Separation of quadrupolar and paramagnetic shift interactions with TOP-STMAS/MQMAS in solid-state lighting phosphors

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Abstract
A new approach for processing satellite-transition magic-angle spinning (STMAS) and multiple-quantum magic-angle spinning (MQMAS) data, based on the two-dimensional one-pulse (TOP) method, which separates the second-rank quadrupolar anisotropy and paramagnetic shift interactions via a double shearing transformation, is described. This method is particularly relevant in paramagnetic systems, where substantial inhomogeneous broadening may broaden the lineshapes. Furthermore, it possesses an advantage over the conventional processing of MQMAS and STMAS spectra because it overcomes the limitation on the spectral width in the indirect dimension imposed by rotor synchronization of the sampling interval. This method was applied experimentally to the $^{27}$Al solid-state nuclear magnetic resonance of a series of yttrium aluminum garnets (YAGs) doped with different lanthanide ions, from which the quadrupolar parameters of paramagnetically shifted and bulk unshifted sites were extracted. These parameters were then compared with density functional theory calculations, which permitted a better understanding of the local structure of Ln substituent ions in the YAG lattice.

KEYWORDS
DFT, inorganic phosphors, MQMAS, paramagnetic NMR, solid-state NMR, STMAS, TOP

1 | INTRODUCTION

In recent years, nuclear magnetic resonance (NMR) has become an established tool for the study of the structural and electronic properties of paramagnetic systems. [1] The hyperfine interactions between the unpaired electrons and observed nucleus that occur in these systems are a rich source of information about the structure, the nature of the bonding, dynamics, and particle shape. [2–5] In systems containing lanthanide ions, these interactions also provide insight into the crystal-field splitting and resulting optical properties. [6–10] From the standpoint of NMR spectroscopy, these interactions are responsible for the paramagnetic shift and shift anisotropy (SA), [11–14] the paramagnetic relaxation enhancement [15] and inhomogeneous broadening due to bulk magnetic susceptibility (BMS) effects, [16–19] which often result in very broad spectra that are difficult to interpret.

Half-integer quadrupolar nuclei, that is, those nuclei with a half-integer spin quantum number $I$ greater than $1/2$, account for the majority of magnetically active nuclides in the periodic table. [20] However, the quadrupolar moment interacts with the electric field gradient (EFG) originating from an asymmetrical electronic charge distribution, which leads to extensive broadening. [21] If this interaction is sufficiently small, the spin system can be

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treated as a spin-1/2 system, while, on the other hand, if comparable with the Zeeman interaction, the spectra will be broadened beyond NMR detection. The central transition (CT) is unaffected by the quadrupolar interaction to a first-order approximation and, consequentially, yields sharper resonances than the satellite transitions (STs). In spite of this, the magnitude of the quadrupolar interaction is often sufficiently large so that a second-order term must consider which results in broadening of the CT resonance that, in contrast to first-order anisotropies, cannot be removed completely via magic-angle spinning (MAS). The quadrupolar-broadened lineshapes can be used to extract the EFG tensor parameters, which are also useful predictors of structural properties, but, their analysis is significantly more difficult when dealing with overlapping resonances from inequivalent chemical sites or with continuous distributions of shifts or quadrupolar parameters.\[22\]

In 1995, Frydman and Hardwood introduced the multiple-quantum magic-angle spinning (MQMAS) experiment,\[23\] which, by correlating a MQ and the CT resonances in a two-dimensional spectrum, permits the refocusing of the second-order quadrupolar interaction and satisfies the demand for a reliable method of recording high-resolution NMR spectra of half-integer quadrupolar nuclear species with conventional MAS probe hardware. Subsequently, Gan proposed an alternative method that correlates the STs with the CT,\[24,25\] which also achieves high-resolution NMR spectra. This experiment, called satellite-transition magic-angle spinning (STMAS), has, in general, enhanced sensitivity when compared with MQMAS but is substantially more demanding to implement because as opposed to the MQ transition, the STs are broadened extensively by the first-order quadrupolar interaction, thus requiring a significantly more accurate magic-angle setting for obtaining high-quality spectra. Additionally, the conventional STMAS also yields unwanted peaks from the undesirable CT–CT autocorrelation.

