Local structure and magnetism of La$_x$Eu$_{1-x}$PO$_4$ solid solutions

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By combining high spinning speed (60 kHz) and low-field (4.7 T) $^{31}$P solid-state NMR with magnetic susceptibility measurements, we experimentally characterized a series of solid solutions belonging to the La$_x$Eu$_{1-x}$PO$_4$ (0 $\leq x \leq 1$) series. Analyses of the magnetic susceptibility data were carried out using the free ion model and crystal field theory calculations allowing to extract the electronic structure. The paramagnetic shifts of the P sites having one Eu$^{3+}$ cation in their surrounding were predicted by combining the determined crystal field and energy level values with density functional theory (DFT) calculations. For the La$_0$Eu$_1$PO$_4$ sample, these theoretical shifts gave a very good overall trend allowing the unambiguous attribution of each P site. This study paves the way for the future analysis of both magnetic susceptibility and NMR data for a broad range of materials containing paramagnetic rare-earth cations.

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I. INTRODUCTION

Owing to their technological and fundamental interest [1,2], lanthanide orthophosphates with the monazite crystalline structure (Ln = La to Gd) have been extensively studied over the past decades. The La$_x$Eu$_{1-x}$PO$_4$ solid solutions represent an important class of these materials, being luminescent [3–5] and being considered as potential matrices for encapsulation of nuclear materials due to their high resistance to radiation damage [6,7]. For this latter purpose, Eu$^{3+}$ is, indeed, often used as a surrogate for Am$^{3+}$ to monitor the structural modifications resulting from ion substitutions, as the two cations have similar outer electronic configuration (n$f^6$, n = 4 for Eu$^{3+}$ and n = 5 for Am$^{3+}$) and ionic radii [8] (Eu$^{3+}$ = 0.947–1.12 Å and Am$^{3+}$ = 0.975–1.09 Å) [9–11]. Additionally, while a solid solution can generally be formed over the whole range of composition [12,13], in the focus are those with low rare-earth contents [1,4] as a high solubility in a LaPO$_4$ matrix does not occur for all lanthanide [14,15] or actinide [16–18] cations.

In order to have a better understanding of the local environment around the $^{31}$P atoms in these solid solutions, magic angle spinning (MAS) NMR has been proven as an efficient analytical tool. Indeed, several authors published data on related crystalline rare-earth orthophosphates, like the LnPO$_4$ series (Ln$^{3+}$ = La$^{3+}$ to Eu$^{3+}$ [19] and Ln$^{3+}$ = La$^{3+}$ to Yb$^{3+}$ [20]) and some of their solid solutions (Ln$^{3+}$ = Ce$^{3+}$, Nd$^{3+}$, and Gd$^{3+}$) [14,15,21]. It was shown that NMR allows to detect, in numerous types of materials, very low paramagnetic content in a unique manner [22]. However, a full attribution of the MAS-NMR signals is not straightforward because the paramagnetic cations cause additional contribution to the nuclear chemical shift [23]. Indeed, it is known that the experimental NMR shift ($\delta_{\text{exp}}$) is the sum of an orbital component ($\delta_{\text{oa}}$), a pseudocontact (PC) shift ($\delta_{\text{PC}}$) and a Fermi contact (FC) shift ($\delta_{\text{FC}}$) [24,25]. The determination of these paramagnetic shifts ($\delta_{\text{p}}$) is currently based on a combination of empirical calculations using the Bleaney’s theory for $\delta_{\text{PC}}$ [26,27] and the McConnell and Robertson approach and its recent improvements for $\delta_{\text{FC}}$ [28–34]. The theoretical prediction of paramagnetic shifts in the rare-earth series is intensively studied [24,35,36] especially for MRI contrast agents [37–44] and in metalloproteins [45–48]. However, these experiments are mostly performed using liquid-state NMR on organic molecules, usually containing conveniently one isolated paramagnetic cation. In inorganic materials, where several paramagnetic cations are present, the numerous unpaired electrons are difficult to handle in the calculations and therefore little has been achieved concerning the full prediction of the paramagnetic shifts [49,50].

Due to the difficulty encountered in predicting the paramagnetic shifts with the monazite crystallographic structure, it is often preferred to limit the discussions to the nature of the paramagnetic shifts through the full lanthanide series [14,15,50–52]. Thus, in their pioneering work, Palke and Stebbins attributed the nature of $\delta_{\text{p}}$ to arise from both FC and PC interactions in the La$_x$L$_n$$_{1-x}$PO$_4$ (Ln$^{3+}$ = Nd and Ce) series [14,15]. This assumption was indirectly deduced from the analysis of the xenotime analogues (containing Ln$^{3+}$ = Tb$^{3+}$ to Lu$^{3+}$) which possess a more symmetric environment around the Ln$^{3+}$ cation.

In the present study, we propose a combined experimental/theoretical approach to go further in the understanding of...
the NMR data in the monazite series by considering this time the series La$_x$Eu$_{1-x}$PO$_4$ (with 0 $\leq$ $x$ $\leq$ 1). To achieve this, we first probe the local environment using 31P high-resolution MAS-NMR and low magnetic field. As numerous peaks are overlapping in most MAS-NMR spectra, we focus our data analysis on the two samples La$_{0.9}$Eu$_{0.1}$PO$_4$ and La$_{0.5}$Eu$_{0.5}$PO$_4$ while a more general discussion is presented about the remaining samples. In the next step, we predict the PC paramagnetic shifts of the P atoms surrounded by one paramagnetic center (vide infra) in these two compounds using calculated energy levels (EL) and crystal field parameters (CFP) obtained by fitting the experimental magnetic susceptibility curves. Finally, we determine indirectly the FC paramagnetic shifts for La$_{0.9}$Eu$_{0.1}$PO$_4$ from EPR parameters obtained by DFT calculations using its Gd$^{3+}$ analogue.

II. METHODS

A. Synthesis

LaPO$_4$ and EuPO$_4$ as well as nine intermediate La$_x$Eu$_{1-x}$PO$_4$ compositions of the solid solution were prepared by sol-gel reaction, using a procedure modified from Geisler et al. [13]. In short, stoichiometric amounts of La$_2$O$_3$ (Alfa Aesar, 99.99%) and Eu$_2$O$_3$ (Merck, 99.99%) were dissolved in HNO$_3$ (Merck, 63%). An excess of H$_3$PO$_4$ (Merck, 85%) ((Eu$^{3+}$ + La$^{3+}$) : PO$_4^{3-}$ = 1 : 1.2) was added dropwise under continuous heating (343 K) and stirring; this initiated the precipitation of a white gel. After 1 h, a 25% NH$_4$OH solution (Merck) was added till achieving a pH = 5. The precipitates were separated from solution by centrifugation and subsequently washed several times with water. After drying in air, the powders were calcined for 5 h under air in alumina crucibles at 873, 1373, and 1873 K, with intermediate drying in air, the powders were calcined for 5 h under air in tumation and subsequently washed several times with water. After

B. NMR

The room temperature (334 K) 31P MAS NMR spectra were recorded at 60 kHz on a Bruker AVANCE III HD 4.7 T spectrometer at a 31P Larmor frequency of 81.02 MHz. One-pulse experiments were performed using a 90° pulse length of 1 $\mu$s. The longitudinal relaxation experiments were performed using a saturation-recovery pulse sequence. The variable temperature spectra were acquired at a spinning rate of 45 kHz. The temperature was calibrated with KBr using the linear law $T = -40\Delta\delta + T$ (\Delta$\delta$ being the shift variation and T the temperature) [53]. To be sure that KBr did not interact with the paramagnetic sample, a layer of Teflon film was added between the powders. All samples were referenced to H$_3$PO$_4$. The spectra were fitted using the DMFIT software [54].

C. Magnetic susceptibility

Measurements of the magnetic susceptibility ($\chi$$_{mol}$) were performed by using a magnetic property measurement system (MPMS – Quantum Design) in the temperature range 2 to 300 K in applied magnetic fields between 0.5 and 7 T. The powders were pressed into pellets and put in a sample holder. The data obtained were then all corrected for the paramagnetic signal of the sample holder.

D. X-ray photoelectron spectroscopy (XPS)

The powder was pressed into indium foil (5 × 5 mm) and mounted on a stainless-steel sample holder. It was kept under vacuum at room temperature for 3 days. High-resolution XPS measurements were performed using a Phoibos 100 hemispherical analyzer. The Al $K_{\alpha}$ ($E$ = 1486.6 eV) radiation was produced by an XRC-1000 microfocus source, equipped with a monochromator and operating at 120 W. The background pressure in the analysis chamber was 2 × 10$^{-10}$ mbar. The spectrometer was calibrated with the 4f$_{7/2}$ line of Au metal to give a value at 83.9 eV BE and the 2p$_{3/2}$ line of Cu metal at 932.7 eV BE for XPS. Photoemission spectra were recorded at room temperature.

