinetic
90 energy cutoff of 100 Ry and optimized Monkhorst–Pack grids given in Table S2 were
91 selected. The data for $BaSn(PO_4)_2$ are given as an example in Table S3.

92 The calculated magnetic shielding parameters and σ_{iso} are defined by the Haeberlen
93 convention^{57,58,59} $|\sigma_{33} - \sigma_{iso}| > |\sigma_{11} - \sigma_{iso}| > |\sigma_{22} - \sigma_{iso}|$ with $\sigma_{iso} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$.

94 The axially of the CSA tensor is defined by $\Delta_{CSA} = \sigma_{33} - \sigma_{iso}$ and its asymmetry by
95 $\eta_{CSA} = \frac{\sigma_{22} - \sigma_{11}}{\sigma_{33} - \sigma_{iso}}$. The same convention was followed to extract the δ_i parameters (i.e.
96 $\Delta_{CSA} = \delta_{33} - \delta_{iso}$ and $\eta_{CSA} = \frac{\delta_{22} - \delta_{11}}{\delta_{33} - \delta_{iso}}$).

97

98 2.4. Cluster DFT calculations

99 The ^{31}P magnetic shieldings of the target compounds were calculated by means of the
100 cluster approach using the Gaussian 09 (G09) software⁶⁰. The model structures (to be
101 discussed later) were subjected to partial geometry optimisations in which the hydrogen
102 atoms were relaxed while the heavy-atom core of the clusters was kept fix. We note that a full
103 optimisation (governed by the hydrogen bonding interactions between close lying OH
104 groups) would destroy the crystal character of the model. For these partial geometry
105 optimisations valence double-zeta basis sets were used: the standard 6-31G** for the light P,
106 O, H, Al, Ca, Si, Ge, Ti atoms, and the relativistic effective core potentials of Hay and Wadt
107 (LANL2DZ): Sr, Ba, Sn,⁶¹ and La, Zr, Hf⁶² for the heavier metals.

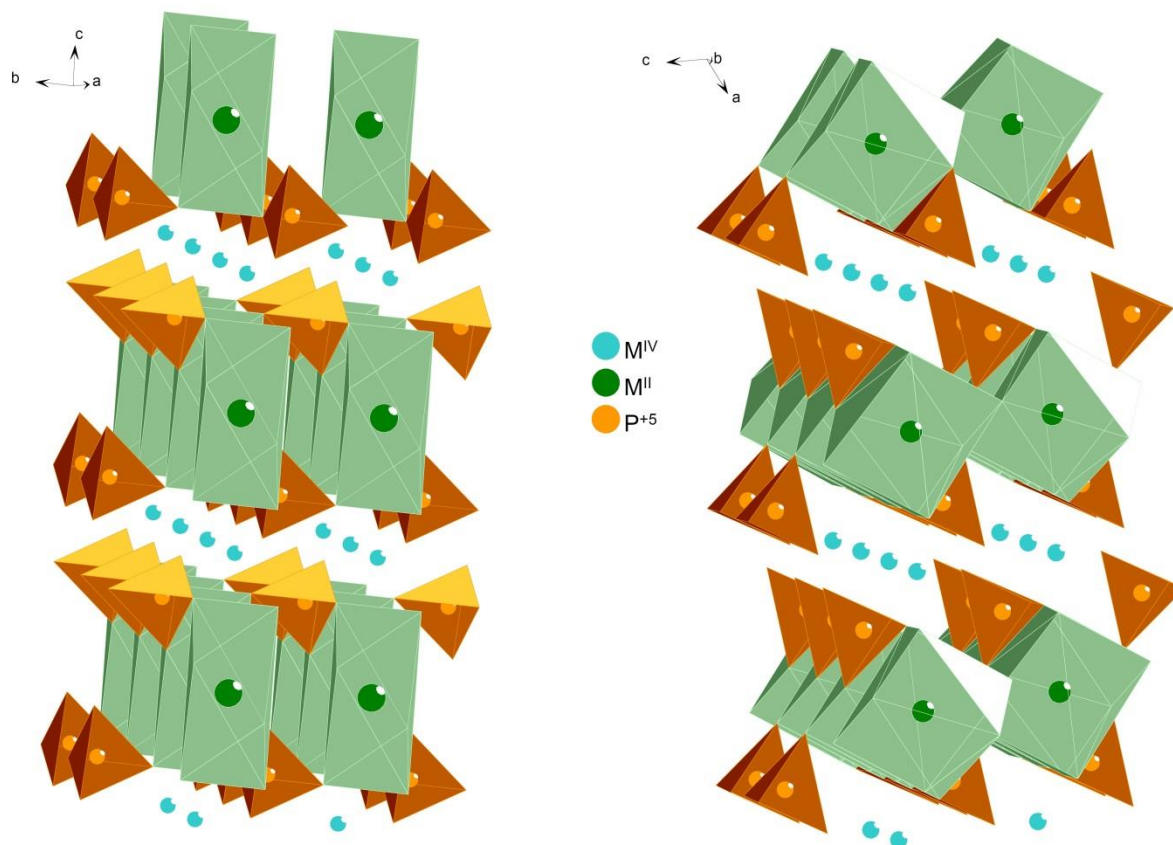
108 All calculations were performed using the B3LYP^{63,64} exchange-correlation functional
109 and the PBE functional⁵². Dunning's correlation-consistent cc-pVTZ basis sets were utilised
110 for the light atoms O, H,⁶⁵ Al, Si, P;⁶⁶ Ca,⁶⁷ Ge,⁶⁸ Ti⁶⁹. For the heavier metals, the following
111 small-core quasi-relativistic pseudopotentials and contracted valence basis sets of the
112 Stuttgart group were used:^{70, 71} Sr, ECP28MWB with 6s6p5d/4s4p2d;⁷² Ba, ECP46MWB
113 with 6s6p5d1f/4s4p2d;⁷⁰ Sn, ECP28MDF with 12s11p9d1f/5s4p3d1f;^{73,74} Zr, ECP28MDF
114 with 41s37s25d2f1g/5s5p4d2f1g;⁷⁵ Hf, ECP60MDF with 41s37s25d2f1g/5s5p4d2f1g⁷⁶
115 contraction schemes and La, ECP28MWB (the number meaning the core electrons replaced
116 by the potential) with a 14s13p10d8f6g/10s8p5d4f3g contraction scheme. NMR calculations
117 on the cluster structures were carried out using in conjunction with the pseudopotentials and
118 basis sets applied in the B3LYP cluster calculations. The magnetic shieldings were calculated
119 with the Gauge-Independent Atomic Orbital (GIAO) formalism.⁷⁷

120

121 3. Results and discussions

122 3.1. Crystalline structures of the $M^II M^IV(\text{PO}_4)_2$ phases

123



124

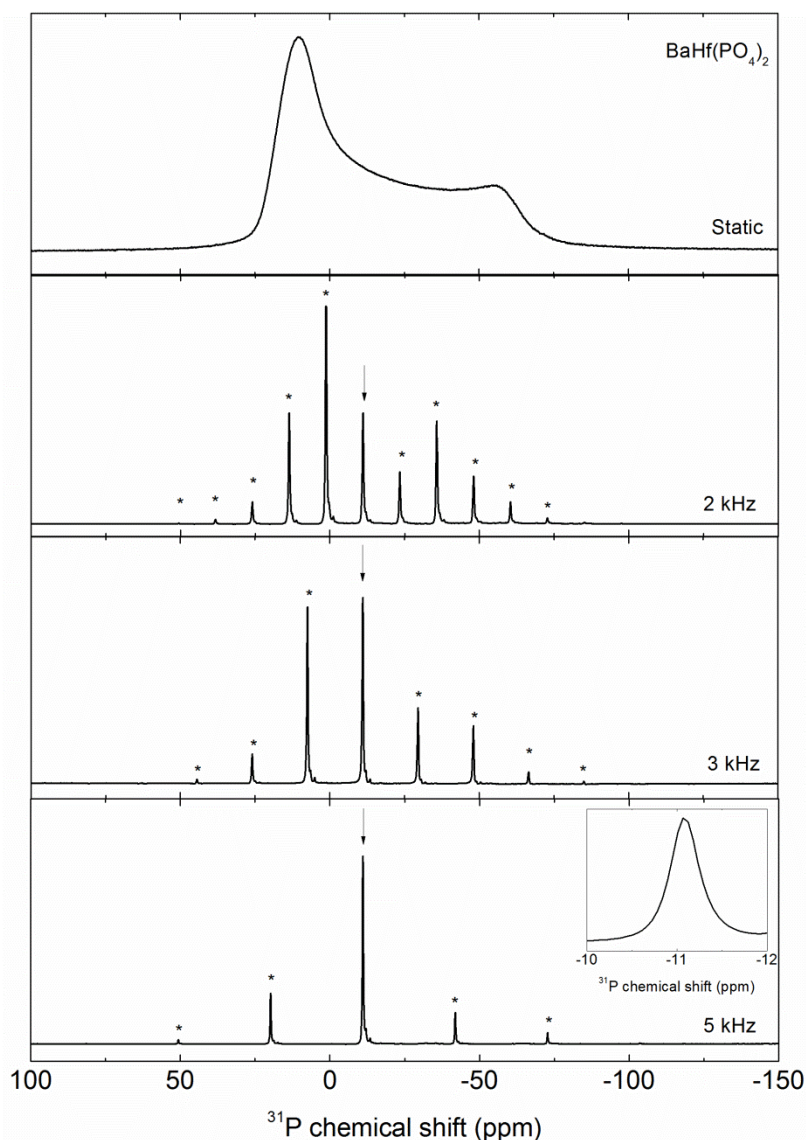
125 Figure 1: Crystalline structure of a) the yavapaiites and b) the low-yavapaiites. The M^{IV}
 126 cations have an octahedral coordination for the two structures.