In paramagnetic systems half-integer quadrupolar nuclei experience both the paramagnetic effects and the quadrupolar interaction, which contributes to the lineshape and, consequentially, makes the extraction of NMR parameters exceedingly complicated. More specifically, BMS effects result in a distribution of paramagnetic shifts that broaden the resonance. This complication is similar to the broadening of the lineshapes found in materials that are amorphous or disordered, where a distribution of local environments results in a distribution of shifts and quadrupolar parameters.\[26,27\]

However, in paramagnetic systems, even if the structure is perfectly crystalline, in which case no distribution of quadrupolar parameters would occur, a BMS-induced shift distribution still broadens the lineshapes.\[1\] For integer-spin paramagnetic nuclei, this problem has been addressed, and a number of pulse sequences have been developed that separate the shift from the quadrupolar interaction.\[28–30\] For half-integer quadrupolar nuclei, it has been shown that by using the rotor-assisted population transfer experiment,\[31\] it is possible to estimate the quadrupolar coupling parameters in systems with NMR spectra that are severely broadened by the paramagnetic SA, BMS, and quadrupolar broadening.\[32–34\] However, this method, unfortunately, does not permit the separation of the shift/SQ and quadrupolar interactions that would facilitate the extraction of information about both interactions. The correlation of anisotropies separated through echo refocusing (COASTER) method,\[35\] which does correlate the SA lineshape against the quadrupolar lineshape, could be applied to address this problem, but requires sample spinning at a rotor angle of 70.12° to remove fourth-rank line broadening and so is not easily implemented using conventional probe hardware. To date, no routinely applicable method has been proposed for extracting quadrupolar interaction parameters from paramagnetic systems for half-integer quadrupolar nuclei.

In this paper, we introduce a new approach for processing STMAS and MQMAS experiments that permits the separation of the isotropic shifts and fourth-rank quadrupolar anisotropy into orthogonal dimensions via a double shearing transformation that is based on the two-dimensional one-pulse (TOP) transformation.\[36–38\] We therefore refer to these experiments as TOP-STMAS and TOP-MQMAS, respectively. The separation of these two interactions is shown, both by simulation and experiment, to facilitate the extraction of quadrupolar parameters in systems with severe inhomogeneous BMS broadening. Additionally, this transformation allows the representation of the high-resolution shift dimension to the directly detected dimension, exploiting its large spectral window to circumvent aliasing problems in systems with large chemical shift dispersion. We proceed to demonstrate this method on a series of yttrium aluminum garnets (YAGs) solid-state lighting phosphors, doped with paramagnetic lanthanide (Ln) ions (neodymium, europium, terbium, and ytterbium) with a composition of Y$_{2.91}$Ln$_{0.09}$Al$_5$O$_{12}$. Using this method, we were able to extract, for the first time, the quadrupolar parameters of the shifted and bulk sites of these materials and, in combination with density functional theory (DFT), improve our understanding of the local structure of Ln substituent ions in the YAG structure.

## 2  THEORETICAL FRAMEWORK

### 2.1  NMR transition frequencies

The Hamiltonian spin operator $\hat{H}$ that describes the NMR interactions in the high-field approximation under MAS
comprises terms from the chemical shielding $\hat{H}_\text{CS}$ and the first- and second-order quadrupolar interactions, $\hat{H}_Q^{(1)}$ and $\hat{H}_Q^{(2)}$.

$$\hat{H}(t) = \hat{H}_\text{CS}(t) + \hat{H}_Q^{(1)}(t) + \hat{H}_Q^{(2)}.$$  

(1)

The chemical shift contribution is given by\[^1,39\]

$$\hat{H}_\text{CS}(t) = -\omega_0 \left[ -\delta_\text{iso} + \sqrt{\frac{2}{3}} \delta_{20}(t) \right] \hat{I}_{1,0}.$$  

(2)

where $\omega_0$ is the Larmor frequency, $\delta_\text{iso}$ is the isotropic shift, and $\delta_{20}$ is the irreducible spherical shielding tensor term of Rank 2. According to the Haberlen convention \((|\delta_{zz} - \delta_\text{iso} | \geq |\delta_{xx} - \delta_\text{iso} | \geq |\delta_{yy} - \delta_\text{iso} |)\), the chemical SA ($\Delta \delta$) and asymmetry parameter ($\eta$) are defined as

$$\Delta \delta = \delta_{zz} - \delta_\text{iso},$$  

(3)

$$\eta = \frac{\delta_{yy} - \delta_{xx}}{\Delta \delta},$$  

(4)

where $\delta_{xx}, \delta_{yy},$ and $\delta_{zz}$ are the Cartesian components of the shift tensor in its principal axis frame.

