Ab initio $^{27}\text{Al}$ NMR chemical shifts and quadrupolar parameters for $\text{Al}_2\text{O}_3$ phases and their precursors

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The Gauge-Including Projector Augmented Wave (GIPAW) method, within the Density Functional Theory (DFT) Generalized Gradient Approximation (GGA) framework, is applied to compute solid state NMR parameters for $^{27}\text{Al}$ in the $\alpha$, $\theta$, and $\kappa$ aluminium oxide phases and their gibbsite and boehmite precursors. The results for well-established crystalline phases compare very well with available experimental data and provide confidence in the accuracy of the method. For $\gamma$-alumina, four structural models proposed in the literature are discussed in terms of their ability to reproduce the experimental spectra also reported in the literature. Among the considered models, the $\text{FeCr}_3\text{O}_4$ structure proposed by Paglia et al. [Phys. Rev. B 71, 224115 (2005)] shows the best agreement. We attempt to link the theoretical NMR parameters to the local geometry. Chemical shifts depend on coordination number but no further correlation is found with geometrical parameters. Instead our calculations reveal that, within a given coordination number, a linear correlation exists between chemical shifts and Born effective charges.

I. INTRODUCTION

Aluminium oxide ($\text{Al}_2\text{O}_3$), also known as alumina, is one of the most important oxides because of its many industrial applications. Corundum ($\alpha$-$\text{Al}_2\text{O}_3$), the most stable and common crystalline form of alumina, is the final product of the calcination of hydroxides or oxhydroxides of aluminium at temperatures above 1273 K, which can vary according to the precursor. The transformation from aluminium hydrates to the final oxide is not direct and a variety of relatively stable intermediate phases can be detected for each combination of starting compound and thermal treatment.

The most commonly used precursors in the synthesis of the various alumina phases are gibbsite [$\gamma$-$\text{Al(OH)}_3$], bayerite [$\alpha$-$\text{Al(OH)}_3$], and boehmite [$\gamma$-$\text{AlO(OH)}$]. The transformation of gibbsite to corundum can proceed through a sequence of hexagonal close packed aluminas ($\chi$ and $\kappa$) or an alternative sequence in which boehmite is initially formed and the $\alpha$ phase is achieved via the cubic spinel transition phases ($\gamma$, $\delta$, and $\theta$)2. Bayerite can also follow this same sequence through boehmite to form corundum3 or an alternative path transforming to $\eta$ and $\theta$ phases4.

Among the transition aluminas, the $\gamma$ phase is highly valued for industrial applications due to its textural properties (surface area, pore volume, pore size), which makes it an important material in many industrial processes acting as an adsorbent, a catalyst and/or catalyst support. In petroleum and petrochemical industries $\gamma$-alumina is used as catalyst support for transition-metal sulphides Co(Ni)MoS in hydrotreatment catalysts and metallic alloys in reforming catalysts6,7. Due to its low crystallinity and the consequent difficulty in characterization, the debate on the structure of $\gamma$-alumina remains open and a series of theoretical and experimental works concerning this subject have been published along the decades8–17.

Since the transition between the distinct intermediate phases is a gradual process, the precise temperature at which each phase is obtained with a high degree of purity can not be determined by X-ray diffraction (XRD) experiments only. Solid-State Nuclear Magnetic Resonance (SS-NMR) is an important technique for material characterization. Long-range order is not a prerequisite to distinguish different phases and the knowledge of $^{27}\text{Al}$ NMR data can allow the detection of the onset of phase changes during alumina calcination18, permitting a discussion of the transition mechanisms19. A detailed interpretation of the results remains, however, a challenge.

The advent of theoretical techniques such as the Gauge-Including Projector Augmented Wave (GIPAW) method20,21 enables the ab initio calculation of isotropic chemical shielding, $\sigma_{iso}$, quadrupolar coupling constant, $C_Q$, and asymmetry parameter, $\eta Q$, in solids. First principles simulations of NMR spectra of structural models for transition aluminas are now possible22,23 and can be compared with available experimental data.

In this paper we apply the GIPAW method to compute solid state Magic Angle Spinning (MAS) NMR parameters for a number of well characterized aluminium oxide phases and for their boehmite and gibbsite precursors. The results are compared with available experimental data to validate the method. In order to contribute to a better characterization of $\gamma$-alumina, a number of structural models, proposed in the literature, are examined and their simulated spectra compared to experimental ones, thus revealing their adequacy.