E. Calculations of the crystal field parameters and the energy levels

For the determination of the CFP data, we have used the SIMPRE computational package [55] introducing the experimental atomic crystallographic coordinates and applying the two fitting parameters [radial displacement vector (D$_r$) and the effective point charge (Z$_e$)] of the radial effective charge (REC) model [56]. The electronic structure of La$_{0.9}$Eu$_{0.1}$PO$_4$ has been calculated using the full basis of microstates in the latest version of the CONDON program [57].

F. DFT calculation of the EPR parameters

We firstly relaxed the LaPO$_4$ crystalline structure using geometry optimizations of the atomic positions (APO) with the QUANTUM ESPRESSO (QE) package [58–60] in order to remove the strain (from a computational point of view) from the experimental structure and to partly correct for the experimental uncertainties. QE relies on a pseudopotential plane-wave expansion formalism of density functional theory (DFT). A 4 × 4 × 4 Monkhorst–Pack k-point grid and a kinetic energy cutoff of 100 Ry were used.

From the APO structure, we designed two cluster models of 54 (C1) and 77 (C2) atoms for the calculation of the EPR parameters shown in Fig. 4 and in Ref. [61]. The fixed cores of these clusters (12 and 47 atoms, respectively) correspond to the APO structure. The outer coordination sites are terminated by 21 and 15 OH groups, respectively. The geometrical parameters of the OH groups were relaxed by partial geometry optimizations using the GAUSSIAN 09 software [62]. The theoretical level of these calculations consisted of the B3LYP exchange-correlation functional in conjunction with the relativistic effective core potential of Hay and Wadt with the associated valence double-zeta basis set (LANL2DZ) for La and with the standard 6–31G** basis set for P, O, and H. The hyperfine tensors $a_{\chi}$ (with and without spin-orbit effects) and the electron g tensor, or the g-shift tensor $\Delta g$ ($\Delta g$ predominant part arises due to spin-orbit effects [63,64]), were determined using the ADF code [65,66]. A previous work showed that this software was efficient for such calculations in the lanthanide series [63]. In these calculations, the scalar (SF) and spin-orbit (SO) relativistic effects were accounted for by utilizing the zeroth-order regular approximation (ZORA) [67]. The SAOP exchange-correlation potential [68,69] was applied, in conjunction with an uncontracted set of Slater-type orbitals.
orbitals (STOs) of triple-zeta-plus-polarization quality (TZ2P-J) [70] containing extra tight (mainly 1s) functions for use in EPR hyperfine calculations. As recommended for systems with heavy elements, the Gaussian finite nucleus model [71] was applied. For the calculation of the matrix products, the MATHEMATICA software was used [72].

III. RESULTS

A. Crystalline structure

The LnPO₄ (Ln = La, Eu) and their solid solutions [13] crystallize in the monazite space group P21/n. This crystallographic structure is composed of chains of alternating PO₄ tetrahedra and Ln-O₉ polyhedra along the c axis. With regard to crystallography, there is one P site, one Ln site and four different O sites. At the Ln site, a C₃ (or C₁h) symmetry is formed as shown in Fig. 1 [73,74]. This symmetry is nonaxial and the symmetry operations are E and σₖ. Each Ln-O₉ polyhedron is surrounded in its first cation coordination shell by seven crystallographically distinct PO₄ (Fig. 1). The P-O-Ln distances (dPO₄) and angles are given in Table S1 [61]. While there is only one crystallographic P site in pure LnPO₄, we differentiate the seven P atoms as it will be necessary for the following NMR discussion on the solid solution.

By decreasing the cation size from La to Eu, the P-Ln distances decrease accordingly (cf. Table S1). The precise determination of the rP-Ln distances in the solid solution samples was not possible. This is usually done via neutron diffraction experiments, which are particularly challenging for Eu-based materials because of their high cross sections. Nonetheless, it can be noticed that P1 and P2 are closer to the Ln cation with rP-Ln < 3.3 Å, while P3 displays an intermediate distance of rP-Ln ~ 3.5 Å and P4 to P7 have relatively similar distances with average distances of rP-Ln = 3.784 Å and rP–Euₙ = 3.672 Å for LaPO₄ and EuPO₄, respectively (see Table S1).

FIG. 1. Example of the C₃ symmetry for the LaPO₄ crystalline structure represented by a 4.5-Å sphere with La as a central atom. The following color code is used: La atoms are in green, P atoms in orange, and O atoms in red. Here, the seven P sites have been differentiated to illustrate the discussion through the paper. In the insert is presented the local environment around the P atom.

B. 31P MAS NMR spectra

As a moderate magnetic field reduces the extent of the spinning sideband pattern and ultrafast MAS increases the spinning sideband separation (reduce their widths and increase coherence lifetimes) [75], the experiments were performed at 4.7 T at a spinning rate of 60 kHz. Moreover, as the frequency range can span around 50 kHz wide at this field, decreasing the spinning rate below 50 kHz or increasing the magnetic field would lead to the overlap between center peaks and spinning sidebands. The 31P MAS NMR spectra of LaPO₄, EuPO₄ and their solid solutions are shown in Fig. S1 [61]. All experimental NMR parameters such as δ(exp), the paramagnetic shift δp, (exp), the full width at half maximum, the relative intensities, and longitudinal relaxation times (T₁) are reported in Table I and Table S2 in Ref. [61]. All T₁ parameters were fitted using a single exponential time constant.

While the LaPO₄ and EuPO₄ spectra present a single peak at −4.5 ppm and 385.4 ppm, respectively (in agreement with the known unique crystallographic P site), the solid solutions spectra feature numerous peaks with pronounced overlapped and broadened features (Fig. S1). Thus we only fitted the spectra of La₀.₈Eu₀.₂PO₄ and La₀.₁Eu₀.₉PO₄ as shown in Fig. 2. For these two samples, only the quantitative spectrum of La₀.₁Eu₀.₉PO₄ presented remaining spinning sidebands, which have been included in the fit as shown in Fig. S2 [61]. The spectrum of La₀.₈Eu₀.₂PO₄ could be fitted using fifteen peaks as depicted in Fig. 2(a), and the one of La₀.₁Eu₀.₉PO₄ could be described by five peaks [Fig. 2(b)]. While an unambiguous fit cannot be obtained for all the spectra, it could be noticed that signals with similar δexp are clearly visible through the whole solid-solution composition range (Tables I and S1). For example, peaks 1 to 7 in La₀.₉Eu₀.₁PO₄ and La₀.₈Eu₀.₂PO₄ or peaks 1 to 5 in La₀.₁Eu₀.₉PO₄ and La₀.₂Eu₀.₈PO₄. Previous studies on solid solutions containing rare-earth elements have shown that finding similar NMR shifts is an evidence for the presence of a similar environment around the nucleus detected by NMR [50–52]. It should also be noted that the line broadening is more important for the Eu-rich solid solutions (Table I), as expected for solid solutions with higher paramagnetic cation content (structural local disorder and/or anisotropic bulk magnetic susceptibility effects) [14,15,21,49].

C. Magnetic susceptibility curves

Based on the NMR results, we decided to focus the magnetic susceptibility measurements on four specific samples to investigate a possible trend: LaPO₄, La₀.₉Eu₀.₁PO₄, La₀.₅Eu₀.₅PO₄, and La₀.₁Eu₀.₉PO₄ (Fig. S5 [61]). As the magnetic susceptibility of EuPO₄ has been previously measured...
### TABLE I. Summary of the NMR parameters extracted from the experimental spectra: the measured experimental shift ($\delta_{\text{exp}}$), experimental paramagnetic shift [$\delta_p(\text{exp})$], the full width at half maximum (FWHM), relative intensity (RI), and longitudinal relaxation time ($T_1$).