The first- and second-order contributions to the Hamiltonian are given by\[^1,39\]

$$\hat{H}_Q^{(1)}(t) = \frac{2\omega_Q}{3eq} V_{2,0}(t) \hat{I}_{2,0}.$$  

(5)

$$\hat{H}_Q^{(2)}(t) = \frac{4\omega_Q^2}{9\omega_0} \left\{ W_{00} \left[ \frac{9}{5}\hat{I}_{3,0} + \frac{4I(I + 1)}{5\sqrt{5}} \hat{I}_{1,0} \right] + W_{20} \left[ -\frac{9}{70} \hat{I}_{3,0} - \frac{2I(I + 1)}{10\sqrt{14}} \hat{I}_{1,0} \right] + W_{40} \left[ \frac{51}{70} \hat{I}_{3,0} - \frac{12I(I + 1) - 9}{10\sqrt{70}} \hat{I}_{1,0} \right] \right\}.$$  

(6)

$V_{2,0}$ is the irreducible spherical tensor component of the EFG tensor, $eq$ is the EFG anisotropy tensor, and $\omega_Q$ is the quadrupolar splitting frequency, which are defined as

$$eq = V_{zz},$$  

(7)

$$\omega_Q = \frac{3\pi C_q}{2I(2I - 1)}. $$  

(8)

Here, $V_{zz}$ is the Cartesian $zz$ component of the EFG tensor in the principal axis frame, where its components are arranged as $|V_{zz}| \geq |V_{xx}| \geq |V_{yy}|$, $I$ is the spin quantum number, and $C_q$ is the quadrupolar coupling defined as follows:

$$C_q = \frac{e^2 Q}{\hbar},$$  

(9)

where $eQ$ is the nuclear quadrupolar moment and $\hbar$ is the Planck constant. The asymmetry parameter of the EFG tensor $\eta^Q$ is defined as

$$\eta^Q = \frac{V_{yy} - V_{xx}}{V_{zz}}.$$  

(10)

The $\hat{i}_{1,0}$ are reduced spin tensor operator of order $\lambda$, which are given by

$$\hat{i}_{00} = \hat{1}$$  

(11)

$$\hat{i}_{10} = \hat{I}_z$$  

(12)

$$\hat{i}_{20} = \hat{I}_z^2 - \frac{1}{3} (I + 1) \hat{1}$$  

(13)

$$\hat{i}_{30} = \frac{1}{3} \left\{ 5\hat{I}_z^3 - [3(I + 1) - 1] \hat{I}_z \right\},$$  

(14)

where $\hat{1}$ is the identity operator and $\hat{I}_z$ is the operator that represents the $z$-component of the nuclear spin. Lastly, the $W_{L0}$ are irreducible spherical tensors formed by contracting two Rank 2 EFG tensor components as follows

$$W_{L0} = \sum_m (2m - m|L0)v_{2m}v_{2-m},$$  

(15)

where $(2m - m|L0)$ are Clebsch–Gordan coefficients and $v$ is the reduced EFG tensor $v = V/eq$. It is worth noting that in paramagnetic systems, the shielding term can decompose in two terms, the orbital contribution $\delta^\text{orb}$ and the contribution, solely due to the unpaired electrons $\delta^\text{orb}$:

$$\delta = \delta^\text{orb} + \delta^\text{S}.$$  

(16)

The Hamiltonian $\hat{H}$ defines the frequency of transition between the nuclear spin states $|m_i\rangle$ and $|m_f\rangle$. This frequency depends on the spatial properties of the interaction via the shielding and EFG terms and on the spin properties via the spin orders $\Xi_{\lambda,M,M_f}$ of rank $\lambda$ for the transitions between $|m_i\rangle$ and $|m_f\rangle$\[^{40}\]:

$$\Xi_{\lambda,M,M_f} = \langle M_f | \hat{i}_{1,0} | M_i \rangle - \langle M_f | \hat{i}_{0,0} | M_i \rangle.$$  

(17)

Following Grandinetti, Ash, and Trease\[^{40}\] we define the different spin orders as $s_{M,M_f} = \Xi_{0,M,M_f}, p_{M,M_f} = \Xi_{1,M,M_f}, d_{M,M_f} = \Xi_{2,M,M_f}$, and $f_{M,M_f} = \Xi_{3,M,M_f}$. For the second-order quadrupolar interaction, where the spatial ranks of 0, 2, and 4 are associated with spin orders of Ranks 1 and 3, it is more convenient to define the C-order parameters $C^{(0)}, C^{(2)},$ and $C^{(4)}$ as follows:

$$C_{M,M_f}^{(0)} = \frac{9}{5} f_{M,M_f} + \frac{4I(I + 1) - 3}{5} p_{M,M_f},$$  

(18)

$$C_{M,M_f}^{(2)} = -\frac{18}{5} f_{M,M_f} + \frac{4I(I + 1) - 3}{10} p_{M,M_f},$$  

(19)

$$C_{M,M_f}^{(4)} = -\frac{51}{5} f_{M,M_f} + \frac{3[4I(I + 1) - 3]}{10} p_{M,M_f}.$$  

(20)