We then examine possible correlations of the predicted chemical shifts with local atomic geometry or local electronic structure, described through Bader analysis24 and Born dynamical effective charges25, finding significant correlations.

The rest of the paper is organized as follows: in Sec. II we describe the theoretical methodology and the structural models used. In Sec. III we present our calculated...
NMR results, compare them with experiments and discuss the resulting correlations. Sec. IV contains our conclusions.

II. DETAILS OF CALCULATIONS

A. Electronic structure

All \textit{ab initio} calculations in this study were performed using the codes available within the Quantum ESPRESSO distribution\textsuperscript{26}, which implements the DFT\textsuperscript{27} framework using a plane waves basis set to expand the one-electron wavefunctions of Kohn-Sham equations\textsuperscript{28}. The effect of exchange-correlation (XC) potential was explored by comparing the results of different descriptions for this term: Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation\textsuperscript{29} and its revision (revPBE) by Zhang and Yang\textsuperscript{30}. Furthermore, we also considered a van der Waals-aware density functional (vdW-DF)\textsuperscript{31,32} recently implemented in Quantum ESPRESSO. Interaction of valence electrons with nuclei and core electrons were treated by the Projector Augmented-Wave (PAW)\textsuperscript{33} method.

The plane wave kinetic energy cut-off and k-points sampling were adjusted to yield less than 1 mRy/atom convergence in total energy for all models. A kinetic energy cut-off of 45 Ry and expansion of augmentation charges up to 220 Ry was sufficient to ensure this criterion. Integration in the Brillouin zone were determined by the Monkhorst-Pack\textsuperscript{34} procedure\textsuperscript{35}. Both atomic positions and cell vectors were fully optimized. NMR chemical shieldings were converged within less than 1 ppm.

The Born effective charge tensor $Z_{\kappa,\alpha\beta}$ is defined\textsuperscript{25} by the macroscopic polarization induced, in direction $\beta$ and under conditions of zero macroscopic electric field, by a zone center phonon displacing atomic sublattice $\kappa$ in direction $\alpha$. Effective charges were calculated within density functional perturbation theory (DFPT)\textsuperscript{36,37} and the values presented in the following sections correspond to their isotropic component obtained by $Z_{\kappa}^0 = Tr[Z_{\kappa,\alpha\beta}/3]$.

B. NMR chemical shifts and quadrupolar parameters

First principles GIPAW calculations\textsuperscript{20,21} yield the absolute chemical shielding tensors for each nucleus, $\delta(r)$. Isotropic chemical shieldings, $\sigma_{iso} = Tr[\delta/3]$, are compared to the experimental isotropic chemical shifts by using the standard expression: $\delta_{iso} = \sigma_{ref} - \sigma_{iso}$. In this work we choose corundum as reference such that $^{27}$Al shift of the $\alpha$ phase is aligned to the experimental one at 0 ppm.

The resulting \textit{ab initio} NMR spectra were obtained by using the QuadFit program\textsuperscript{38} with the theoretically calculated chemical shifts and quadrupolar interaction parameters, using the experimental magnetic field intensity, and normalizing each spectral component to reflect the relative number of aluminium types. A Lorentzian broadening was added to each spectral feature to obtain the best comparison with the experimental lineshape.

C. Structural models

Among the oxide phases with well characterized structures, we studied the final product $\alpha$ and the transitional aluminas $\beta$ and $\kappa$.

The structural model for $\alpha$-alumina, used as a reference for all simulated NMR spectra in this work, was published by Ishizawa et al.\textsuperscript{39} in an XRD study. The structure was reported as a corundum-type, with an hexagonal crystal system and $P6_3$ space group. The crystallographic cell contains six $Al_2O_3$ units in which all aluminium sites are coordinated by six oxygens.

The $\beta$ phase is present along the $\gamma \rightarrow \alpha$ transition in different dehydration paths and its structure has been characterized by Zhou and Snyder\textsuperscript{3}, with a monoclinic crystal system and $C2/m$ space group. In that work the structure was refined from Rietveld analysis resulting in a crystallographic cell with four $Al_2O_3$ units, in which half of the aluminium atoms are octahedrally ($Al_{oct}$) and half are tetraedrally ($Al_{tet}$) coordinated.