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Peak</th>
<th>$\delta_{\text{exp}}$ (ppm)</th>
<th>$\delta_p(\text{exp})$ (ppm)</th>
<th>FWHM (ppm)</th>
<th>RI (%)</th>
<th>$T_1(s)$ (±5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaPO$_4$</td>
<td>1</td>
<td>−4.5</td>
<td></td>
<td>2.5</td>
<td></td>
<td>1714</td>
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<tr>
<td>La$<em>{0.6}$Eu$</em>{0.1}$PO$_4$</td>
<td>1</td>
<td>220.1</td>
<td>225.2</td>
<td>13.5</td>
<td>4.9</td>
<td>0.296</td>
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<tr>
<td></td>
<td>2</td>
<td>121.4</td>
<td>126.5</td>
<td>15.9</td>
<td>5.9</td>
<td>0.523</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>42.0</td>
<td>47.1</td>
<td>10.1</td>
<td>5.3</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>16.5</td>
<td>21.6</td>
<td>11</td>
<td>6.1</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>−5.1</td>
<td></td>
<td>9.6</td>
<td>49.7</td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>−39.1</td>
<td>−34</td>
<td>10.6</td>
<td>9.9</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>−62.6</td>
<td>−57.5</td>
<td>12</td>
<td>5.6</td>
<td>2.9</td>
</tr>
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<td>8</td>
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<td>17.5</td>
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<td>12.8</td>
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<tr>
<td></td>
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<td></td>
<td>9.2</td>
<td>0.9</td>
<td></td>
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<tr>
<td></td>
<td>11</td>
<td>164.1</td>
<td></td>
<td>11.9</td>
<td></td>
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<tr>
<td></td>
<td>12</td>
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<td>21.6</td>
<td>1.8</td>
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<tr>
<td></td>
<td>15</td>
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<td>−15.4</td>
<td>15.4</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>EuPO$_4$</td>
<td>1</td>
<td>385.4</td>
<td></td>
<td>45.4</td>
<td></td>
<td>0.21</td>
</tr>
</tbody>
</table>

[76,77], the magnetic susceptibility curve acquired by Golbs et al. [77] was extracted and analyzed alongside the data we recorded for the other samples (Fig. S5). For LaPO$_4$, the experimental value of $\chi = -0.2 \times 10^{-3}$ emu mol$^{-1}$ obtained is, as expected, characteristic of its diamagnetic behavior. A small diamagnetic upturn is also present (Fig. S5). The magnetic susceptibility curve of EuPO$_4$ is characteristic of a pure Van Vleck (VV) behavior with low-temperature independent variation up to $\sim 100$ K (due to the diamagnetic $J = 0$ ground state of Eu$^{3+}$) [78], then it becomes temperature dependent. At higher temperatures, a Curie-Weiss like behavior is visible as observed in other Eu$^{3+}$-based material [78–80].

For a coherent approach, the magnetic susceptibilities of the solid solutions have also been normalized considering the Eu$^{3+}$ content ($\chi_{\text{mol}}(\mu_{\text{eff}})$ and $\chi_{\text{mol}}(\mu_{\text{eff}},\text{Eu}^{3+})$. The values are reported in Table II. Through the series, there is a decrease of $\mu_{\text{eff}}$ with decreasing Eu-content as expected from the diamagnetic character of LaPO$_4$. The $\mu_{\text{eff},\text{Eu}^{3+}}$ values are consistent with the value of 3.51 $\mu_B$ determined for a free Eu$^{3+}$ ion [81,82], while they are slightly decreasing with decreasing Eu$^{3+}$ content.

### IV. DISCUSSION

#### A. Analysis of the $^{31}$P MAS NMR data

1. The quantitative spectra

The spectra of the solid solutions with paramagnetic cations allow us to characterize the local structure around the NMR active spin-bearing nucleus in a unique manner [51]. Thus, in the ideal case of a randomly distributed network (RDN), depending on the composition of the solid solution, the NMR peaks can be assigned to $P(\text{La})_{7-m}(\text{Eu})_m(0 \leq m \leq 7)$ units (i.e., a P atom surrounded by “m” La atoms and “7-m” Eu atoms). Their relative intensities can be predicted thanks to the formula:

$$I_k = (p^k(1-p)^{n-k})(\frac{n!}{k!(n-k)!}),$$

(1)

for all compositions considering the magnetic susceptibility value at this temperature. This was done considering $\chi_{\text{mol}}(\mu_{\text{eff}})$ and $\chi_{\text{mol},\text{Eu}^{3+}}(\mu_{\text{eff},\text{Eu}^{3+}})$. The values are reported in Table II. Through the series, there is a decrease of $\mu_{\text{eff}}$ with decreasing Eu-content as expected from the diamagnetic character of LaPO$_4$. The $\mu_{\text{eff},\text{Eu}^{3+}}$ values are consistent with the value of 3.51 $\mu_B$ determined for a free Eu$^{3+}$ ion [81,82], while they are slightly decreasing with decreasing Eu$^{3+}$ content.
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where $p$ is the probability of $\text{Ln}^{3+}$ replacing an Eu-O$_9$ site, which is equal to the concentration of Eu$^{3+}$, $k = 7 - m$ is the number of Eu$^{3+}$ interacting with the $31\text{P}$ nucleus for the specific peak, $n$ is the total number of sites into which Eu$^{3+}$ can enter and cause a specific paramagnetically shifted peak (equal to 7 here for the seven distinct first-shell $31\text{P} - \text{Eu}^{3+}$ configurations). With this approach, we obtained the values displayed in Table S3 [61]. Thus, for example, the spectrum of $\text{La}_{0.9}\text{Eu}_{0.1}\text{PO}_4$ should have four signals corresponding to the $\text{P(La)}^7(\text{Eu})^0$, $\text{P(La)}^6(\text{Eu})^1$, $\text{P(La)}^5(\text{Eu})^2$, and $\text{P(La)}^4(\text{Eu})^3$ units with the relative intensities of 48%, 37%, 13%, and 2%, respectively. Similarly, for $\text{La}_{0.1}\text{Eu}_{0.9}\text{PO}_4$, four signals with the same relative intensities are also expected except that they should correspond to the $\text{P(La)}^0(\text{Eu})^7$, $\text{P(La)}^1(\text{Eu})^6$, $\text{P(La)}^2(\text{Eu})^5$, and $\text{P(La)}^3(\text{Eu})^4$ units respectively. By comparing the experimental data with the theoretical number of peaks and relative intensities, one can but notice the differences. Indeed, the experimental spectrum of $\text{La}_{0.9}\text{Eu}_{0.1}\text{PO}_4$ presents 15 peaks and the one of $\text{La}_{0.1}\text{Eu}_{0.9}\text{PO}_4$ five peaks with relative intensities different from the RDN values. A straightforward explanation to these differences can be deduced from the similar spectra previously recorded for the $\text{La}_x\text{Ce}_{1-x}\text{PO}_4$ monazite...
series (with x = 0.97, 0.9, 0.84, 0.68) [15]. Indeed, instead of having peaks with the relative intensities calculated with Eq. (1), the authors observed (of having peaks with the relative intensities calculated for the P(La)0(Eu)7 units with a relative intensity of 48% and spectrum. Thus, the observable signals should be: one peak (RDN) relative intensity of 2% is divided over 35 peaks. Units will most probably not be detected as the calculated relative intensities of 0.6%. Experimentally, some of these signals can be detected, but due to the low intensities, it will be difficult to analyze them further. Finally, the P(La)4(Eu)3 signals can be detected, but due to the low intensities, it will be made of one signal with a relative intensity of about 48%. This theoretical value is in good agreement with the relative intensity of 49.7% determined experimentally for peak 5. The main difference with the values obtained from Eq. (1) will be indeed observed for k ≠ 0 as it corresponds to the insertion of paramagnetic cations in the diamagnetic matrix. Thus, by considering now the P(La)7(Eu)0 units (k = 1), seven signals are expected with relative intensities of about 5.3% each. And it is exactly the relative intensities obtained for the experimental peaks 1–4, 6, and 7 (peak 6 being the overlapping of two components). Due to spatial invariance, 21 peaks for the P(La)5(Eu)2 units should appear on the spectrum, with relative intensities of 0.6%. Experimentally, some of these signals can be detected, but due to the low intensities, it will be difficult to analyze them further. Finally, the P(La)4(Eu)1 units will most probably not be detected as the calculated (RDN) relative intensity of 2% is divided over 35 peaks.

We also did a similar approach for the La0.10Eu0.90PO4 spectrum. Thus, the observable signals should be: one peak for the P(La)0(Eu)7 units with a relative intensity of 48% and seven peaks for the P(La)1(Eu)6 units of about 5.3% each. It is clear that part of the signal intensity corresponding to peak 1 [Fig. 2(b)] belongs to the P(La)5(Eu)2 units as it is the most intense (77%). Unfortunately, it is here less straightforward to attribute the seven signals to the P(La)1(Eu)6 units mostly because the peaks are broad and overlapping. With these results in mind, one can easily understand the increased complexity observed in the spectra of the other solid solutions.