The frequencies of the transitions due to the chemical shift $\Omega_\text{CS}$, first- and second-order quadrupolar $\Omega_Q^{(1)}$ and $\Omega_Q^{(2)}$ interaction, are therefore given by

$$\Omega_\text{CS}(\Omega_\text{SC}, \Omega_\text{CR}, M_i, M_f) = \gamma_\text{CS} P_{M,M_f} + \gamma_2 \Omega_\text{CS}(\Omega_\text{SC}, \Omega_\text{CR}) \cdot P_{M,M_f},$$  

(21)

$$\Omega_Q^{(1)}(\Omega_\text{QC}, \Omega_\text{CR}, M_i, M_f) = \gamma_Q^{(1)}(\Omega_\text{QC}, \Omega_\text{CR}) \cdot d_{M,M_f}. $$  

(22)
\[
\Omega_Q^{(2)}(\Omega_{QC}, \Omega_{CR}, M, M_f) = Y_{0,0}^{Q_{20}} \cdot C_{M,M_f}^{(0)} + Y_{2,0}^{Q_{20}} (\Omega_{QC}, \Omega_{CR}) \cdot C_{M,M_f}^{(2)} + Y_{4,0}^{Q_{20}} (\Omega_{QC}, \Omega_{CR}) \cdot C_{M,M_f}^{(4)}.
\]  

(23)

The chemical shift interaction depends on the \(p\) order with an isotropic rank 0, \(Y_{0,0}^{CS}\), and anisotropic rank 2, \(Y_{2,0}^{CS}\), spatial dependencies. The first-order quadrupolar interaction contributes with a second-rank spatial anisotropy, \(Y_{2,0}^{Q_{20}}\), and a spin part dependent on \(d\). Lastly, the second-order quadrupolar interaction, similarly to the chemical shift, contributes with isotropic and anisotropic spatial parts, of ranks 2 and 4. The isotropic term gives rise to the second-order quadrupolar shift \(\delta_q\), which is defined as

\[
\delta_q = \frac{3C_q^2 (1 + \frac{d^2}{\gamma}) [3 - 4I(I + 1)]}{1600q^2(2I - 2)^2},
\]  

(24)

and depends \(C_{M,M_f}^{(0)}\). The Rank 2 term, \(Y_{2,0}^{Q_{20}}\), depends on \(C_{M,M_f}^{(2)}\) and the Rank 4 term, \(Y_{4,0}^{Q_{20}}\), on \(C_{M,M_f}^{(4)}\). The sets of Euler angles \(\Omega_{SC} = (\alpha_{SC}, \beta_{SC}, \gamma_{SC})\) and \(\Omega_{QC} = (\alpha_{QC}, \beta_{QC}, \gamma_{QC})\) define the orientation of the PAFs of the shielding and EFG tensors with respect to the crystal frame, and \(\Omega_{CR} = (\alpha_{CR}, \beta_{CR}, \gamma_{CR})\) defines the orientation of the crystal frame to the rotor-fixed frame.

The Rank 0 terms are independent of the orientation of the crystallites and are, therefore, unaffected by MAS. The Rank 2 terms due to the SA and first- and second-order quadrupolar interaction, because they depend on the orientation crystal frame with respect to the rotor-fixed frame, which is time dependent under sample rotation, represent broadening that is removed by MAS and split into a manifold of spinning sidebands. Finally, the Rank 4 term, is also time dependent, but as opposed to the Rank 2 terms, MAS only scales down the range of time independent frequencies that define the linewidth by a factor of \(-7/18\). Similarly to the Rank 0 terms, a distribution of quadrupolar parameters will also further broaden the lineshape.

2.2 MQMAS/STMAS

The MQMAS and STMAS experiments overcome the second-order quadrupolar-induced broadening due to the Rank 4 contribution using a \(C_{ij}^{(4)}\) echo.\footnote{The pulse sequence used for both experiments is shown in Figure 1a. In the STMAS experiment, as shown by the coherence transfer pathways in Figure 1b, during \(t_1\) evolution, the transition pathway passes through single-quantum ST pathway and end on the single-quantum CT during \(t_2\), whereas in the MQMAS experiment (Figure 1c) during \(t_1\), the CTP passes through a symmetric (\(|m| \leftrightarrow |m|\)) MQ transition (here 3Q), and then, similarly to STMAS, ends on the CT. For both experiments, the recorded two-dimensional time-domain signal for both the N-type and P-type pathways is given by

\[
S(t_1, t_2) = \exp \left ( \frac{i}{\hbar} \left ( Y_{0,0}^{CS} \cdot P_{M,M_f} + \frac{\gamma}{\hbar} \cdot C_{M,M_f}^{(0)} + Y_{2,0}^{Q_{20}} \cdot C_{M,M_f}^{(2)} + Y_{4,0}^{Q_{20}} \cdot C_{M,M_f}^{(4)} \right ) t_1 \right )
\]

\[
\times \exp \left ( \frac{i}{\hbar} \left ( -Y_{0,0}^{CS} + Y_{2,0}^{Q_{20}} \cdot C_{-1,2,1/2}^{(0)} + Y_{4,0}^{Q_{20}} \cdot C_{-1,2,1/2}^{(4)} \right ) t_2 \right )
\]