127 In Figure 1 the two crystalline structures of the M^{II}M^{IV}(PO₄)₂ are presented. The
 128 yavapaiite crystalline structures the M^{IV} cations have an octahedral coordination and are
 129 corner-linked to six separate phosphate tetrahedra through the oxygen atoms, forming two
 130 different sheets. In between these sheets, a layer of 10-coordinated M^{II} cations is located,
 131 being also linked to the PO₄ units.⁷⁸ The low-yavapaiite structure can be described as a
 132 distorted yavapaiite with a double lattice along the a-axis. Compared to the yavapaiite, the
 133 tetravalent cations remain in an octahedral environment, whereas the 10-coordination of the
 134 divalent cations decreases to eight (capped with 2 additional oxygen atoms).²³

135

136 3.2. ³¹P NMR spectra

137



138

139 Figure 2: ^{31}P spectra of $\text{BaHf}(\text{PO}_4)_2$ acquired in static conditions and at different spinning
 140 rates. The arrow indicates the isotropic band while the stars stand for the spinning sidebands.
 141 The insert presents the central peak.

142

143 For all samples, the ^{31}P MAS NMR spectra were acquired in static conditions and at
 144 three spinning rates (2, 3 and 5 kHz). As similar data were obtained for all samples, only the
 145 $\text{BaHf}(\text{PO}_4)_2$ spectra are given in Figure 2 as example to show the spinning rate effects.
 146 Additionally, in Figure S1, the spectra of all the other $\text{M}^{\text{II}}\text{M}^{\text{IV}}(\text{PO}_4)_2$ compounds are depicted
 147 at the spinning rates of 5 and 2 kHz.

148

149 The static spectrum presents a typical CSA dominated powder pattern, and combined
 150 with slow MAS rates it has been possible to identify the isotropic bands and extract the CSA
 151 parameters. The observation of a single isotropic band for each compound is in agreement
 with the single P site expected from these crystalline structures. All the NMR parameters

152 (δ_{iso} , δ_{ii}) extracted from the spectra are gathered in Table 1. Small differences were found
 153 between static and MAS values of the CSA most probably due to ^{31}P - ^{31}P coupling. These
 154 differences were accounted in the uncertainties.

155
 156 Table 1: The experimental ^{31}P isotropic chemical shifts, δ_{iso} , and the anisotropic parameters
 157 (δ_{11} , δ_{22} , δ_{33} , Δ_{CSA} , η_{CSA}) of the crystalline phosphates. Each compound was attributed a
 158 random number (N°) with which it will be labelled with. Data for compounds 1-7 were
 159 obtained in the present study while for compounds 8-12 they were extracted from the
 160 literature indicated by the references.

N°	Name	δ_{iso} (ppm)	Δ_{CSA} (ppm)	η_{CSA}	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
1	BaHf(PO ₄) ₂	-11.1 ± 1	-53.1 ± 1	0.21± 0.1	21.0	9.9	-64.2
2	BaSn(PO ₄) ₂	-11.7 ± 1	-52.6 ± 1	0.23± 0.1	21.5	9.1	-65.7
3	BaGe(PO ₄) ₂	-21.2 ± 1	-52.6 ± 1	0.19± 0.1	10.1	0.1	-73.8
4	BaZr(PO ₄) ₂	-15.5 ± 1	-51.2 ± 1	0.21± 0.1	15.5	4.7	-66.8
5	BaTi(PO ₄) ₂	-16.1 ± 1	-50.9 ± 1	0.15± 0.1	13.2	5.5	-67.0
6	CaGe(PO ₄) ₂	-17.6 ± 1	-64.3 ± 1	0.17± 0.1	20.0	9.1	-81.9
7	β - SrGe(PO ₄) ₂	-19 ± 1	-58.9 ± 1	0.15± 0.1	14.9	6.0	-77.9
8	Si ₅ O(PO ₄) ₆	-44.1 ± 1 ^{43*}	39.6	0.5	-73.6	-53.8	-4.5
9	Ge ₅ O(PO ₄) ₆	-32.9 ± 1 ^{44*}	--	--	--	--	--
10	LaPO ₄	-4.4 ± 1 ^{38,39*}	19.3	0.75	-21.2	-6.7	15
11	AlPO ₄	-25.9 ²⁵ / 26.3 ± 1 ^{83*}	--	--	--	--	--
12	AlPO ₄ -c	-30.7 ± 1 ^{42*}	--	--	--	--	--

161 *the uncertainties are not given in the following papers, but deduced from the spectra.

162

163

164 3.3. Effect of DFT optimisation on the crystalline structures

165 Computed parameters often suffer from experimental errors intrinsically as the
166 experimental crystalline structures are more representative of a thermal average than the true
167 local environment.^{51,89} To overcome this drawback, the optimisation of the atomic positions
168 and/or the unit cell parameters is often done. To render these effects the different
169 optimisation procedures are discussed in the following paragraph. Additionally, due to the
170 small range of the ³¹P δ_{iso} values (~10 ppm) in this phosphate series, we also considered the
171 chemical shifts (Table 1) of previously published crystalline compounds (denoted thereafter
172 as M'PO₄ as they possess only one metal cation, M') which, conveniently, have a single
173 crystallographic P site: Ge₅O(PO₄)₆⁴⁴ (R-3 H⁷⁹), Si₅O(PO₄)₆^{43,80} (R -3 H⁸¹), AlPO₄⁴² (P 3₁ 2
174 1⁸²), AlPO₄⁴² (C 2 2 2₁⁸³) and LaPO₄^{38, 39} (P 1 2 1/a 1⁸⁴). This approach is similar to the work
175 done by several other authors^{85,86} as it gives an overview over a broader range of chemical
176 shifts.

177 In the present study three different optimisation approaches have been used: *i*) the
178 atomic position optimisation (APO) in which only the atom positions are relaxed, *ii*) the full
179 optimisation (FO) in which both the atom positions and cell parameters are relaxed and *iii*)
180 full optimisation followed by scaling of the obtained structure back to the original
181 experimental cell parameters (FOS). This last approach can be particularly advantageous in
182 the case of the PBE GGA functional, which is known to lead to an increase of the cell
183 dimension (by typically few %) and therefore a rescaling sometimes improves the σ_{iso} .^{87,88}

184 In the assessment of the optimisation effects and how it will later influence the
185 computed shielding, we considered three averaged structural parameters: *i*) the phosphorus-
186 oxygen bond distance ($\langle r_{P-O} \rangle$), *ii*) the metal-oxygen bond distance ($\langle r_{M-O} \rangle$, M = M', M^{II},
187 M^{IV}) and, *iii*) the metal-oxygen-phosphorus bond angle ($\langle \theta_{M-O-P} \rangle$, M = M', M^{II}, M^{IV}). To
188 compare the optimized (Opt) values with those of the experimental structure (ES) we
189 considered the following classical statistics:

$$190 \frac{\Delta \langle r_{P-O} \rangle}{\langle r_{P-O} \rangle_{ES}} = \frac{\langle r_{P-O} \rangle_{Opt} - \langle r_{P-O} \rangle_{ES}}{\langle r_{P-O} \rangle_{ES}} * 100 \quad (1)$$

$$191 \frac{\Delta \langle r_{M-O} \rangle}{\langle r_{M-O} \rangle_{ES}} = \frac{\langle r_{M-O} \rangle_{Opt} - \langle r_{M-O} \rangle_{ES}}{\langle r_{M-O} \rangle_{ES}} * 100 \quad (2)$$

$$192 \frac{\Delta \langle \theta_{M-O-P} \rangle}{\langle \theta_{M-O-P} \rangle_{ES}} = \frac{\langle \theta_{M-O-P} \rangle_{Opt} - \langle \theta_{M-O-P} \rangle_{ES}}{\langle \theta_{M-O-P} \rangle_{ES}} * 100 \quad (3)$$

193 where Opt = APO, FO, FOS and M = M', M^{II}, M^{IV}.