### 2. MAS- NMR spectra of other rare-earth monazites

For the low Eu3+ content, our spectrum can be compared to the one previously published for other La0.995Ln0.005PO4 compounds (Ln = Ce [15] and Nd [14]). All the three spectra feature a similar unshifted peak with the highest relative intensity which can easily be attributed to the P(La)7(Eu)0 units. However, as expected, the peak positions of the seven P(La)7(Eu)0 units depend upon the nature of Ln3+ cation. Indeed, four peaks have positive frequencies for Eu3+ compared to the two ones for Ce3+ and to the three ones for Nd3+. The other peaks have negative shifts. A more detailed comparison between spectra from the same composition but with a different Ln3+ cation is not possible as the different peaks corresponding to these P(La)7(Eu)x units were not previously assigned. To our knowledge, for such a high content of paramagnetic cation, only the La0.25Nd0.75PO4 NMR spectrum has been published [20]. However, the authors did not achieve a sufficient spectral resolution due to the strong overlap between the main signal and the spinning sidebands.

### 3. Longitudinal relaxation times

A very long T1 is observed for LaPO4 (1714 s, see Table I) as expected for this diamagnetic compound [14]. Our value differs from the one of 600 s published previously [21,83], probably due to the presence of different small quantities of impurity. EuPO4 possesses a short T1 of 210 ms being close to that of the paramagnetic GdPO4 (460 ms) [21]. For La0.90Eu0.10PO4 (x = 0.1, 0.2, 0.8, 0.9), the T1 values were determined for peaks 1–7 (low Eu3+-content) and peaks 1–5 (high Eu3+-content), as these peaks could easily be differentiated and possess similar shifts (Fig. 2, Table I, and Table S3). Peak 5, attributed to the P(La)7(Eu)0 units, possesses accordingly the longest T1 compared to the other peaks, while being much shorter than the peak of neat LaPO4. This confirms the presence of Eu3+ in the outer coordination sphere of such P atoms. Peaks 1 and 2 display the shortest T1, a fact which also points toward a closer proximity to the paramagnetic cation as T1 is proportional to r6 according to the general equation [21,27,49,84,85]:

\[ \frac{1}{T_1} = \frac{2}{5} \left( \frac{1}{4\pi} \right)^2 \frac{\gamma_p^2 g_e^2 \mu_B^2}{r^6} (S_z)^2 \frac{3\tau_r}{1 + \omega_p^2 \tau_r^2} \]  

(2)

with \( \gamma_p \) being the phosphorus gyromagnetic ratio, \( g_e \) the electron g-factor, \( \mu_B \) the Bohr magneton, r the Eu-P distance, \( S_z \) the thermal average of the z component of the electron spin, \( \tau_r \) the electronic longitudinal relaxation time, and \( \omega_p \) the 31P Larmor frequency.

The shortest T1 values indicate that peaks 1 and 2 might be, at first sight, respectively assigned to P1 and P2 for the P(La)0(Eu)7 units, as they possess the shortest Eu-P distance (Table S1). For x = 0.8, in a similar approach, the peaks at \( \delta_{exp} \sim -5, 220, \) and 121 ppm might be attributed to P(La)7(Eu)0, and to P1 and P2 of P(La)0(Eu)1, respectively. We want to underline that this statement is made as a first approximation, as peak attribution solely based on T1 is not always true [24]. For the two highest Eu3+-content samples (x = 0.1 and 0.2), all peaks possess relatively similar and
short $T_1$ values, precluding an assignment from considerations on distances alone.

For the other compositions, as it was not straightforward to fit all peaks, the spectra were divided into three regions of $\delta_{\text{exp}}$, the shifts ranges and $T_1$ values being specified in Table S2. R1 corresponds to species with shifts close to pure EuPO$_4$, R2 to species with $\delta_{\text{exp}}$ in between pure EuPO$_4$ and LaPO$_4$ and R3 to species with shifts close to pure LaPO$_4$. $T_1$ is the shortest for the peaks belonging to R1 and R2 peaks have intermediate $T_1$ values and R3 the longest $T_1$ values. There is a slight $T_1$ increase with increasing La content as observed for La$_n$Nd$_1-x$PO$_4$ [21,22].

4. Temperature effects compared with La$_{0.99}$Nd$_{0.01}$PO$_4$

As previously done by Palke and Stebbins [14] for a lanthanum-neodymium orthophosphate with very low Nd$^{3+}$ content, we also performed variable temperature experiments on the lowest Eu$^{3+}$-doped sample as it presents the best spectral resolution (Fig. S3 [61]). The peaks corresponding to the seven P sites surrounded by one Eu$^{3+}$ and six La$^{3+}$ cations gave the best resolution and are therefore the ones discussed here. Peaks 1, 2, 3, 6, and 7 have their positions affected by temperature. The range of paramagnetic shifts in the present study is much broader than the one observed for La$_n$Nd$_1-x$PO$_4$ as the measurements were performed on one Eu$^{3+}$ and six La$^{3+}$ cations. The peaks 1 and 2 have the most important temperature variations similarly to peaks A and B in the La$_{0.99}$Nd$_{0.01}$PO$_4$ spectrum (Fig. S4). Signals with positive paramagnetic shifts will move upfield while those with negative paramagnetic shifts will move downfield with increasing temperature. We do not believe that these similarities are random and it might thus be possible that peaks A and B in the La$_{0.99}$Nd$_{0.01}$PO$_4$ spectrum correspond to the P1 and P2 sites, respectively. However, our suggestion is only speculative because no $T_1$ measurements were shown by Palke and Stebbins [14]. On the other hand, Maron et al. [21] published $T_1$ measurements on a La$_{0.99}$Nd$_{0.01}$PO$_4$ sample, but they only provided an average value over all peaks.

B. Prediction of the $^{31}$P paramagnetic shifts

1. Pseudocontact and contact shifts

The formula for the experimental NMR shifts of a paramagnetic compound caused by a rare-earth center is [37,39,49]

$$
\delta_{\text{exp}} = \delta_{\text{dia}} + \delta_{\text{PC}} + \delta_{\text{FC}}
$$

The anisotropic part of the shift by Eu$^{3+}$ has been analyzed by Bleaney separately from the other rare-earth cations due to its nonmagnetic ground state ($J = 0$). He considered that the PC is only due to the anisotropy in the magnetic susceptibility, that the ELs are nondegenerate (original Van Vleck theory) and the excited states ($J = 1, 2, 3$) have to be considered [26,86].

The formula applied to calculate the $\delta_{\text{PC}}$ directly has been derived from Bleaney’s theory and is currently the most used [24,27,37,39,87]:

$$
\delta_{\text{PC}} = C_J B_0^3 \frac{3z^2 - r^2}{r^5} + \sqrt{6} C_J B_0^2 \frac{3x^2 - y^2}{r^5}
$$

with $C_J$ being a constant equal to 4 for Eu$^{3+}$ (relative to $-100$ ppm for Dy$^{3+}$) calculated by Golding and Pyykko [29] for LnCl$_3$ matrices with $B_0^2 = 274$ cm$^{-1}$ at 300 K [37,39]. $C_J$ includes the excited states and the temperature dependency and is commonly applied for the Ln$^{3+}$ series giving already successful results to calculate the $\delta_{\text{PC}}$ [37,39,85]. We will denote this approach as Golding and Pyykko approach (GPA) in the following discussion.

Another formula has been determined by Bleaney [26] in its original theory and allows, to calculate the PC shielidings. The following equation for the PC with temperature dependency is [26]

$$
\sigma_{\text{PC}} = L F'' \left[ \frac{1 - f(T) e^{-x}}{1 + 3 e^{-x}} \right].
$$

The $L$ constant is proportional to $r^{-3}$ ($r$ being the Eu-P radial distance) and to the $J = 1, 2, 3$ nondegenerate multiplets; $F''$ is a constant which depends on the radial angle $\theta$, the polar angle $\varphi$, and the crystal field parameters $B_0^2$ and $B_2^2$; $f(T)$ is a temperature dependent function which includes the nondegenerated excited levels; finally $x = E_1/k_B T$ (where $E_1$ is the energy of the first excited state $J = 1$ in $J$, $k_B$ is the Boltzmann constant in K$^{-1}$ and $T$ in K) is the classical Boltzmann distribution. All these terms are compiled in Table III. We will denote this approach as the Bleaney theory (BT) in the following discussion.

By comparing the two formulas to retrieve $\delta_{\text{PC}}$ and the $\sigma_{\text{PC}}$, one can notice that for the shielding calculations all the parameters can be set and the use of a pre-calculated $C_J$ constant—with CFP which might not correspond to our compound—is not necessary.