(25)

where \(t_{-1/2,1/2} = -1\) and, for convenience, we have only included the time-independent components of the signal. Here, \(m_i\) and \(m_f\) have values pertaining either to the MQ or ST, as required. It is worth noting that due to the rotor synchronization of the sampling interval, the time-dependent terms are refocused by MAS in \(t_1\). Additionally, for MQMAS because the multiple-quantum transition is symmetric, \(d_{M,-M} = 0\), and the contribution of the first-order quadrupolar interaction also vanishes. This result also holds true for the CT transition in \(t_2\) provided that the last pulse is CT selective. Applying a shearing and scaling transformation parallel to \(t_2\), it is possible to construct a two-dimensional time-domain signal where \(Y_{2,0}^{Q_{20}}\) does not evolve in (i.e., is refocused along) \(t_1\), as shown in Figure 2a for STMAS and Figure 2b for MQMAS.

2.3 Double sheared TOP-MQMAS/STMAS

The STMAS/MQMAS time-domain data, when processed as shown in Figure 2, do not separate the chemical shift and the Rank 4 quadrupolar lineshapes into orthogonal
dimensions and so do not remove the quadrupolar interference of the BMS broadening from the quadrupolar lineshapes. Additionally, due to rotor synchronization in $t_1$, the spectral window may not be sufficiently large to accommodate the chemical shift dispersion, especially for paramagnetic systems. Peaks that lie outside the spectral window are folded, or aliased, back into the spectral window, which further complicates their analysis. Both the limitations of the inhomogeneous BMS broadening and the spectral window in $\omega_1$ can be addressed via a double shearing transformation similar to the scheme proposed in for TOP,[36–38,41,42] pure shift NMR in solution,[43] and COASTER.[45] After this transformation, a new $(t'_1, t'_2)$ two-dimensional time-domain system where the frequency terms that depend on $p$ do not evolve in $t'_1$ is constructed, which eliminates the BMS broadening and shift in $\omega'_1$, and instead transfers them to $\omega'_2$ where we can benefit from the large spectral window of directly acquired dimension, analogously to TOP processing[36–38] as demonstrated by Walder et al.[41] and Paruzzo et al.[42] In this time-domain system, $C^{(4)}$ is refocused along $t'_2$, and, consequently, the indirect dimension accommodates the Rank 4 second-order quadrupolar-induced anisotropy, which is usually sufficiently small to be represented within the limited spectral window. Furthermore, it is worth noting that this double shear transformation is done entirely via passive transformations, which do not require any undesirable interpolation of data, and are carried out on the full $t_1 - t_2$ quadrant system, generated via TOP processing, thus avoiding possible folding artefacts introduced by the shear transformations.[40]

Figures 3a–c and 4a–c give a visual outline of the echo ridges for the different interactions and how they are affected by the shear transformations together with a representation of simulated data in both time- (Figures 3d–f and 4d–f) and frequency domains (Figures 3g–i and 4 g–i), for triple quantum magic-angle spinning and STMAS acquired for a system of three independent spin $5/2$ sites whose resonances are affected by BMS. After the first shear transformation along $t_2$ with a shear ratio $k(t_2)$, a new $t'_1$ dimension is created (Figures 3b and 4b) along which the evolution of the BMS broadening and shift are refocused. Consequently, after this transformation, the folding/aliasing in $\omega_1$, arising due to the large chemical shift dispersion, is also removed, as shown in
FIGURE 3  Simulation of a $z$-filtered satellite-transition magic-angle spinning spectrum with rotor-synchronized indirect dimension $t_1$, for a system comprising three independent spins $5/2$. In (a–c) are shown the different echo ridges for the first (solid lines) and second satellites (dashed lines). The echo central transition ridge, as opposed to the satellites, lies along the $p$ ridge. In (d–f) and (g–i), the corresponding signals are shown in the time and frequency domains, respectively. In (g–i), the main diagonal $\omega_1 = \omega_2$ is indicated by the dotted line. After the first shear transformation, the $t_1'$ and $\omega_1'$ dimensions contain no shift components ($p$) from the first satellites and, likewise, after the second transformation, the $t_2'$ and $\omega_2'$ dimensions contain no quadrupolar broadening ($C(4)$), from the first satellites as well. In figures (j) and (k), expansions of the centerband of each spin resonance of the double sheared spectrum (i) are shown. The simulation was carried out using a Larmor frequency of 156.6 MHz, 60 kHz magic-angle spinning frequency, $\{\delta_{iso}, [\text{ppm}], C_q, \eta^Q\} = \{77.5, 6.15, 0.05\}, \{47.5, 6.15, 0.9\}, \{-1000, 6.15, 0.05\}$. All chemical sites were simulated including inhomogeneous Gaussian broadening of the isotropic shifts and chemical shift anisotropy of $\Delta \delta = 640$ (ppm) and $\eta = 0.0$