The $\kappa$ phase is one of the intermediate products of the dehydration path from gibbsite to corundum. Olivier et al.\textsuperscript{40} describes the $\kappa$ phase with an orthorhombic system and $Pna2_1$ space group. The cell contains six $Al_2O_3$ units and 25% of the $Al^{3+}$ sites are tetrahedral, 50% octahedral and 25% in a very distorted octahedral.

We have also studied the NMR spectra of precursor phases gibbsite and boehmite. For gibbsite we started from the structure resolved by Saalfeld and Wedde in a single-crystal XRD study\textsuperscript{41}. The structure is monoclinic with $P2_1/n$ space group where the $Al^{3+}$ cations are octahedrally coordinated by 6 $OH^-$ groups forming double layers and occupy two thirds of the octahedral holes in alternate layers\textsuperscript{42}. The interlayer cohesion is granted by hydrogen bonds between these $OH^-$ groups.

In the also layered boehmite structure, described by Christensen et al.\textsuperscript{43}, each $Al^{3+}$ cation is octahedrally coordinated by 2 $OH^-$ groups and 4 intralayer $O^{2-}$ anions in an orthorhombic system with $Cmcm$ space group. As in the gibbsite structure, the boehmite double layers interact with each other via hydrogen bonds, which are exclusively interlayer. In this phase, hydrogen bonds are organized in chains along [001] direction and different bond networks are possible depending on the relative orientation of neighboring chains. In our calculations we considered all possible combinations compatible with a 2×2 supercell. The structure with the lowest energy was found to be the one where nearest neighbor chains are antiparallel. However energy differences among various combinations are found to be less than 1 mRy/cell which is consistent with the experimentally observed disorder.
in this phase. As one of the aims of this work is to contribute to the characterization of γ-alumina phase, four different γ-alumina structural models from published theoretical works have been studied.

The first γ-phase model, γ-Al₂O₃(A), considered here was proposed by Gutierrez et al. This model, also called defect spinel or spinel-like structure, consists of a cell with 8 Al₂O₃ units, in which 37.5% of the cations are Al₃tet and 62.5% are Al₃oct. Among the 24 O atoms, 12 are four-fold coordinated (O₄-fold) and 12 are three-fold coordinated (O₃-fold) to aluminium atoms. It is important to note that in this model only spinel sites are occupied by the Al³⁺ cations.

The next γ-phase model, γ-Al₂O₃(B), used in this work was published by Digne et al. and proposed by Krokidis et al. The model has 8 Al₂O₃ units in the cell, 25% of all aluminium atoms are Al₃tet sites, in a sublattice of O²⁻ anions. The crystal system is monoclinic, but very close to an orthorhombic one with the Pn/m space group. In this model cations occupy also non-spinel sites.

Two other γ-phase models were published by Paglia et al. and proposed by Krokidis et al. The unit cells of these models contain a large number of atoms, 32 Al₂O₃ units, and were generated from an extensive search on all structural possibilities of the γ-Al₂O₃ structures using Fd3m and I41/amd space groups. In the Fd3m model, γ-Al₂O₃(C), among the 64 Al³⁺ sites 22 are Al₃tet, 41 are Al₃oct and 1 is Al₅pen (five-coordinated), while in the I41/amd model, γ-Al₂O₃(D), there are 21 Al₃tet and 43 Al₃oct sites. In these two models, due to the breaking of the local symmetry by the variations in cation occupancies and related distortions in octahedral and tetrahedral sites, the symmetry is actually P1.

### III. RESULTS AND DISCUSSION

#### A. Structure optimization and approximations on exchange-correlation functional

Geometry optimization was performed for all phases, allowing both the atomic positions and cell vectors to relax keeping the group symmetry fixed. To investigate the effect of approximations on exchange-correlation functionals, each geometry optimization was repeated with PBE, rev-PBE, and the vdw-DF functionals as described in Sec. II A. All XC functionals considered overestimate the experimental volume, PBE by about 1.8% on average, rev-PBE by 4.2%. The use of van der Waals functional was found to have negligible effect, inducing a tiny further expansion, on all structures except for gibbsite (γ-Al(OH)₃) [see Table I] where a slight contraction was observed. The exception in the case of gibbsite can be understood considering its layered and open structure.