The isotropic part of the contact shift for a free ion has been calculated by some authors using the formula [23,30,37,39,88,89]:

$$
\delta_{\text{FC}} = \frac{A_{\text{iso}}}{\hbar} \frac{\mu_B}{3 \gamma_p k_B T} \times 10^6,
$$

where $A_{\text{iso}}/\hbar$ is the electron-nucleus transferred hyperfine coupling constant (in Hz, $A_{\text{iso}}$ in $J$ and $\hbar$ the inverse of the Planck constant in Js), $(S_z)$ is the reduced value of the average spin polarization (no unit), $\gamma_p$ is the gyromagnetic ratio of the observed nucleus $^{31}$P (Hz T$^{-1}$), $\mu_B$ (J T$^{-1}$ or $\text{A m}^2$), $k_B$ is the Boltzmann constant, and $T$ in K. However, more recent works [31–33] have shown that the $g$ factor is missing from Eq. (7) and the correct expression is the following:

$$
\delta_{\text{FC}} = \frac{\mu_B}{3 \gamma_p k_B T} \text{tr}[\sigma] \times 10^6,
$$

with $g$ the $g$-tensor and $\sigma$ is the hyperfine coupling tensor of the probe nucleus. The value of the $g$-tensor is obtained from $g = g_e + \Delta g$ with $g_e = 2.0023$ [63].

As the empirical formulas for both the PC and FC shifts include temperature dependence, the variation of peaks position with increasing temperatures can now be understood.
two oxidation states \([102–104]\), as it is a high-sensitive surface technique facilitating a detection down to one atomic percent.

Thus the La\(_{0}\) binary compounds (Eu-O, Eu-F) \([103]\). The received sample presented in Fig. S7 \([61]\). First the Eu-4\(_d\) line was considered. The 4\(_d\) photoemission lines of Eu \(2^+\) for several binary compounds (Eu-O, Eu-F) \([103]\). The received sample does not show any intensity that could be attributed to Eu \(2^+\). The peak at 132.2-eV BE, attributed to P-2\(p\), is separated by 3 eV from the Eu\(_{4d5/2}\) line. To completely exclude its possible assignment to Eu \(2^+\) (4\(_d\)-5/2), we exposed the surface to atomic oxygen at room temperature—which would oxidize surface Eu \(2^+\) to Eu \(3^+\). There was no spectral modification, which is consistent with the P-2\(p\) nature of this peak or the exclusive presence of Eu \(2^+\) in the sample. Finally, the Eu-3\(d\) spectrum shows the presence of the Eu \(3^+\)-3\(d\) peaks and the absence of Eu \(2^+\)-3\(d\) (which would also appear shifted to 9 eV lower BE than the Eu \(3^+\) peaks). The present analysis clearly excludes the Eu \(2^+\) cation as the cause of this low-temperature upturn on the magnetic susceptibility curves. It is worth mentioning that it is difficult to obtain neat Eu \(3^+\) and that as other rare-earth ions might be also present, they can be the cause of this low-temperature upturn. Another hypothesis to this low-temperature upturn, which is more important for the La\(_{0}\)PO\(_4\) sample, would be a slight effect of the diamagnetic contribution as observed for LaPO\(_4\).

### 2. Fitting with the free Eu \(3^+\) ion model

Due to its electronic configuration, Eu \(3^+\) possesses a diamagnetic ground state, and it is the mixing with the excited states which leads to the peculiar Van Vleck paramagnetism \([81,82,105,106]\). In the case of a free Eu \(3^+\) ion, all the energy levels are nondegenerate and the magnetic susceptibility can be fitted using a pure VV interaction following the equation \([78]\):

\[
\chi_{VV} = \left( N A \mu_B^2 \right) \left/ \left( 1 + 3 \exp \left( -\frac{\lambda}{T} \right) + 5 \exp \left( -\frac{3\lambda}{T} \right) + 7 \exp \left( -\frac{6\lambda}{T} \right) + 9 \exp \left( -\frac{10\lambda}{T} \right) + 11 \exp \left( -\frac{15\lambda}{T} \right) \right),
\]

\[
+ 13 \exp \left( -\frac{21\lambda}{T} \right) \right) \times \left( 24 + 13.5 \left( \frac{\lambda}{T} \right) - 1.5 \right) \exp \left( -\frac{\lambda}{T} \right) + 67.5 \left( \frac{\lambda}{T} \right) - 2.5 \right) \exp \left( -\frac{3\lambda}{T} \right) \right),
\]

\[
+ \left( 189 \left( \frac{\lambda}{T} \right) - 3.5 \right) \exp \left( -\frac{6\lambda}{T} \right) + \left( 405 \left( \frac{\lambda}{T} \right) - 4.5 \right) \exp \left( -\frac{10\lambda}{T} \right) + \left( 742.5 \left( \frac{\lambda}{T} \right) - 5.5 \right) \exp \left( -\frac{15\lambda}{T} \right) \right) + \left( 1228.5 \left( \frac{\lambda}{T} \right) - 6.5 \right) \exp \left( -\frac{21\lambda}{T} \right) \right)/((3\lambda k_B) 10^{-1}) \right). \tag{8}
\]

In this approach (called thereafter model 1), the only variable is the \(\lambda\) parameter which corresponds to the energy of the first excited state \((E_i)\). \(E_i\) is related to the other energy levels as shown in the diagram in Fig. S8 \([61]\). The best fit parameters of \(\lambda\) [Fig. 3(b)] are reported in Table II. The susceptibility curves were fitted limiting the space to the lowest three multiplets \((J = 0, 1, 2)\), since the inclusion of further excited states did not improve the quality significantly. Similarly, releasing the constraint between the energy levels \((E_1 = 3E_2 = 6E_3)\) did not improve the fits. While model 1 properly describes the low-temperature VV constant behavior important for setting the energy level values, it does not
reproduce the very low-temperature upturn previously discussed. Therefore the curves were also fitted using model 2 which includes the upturn in the fit by adding a scaled Curie-Weiss law to the Van Vleck paramagnetism formula (VVCW) using the following equation:

\[ \chi_{VVCW} = \frac{C}{T - \theta_p} + (1 - f_i) \chi_V \]  

(9)

with \( f_i \) being the percentage of paramagnetic impurities leading to a CW behavior, \( C \) the Curie-Weiss constant, and \( \theta_p \) the Weiss temperature. Some authors proceeded similarly to fit their curves [92]. There is now a better fit of the global magnetic susceptibility curves, especially for La\( _{0.9} \)Eu\( _{0.1} \)PO\( _4 \).

3. Theoretical calculations for the La\( _{0.9} \)Eu\( _{0.1} \)PO\( _4 \) sample

Using the following approach, denoted thereafter as Model 3, it was possible to determine both the energy levels and the CFP (\( B_{q}^{0} \), \( A_{q}^{j} \)). As such crystal field calculations are limited to a magnetic center completely isolated from other magnetic ions, we focused on the sample with the lowest Eu-content. The full set of CFP has been determined using the REC [56] model in the SIMPRE computational package [55]. As the energy level fitting in the SIMPRE code is limited to the ground \( J \) multiplet being \( J = 0 \) for Eu\( ^{3+} \), we took advantage of the spectroscopic energy levels reported for the isoostrucrual NdPO\( _4 \) derivative [107] \( J_{\text{Nd}^{3+}} = 9/2 \). This allowed us to obtain the REC parameters that model the crystal field effect of the phosphonate ligands (\( D_r = 0.749 \) Å and \( Z_i = 0.371 \)). Then, we applied them to the experimental coordinates of La\( _{0.9} \)Eu\( _{0.1} \)PO\( _4 \) in order to calculate the 27 CFP using the following expressions:

\[ A_{k}^{0} = \frac{4\pi}{2k + 1} \sum_{i=1}^{N} \frac{Z_i e^2}{R_i^{k+1}} Z_{40}(\theta_i, \varphi_i) p_{kq}, \]  

(10)

\[ A_{k}^{q} = \frac{4\pi}{2k + 1} \sum_{i=1}^{N} \frac{Z_i e^2}{R_i^{k+1}} Z_{q}(\theta_i, \varphi_i) p_{kq} \quad (q > 0), \]  

(11)

\[ A_{k}^{q} = \frac{4\pi}{2k + 1} \sum_{i=1}^{N} \frac{Z_i e^2}{R_i^{k+1}} Z_{q}(\theta_i, \varphi_i) p_{kq} \quad (q < 0), \]  

(12)

where \( R_i, \theta_i, \) and \( \varphi_i \) are the effective polar coordinates of the point charges; \( Z_i \) is the effective point charge, associated to the \( i \)th donor atom with the lanthanide at the origin; \( N \) is the number of ligands; \( e \) is the electron charge; \( p_{kq} \) are the prefactors of the spherical harmonics and \( Z_{kq} \) are the tesseral harmonics expressed in terms of the polar coordinates for the \( i \)th donor atom. The full set of EL and CFP are given in Tables S4 and S5 [61].