Figures 3h and 4h. The second shear transformation, now parallel to $t_1'$ with shear ratio $k(t_1)$, removes the quadrupolar broadening from $t_2'$ (Figures 3c and 4c), which in turn removes it from $\omega_2$ and thus yielding pure quadrupolar and pure shift dimensions (Figures 3f and 4f) analogous to pure shift experiments in solution NMR spectroscopy.[43]

In Figures 3j–k and 4j–k we show an expansion of the processed spectra around the resonances of each simulated
FIGURE 4  Simulation of a z-filtered triple quantum magic-angle spinning spectrum with rotor-synchronized indirect dimension $t_1$, for a system comprising three independent spin 5/2 sites. In (a–c) are shown the different echo ridge for the triple-quantum central transition correlation. In (d–f) and (g–i), the corresponding signals are shown in the time and frequency domains, respectively. In (g–i), the main diagonal $\omega_1 = \omega_2$ is indicated by the dotted line. After the first shear transformation, the $t'_1$ and $\omega'_1$ dimensions contain no shift components ($p$) and, likewise, after the second transformation, the $t'_2$ and $\omega'_2$ dimensions contain no quadrupolar broadening ($C_q$). In figures (j) and (k), expansions of the centerbands of each spin resonance of the double sheared spectrum (i) are shown. The simulation was carried out using a Larmor frequency of 156.6 MHz, 60 kHz magic-angle spinning frequency, $\{\delta_{iso}\ \text{[ppm]}, C_q, \eta^Q\} = \{77.5, 6.15, 0.05\}, \{47.5, 6.15, 0.9\}$, and $\{-1000, 6.15, 0.05\}$. All chemical sites were simulated including inhomogeneous Gaussian broadening of the isotropic shifts and chemical shift anisotropy of $\Delta \delta = 640$ (ppm) and $\eta = 0.0$

site to better illustrate how this transformation greatly facilitates spectral interpretation and extraction of both shift and quadrupolar parameters. It is also worth noting that in the TOP-STMAS spectra, other than the cross-peak arising from the correlation of first ST (ST$_1$) with the CT, different correlation ridges of CT and second ST (ST$_2$) with the CT are visible. These additional correlations can, however, be removed using the double-quantum-filtered
TABLE 1  Shear ratios (SRs) in the time domain, scaling factors (SCs), and quadrupolar shift coefficients (SCs) for the TOP-STMAS experiment. The quadrupolar shift coefficients are defined so that the total shift is given by \( \delta_{\text{shift}} = \delta_{\text{iso}} + SC_{\text{iso}} \cdot \delta_{q} \) and \( \delta_{\text{Quad}} = SC_{\text{quad}} \cdot \delta_{q} \).

| First shear | Second shear |
|-------------|-------------|
| \( k_{1}^{(1)} \) | \( C_{4}^{(4)} \) |
| \( k_{2}^{(1)} \) | \( C_{4}^{(4)} \) |
| \( k_{3}^{(1)} \) | \( C_{4}^{(4)} \) |
| \( k_{4}^{(1)} \) | \( C_{4}^{(4)} \) |

\( k_{1}^{(1)} = C_{M, M}^{(4)} \cdot \frac{1 + |k_{1}^{(1)}|}{C_{4}^{(4)} - k_{1}^{(1)} C_{4}^{(4)}} \) (31)

In order to facilitate the extraction of NMR parameters, the chemical shift and quadrupolar dimensions are then scaled so that they can be readily compared with a one-dimensional MAS spectra,

\( \omega_{\text{quad}} = -C_{M, M}^{(4)} \cdot \frac{1 + |k_{1}^{(1)}|}{C_{4}^{(4)} - k_{1}^{(1)} C_{4}^{(4)}} \cdot \omega_{1, 0}^{t} \) (32)

\( \omega_{\text{iso}} = \omega_{2}^{t} (1 + |k_{1}^{(1)}|) \) (33)

The values for the shear ratios and scaling coefficients for all relevant spin quantum numbers and transitions are given in Table 1 for TOP-STMAS and Table 2 for TOP-MQMAS.