Since ab initio NMR calculations are very sensitive to structural details, we performed all NMR calculations at optimized positions for each XC functional. In spite of the discrepancy in calculated equilibrium volume, the average difference in σ_{000}, |C_Q| and η₂ between PBE and revPBE were calculated as 1.15 ppm, 0.14 MHz and 0.03, respectively. These values were found to have negligible effect on total spectra and, except for gibbsite, only the PBE spectra will be shown. The numerical values for the three XC functionals are reported in Table II.

#### B. NMR parameters and spectra for well characterized structures

In this section, we present a detailed comparison of our ab initio calculated chemical shifts and quadrupolar interaction parameters for all the well characterized structural phases mentioned in Sec. II C with experimental data, as well as with very recent theoretical results from the literature. All relevant data are shown in Table II.

#### 1. α and θ phases

Corundum, α-Al₂O₃, shows a single well defined NMR peak that we take as reference when comparing spectra for other structures.

For the θ phase, we compare our results with the ones reported in Ref. 19, where a mixture of α and θ phases were examined, and the NMR parameters (see Table II) for these two coexisting phases were extracted from the experimental spectrum by lineshape fitting.

The overall good agreement between experimental and theoretical spectra can be seen in Fig. 1, upper curves. The decomposition in individual contributions is also given. The main difference between experiment and theory is in the asymmetry parameter η₂ for the Al₃tet site. For this peak, it should be noted that a recent theoretical work has also reported a value similar to ours.
TABLE II. Comparison between chemical shifts and quadrupolar coupling parameters calculated in this work and experimental and theoretical data from the literature.

| Structure | $\delta_{iso}$ (ppm) | $C_Q$ (MHz) | $\eta_Q$ |
|-----------|----------------------|-------------|----------|
|           | previous this work   | previous this work | previous this work |
| $\alpha$-$\text{Al}_2\text{O}_3$ | | | |
| $\text{Al}_{\text{oct}}$ | 0.0 (1)$^a$ | 0.0$^b$ | 0.0 | 2.38$^a$ | 2.33$^b$ | 2.05/1.98/2.10 | 0.00$^a$ | 0$^b$ | 0.04/0.04/0.03 |
| $\theta$-$\text{Al}_2\text{O}_3$ | | | | |
| $\text{Al}_{\text{oct}}$ | -3.0 (1.0)$^a$ | -5.9$^b$ | -4.9/-4.8/-5.0 | 3.50 (0.30)$^a$ | 3.44$^b$ | 2.91/2.81/2.71 | 0.00 (0.10)$^a$ | 0.18$^b$ | 0.26/0.36/0.29 |
| $\text{Al}_{\text{tet}}$ | 66.5 (1.0)$^a$ | 62.3$^b$ | 62.6/60.2/61.1 | 6.40 (0.10)$^a$ | 6.34$^b$ | 5.63/5.53/5.37 | 0.65 (0.02)$^a$ | 0.42$^b$ | 0.43/0.37/0.42 |
| $\kappa$-$\text{Al}_2\text{O}_3$ | | | | |
| $\text{Al}_{\text{oct}}(1)$ | 0.0$^c$ | 0.3$^b$ | 2.0/2.3/2.0 | 0.50$^c$ | -9.98$^b$ | -9.53/-9.45/-9.41 | – | 0.33$^b$ | 0.29/0.29/0.28 |
| $\text{Al}_{\text{tet}}(3)$ | 68.5$^c$ | 60.7$^b$ | 62.6/60.2/61.2 | 0.76$^c$ | -5.3$^b$ | -4.83/-4.67/-4.49 | 0.3$^c$ | 0.33$^b$ | 0.33/0.31/0.32 |
| $\text{Al}_{\text{oct}}(4)$ | 5.0$^c$ | 4.4$^b$ | 3.8/3.6/3.5 | 0.85$^c$ | 4.51$^b$ | 4.99/-4.96/5.06 | – | 0.77$^b$ | 0.99/1.00/1.00 |
| $\gamma$-$\text{Al}(\text{OH})_3$ Gibbsite | | | | |
| $\text{Al}_{\text{oct}}(1)$ | -5.6$^d,g$ | 2.2$^c$ | 2.2/2.3/2.1$^b$ | 4.70$\pm0.20$$^d$ | 5.10$^b$ | -5.30/-4.74/-4.43 | 1.00$\pm0.05$$^d$ | 0.35$^c$ | 0.32/0.35/0.35 |
| $\text{Al}_{\text{oct}}(2)$ | 0.0$^d,g$ | 0.0$^c$ | 0.0$^b$ | 2.20$\pm0.20$$^d$ | 2.80$^b$ | 2.33/2.06/1.81 | 0.75$\pm0.05$$^d$ | 0.66$^c$ | 0.81/0.71/0.66 |
| $\gamma$-$\text{Al}(\text{OH})_3$ Boehmite | | | | |
| $\text{Al}_{\text{oct}}$ | -1.0$^d,g$ | – | -0.9/-0.5/-0.2$^h$ | 1.8 - 2.8$^d$ | – | 2.16/2.08/2.27 | 0.5 - 1.0$^d$ | – | 0.45/0.46/0.67 |