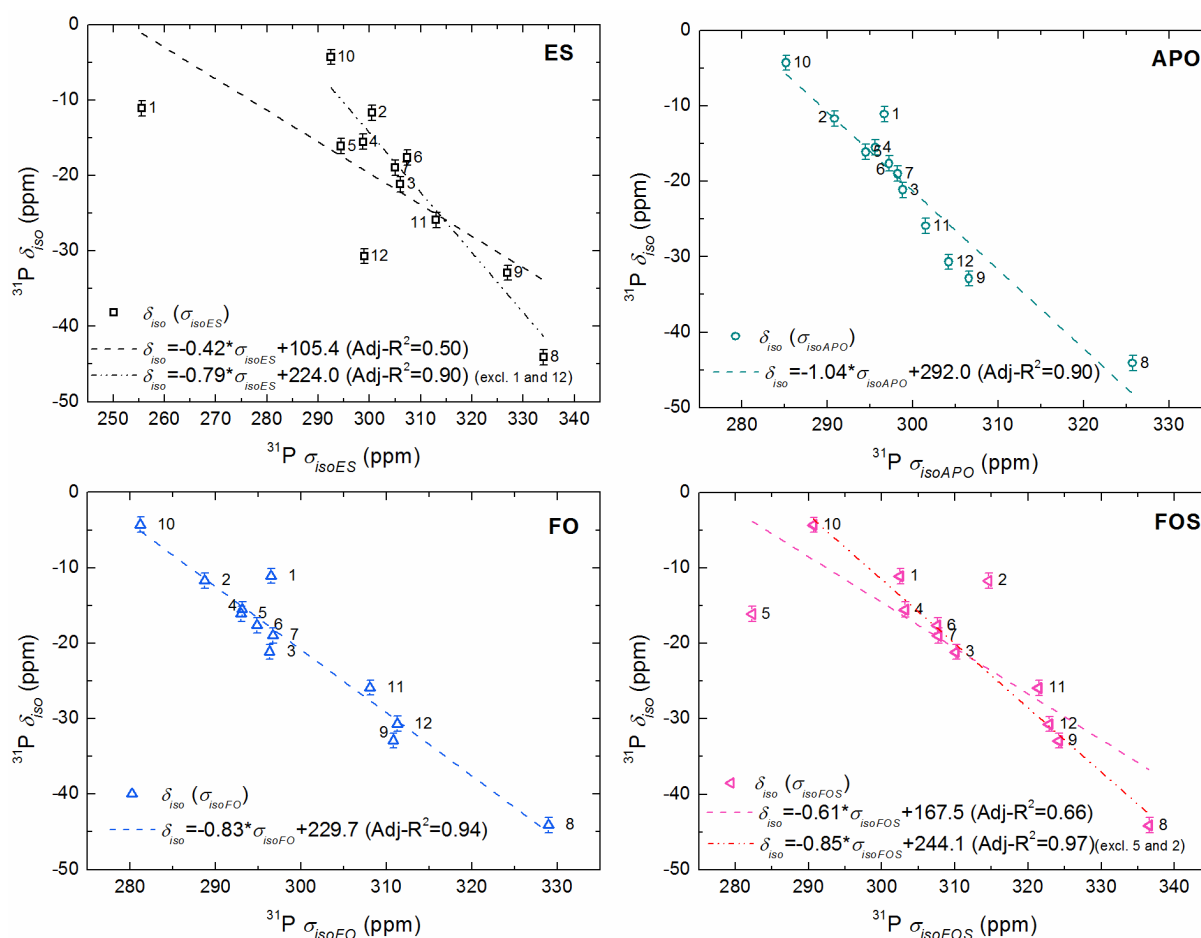
194 The results from Equation 1 are presented in Figure S2. The $\langle r_{P-O} \rangle$ data of
 195 $BaHf(PO_4)_2$ and $Si_5O(PO_4)_6$ are mostly influenced by structure optimisation with deviation
 196 from the ES values of $\sim 6\%$. It is interesting to note that the optimisation effects with the FO
 197 and APO approaches lead to quite similar $\langle r_{P-O} \rangle$ values. In Figure S3, the optimisation
 198 effects on the average metal-oxygen distances $\langle r_{M^{II}-O} \rangle$, $\langle r_{M^{IV}-O} \rangle$ and $\langle r_{M'-O} \rangle$ are depicted as
 199 obtained using Equation 2. With $\sim 4\%$, $\langle r_{M^{IV}-O} \rangle$ for $BaGe(PO_4)_2$ and $\langle r_{M'-O} \rangle$ for $Ge_5O(PO_4)_6$
 200 represent the largest differences compared to the ES values. Finally, Figure S4 shows the
 201 optimisation effects on the bond angles (Equation 3). The largest deviations from the ES
 202 values are again observed for $BaHf(PO_4)_2$ independent from the optimisation approach used.
 203 This analysis underlines errors more specifically in the experimental structural data of
 204 $BaHf(PO_4)_2$.

205

206 3.4. Calculation of chemical shieldings

207 3.4.1. The periodic calculations

208



209

210 Figure 3: Plot of the experimental ^{31}P δ_{iso} against the calculated ^{31}P σ_{iso} obtained from
211 periodic calculations. "excl." means excluding extremely deviating σ_{iso} data (see text). For the
212 compound numbers see Table 1.

213

214 In Figure 3, the experimental δ_{iso} are plotted against the theoretical σ_{iso} data. The
215 corresponding values are given in Table S4. As the two parameters are related through the
216 relation⁵¹, $\delta_{iso} = \sigma_{ref} + a\sigma_{iso}$ (with a being the slope and σ_{ref} the "reference" shielding from
217 the fittings), the data can be fitted using a linear equation. Among the σ_{iso} values based on the
218 ES structures a few large deviations can be observed from the regression line fitted to all the
219 data. The largest σ_{iso} deviations belong to $\text{BaHf}(\text{PO}_4)_2$ and $\text{AlPO}_4\text{-c}$. Indeed, after removing
220 these values from the fit, an improvement of the linear relationship measured by the adjusted
221 R-squared ($Adj\text{-}R^2$) was obtained as it increased from 0.50 to 0.90. The former very poor $Adj\text{-}$
222 R^2 reflects the deficiencies of the ES parameters as already discussed by other authors.^{51,89}
223 The above situation can be improved by quantum chemical geometry optimisation which can
224 (partly) correct the experimental errors.⁵¹ There are a few optimisation procedures for that
225 purpose. In the present study we probed three procedures (APO, FO and FOS), introduced in
226 section 3.3. For the σ_{iso} data determined using the optimized crystalline structures we
227 obtained a considerable improvement of the correlations between the δ_{iso} and the σ_{iso} values
228 (Figure 3), particularly on the basis of the APO and FO structures ($Adj\text{-}R^2$ equal to 0.90 and
229 0.94 respectively). $\text{BaHf}(\text{PO}_4)_2$ and $\text{AlPO}_4\text{-c}$ present now isotropic shieldings more in line
230 with the others. These better correlations can indeed be traced back to the improved structural
231 parameters of the APO and FO structures with respect to ES (Figure S2-Figure S4). BaHfPO_4
232 is the most demonstrative example, as here large changes occurred in all structural parameters
233 upon optimisation compared to the ES.