3 | MATERIALS AND METHODS

3.1 | Sample preparation

The samples of \( Y_{3}Al_{5}O_{12} \) (YAG:Ln) with Ln=Nd, Eu, Tb, and Yb, were prepared according to the procedure described previously for the microwave synthesis of YAG:Ce. Stoichiometric amounts of \( Y_{2}O_{3} \) (99.99%, Sigma-Aldrich), \( Al_{2}O_{3} \) (99.99%, Sigma-Aldrich), and \( Ln_{2}O_{3} \) (Ln=Nd, Eu, Tb and Yb) were mixed and ground in an agate mortar and pestle for 30 min in acetone. The lanthanide ion dopant amount was fixed at 9 mol for all samples, resulting in the intended composition of \( Y_{2}91Ln_{0.99}Al_{5}O_{12} \). BaF₂ (99%, Materion) and NH₄F (≥ 99.99%, Sigma-Aldrich) were added (5 and 0.5 wt%, respectively) as sintering agents (flux). For each sample,
6 g of granular activated charcoal (12–20 mesh, DARCO®, Sigma-Aldrich) was used as the microwave susceptor and placed in an alumina crucible (50 mL, Advalue). Roughly 0.5 g of mixed, unreacted, sample powder was placed in a smaller alumina crucible (10 mL, Advalue), which was pushed into the carbon containing 50-mL crucible and covered with an alumina lid (Advalue). This dual-crucibles setup was put in a carved-out block of high-temperature alumina insulation foam and placed in a household microwave (Panasonic NN-SN667B, 600 W) operated at 40 kHz with a 2 µs pulse length. All spectra were recorded with a sampling interval in $t_1$ of 33.33 µs, except the Tb:YAG spectrum, which was recorded with a sampling interval in $t_1$ of 16.67 µs. The spectra of pristine YAG and Nd:YAG were recorded with 128 increments in the indirect dimension and with 8 and 576 transients per $t_1$ increment and recycle delays of 32 and 0.4 s, respectively. The spectra of Eu:YAG and Yb:YAG were recorded with 256 increments in $t_1$, 32 and 896 transients per increment and recycle delays of 16 and 0.5 s. Lastly, the Tb:YAG was recorded with 512 $t_1$ increments, 24 transients per increment, and a recycle delay of 4.6 s. The spectra were processed in MATLAB using in-house written scripts.

### 3.2 Solid-state NMR

The $^{27}$Al NMR experiments were performed on a Bruker 600 Avance-III spectrometer operating at a Larmor frequency of 156.375 MHz, equipped with a 1.3-mm HX probe with MAS frequency of 60 kHz. A solution of 1 M Al(NO$_3$)$_3$$_3$ was used for referencing and calibrating the radio frequency (RF) pulses. The one-dimensional MAS spectra were recorded using an RF pulse with a 131-kHz nutation frequency and small flip angles (0.25 µs length), to ensure quadrupolar nutation effects did not alter the relative signal intensities. The relaxation delays ($\tau_{rec}$) ranged between 20 and 45 s to ensure quantitative results. For Ln:YAGs, additional MAS spectra were recorded with a 50 ms recycle delay to emphasize the shifted paramagnetic sites of lower intensity that, due to the PRE, have faster spin–lattice relaxation.

STMAS experiments were performed using the z-filtered STMAS pulse sequence, preceded by a saturation recovery block, as shown in Figure 1a.[25] All nonselective pulses used an RF amplitude of 122 kHz, employing a 1.5 µs pulse for both excitation and reconversion of the satellite coherences, optimized experimentally. The CT selective pulse operated at 40 kHz with a 2.1 µs pulse length. All spectra were recorded with a sampling interval in $t_1$ of 33.33 µs, except the Tb:YAG spectrum, which was recorded with a sampling interval in $t_1$ of 16.67 µs. The spectra of pristine YAG and Nd:YAG were recorded with 128 increments in the indirect dimension and with 8 and 576 transients per $t_1$ increment and recycle delays of 32 and 0.4 s, respectively. The spectra of Eu:YAG and Yb:YAG were recorded with 256 increments in $t_1$, 32 and 896 transients per increment and recycle delays of 16 and 0.5 s. Lastly, the Tb:YAG was recorded with 512 $t_1$ increments, 24 transients per increment, and a recycle delay of 4.6 s. The spectra were processed in MATLAB using in-house written scripts.