$^a$Ref. [19]; $^b$Ref. [23]; $^c$Ref. [40]; $^d$Ref. [44]; $^e$Ref. [51]. $^f$Aluminium sites are labeled according to Ref. [40] and the sites symmetry, see Table III. $^g$The experimental $\delta_{iso}(\text{Al}_{\text{oct}}(2)) = 11.5 \pm 0.2$ ppm from gibbsite is taken as reference. $^h$The calculated $\sigma_{iso}(\text{Al}_{\text{oct}}(2)) = 562.72$ ppm from gibbsite is taken as reference.

FIG. 1. (color on-line) Comparison between our theoretical results and the experimental $^{27}$Al MAS NMR spectra from Ref. [19] for a mixture of the $\alpha$ and $\theta$ alumina phases (upper curves). Decomposition of the theoretical spectrum in its individual components (lower curves).

TABLE III. Optimized Al–O distances for the $\kappa$-$\text{Al}_2\text{O}_3$ structure. Additionally, for the experimental$^{40}$ and the optimized structures, we present the average absolute deviation in the distances, $D_{\text{dist.}}$, and in the $O$–Al–$O$ angles, $D_{\text{ang.}}$, according to equations (1) and (2).

| $\text{Al}_{\text{oct}}(1)$ | $\text{Al}_{\text{tet}}(3)$ | $\text{Al}_{\text{oct}}(4)$ |
|-------------------------|-------------------------|-------------------------|
| Distances (Å)           |                         |                         |
| Th.                     | 1.962                   | 1.991                   | 1.797                   | 1.879                   |
| Exp.                    | 1.961                   | 2.269                   | 1.772                   | 1.959                   |
|                         | 1.936                   | 1.848                   | 1.756                   | 1.821                   |
|                         | 1.820                   | 1.829                   | 1.784                   | 2.026                   |
|                         | 1.917                   | 2.038                   | –                       | 1.838                   |
|                         | 1.968                   | 1.844                   | –                       | 2.215                   |
| $D_{\text{dist.}}$ (Å)  |                         |                         |                         |
| Th.                     | 0.039                   | 0.130                   | 0.013                   | 0.111                   |
| Exp.                    | 0.058                   | 0.171                   | 0.025                   | 0.105                   |
| $D_{\text{ang.}}$ (°)   |                         |                         |                         |
| Th.                     | 5.028                   | 8.392                   | 3.572                   | 7.305                   |
| Exp.                    | 5.150                   | 8.590                   | 5.081                   | 6.888                   |
assigned to the strongly distorted quadrupolar coupling. The high coupling component was lap of three distinct peaks: two with high, one with low shielding. As it can be seen, at low magnetic field intensity, Al(1) peak broadens considerably due to its high quadrupolar coupling constant, making it difficult to observe over the background in the experiment. This demonstrates that, even though experiments can provide accurate structural information, \textit{ab initio} NMR calculations might be essential for an unambiguous peak assignment.

3. \textit{gibbsite and boehmite phases}

The structures and NMR properties of gibbsite and boehmite are experimentally well characterized.\cite{44,51–53}

As can be seen in Fig. 3, the gibbsite NMR spectrum simulated with the theoretically determined parameters agrees very satisfactorily with the experimentally obtained spectrum by Hill \textit{et al.}\cite{18}. This structure is the only one for which we observed a noticeable dependence of the theoretical spectra on the exchange correlation functional used, showing improved results when using vdW-DF\textsuperscript{31} functional (see inset in Fig. 3). In Table II, we present a quantitative comparison between our calculated NMR parameters and the experimental results reported by Damodaran \textit{et al.}\cite{44}. Our results for $C_Q$ and $\eta_Q$ are in good agreement with both of these experiments and can accurately reproduce the asymmetry of the peak.