In order to obtain the energy levels and the magnetic susceptibility curve of the system, the calculated CFP were introduced into the CONDON package that uses the following full Hamiltonian:

\[
\hat{H}_{\text{Full}} = \hat{H}_{0} + \sum_{i=1}^{N} \left[ \frac{-\hbar^2}{2m_e} \nabla_i^2 + V(r_i) \right] + \sum_{i>j}^{N} \frac{\epsilon_{ij}}{r_{ij}} + \sum_{i>j}^{N} \left( \xi(r_{ij}) \mathbf{I}_i \cdot \mathbf{S}_j \right) - \mu_B (\mathbf{I} + g \mathbf{S}) \cdot \mathbf{B},
\]

(13)

where \( \hat{H}_0 \) represents the energy in the central field approximation (which is neglected), \( \hat{H}_{\text{ee}} \) the interelectronic repulsion, \( \hat{H}_{\text{CF}} \) the crystal field with \( C_{k}^{q} \) the spherical tensors, \( \hat{H}_{\text{sph}} \) the spin-orbit coupling, and \( \hat{H}_{\text{mag}} \) the Zeeman effect of an external magnetic field \( \mathbf{B} \). The calculated magnetic susceptibility is finally plotted with the experimental one in Fig. 3(c) showing how well such an approach is able to reproduce the experimental data. With model 3, the values of the degenerate EL (\( J \) up to 4) can now be determined, which was not possible with the free ion approach.

The \( B_{q}^{0} \) and \( B_{q}^{j} \), which are of interest for the \( \delta_{BC} \) calculations, are also compared with the experimentally determined ones for a LaPO\( _4 \) matrix doped with low Eu\( ^{3+} \)-content and the ones determined by Antic-Fidancev et al. [107] (see Table IV). The agreement is remarkable considering that the previous works assumed an axial \( C_{2v} \) symmetry around the Eu\( ^{3+} \) cation (this approximation often done for other rare earths [108,109]) while we used experimental coordinates.

**TABLE IV. Calculated crystal field parameters.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( B_{q}^{0} ) cm(^{-1} )</th>
<th>( B_{q}^{j} ) cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>La( _{0.9} )Eu( _{0.1} )PO( _4 ) (this work)</td>
<td>-623</td>
<td>71</td>
</tr>
<tr>
<td>1% - 5% Eu( ^{3+} ) LaPO( _4 ) (Antic-Fidancev [107])</td>
<td>-649 (23)</td>
<td>129 (13)</td>
</tr>
<tr>
<td>EuPO( _4 ) [110]</td>
<td>-707 (9)</td>
<td>-62 (4)</td>
</tr>
</tbody>
</table>
The $\lambda$ values (Table II) between models 1 and 2 are not very different ($\sim 30 \text{ cm}^{-1}$) meaning that both approaches are equivalent in describing the EL. While a better fit is obtained with Model 2, the physics behind the constants $C$ and $\theta_p$ can be questioned. Indeed, the meaning of the Curie constant, which is characteristic of the effective magnetic moment, gives incoherent values (Table II) in the way that, effective moments equal to 0.1 and 0.2 can be calculated for EuPO$_4$ and La$_{0.9}$Eu$_{0.1}$PO$_4$, respectively. These peculiar values exclude the presence of Eu$^{2+}$ cations as an impurity ($\mu_{\text{eff}} = 7.94 \mu_B$) and might be attributed to a mixing of several rare-earth paramagnetic cations. Also, the percentage of paramagnetic impurity leading to this upturn is very small (Table II). Overall, considering Model 1 or 2, there is an increase of the EL values with increasing La content. To compare this evolution with the one obtained theoretically, we have to suppose that the energy levels are also nondegenerate (average value of the three calculated $M_S$ levels for $J = 1$). Accordingly, for the low Eu$^{3+}$ content, $^{7}F_1 = 391.2 \text{ cm}^{-1}$ was determined. For EuPO$_4$, calculations of the EL were previously done [76] (Table S4) and a $^{7}F_1 = 371 \text{ cm}^{-1}$ was deduced. These higher theoretical values compared to those determined using the free ion approach are not surprising as the full Hamiltonian is now considered. Overall, there is always a decrease of the EL with increasing Eu$^{3+}$ content independently from the model used.

D. Calculations of the EPR parameters using cluster models

In these calculations, we modelled the Eu$^{3+}$ dilution in a diamagnetic matrix, i.e., the effect of a single Eu$^{3+}$ ion on the NMR shift of $^{31}$P. To predict the $\delta_{\text{FC}}$ [Eqs. (7) and (8)], we need $A_{\text{iso}}$ or $\text{tr}[ga_y]$. They can be determined by DFT calculations on an appropriate model structure containing one P atom surrounded by six La$^{3+}$ cations and one paramagnetic center. Unfortunately, due to its nonmagnetic ground state, the calculation of EPR parameters using DFT calculations for the Eu$^{3+}$ cation is not straightforward. However, a team of researchers [37–39] overcame this drawback by substituting this 4$f^6$ cation by Gd$^{3+}$ (4$f^7$). They multiplied the obtained $A_{\text{iso}}$ values by a factor of 0.34 and succeeded in predicting the paramagnetic shifts. Luckily in our case, the La$_x$Gd$_{1-x}$PO$_4$ [21,111] system still belongs to the monazite series and thus this approach can be used.

Hence, we relaxed the LaPO$_4$ crystalline structure using the QUANTUM ESPRESSO software (details in the Experimental Part). Then, the full structure was approximated by cluster models. Recent results [112,113] on 3d-element-based materials (Mn, Fe, Co, Ni) showed that the paramagnetic shifts were similarly well reproduced using the cluster model approach as by solid-state calculations. To render the local environment effects on the EPR parameters, we considered two cluster models presented in Fig. 4.

In the C1 model structure with the molecular formula of P$_1$La$_6$Gd$_1$O$_{25}$H$_{21}$ the P atom is in the center surrounded by four O atoms as the first coordination sphere. Seven Ln (Ln = La, Gd) atoms form the second coordination sphere. The fixed coordinates of these atoms correspond to the APO structure. The outer coordination sites of the Ln atoms (third coordination sphere) are terminated by relaxed OH groups. The cluster has a charge of $-3 \text{ e}$. In this model the surrounding of the central P atom corresponds to that in the crystal, therefore it is described very well. The description of the Ln atoms in the second coordination sphere, however, may somewhat suffer from the replacement of the crystal O atoms by relaxed OH groups. In order to account for the seven magnetically different environments; seven C1 clusters were implemented substituting each time a different La$^{3+}$ atom
TABLE V. Isotropic hyperfine coupling constants \( (A_{iso}/\hbar, \text{MHz}) \) and shifts due to the Fermi contact interaction \( (\delta_{PC}, \text{ppm}) \) calculated based on the \( P_1 \)La\(_0\)Gd\(_x\)O\(_{2x}\)H\(_y\) (C1) and Gd\(_x\)P\(_2\)La\(_{11}\)O\(_{20}\)H\(_{11}\) (C2) clusters. As suggested previously [37–39], the \( A_{iso}/\hbar \) values determined from the Gd\(^{3+}\) clusters were scaled by a factor of 0.34 in order to predict the ones expected for an Eu\(^{3+}\) cluster.

<table>
<thead>
<tr>
<th>P site</th>
<th>( A_{iso}/\hbar )</th>
<th>( \delta_{PC1} ) (C1)</th>
<th>( A_{iso}/\hbar )</th>
<th>( \delta_{PC2} ) (C2)</th>
<th>( \text{tr}[g_{av}] )</th>
<th>( \delta_{PC3} ) (C2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.177</td>
<td>73.4</td>
<td>0.166</td>
<td>69.1</td>
<td>0.599</td>
<td>248.8</td>
</tr>
<tr>
<td>P2</td>
<td>0.129</td>
<td>53.8</td>
<td>0.107</td>
<td>44.6</td>
<td>0.382</td>
<td>158.7</td>
</tr>
<tr>
<td>P3</td>
<td>0.061</td>
<td>25.3</td>
<td>0.043</td>
<td>18.0</td>
<td>0.173</td>
<td>71.9</td>
</tr>
<tr>
<td>P4</td>
<td>0.017</td>
<td>7.2</td>
<td>0.016</td>
<td>6.5</td>
<td>0.060</td>
<td>25.0</td>
</tr>
<tr>
<td>P5</td>
<td>−0.012</td>
<td>−4.97</td>
<td>−0.016</td>
<td>−6.7</td>
<td>−0.059</td>
<td>−24.5</td>
</tr>
<tr>
<td>P6</td>
<td>−0.015</td>
<td>−6.2</td>
<td>−0.003</td>
<td>−1.1</td>
<td>−0.001</td>
<td>−0.5</td>
</tr>
<tr>
<td>P7</td>
<td>−0.041</td>
<td>−16.9</td>
<td>−0.017</td>
<td>−7.1</td>
<td>−0.059</td>
<td>−24.7</td>
</tr>
</tbody>
</table>

by a Gd\(^{3+}\) atom. The calculated \( A_{iso}/\hbar \) values are given in Table V. For P1 and P2, possessing the highest \( A_{iso}/\hbar \) values, we tested the larger QZ4P-J basis set in order to see how it influences this parameter. Very similar values of 0.170 and 0.123 MHz, respectively, were obtained. This shows that, in the present case, the TZ2P-J basis set is good enough for this parameter.