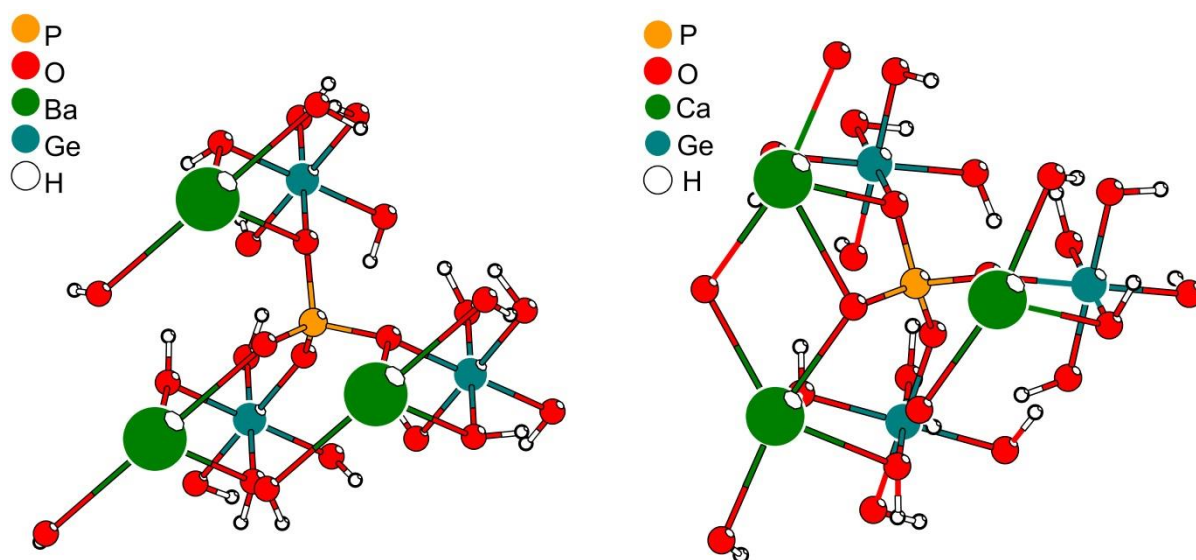
234 Contrary to the two above used procedures, the FOS method does not seem to
235 improve significantly the general correlation compared to ES ($Adj\text{-}R^2=0.66$ vs $Adj\text{-}R^2=0.50$).
236 This is mostly due to the σ_{iso} values of $\text{BaTi}(\text{PO}_4)_2$ and $\text{BaSn}(\text{PO}_4)_2$ which deviate
237 considerably from the fitted line. Removing their σ_{iso} values from the plot lead to an increase
238 of $Adj\text{-}R^2$ from 0.66 to 0.97. For $\text{BaTi}(\text{PO}_4)_2$, it is the $\langle\theta_{\text{M}}^{\text{IV}}\text{-OP}\rangle$ parameter which seems to be
239 too underestimated. After FO, the unit-cell parameters of $\text{BaTi}(\text{PO}_4)_2$ decreases from 1115.4
240 to 1056.4 a.u.³ contrary to the other unit cells which are increasing. Therefore, rescaling the
241 optimized cell parameters to the original experimental ones worsened considerably the

242 achievements of the FOS. For $\text{BaSn}(\text{PO}_4)_2$, we believe that, the error of FOS might be the
243 result of the optimisation headed towards a different local minimum.

244 It is also noteworthy that both a and σ_{ref} vary slightly, depending on the type of
245 structure used to calculate σ_{iso} . This is the consequence of the shielding being sensitive to
246 small changes in structural parameters. In fact, Vasconcelos et al.⁸⁵ have already reported
247 such behaviour in phosphate based materials underlining the difficulty to choose a uniform
248 σ_{ref} . Also, while the ideal slope must be -1, nuclear quantum effects, incomplete basis sets,
249 and other systematic errors in the DFT calculations can lead to deviations from this ideal
250 value.⁹⁰

251

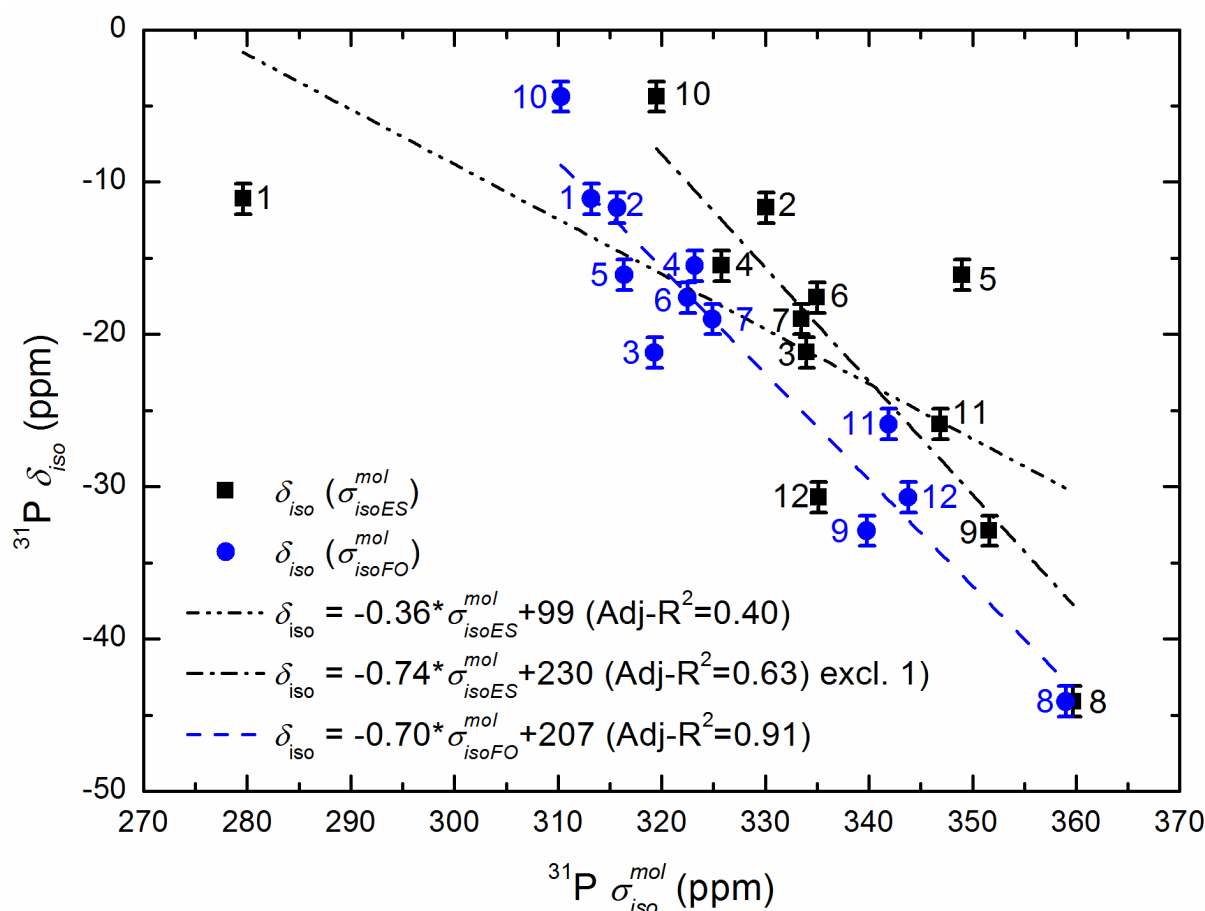
252 3.4.2. Small clusters approach



254 Figure 4: A typical cluster model structure used for the calculations of $\text{M}^{\text{II}}\text{M}^{\text{IV}}(\text{PO}_4)_2$
255 yavapaiite (left) and low-yavapaiite (right). More details are given in the Supporting
256 Information.

257 As examples for our cluster models for the yavapaiite and low-yavapaiite structures,
258 the clusters for $\text{BaGe}(\text{PO}_4)_2$ and $\text{CaGe}(\text{PO}_4)_2$, respectively, are shown in Figure 4. The cores
259 of the clusters consist of atoms, up to the third coordination shell (PO_4 , metals, oxygens),
260 taken from the ES and FO structures. The choice for FO from the three solid-state optimized
261 structure types is reasoned by the found best linear correlation between δ_{iso} and σ_{iso} . The
262 hydrogen atoms were added to the terminal oxygen atoms in order to compensate for the very
263 large negative charges of the core structures. The final charges of our clusters were -5 e
264 except for Al and La with charges of -3 e. The strain due to the manually added hydrogens
265 was removed by partial geometry optimisations, in which the hydrogen atoms were subjected

266 to geometry optimisation while the core of the cluster was kept fixed. Test calculations by
 267 varying the hydrogen bonding pattern around the fixed cores revealed only a slight influence
 268 (up to 2 ppm) on the calculated ^{13}P shieldings. The present reported cluster sizes were most
 269 suitable for the description of the NMR properties of the target compounds as reducing them
 270 to the second coordination shell resulted in unreliable chemical shieldings while expanding
 271 them led to serious SCF convergence problems. The exact compositions and pictures of the
 272 clusters together with the Cartesian coordinates of the final structures are given in the
 273 Supplementary Information.
 274



275
 276 Figure 5: Plot of the experimental ^{31}P δ_{iso} against the calculated ^{31}P σ_{iso}^{mol} obtained based on
 277 the cluster models. For the compound numbers see Table 1.

278
 279 In Figure 5 the experimental δ_{iso} values are plotted against the theoretical shielding (σ_{iso}^{mol})
 280 obtained from our cluster models.