In agreement with the previous theoretical work by Vyalikh \textit{et al.}\cite{51}, in Fig. 3 we show that this resonance profile can be decomposed as the superposition of two distinct peaks with different second-order quadrupolar structure, belonging to two distinct $Al_{oct}$ sites in gibbsite.

As described in Ref. [51] the two sites differ in the OH groups surrounding them. This can be seen in Fig. 4 where a single Al(OH)$_3$ layer is drawn showing that among the six OH groups surrounding $Al_{oct}(1)$, two participate in interlayer hydrogen-bonds as donors while the remaining four are oriented in-plane and participate to interlayer hydrogen-bonds as acceptors. For $Al_{oct}(2)$ the
opposite occurs. We further characterize the two aluminium sites reporting, in Table IV, the $^{17}$O chemical shifts, the Born effective charges and the hydrogen-bond connectivity of the six oxygen types (labeled in Fig. 4) surrounding them. This analysis reveals that the two aluminium sites are mostly surrounded by the same types of oxygens and the distinction is based on just two different oxygen environments ($O_c$ and $O_d$), each one neighboring only one type of aluminium site.

![Graph](image)

**FIG. 3.** (color on-line) Comparison between the experimental $^{27}$Al MAS NMR spectra from Ref. [18] for gibbsite and the theoretical spectrum obtained with the vdW-DF functional. Decomposition of the spectrum in individual components is also given. The effect of different exchange and correlation functionals on the simulated spectrum is shown in the inset.

![Graph](image)

**FIG. 4.** (color on-line) View from direction (001) of a single Al(OH)$_3$ layer in gibbsite showing the arrangement of the different types of hydroxyl groups around the aluminium cations (large gray atoms). Oxygen (small red atoms) are labeled according to their different environments as referred in Table IV.

The oxyhydroxide polymorph boehmite, $\gamma$-AlO(OH), was detected by XRD in the experiment by Hill et al.\textsuperscript{18} in the temperature range from 200 to 400°C in a mixture with gibbsite or the transitional $\chi$ phase. A direct comparison between a simulated NMR spectrum for this phase with that experiment is therefore not possible. In the experiment by Damodaran et al.\textsuperscript{44} the lack of high resolution in the boehmite NMR spectrum is suggested to be due to the disorder in Al positions in the sample used, leading to small variations in the isotropic chemical shift and quadrupolar couplings. Nevertheless, it was possible to extract experimental estimates for $C_Q$ and $\eta_Q$, which are in good agreement with our calculated values, as presented in Table II.

**C. The $\gamma$-Al$_2$O$_3$ phase and its structural models**

As previously mentioned, $\gamma$-alumina structure is not yet well characterized in the literature and a vast discussion about this subject persists. Experimental NMR spectra of $\gamma$-alumina have been reported in a number of studies. In the work by O’Dell et al.\textsuperscript{19}, the samples obtained with calcination temperatures from 600°C to 1000°C are attributed to mixtures of cubic spinel transitional phases, as indicated by the presence of a tetrahedral peak around 60 ppm (taking the $\alpha$ phase as a reference). The fivefold-coordinated peak that has been observed in this phase has been attributed to inherent disorder\textsuperscript{19} or surface atom contributions\textsuperscript{54}. The MAS NMR study of Pecharromán et al.\textsuperscript{55} reported a small percentage of AlO$_5$ sites as well, along with an occupation of 76.3% and 21% for Al$_{oct}$ and Al$_{tet}$ sites, respectively. However, no evidence of a fivefold-coordinated Al peak is present in some other experiments, such as the one of Ref. [56], obtained from a hydrogenated boehmite precursor calcinated at 600°C for several hours and the one of Ref. [18], in which the sample was obtained from the calcination of gibbsite at 700°C through the formation of boehmite at 300°C.

To gain further insight on the structure of this phase, we have calculated the ab initio NMR parameters and obtained the simulated spectrum for each one of the four $\gamma$-alumina structural models that have been mentioned in Section II C. From the comparison of the calculated spectra with the experimental ones obtained for calcination conditions associated to $\gamma$-alumina, an evaluation of
the adequacy of these structural models will be possible. Since NMR is a sensitive probe of the local structural and chemical environment, comparisons based on NMR parameters will provide complementary constraints with respect to X-ray and neutron diffraction methods used, for instance, in the detailed structural search of Ref. [49].