To better describe the local environment around the Gd atom, we implemented the cluster C2 model with the molecular formula of Gd\(_x\)P\(_2\)La\(_{11}\)O\(_{20}\)H\(_{11}\). It contains a Gd\(^{3+}\) atom in the center surrounded by seven PO\(_4\) groups as the first coordination sphere. The second coordination sphere consists of eleven La atoms. The fixed coordinates of these atoms correspond to the APO structure. The outer coordination sites of the La atoms are terminated by relaxed OH groups. The cluster has a charge of 0 e. In this model, the surrounding of the central Gd atom corresponds to that in the crystal, therefore it is described very well. The description of the P atoms in the second coordination sphere should be also very good, because they are surrounded with O atoms and at a further distance by the closest La atoms, exactly as in the crystal structure. On the other hand, the description of the outer La atoms may somewhat suffer from the replacement of the crystal O atoms by relaxed OH groups. Due to the better description of Gd and the P atoms, the C2 model should be superior to C1. Using this C2 model, the \( A_{iso}/\hbar \) values of the seven P sites could conveniently be obtained in one calculation (Table V). One can observe that the two sets of \( A_{iso}/\hbar \) values from the C1 and C2 model structures are quite similar except for P6 and P7.

In addition, using the C2 model, we calculated also the \( a_N \) and \( g \) tensors and from them evaluated the \( g \)-factor by matrix operations. The obtained value of 1.236 is much lower than the experimental \( g \)-factor of 1.995 [111]. We therefore do expect that this approach will lead to important uncertainties.

E. Nature and prediction of the \( ^{31}\text{P} \) paramagnetic shifts

1. The LnPO\(_4\) series (Ln = La, Ce, Pr, Nd, Sm, and Eu)

In order to understand the origin of the paramagnetic shift in EuPO\(_4\), we considered the \( ^{31}\text{P} \) \( \delta_{exp} \) for the given series as was previously done for other crystalline phases [20,50,52]. Thus the \( \delta_{exp} \) data recorded at 31.25 kHz by Bregiroux et al. [19] were plotted against the average electron spin polarization \( \langle S_z \rangle \) determined by Golding and Halton [30] in Fig. 5. A good linear correlation is observed through the series suggesting a constant \( A_{iso} \) in contrast to previous results [20]. As the \( \delta_{exp} \) data were determined from static conditions [20], this difference might be linked with higher uncertainties on the NMR shifts in such conditions. This linear relation also shows that the Fermi contact interaction is the dominant one. Furthermore, by plotting the \( \delta_{exp} \) against the \( C_j \) parameters calculated by Golding and Pyykkö [29], we can attribute the variation of the paramagnetic shifts to the PC interaction. Here, as shown in Fig. S9 [61], we did not obtain a linear correlation, excluding any significant role of this interaction in the variation of the shifts.

2. \( \text{La}_{0.1}\text{Eu}_{0.9}\text{PO}_4 \)

The \( \delta_{PC1} \) and \( \sigma_{PC1} \) data were calculated for this rich Eu\(^{3+}\)-doped solid solution using the CFP previously determined in pure EuPO\(_4\) [110] and the energy levels published by Bronova et al. [76]. The atomic coordinates required for the calculations [Eq. (5), Eq. (6), and Table III] are those from EuPO\(_4\). The calculated values are presented in Table VI. As expected, the \( \sigma_{PC1} \) and the \( \delta_{PC1} \) values possess opposite signs. As the same interaction acts for the shielding and the shift, we considered that a linear relation exists between these two parameters following the equation \( \delta_{PC2} = a\sigma_{PC1} \) (with \( a \) as the scaling factor). This rescaling was previously applied by Bleaney et al. [86] and gave good results. The two approaches provided similar pseudocontact shift values (\( \delta_{PC1} \) and \( \delta_{PC2} \), cf. Table VI). It is interesting to notice that the \( \delta_{PC} \) values (with similar signs) determined for the different P sites have very close values. This might be a good explanation for the fewer signals (due to overlapping) in this rich Eu\(^{3+}\)-doped sample. However, these empirically calculated shifts are very different from the experimental \( \delta_{exp} \) ones. It is clear that, for this sample, the PC interaction is not the only one responsible for
on the Golding and Pyykkö approach, then to calculate the pseudocontact shift based on Bleaney’s theory (BT) or Golding and Pyykkö approach (GPA) were used for their prediction. Like values (Table VI) and three others have opposite signs. By comparing the experimental peaks with relative intensities obtained for P6 and P7, the δ(exp) shifts. Unfortunately, it was not possible to predict the FC interaction by determining the Aiso values, we subtracted the diamagnetic contribution from the experimental shifts and that FC, which is the dominant interaction in EuPO₄, contributes probably in a substantial degree. This may also be the source of the different behavior: the calculated δPC values change sign for some P sites while all the experimental peaks with relative intensities ≥4% have positive δ(exp) shifts. Unfortunately, it was not possible to predict the FC interaction by determining the Aiso using an appropriate model structure for La₀₉Eu₀₉PO₄, as our DFT calculations failed for structures containing more than one Ln with unpaired electrons.

### 3. La₀₉Eu₀₉PO₄

Based on Eqs. (5)–(8), we attempted to attribute the different signals of the P(La)₆(Eu)₁ units by calculating theoretically the paramagnetic shifts and comparing them with the experimental paramagnetic shifts, δp (exp). In order to obtain δp (exp), we subtracted the diamagnetic contribution (δdia, the shift corresponding to the P(La)₇ units, i.e., the unshifted peak at −4.5 ppm) from the experimental shifts, δexp, following the equation δp(exp) = δexp − δdia [14,37,39,44,114] (Table I). Then, to calculate empirically the pseudocontact shift based on the Golding and Pyykkö approach, δPC1 [Eq. (5)], and the paramagnetic shielding based on Bleaney’s theory, σPC2 [Eq. (6)], we used the theoretical CFP and EL values evaluated in the present study (PS) and compared the results with those previously published by Antic-Fidancev (AF) et al. [107]. Like δp(exp), four P sites have positive calculated δPC1/σPC2 values (Table VI) and three others have opposite signs. By comparing δPC2 determined using the two sets of CFP and EL (Table VI, Fig. S10(a) [61]), one can notice a difference of ~20%–25% (in relative intensity) for P1, P2, P3, P4, and P6; while for the σPC2 this difference is less significant reaching max. ~11% for P6. As previously described, the σPC2 data have been rescaled based on δPC3 (similarly to reference 83) to obtain the δPC4 values. Very close scaling factors of ~6.04 and ~5.85 were determined using the CFP and EL data from the PS and AF works, respectively. As the pseudocontact shifts determined with the CFP and EL from the present study give more coherent results, we will focus our discussion on these values. Both approaches (i.e., BT and GPA), give differences up to ~17%, the minimum differences obtained for P5 (2%) and P7 (~3%) [Fig. S10(b)].

As the FC interaction is missing from these calculations, the theoretical FC shifts, δFC, were separately calculated taking advantage of the “dilution” of a paramagnetic cation in a diamagnetic matrix. To do so, the reduced value of the average energy level of the J states. Also, similarly to Pinkerton et al. [115], we set g the Landé g factor to 4.4, the γ orbital reduction factor to 1, while the k Boltzmann constant is equal to 0.695 cm⁻¹/K. A (S₁) value of 10.56 has been determined at 334 K (the temperature corresponding to the experimental conditions). This value is really close to the S₁ = 10.68 value, determined previously by Golding and Pyykkö [29].

Using the two sets of Aiso values and the tr[gaₙ] product obtained in our cluster model calculations (vide supra), three sets of paramagnetic shifts due to the Fermi Contact interaction were determined (Table V). By comparing δPC determined using Cluster 1 (δPC1) to those from Cluster 2 (δPC2), large differences were obtained for P6 (~82%) and P7 (~58%), originating from the largely different Aiso values. It is also noteworthy that, both Fermi contact shifts are of highest importance for P1 and P2, which possess the shortest distances to the paramagnetic center. This observation seems to confirm the previous statement based on T₁. As expected, δPC1 present different and larger values of shifts than both δPC1 and δPC2.