281 The corresponding values are given in Table S5. Similarly to the solid-state calculations,
 282 the δ_{iso} vs σ_{isoES}^{mol} have a poor correlation due mainly to the above shown error in the

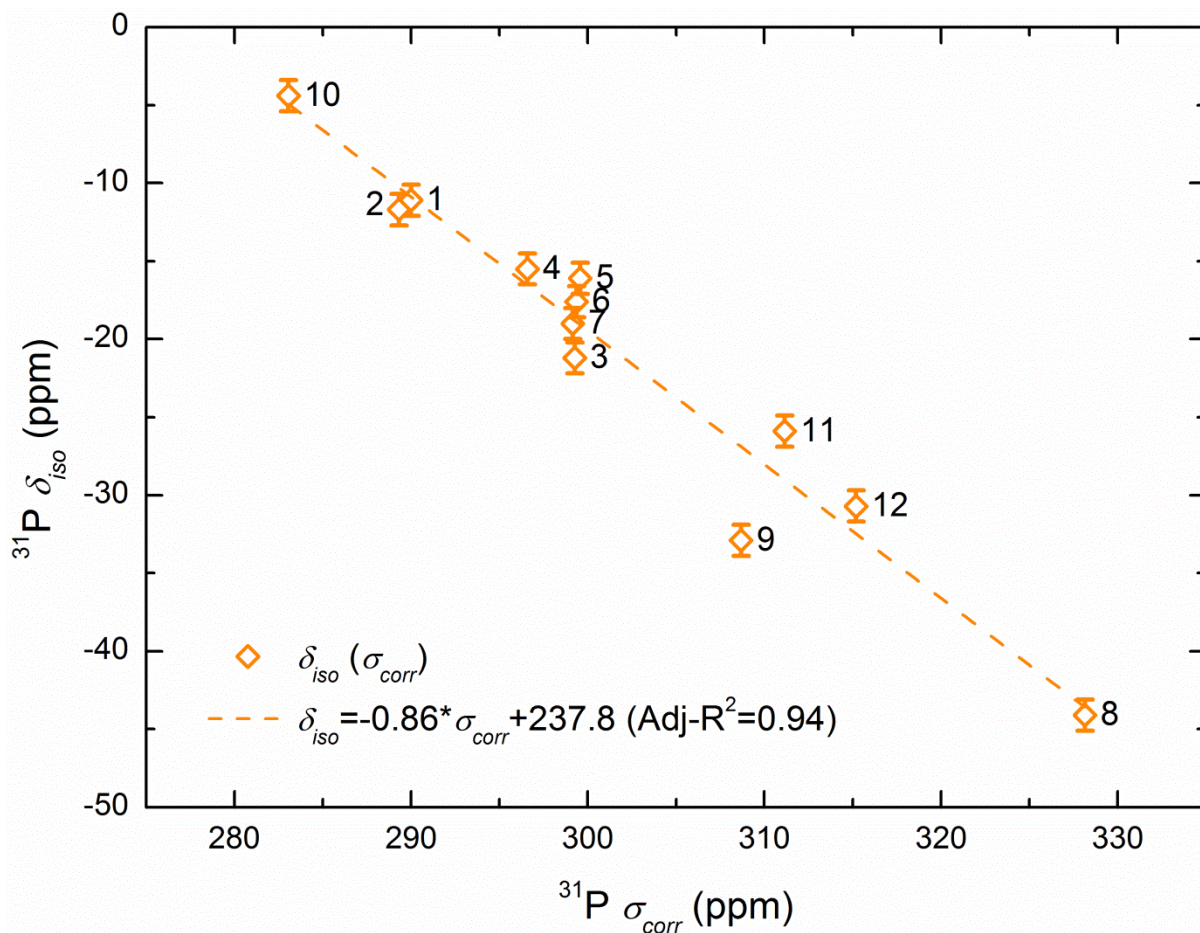
283 experimental structural data of BaHf(PO₄)₂. The correlation is thus improved from Adj- $R^2 =$
284 0.40 to 0.63 after omitting its chemical shielding. Using the clusters based on the FO
285 structures, the σ_{isoFO}^{mol} data correlate now well with δ_{iso} with an Adj- R^2 equal to 0.84. This
286 result reflects the efficiency of using small molecular cluster models to represent the solid-
287 state, as already shown by some authors in other phosphate series^{85,91}.

288 To go beyond these two classical approaches (*i.e.* periodic and cluster) and to capture the
289 full periodic nature of the crystal while also obtaining the higher accuracy associated with
290 computational models, we applied the new method recently suggested by Dračinský et al.⁹². It
291 consists in correcting the GIPAW calculated shieldings (σ_{corr}) by considering the difference
292 between the shielding calculated with the B3LYP and the PBE functionals employed in the
293 GIPAW calculation. For our study, we considered the FO structure and applied the following
294 equation:

$$295 \quad \sigma_{corr} = \sigma_{cryst}^{GIPAW} - \sigma_{mol}^{PBE} + \sigma_{mol}^{B3LYP} \quad (4)$$

296 with σ_{cryst}^{GIPAW} corresponding to the σ_{isoFO} obtained using the GGA-based GIPAW method
297 and; σ_{mol}^{PBE} and σ_{mol}^{B3LYP} corresponding to the σ_{isoFO}^{mol} obtained based on the clusters using the
298 PBE (same GGA as the GIPAW calculation) and B3LYP (hybrid) functionals.

299



300

301 Figure 6: Plot of the experimental $^{31}\text{P } \delta_{iso}$ against the calculated $^{31}\text{P } \sigma_{corr}$ obtained based on
 302 equation 4. For the compound numbers see Table 1.

303 In Figure 6, we plotted the experimental δ_{iso} values against the corrected shielding.
 304 The first observation is an increase of the linear slope from -0.83 to -0.86 which is positively
 305 getting closer to the ideal value of -1. In Table 2, we determined the theoretical δ_{iso} values
 306 based on the GIPAW and Dračinský approaches. This allows to easily compare them with the
 307 experimental values. The lowest mean absolute error (MAE) is obtained for the corrected
 308 shielding values confirming again that this method does lead to data improvements. The
 309 maximal absolute error for δ_{corr} of 6 ppm is obtained for $\text{Ge}_5\text{O}(\text{PO}_4)_6$. Nonetheless, this value
 310 also corresponds to an improvement from the non-corrected shielding (decrease of about 2
 311 ppm). It is worth mentioning that this theoretical δ_{iso} is not well represented independently of
 312 the type of calculations approach or optimization considered. This might imply a larger error
 313 of the δ_{iso} value. It is also interesting to notice that the shielding of $\text{BaHf}(\text{PO}_4)_2$ is specifically
 314 improved with this correction most probably implying the problems in GGA-PBE in addition
 315 to the structural parameter errors previously discussed.

316 Table 2: Theoretical δ_{iso} in ppm with $\delta_{cryst}^{GIPAW} = -0.83 * \sigma_{cryst}^{GIPAW} + 229.7$ and $\delta_{corr} =$
 317 $-0.86 * \sigma_{corr} + 237.8$. The MAE and maximal absolute errors (ppm) are also given.