In Fig. 5 we compare the theoretical spectra with the experimental data by O’Dell et al. [19] (left panel, 14.1 T), and by Hill et al. [18] (right panel, 9.4 T). We also compared with the 9.4 T spectrum by Pecharromán et al. [55] (not shown) which agrees very well with the one by Hill et al.

From Fig. 5, it is clear that the simulated MAS NMR spectra for the $\gamma$-$\text{Al}_2\text{O}_3$ (C) structural model proposed by Paglia et al. [49] best reproduces all the experimental results considered. The agreement is very satisfactory and even better for the more precise spectrum at the higher magnetic field [left panel of Fig. 5].

It may appear natural that the two models that display lesser agreement with the experimental spectra are the two (models A and B) whose unit cells only contain 8 $\text{Al}_2\text{O}_3$ formula units and a reduced number of non-equivalent aluminium environments, while model C contains a large number of $\text{Al}_2\text{O}_3$ formula units allowing a distribution of NMR parameters, which is more suitable for the representation of the broad features observed experimentally. Notice however that having a large number of non-equivalent aluminium environments may be considered a necessary, but not a sufficient condition to properly reproduce the experimental NMR spectra. In fact both Paglia’s structural models (C and D) contain 64 $\text{Al}_2\text{O}_3$ formula units and reproduce neutron diffraction data [49] equally well but only model C (the one associated to $F\overline{4}d$ symmetry) satisfactorily reproduces the spectral region of the tetrahedrally coordinated Al atoms and even for this model the sharpness of the octahedral-

![Figure 5](color on-line) Comparison of the theoretical spectra (dashed red lines) for the four $\gamma$-alumina models considered in this study and the experimental $^{27}$Al MAS NMR spectra (black solid lines) from Ref. [19] (left panel) and Ref. [18] (right panel). A Lorentzian broadening of 0.5 KHz was added to each component which were properly normalized to reflect relative site abundance.

| TABLE V. Average values and corresponding standard deviations for $^{27}$Al chemical shifts, absolute quadrupolar coupling, asymmetry parameter, and site occupation, decomposed according to Al coordination number, for the four $\gamma$-alumina models considered in this work. |
|-------------------------------|-----------------|-------------|-----|
| $\gamma$-$\text{Al}_2\text{O}_3$(A) | $\text{AlO}_6$ | -0.6±1.8 | 4.90±0.47 | 0.86 ± 0.12 | 62.5 |
|                                | $\text{AlO}_4$ | 52.1±3.0 | 6.36±2.65 | 0.14 ± 0.08 | 37.5 |
| $\gamma$-$\text{Al}_2\text{O}_3$(B) | $\text{AlO}_6$ | -0.7±4.9 | 7.98±3.25 | 0.41±0.23 | 75 |
|                                | $\text{AlO}_4$ | 52.0±0.1 | 4.51±0.91 | 0.47±0.35 | 25 |
| $\gamma$-$\text{Al}_2\text{O}_3$(C) | $\text{AlO}_6$ | -0.8±4.3 | 5.93±2.45 | 0.52±0.26 | 64.0 |
|                                | $\text{AlO}_5$ | 15.9 | 7.43 | 0.34 | 1.6 |
|                                | $\text{AlO}_4$ | 59.9±4.7 | 7.70±3.00 | 0.64±0.25 | 34.4 |
| $\gamma$-$\text{Al}_2\text{O}_3$(D) | $\text{AlO}_6$ | -0.1±4.2 | 6.25±2.38 | 0.57±0.23 | 67.2 |
|                                | $\text{AlO}_4$ | 52.7±6.5 | 8.27±2.92 | 0.58±0.27 | 32.8 |

Al peak is not completely satisfactory. Table V shows that, on average, model C gives a higher average value for $\delta_{iso}$ for the $\text{Al}_{tet}$ peak while the other models display rather similar values that underestimate the experiment.

Furthermore, in the $\gamma$-$\text{Al}_2\text{O}_3$ structural model C, a truly $\text{AlO}_5$ site is evident, and its calculated $\delta_{iso}$ of 15.9 ppm is easily separated from the peaks of octahedrally (-9.4 to 9.4 ppm) and tetraedrally (42.6 to 68.0 ppm) coordinated sites. Although the small occupation of this site in model C cannot reproduce the $\text{AlO}_5$ peak observed by some experiments, the $\delta_{iso}$ is in the experimentally measured range, implying that an increase in $\text{AlO}_5$ sites
due to defects and/or surface effects would explain the observed feature.