Finally, in Table VII, the theoretical paramagnetic shift values are shown as determined by summing the pseudocontact shifts (δPC3 and δPC4 in Table VI) with the Fermi contact shifts (δFC1, δFC2, and δFC3 in Table V). The experimental and theoretical paramagnetic shifts are compared in Fig. 6. We first compare δp1 with δp2, δp3 with δp4 and, δp5 with

<table>
<thead>
<tr>
<th>La₀₉Eu₀₉PO₄</th>
<th>δPC1, GPA</th>
<th>σPC1, BT</th>
<th>δPC2, BT</th>
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<td>45.3</td>
<td>-309.3</td>
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<td>253.8</td>
<td>-45.7</td>
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<td>295.7</td>
<td>-53.3</td>
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<td>44</td>
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</table>

<table>
<thead>
<tr>
<th>La₀₉Eu₀₉PO₄</th>
<th>δPC1, GPA</th>
<th>σPC1, BT</th>
<th>δPC2, BT</th>
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<td>48.1</td>
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<td>70.8</td>
<td>84.1</td>
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<td>-12.6</td>
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<td>91.2</td>
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<td>-77.8</td>
<td>442.5</td>
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<tr>
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<td>50.6</td>
<td>66.0</td>
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<tr>
<td>P7</td>
<td>-27.4</td>
<td>-26.8</td>
<td>170.8</td>
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As the FC interaction is missing from these calculations, the theoretical FC shifts, δFC, were separately calculated taking advantage of the “dilution” of a paramagnetic cation in a diamagnetic matrix. To do so, the reduced value of the average spin polarization parameter (S₁) needs to be determined, as expressed by Eqs. (7) and (8). Then, assuming a Boltzmann distribution, this parameter can be obtained using the following equation [115]:

\[
\langle S_i \rangle = \frac{\sum_j \langle S_i \rangle J(J+1)}{\sum_j J(J+1)} \exp \left[ -E_J/J(1+2kT) \right] \tag{14}
\]

with E_J being the energy level of the J states. Also, similarly to Pinkerton et al. [115], we set g the Landé g factor to 4.4, the γ orbital reduction factor to 1, while the k Boltzmann constant is equal to 0.695 cm⁻¹/K. A (S₁) value of 10.56 has been determined at 334 K (the temperature corresponding to the experimental conditions). This value is really close to the S₁ = 10.68 value, determined previously by Golding and Pyykkö [29].

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δ_pσ (Fig. S11(a) [61]) to render the effect of replacing δ_PC3 with δ_FC3. For most P sites, there are only small differences (up to ~20%) between the two paramagnetic shifts except for P4 (up to ~40%) probably because for this site there is a small theoretical paramagnetic shift value. Next, by fixing the PC shifts and changing the FC approach based on Eq. (7), one can note that the type of cluster model influences the paramagnetic shifts only moderately with differences up to ~30% for P7 [Fig. S11(b)]. Also, independent from the type of cluster model used, the theoretical paramagnetic shifts values (considering δ_FC1 and δ_FC2) are underestimated with respect to the experimental ones for P1, P2, and P4, while they are overestimated for the other P sites. At last, by using Eq. (8) to calculate δ_FC3 (Fig. 6), there is an overall overestimation with respect to the experimental paramagnetic shifts values. This observation is not surprising, as the g-tensor might not be very well predicted underlining the rough approximation character of substituting Eu^{3+} to Gd^{3+}. Yet, there is a similar trend in the shifts based on the experiment and the two other theoretical approaches. This implies that it may still be a helpful approach for helping in the assignment of the different sites in a solid sample based on the overall trend.

Thus, we note that compared to the most recent works on calculated paramagnetic shifts for solid-state materials (mostly on 3d metals) using state-of-the-art DFT methods [112,113], the agreement between the present experimental and theoretical shifts is still very good. Moreover, whatever methods used, we obtained a clear trend allowing us to assign the NMR peaks unambiguously. Considering the numerous approximations needed because of the specific ground state of Eu^{3+} (namely, using Nd^{3+} to calculate CFP and EL, the cluster models and Gd^{3+} substituted to Eu^{3+}), it is quite encouraging to observe such trends and to achieve the distinction and attribution of each P(La)_{6}(Eu)_{1} unit.

### V. CONCLUSION

We have recorded $^{31}$P MAS NMR spectra and magnetic susceptibility curves for a series of La$_x$Eu$_{1-x}$PO$_4$ solid solutions. The spectra of the Eu-containing samples are complex due to the paramagnetic character of Eu$^{3+}$: instead of a single peak expected from the unique crystallographic P site, several signals attributed to magnetically inequivalent P sites were detected. For the spectrum of La$_{0.9}$Eu$_{0.1}$PO$_4$, for example, we identified (i) one peak belonging to the P(La)$_7$ units, (ii) seven peaks with equivalent intensities for the P(La)$_5$(Eu)$_1$ units, and (iii) remaining intensities corresponding to the twenty one peaks belonging to the P(La)$_5$(Eu)$_2$ units.

We measured the $T_1$ relaxation time over the whole range of composition. The obtained faster longitudinal relaxation upon increase of the paramagnetic cation concentration facilitated the attribution of peaks 1 and 2 to the P1 and P2 sites, respectively, in the La$_{0.9}$Eu$_{0.1}$PO$_4$ and La$_{0.8}$Eu$_{0.2}$PO$_4$ spectra.

We were also able to better understand the magnetic properties by recording magnetic susceptibility curves for LaPO$_4$, La$_{0.9}$Eu$_{0.1}$PO$_4$, La$_{0.5}$Eu$_{0.3}$PO$_4$, and La$_{0.1}$Eu$_{0.9}$PO$_4$ and comparing them to the one previously published for EuPO$_4$. We observed the Van Vleck behavior for all the composition having paramagnetic Eu$^{3+}$ cations. LaPO$_4$ displays a diamagnetic behavior. By fitting empirically the $\chi_{mol}$Eu$^{3+}$ using the free ion model, we extracted the nondegenerate energy levels. Furthermore, for La$_{0.9}$Eu$_{0.1}$PO$_4$, it was possible to fit theoretically the curve and predict the energy levels and crystal field parameters. Overall, there was a decrease of the EL values with increasing La$^{3+}$ content.

The so-obtained energy levels and CFP allowed us to predict the pseudocontact shifts for both La$_{0.1}$Eu$_{0.9}$PO$_4$ and La$_{0.9}$Eu$_{0.1}$PO$_4$ using the BT and GPA methods for the P(La)$_5$(Eu)$_1$ units. We found that the use of the $C_j$ constant gave δ_PC more dependents on the energy levels and crystal field parameters. These calculations confirmed that

<table>
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<th>P site</th>
<th>δ_p1 = δ_FC1 + δ_PC1</th>
<th>δ_p2 = δ_FC1 + δ_PC2</th>
<th>δ_p3 = δ_FC2 + δ_PC3</th>
<th>δ_p4 = δ_FC2 + δ_PC4</th>
<th>δ_p5 = δ_FC3 + δ_PC3</th>
<th>δ_p6 = δ_FC3 + δ_PC4</th>
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<tbody>
<tr>
<td>P1</td>
<td>136.7</td>
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<td>92.7</td>
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<td>P6</td>
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<td>49.4</td>
<td>43.1</td>
<td>50.0</td>
</tr>
<tr>
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</table>
this interaction plays an important role in the shifts, but the FC interaction has also to be considered. The Fermi contact shifts for a P atom surrounded by one paramagnetic cation were evaluated from theoretical EPR parameters obtained by DFT calculations. The diamagnetic electronic ground state of Eu$^{3+}$ was circumvented substituting Eu$^{3+}$ by the Gd$^{3+}$ ion. Nonetheless, as expected, some differences have been observed between experimental and theoretical shifts due to these approximations. Thanks to a similar trend in the shifts, it has yet been possible to assign each signal of the P(La)$_{6}$(Eu)$_{1}$ units, and on its basis to achieve the interpretation of the La$_{0.9}$Eu$_{0.1}$PO$_{4}$ spectrum.

As these crystalline phases are also considered as matrices for radioactive materials, we plan to use the same approach on similar matrices doped with actinide cations.

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software package to calculate crystal field parameters, energy levels, and magnetic properties on mononuclear lanthanoid complexes based on charge distributions, J. Comput. Chem. 34, 1961 (2013).


[61] See Supplemental Material at http://link.aps.org/ supplemental/10.1103/PhysRevB.100.054412 for additional crystallographic, NMR, magnetic susceptibility and XPS experimental data for the whole La2Eu1-xPO4 series; full theoretical energy levels and CFP data; and description of the small clusters used for DFT calculations.

[62] M. J. Frisch et al., GAUSSIAN 09, Revision D.01. (Gaussian, Inc., Wallingford CT, 2010).