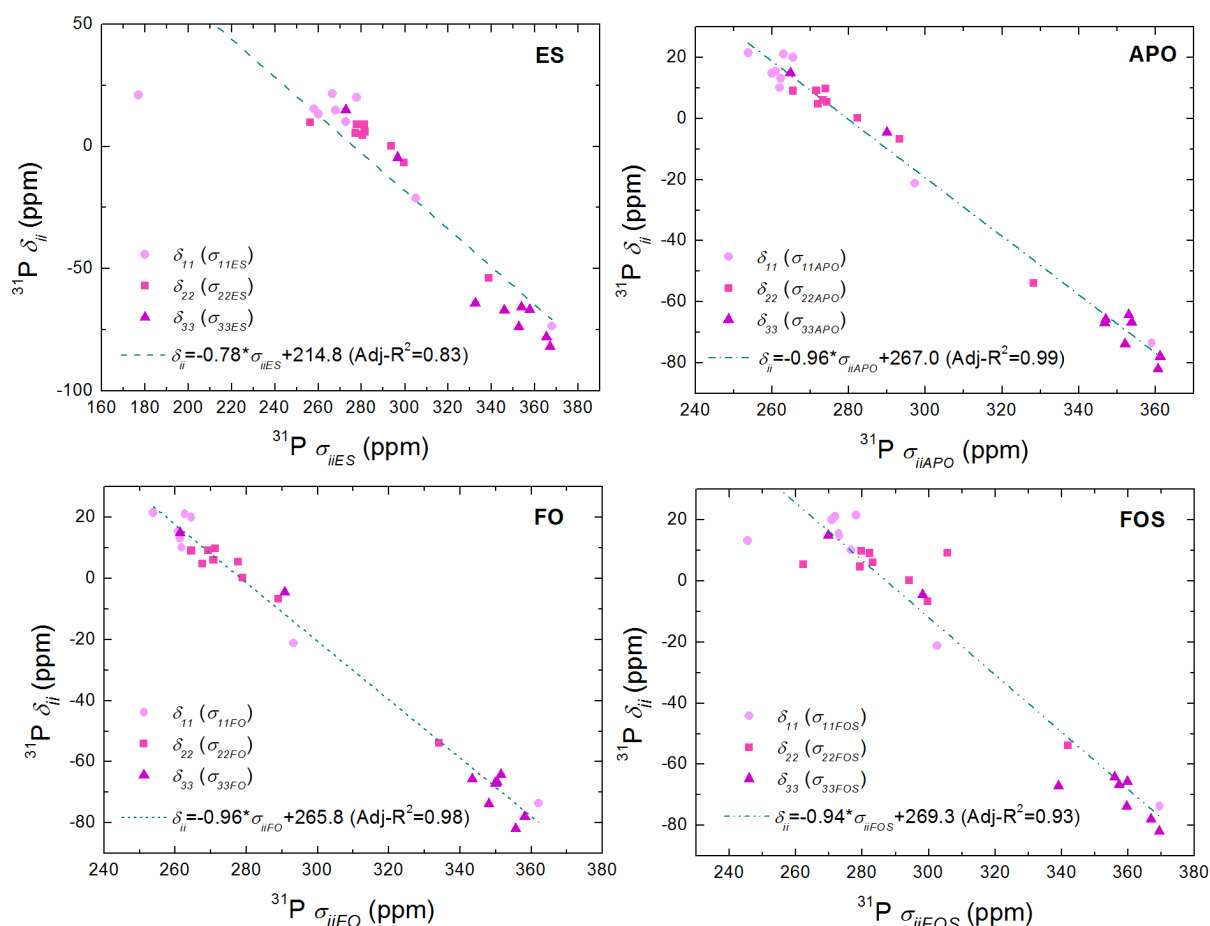
N°	Name	δ_{cryst}^{GIPAW}	δ_{corr}
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1	BaHf(PO ₄) ₂	-16.8	-10.9
2	BaSn(PO ₄) ₂	-11.5	-10.3
3	BaGe(PO ₄) ₂	-17.8	-18.9
4	BaZr(PO ₄) ₂	-15.0	-16.6
5	BaTi(PO ₄) ₂	-17.8	-19.1
6	CaGe(PO ₄) ₂	-16.6	-18.9
7	β -SrGe(PO ₄) ₂	-18.1	-18.8
8	Si ₅ O(PO ₄) ₆	-45.0	-43.6
9	Ge ₅ O(PO ₄) ₆	-41.0	-26.9
10	LaPO ₄	-5.2	-5.0
11	AlPO ₄	-27.6	-29.0
12	AlPO ₄ -c	-30.3	-32.5
	MAE	2.1	1.8
	Max. Abs. Err.	8.1	6.0

318

319 3.4.3. Chemical shift shieldings

320



321

322 Figure 7: Plot of the experimental δ_{ii} against the calculated σ_{ii} values and their corresponding
323 fits (dashed lines).

324

325 The σ_{ii} values correspond to the eigenvalues of the chemical shielding tensor which is
 326 a 3 x 3 matrix in the laboratory frame^{93,94}:

$$\sigma_{lab} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

327 The chemical shielding tensor and the associated σ_{ii} values are given as part of the QE
 328 output file. We noticed that contrary to the good results on δ_{iso} vs σ_{iso} , the σ_{ii} from the output
 329 files gave a poorer linear correlation with the δ_{ii} as shown in Figure S5. We checked the
 330 eigenvalues by recalculating them with the Mathematica software® and the results are shown
 331 in Figure 7. One can notice that a much better overall correlation is now obtained with Adj-
 332 R^2 coefficient improved from 0.25 to 0.83 for the ES, 0.92 to 0.99 for the APO, 0.93 to 0.98
 333 for the FO and, 0.87 to 0.93 for the FOS. These differences suggest an erroneous
 334 determination of the eigenvalues in the QE code. We also show here that both slope and σ_{ref}
 335 are dependent upon the type of optimisation.

336 In the literature, while most review papers^{51,43} suggest to plot δ_{ii} vs σ_{ii} , as done in the
 337 present work, some authors prefer the σ_{ii} vs δ_{ii} representation as a slope of -1 is most easily
 338 obtained. We therefore gave in Table 3 the values of the linear relations $\sigma_{ii} = \sigma_{iiref} + b * \delta_{ii}$ in
 339 order to compare with the published data. Holmes et al.⁹¹ found a linear correlation of $\sigma_{ii} =$
 340 $1.09 * \delta_{ii} + 270$ for a set of 57 compounds and our results are in line with their observations.

341

342 Table 3: Linear fit considering $\sigma_{ii} = \sigma_{iiref} + b * \delta_{ii}$.

<i>Opt.</i>	<i>b</i>	σ_{iiref}	R^2
ES	-1.1	280.1	0.83
ES excl. 1	-1.0	286.2	0.97
APO	-1.03	279.6	0.99
FO	-1.03	278.4	0.98
FOS	-0.99	288.4	0.93
FOS excl. 5	-0.98	291.5	0.97

343

344

345 4. Conclusion

346 We studied here the local P environment in a series of crystalline phosphates by combing
 347 ³¹P NMR with periodic and small cluster DFT calculations. All the ³¹P spectra acquired

348 possess a good resolution with a clear identification of a single P signal in agreement with
349 their crystallographic structures. Using the GIPAW approach, optimisations of the crystalline
350 structure parameters using three types approaches (APO, FO and FOS) led to an overall
351 improvement of the calculated NMR parameters, especially for BaHf(PO₄)₂. Good linear
352 correlations, δ_{iso} vs σ_{iso} , were achieved with both APO ($Adj-R^2=0.90$) and FO ($Adj-R^2=0.94$)
353 structures, with a preference on the latest optimisation approach. Using the ES and FO
354 structures, small cluster models were constructed. The isotropic chemical shielding (σ_{iso}^{mol})
355 extracted presented a good correlation with the isotropic chemical shifts. This underlines the
356 efficiency of such clusters and its eventual use as substitute to model the infinite crystal
357 especially in the case of paramagnetic systems. Nonetheless, a better improvement of the
358 theoretical isotropic chemical shift was achieved by combining the advantages of both plane-
359 wave and molecular computational approaches (MAE decreasing from 2.1 to 1.8). For the
360 CSA parameters, good linear correlations were also obtained between the δ_i and the σ_i data
361 determined on the basis of the APO ($Adj-R^2=0.99$) and FO ($Adj-R^2=0.98$) relaxed structures,
362 with this time slightly better results with the first optimisation approach. The present paper
363 show a first step in the NMR study of M^{II}M^{IV}(PO₄)₂ compounds using periodic and cluster
364 calculations with an extension to any phosphates.