It should be noted that in the study by Pecharromán et al., the complex NMR spectrum in the γ-alumina region was analyzed as superposition of a small number of peaks for which the quadrupolar interaction parameters were estimated for tetrahedral ($Q_1 = 4.7 - 4.9$ MHz) and octahedral ($Q_2 = 3.6 - 3.9$ MHz) sites. These estimated values do not agree with the ones obtained for model C. Since model C shows very good agreement for the total spectrum, this implies that extracting NMR parameters from a complex spectrum, in absence of further experimental or theoretical characterization, is likely an unreliable procedure as it can result in widely different distributions of NMR parameters for the same spectrum.

### D. Correlation analysis

In the literature there have been several attempts to correlate features in NMR spectra with local structural details such as coordination numbers, local atomic bondlength and angular distortion, shortest bondlength, Mulliken charge population etc.

Our calculations confirm the dependence of chemical shifts on aluminum coordination numbers, such that 4-, 5- and 6-coordinated aluminum sites show chemical shifts in well separated ranges: the lower the coordination number the larger is the chemical shift.

However, the internal distribution within a given coordination number does not correlate with local geometric descriptors such as local bondlength, angular distortions, or shortest bondlength. To explain this we performed a simple test in the non-spinel model B for γ-alumina by displacing an oxygen atom while keeping the rest fixed and we observed that the NMR parameters were affected in a region extending up to the third coordination shell, thus demonstrating the sensitivity of NMR to non-local structural details.

The only properties that we found to display a significant correlation with the NMR shieldings were aluminum Bader charges and Born dynamical effective charges. For both charges the correlation is linear and structure independent as demonstrated by the linear fits obeyed equally well by all phases, as shown in Fig. 6.

It should be mentioned that Bader charges and Born effective charges correlate very strongly with each other so that no additional information can be gained by considering the two charges together. This is because γ-alumina is a crystal with a high degree of ionicity, where these two quantities are strongly related.

Furthemore, we can understand the correlation of NMR shieldings with Born effective charges because they both originate from local electronic susceptibility, one being determined from the current induced by the magnetic field, the other measuring the charge flow associated to vibrational motion.

As an historical curiosity, we mention that proposing a correlation between NMR chemical shifts and effective charges is not a complete novelty since in a couple of papers in the late seventies a correlation was reported to exist for binary semiconductors among Szegiti's effective charges and $^{27}$Al and $^{31}$P NMR chemical shifts.

### IV. CONCLUSIONS

We investigated from first principles the $^{27}$Al NMR properties of several well characterized crystalline phases of $Al_2O_3$ and of two of its calcination precursor phases, obtaining very good agreement with available experimental results. New insight for the peak assignments in the spectra were proposed for some structures.

This gave confidence in the theoretical approach and allowed us to address the open problem of the structural characterization of the technologically important γ-alumina phase by comparing the experimental spectra with the theoretical predictions calculated for four structural models recently appeared in the literature: our study supports the model structure with $Fd\bar{3}m$ symmetry proposed by Paglia et al. in Ref. [49] as the one that best reproduces the NMR experimental results in the bulk.

Calculations confirm that chemical shifts strongly depend on coordination number. Moreover, within a given coordination number, a linear correlation exists between chemical shifts and Born effective charges or Bader charges.

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FIG. 6. (color on-line) Correlations between chemical shifts and effective charges, $Z^*$, (above) or Bader charges (below). Left panels collect the data for all the structures considered in this work except the $\gamma$-alumina models C and D, that contain many different Al sites. For these models the data are reported separately in the right panels. Lines correspond to linear fit to $A_{\text{oct}}$ and $A_{\text{tet}}$ data for all the structures.

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The k-point meshes for each structure are as follows: Boehmite 3x1x3; Gibbsite 2x2x2; α-Al2O3 2x2x1; κ-Al2O3 3x2x2; θ-Al2O3 1x4x2; γ-Al2O3(A) 2x2x1; γ-Al2O3(B) 2x2x1; γ-Al2O3(C) 2x2x1; γ-Al2O3(D) 1x2x1. All meshes were shifted by half of the mesh interval in each direction.