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- 1 E. Morin, G. Wallez, S. Jaulmes, J. C. Couturier, M. Quarton, *J. Solid State Chem.* 137 (1998) 283–288, <https://doi.org/10.1006/jssc.1997.7735>.
- 2 K. Fukuda, A. Moriyama, T. Iwata, *J. Solid State Chem.* 178 (2005) 2144–2151, <https://doi.org/10.1016/j.jssc.2005.04.022>.
- 3 G. Blasse, G. J. Dirksen, *Chem. Phys. Lett.* 62 (1979) 19–20, [https://doi.org/10.1016/0009-2614\(79\)80403-0](https://doi.org/10.1016/0009-2614(79)80403-0).
- 4 C. R. Miao, C. C. Torardi, *J. Solid State Chem.* 155 (2000) 229–232, <https://doi.org/10.1006/jssc.2000.8938>.
- 5 Z. J. Zhang, J. L. Yuan, X. J. Wang, D. B. Xiong, H. H. Chen, J. T. Zhao, Y. B. Fu, Z. M. Qi, G. B. Zhang, C. S. Shi, *J. Phys. D: Appl. Phys.* 40 (2007) 1910–1914, <https://doi.org/10.1088/0022-3727/40/7/012>.
- 6 B. Yan, J. Gu, X. Xiao, *J. Nanopart. Res.* 12 (2010) 2145–2152, <https://doi.org/10.1007/s11051-009-9776-x>.
- 7 X. Xiao, B. Yan, *J. Amer. Ceram. Soc.* 93 (2010) 2195–2201, <https://doi.org/10.1111/j.1551-2916.2010.03716.x>.
- 8 R. R. Parrish, *Canadian Journal of Earth Science* 27 (1990) 1431–1450, <https://doi.org/10.1139/e90-152>.
- 9 J.-M. Montel, S. Foret, M. Veschambre, C. Nicollet, A. Provost, *Chemical Geology* 131 (1996) 37–53, [https://doi.org/10.1016/0009-2541\(96\)00024-1](https://doi.org/10.1016/0009-2541(96)00024-1).
- 10 V. Brandel, N. Dacheux, E. Pichot, M. Genet, J. Emery, J. Y. Buzare, R. Podor, *Chem. Mater.* 10 (1998) 345–350, <https://doi.org/10.1021/cm970513d>.
- 11 O. Terra, N. Dacheux, F. Audubert, R. Podor, *J. Nuc. Mater.* 352 (2006) 224–232, <https://doi.org/10.1016/j.jnucmat.2006.02.058>.
- 12 O. Terra, N. Clavier, N. Dacheux, R. Podor, *New J. Chem.* 27 (2003) 957–967, <https://doi.org/10.1039/B212805P>.
- 13 D. M. Bykov, A. I. Orlova, S. V. Tomilin, A. A. Lizin, A. N. Lukinykh, *Radiochemistry* 48 (2006) 234–239, <https://doi.org/10.1134/S1066362206030052>.
- 14 D. Bregiroux, O. Terra, F. Audubert, N. Dacheux, V. Serin, R. Podor, D. Bernache-Assollant, *Inorg. Chem.* 46 (2007) 10372–10382, <https://doi.org/10.1021/ic7012123>.
- 15 P. Sengupta, *J. Hazard. Mater.* 235–236 (2012) 17–28, <https://doi.org/10.1016/j.jhazmat.2012.07.039>.
- 16 I. W. Donald, B. L. Metcalfe, R. N. J. Taylor, *J. Mater. Sci.* 32 (1997) 5851–5887, <https://doi.org/10.1023/A:1018646507438>.
- 17 W. E. Lee, M. I. Ojovan, M. C. Stennett, N. C. Hyatt, *Adv. Appl. Ceram.* 105 (2006) 3–12, <https://doi.org/10.1179/174367606X81669>.
- 18 K. Popa, D. Bregiroux, R. J. M. Konings, A. F. Popa, T. Gouder, T. Geisler, P. E. Raison, *J. Solid State Chem.* 180 (2007) 2346–2355, <https://doi.org/10.1016/j.jssc.2007.06.006>.
- 19 S. Neumeier, Y. Arinicheva, Y. Ji, J. M. Heuser, P. M. Kowalski, P. Kegler, H. Schlenz, D. Bosbach, G. Deissmann, *Radiochim. Acta* 105 (2017) 961–984, <https://doi.org/10.1515/ract-2017-2819>.
- 20 K. Popa, R. J. M. Konings, T. Wiss, H. Leiste, *J. Radioanal. Nucl. Chem.* 273 (2007) 563–567, <https://doi.org/10.1007/s10967-007-0910-x>.
- 21 K. Popa, T. Shvareva, L. Mazeina, E. Colineau, F. Wastin, R.J.M. Konings, A. Navrotsky, *Am. Mineral.* 93 (2008) 1356–1362, <https://doi.org/10.2138/am.2008.2794>.
- 22 Y. Arinicheva, K. Popa, A.C. Scheinost, A. Rossberg, O. Dieste Blanco, P.E. Raison, A. Cambriani, J. Somers, D. Bosbach, S. Neumeier, *J. Nucl. Mater.*, 493 (2017) 404–411, <https://doi.org/10.1016/j.jnucmat.2017.06.034>.

- 23 D. Bregiroux, K. Popa, G. Wallez, *J. Solid State Chem.* 230 (2015) 26-33, <https://doi.org/10.1016/j.jssc.2015.06.010>.
- 24 D. Bregiroux, G. Wallez, K. Popa, *Solid State Sci.* 41 (2015) 43-47, <http://dx.doi.org/10.1016/j.solidstatesciences.2015.02.004>.
- 25 A. K. Cheetham, N. J. Clayden, C. M. Dobson, R. J. B. Jakeman, *J. Chem. Soc., Chem. Commun.*, 1986, 195-197, <https://doi.org/10.1039/C39860000195>.
- 26 I. D. Brown, R. D. Shannon, *Acta Cryst.* A29 (1973) 266-282, <https://doi.org/10.1107/S0567739473000689>.
- 27 A. C. Palke, J. F. Stebbins, *Am. Miner.* 96 (2011) 343-353, <https://doi.org/10.2138/am.2011.3816>.
- 28 A. C. Palke, J. F. Stebbins, L. A. Boatner, *Inorg. Chem.* 52 (2013) 12605-12615, <https://doi.org/10.1021/ic401757z>.
- 29 L. Martel, J.-F. Vigier, D. Prieur, S. Nourry, A. Guiot, K. Dardenne, J. Boshoven, J. Somers, *J. Phys. Chem. C* 118 (2014) 27640-27647, <https://doi.org/10.1021/jp507088t>.
- 30 F. Gendron, K. Sharkas, J. Autschbach, *J. Phys. Chem. Lett.* 6 (2015) 2183-2188, <https://doi.org/10.1021/acs.jpcclett.5b00932>.
- 31 F. Gendron, B. Pritchard, H. Bolvin, J. Autschbach, *Inorg. Chem.* 53 (2014) 8577-8592, <https://doi.org/10.1021/ic501168a>.
- 32 D. E. Smiles, G. Wu, P. Hrobárik, T. W. Hayton, *J. Am. Chem. Soc.* 138 (2016) 814-825, <https://doi.org/10.1021/jacs.5b07767>.
- 33 L. Martel, A. Rakhmatullin, J. J. Baldoví, M. Perfetti, K. Popa, M. Deschamps, T. Gouder, E. Colineau, A. Kovács, J.-C. Griveau, *Phys. Rev. B* 100 (2019) 054412, <https://doi.org/10.1103/PhysRevB.100.054412>.
- 34 A. Mondal, M. W. Gaultois, A. J. Pell, M. Iannuzzi, C. P. Grey, J. Hutter, M. Kaupp, *J. Chem. Theory Comput.*, 14 (2018) 377-394.
- 35 E. J. Graeber, A. Rosenzweig, *Am. Miner.* 56 (1971) 1917-1933.
- 36 J. W. Anthony, W. J. McLean, *Am. Miner.* 57 (1972) 1546-1549.
- 37 K. Popa, G. Wallez, D. Bregiroux, P. Loiseau, *J. Solid State Chem.* 184 (2011) 2629-2634, <https://doi.org/10.1016/j.jssc.2011.07.037>.
- 38 D. Bregiroux, F. Audubert, T. Charpentier, D. Sakellariou, D. Bernache-Assollant, *Solid State Sci.* 9 (2007) 432-439, <https://doi.org/10.1016/j.solidstatesciences.2007.03.019>.
- 39 K. Popa, P. E. Raison, L. Martel, P. M. Martin, D. Prieur, P. L. Solari, D. Bouëxière, R. J. M. Konings, J. Somers, *J. Solid State Chem.* 230 (2015) 169-174, <https://doi.org/10.1016/j.jssc.2015.07.002>.
- 40 D. Müller, E. Jahn, G. Ladwig, U. Haubenreisser, *Chem. Phys. Lett.*, 109 (1984) 332-336, [https://doi.org/10.1016/0009-2614\(84\)85596-7](https://doi.org/10.1016/0009-2614(84)85596-7).
- 41 K. Kanehashi, T. Nemoto, K. Saito, *J. Non-Cryst. Solids*, 2007, **353**, 4227-4231, <https://doi.org/10.1016/j.jnoncrysol.2007.05.020>.
- 42 D. M. Dawson, S. E. Ashbrook, *J. Phys. Chem. C*, 118 (2014) 23285-23296, <https://doi.org/10.1021/jp507644z>.
- 43 C. Bonhomme, C. Gervais, C. Coelho, F. Pourpoint, T. Azaïs, L. Bonhomme-Courry, F. Babonneau, G. Jacob, M. Ferrari, D. Canet, J. R. Yates, C. J. Pickard, S.A. Joyce, F. Mauri, D. Massiot, *Magn. Reson. Chem.* 48 (2010) S86-S102, <https://doi.org/10.1002/mrc.2635>.
- 44 E. R. Losilla, A. Cabeza, S. Bruque, M. A. G. Aranda, J. Sanz, J. E. Iglesias, J. A. Alonso, *J. Solid State Chem.* 156 (2001) 213-219, <https://doi.org/10.1006/jssc.2000.8984>.
- 45 K. Popa, R. J. M. Konings, P. Boulet, D. Bouëxière, A. F. Popa, *Thermochim. Acta* 436 (2005) 51-55, <https://doi.org/10.1016/j.tca.2005.06.035>.
- 46 K. Popa, R.J.M. Konings, O. Beneš, T. Geisler, A.F. Popa, *Thermochim. Acta*, 451 (2006) 1-4, <https://doi.org/10.1016/j.tca.2006.08.011>.

-
- 47 T. Geisler, K. Popa, R. J. M. Konings, A. F. Popa, *J. Solid State Chem.* 179 (2006) 1490-1495, <https://doi.org/10.1016/j.jssc.2006.01.065>.
- 48 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, G. Hoatson, *Magn. Reson. Chem.* 40 (2002) 70-76, <https://doi.org/10.1002/mrc.984>.
- 49 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P Seitsonen, A. Smogunov, P. Umari, R. M Wentzcovitch, *J. Phys.: Condens. Matter* 21 (2009) 395502, <https://doi.org/10.1088/0953-8984/21/39/395502>.
- 50 C. J. Pickard, F. Mauri, *Phys. Rev. B*, 63 (2001) 245101, <https://doi.org/10.1103/PhysRevB.63.245101>.
- 51 T. Charpentier, *Solid State NMR*, 40 (2011) 1-20, <https://doi.org/10.1016/j.ssnmr.2011.04.006>.
- 52 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865-3868, <https://doi.org/10.1103/PhysRevLett.77.3865>.
- 53 N. Trouiller, J. Martins, *Phys. Rev. B*, 43 (1991) 1993-2006, <https://doi.org/10.1103/PhysRevB.43.1993>.
- 54 <http://www.quantum-espresso.org/pseudopotentials/pslibrary/>.
- 55 <https://sites.google.com/site/dceresoli/pseudopotentials>.
- 56 <http://www.quantum-espresso.org>.
- 57 U. Haeberlen, In *Advances in Magnetic Resonance*; Suppl. 1; J. S. Waugh, Ed.; Academic Press: New York, 1976.
- 58 M. Mehring, *Principles of High Resolution NMR in Solids*, 2nd. ed.; Springer Verlag: Berlin, 1983.
- 59 H. W. Spiess, In *NMR Basic Principles and Progress*; P. Diehl, E. Fluck, R. Kosfeld, Eds.; Springer Verlag, Berlin, 1978, Vol. 15.
- 60 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01. Gaussian, Inc., Wallingford CT, 2010.
- 61 W. R. Wadt, P. J. Hay, *J. Chem. Phys.*, 82 (1985) 284, <https://doi.org/10.1063/1.448800>.
- 62 W. R. Wadt, P. J. Hay, *J. Chem. Phys.* 82 (1985) 299, <https://doi.org/10.1063/1.448975>.
- 63 A. D. Becke, *J. Chem. Phys.*, 98 (1993) 5648-5652, <https://doi.org/10.1063/1.464913>.
- 64 C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 37 (1988) 785-789, <https://doi.org/10.1103/PhysRevB.37.785>.
- 65 T. H. Dunning, Jr., *J. Chem. Phys.* 90 (1989) 1007, <https://doi.org/10.1063/1.456153>.
- 66 D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* 98 (1993) 1358, <https://doi.org/10.1063/1.464303>.

- 67 J. Koput and K.A. Peterson, *J. Phys. Chem. A* 106 (2002) 9595–9599, <https://doi.org/10.1021/jp026283u>.
- 68 A. K. Wilson, D. E. Woon, K. A. Peterson, T. H. Dunning, Jr., *J. Chem. Phys.* 110 (1999) 7667, <https://doi.org/10.1063/1.478678>.
- 69 N.B. Balabanov and K.A. Peterson, *J. Chem. Phys.* 123 (2005) 064107, <https://doi.org/10.1063/1.1998907>.
- 70 X. Cao, M. Dolg, *J. Chem. Phys.* 115, 7348 (2001), <https://doi.org/10.1063/1.1406535>.
- 71 X. Cao, M. Dolg, *J. Molec. Struct. (Theochem)* 581 (2002) 139, [https://doi.org/10.1016/S0166-1280\(01\)00751-5](https://doi.org/10.1016/S0166-1280(01)00751-5).
- 72 M. Kaupp, P. v. R. Schleyer, H. Stoll, H. Preuss, *J. Chem. Phys.* 94 (1991) 1360, <https://doi.org/10.1063/1.459993>.
- 73 B. Metz, H. Stoll, M. Dolg, *J. Chem. Phys.* 113 (2000) 2563, <https://doi.org/10.1063/1.1305880>.
- 74 K. A. Peterson, *J. Chem. Phys.* 119 (2003) 11099, <https://doi.org/10.1063/1.1622923>.
- 75 K. A. Peterson, D. Figgen, M. Dolg, H. Stoll, *J. Chem. Phys.* 126 (2007) 124101, <https://doi.org/10.1063/1.2647019>.
- 76 D. Figgen, K.A. Peterson, M. Dolg, H. Stoll, *J. Chem. Phys.* 130 (2009) 164108, <https://doi.org/10.1063/1.3119665>.
- 77 J. R. Cheeseman, G. W. Trucks, T. A. Keith, M. J. Frisch, *J. Chem. Phys.* 104 (1996) 5497–5509, <https://doi.org/10.1063/1.471789>.
- 78 D. Bregiroux, K. Popa, R. Jardin, P. E. Raison, G. Wallez, M. Quarton, M. Brunelli, C. Ferrero, R. Caciuffo, *J. Solid State Chem.* 182 (2009) 1115–1120, <https://doi.org/10.1016/j.jssc.2009.02.012>.
- 79 H. Mayer, H. Völlenkle, *Monatsh. Chem.* **103** (1972) 1560.
- 80 C. Coelho, T. Azais, L. Bonhomme-Courty, G. Laurent, C. Bonhomme, *Inorg. Chem.* 46 (2007) 1379–1387, <https://doi.org/10.1021/ic061964f>.
- 81 H. Mayer, *Monatsh. Chem.* 105 (1974) 46–54, <https://doi.org/10.1007/BF00911286>.
- 82 H. N. Ng, C. Calvo, *Can. J. Phys.* 54 (1976) 638–647, <https://doi.org/10.1139/p76-070>.
- 83 B. L. Phillips, J. G. Thompson, Y. Xiao, R. J. Kirkpatrick, *Phys. Chem. Miner.* 20 (1993) 341–352, <https://doi.org/10.1007/BF00215105>.
- 84 S. Jaulmes, *Bull. Soc. fr. Minéral. Cristallog.* 95 (1972) 42–46.
- 85 F. Vasconcelos, S. Cristol, J.-F. Paul, L. Montagne, F. Mauri, L. Delevoye, *Magn. Reson. Chem.* 48 (2010) S142–S150, <https://doi.org/10.1002/mrc.2667>.
- 86 K. Pilar, Z. Deng, M. B. Preefer, J. A. Cooley, R. Clément, R. Seshadri, A. K. Cheetham, *Phys. Chem. Chem. Phys.* 21 (2019) 10070–10074, <https://doi.org/10.1039/c9cp01420a>.
- 87 T. Charpentier, S. Ispas, M. Profeta, F. Mauri, C. J. Pickard, *J. Phys. Chem. B* 108 (2004) 4147–4161, <https://doi.org/10.1021/jp0367225>.
- 88 M. Profeta, F. Mauri, C. J. Pickard, *J. Am. Chem. Soc.* 125 (2003) 541–548, <https://doi.org/10.1021/ja027124r>.
- 89 J. R. Yates, S. E. Dobbins, C. J. Pickard, F. Mauri, P. Y. Ghi, R. K. Harris, *Phys. Chem. Chem. Phys.* 7 (2005) 1402–1407, <https://doi.org/10.1039/B500674K>.
- 90 M. Dračinský, P. Hodgkinson, *Chem. Eur. J.*, 20 (2014) 2201–2207, <https://doi.org/10.1002/chem.201303496>.
- 91 S. T. Holmes, R. J. Iuliucci, K. T. Mueller, C. Dybowski, *J. Chem. Theory Comput.* 11 (2015) 5229–5241, <https://doi.org/10.1021/acs.jctc.5b00752>.
- 92 M. Dračinský, P. Unzueta, G. J. O. Beran, *Phys. Chem. Chem. Phys.*, 21 (2019) 14992, <https://doi.org/10.1039/c9cp01666j>.
- 93 R. P. Young, C. R. Lewis, C. Yang, L. Wang, J. K. Harper, L. J. Mueller, *Magn Reson Chem.* 57 (2019) 211–223, <https://doi.org/10.1002/mrc.4793>

94 L. J. Mueller, *Concept. Magn. Reson. A*, 38 (2011) 221–235,
<https://doi.org/10.1002/cmr.a.20224>