### 3.3 Computational details

Numerical simulations of the NMR spectra were performed in SIMPSON.[47] For simulations of one-dimensional signal spectra, powder averaging was performed using the REPULSION scheme[48] with 2,000 crystallites, whereas simulations of two-dimensional spectra employed 678 crystallites. To fit the one-dimensional STMAS slices and extract the quadrupolar parameters, the Levenberg–Marquardt damped least square mini-
mization algorithm\cite{49} implemented in C++\cite{50} was used. The errors of the quadrupolar parameters were generated using Monte-Carlo\cite{50} following the procedure described previously.\cite{30}

The geometry optimizations of the structures of the pristine YAG and YAG doped with a composition of \(\text{Y}_{2.875}\text{La}_{0.125}\text{Al}_3\text{O}_12\) were performed using plane-wave DFT\cite{51,52} using the QUANTUM ESPRESSO code.\cite{53} The generalized gradient approximation\cite{54} exchange-correlation functional of Perdew, Burke, and Ernzerhof\cite{55} with Grimme D2 dispersion correction\cite{56} was used with standard pseudo potentials from QUANTUM ESPRESSO. The plane wave energy cutoff was set to 80 Ry and a \(2\times 2\times 2\) Monkhorst–Pack grid for Brillouin zone was employed. The calculations were converged within a \(10^{-8}\) Ry and ionic relaxation forces within \(10^{-4}\) Ry/bhor. The EFG tensors were calculated using gauge including projector augmented wave (GIPAW) approach.\cite{57}

The EFG tensor was also calculated using the CRYS- TAL 17 code\cite{58} using Perdew, Burke, and Ernzerhof approximation of the exchange-correlation functional with \(2\times 2\times 2\) Monkhorst–Pack grid with self-consistent field cycle convergence of \(10^{-7}\). For the aluminum and oxygen atoms the Peintinger, Oliveira, and Bredow triple zeta valence with polarization quality were used\cite{59} with formats \((10s6p1f)/[4s3p1f]\) and \((14s9p1f)/[5s4p1f]\), respectively. Due to SCF instabilities, the Nd, Eu, Tb, and Yb in the structure were replaced with La and Lu using a small-core basis set with format ECP28MWB-(11s11p7d8f)/[4s4p2d3f].\cite{60}

FIGURE 5 (a) Structure of Ln:yttrium aluminum garnet with two distinct aluminum sites and (b) a molecular cluster defined by the atoms in the Ln–Y coordination shell. Density functional theory calculations predict three distinct local environments, one six-coordinated AlO\(_6\) (1) and two four-coordinated AlO\(_4\) (2 and 3), which are distinguished by the distance to the lanthanide ion.

FIGURE 6 (a) \(\text{ }^{27}\text{Al}\) solid-state nuclear magnetic resonance spectrum of pristine yttrium aluminum garnet where two signals arising from the AlO\(_4\) and the AlO\(_6\) are clearly distinguishable. The spectra with the full spinning sideband manifolds in view are shown in the SI. (b) \(\text{ }^{27}\text{Al}\)–Filtered TOP-STMAS spectrum indicating the CT-ST\(_1\) correlation cross-peak and the CT–CT diagonal peak, of lower intensity. In (c) are shown the extracted slice together with the best fit tabulated chemical shift and quadrupolar interaction parameters extracted experimentally, compared with those calculated by DFT. The quadrupolar interaction parameters reported in Florian et al.\cite{61} and Vosegaard et al.\cite{62} were also included for comparison. Both spectra were acquired at 14.1 T and 60 kHz magic-angle spinning.
4 | RESULTS AND DISCUSSION

4.1 | Pristine YAG

In order to access the accuracy of the TOP-STMAS method, we investigated its performance on the pristine YAG system. STMAS was chosen to study the pristine YAG and Ln:YAG materials due to its high sensitivity relative to MQMAS, which is crucial as a result of the low concentration of aluminum sites in close proximity to the lanthanide dopant ions, as discussed below. Moreover, STMAS sensitivity, as opposed to MQMAS, is not affected by the very fast MAS rate of 60 kHz. There are two crystallographically distinct aluminum sites in the structure of pristine YAG, (Figure 5a): a six-coordinated (AlO$_6$) and a four-coordinated sites (AlO$_4$). In the $^{27}$Al solid-state NMR spectra, both corresponding resonances are well resolved (Figure 6) and have been previously characterized.[61] Figure 6b shows TOP-STMAS spectrum where the peaks from both the CT–CT and ST1–CT correlations are visible but no discernible peak arising from the ST2–CT was detected. A slice from the ST1–CT cross-peak was then extracted to fit quadrupolar parameters. The quadrupolar parameters are reported in Figure 6c along with the DFT calculated values, and those previously measured by Florian et al.[61] and Vosegaard et al.[62] on a single YAG crystal. The predicted quadrupolar parameters of the TOP-STMAS experiment agree within error with both literature values, which further validates the method. Additionally, the quadrupolar interaction parameters predicted by the CRYSTAL code are also in better agreement with the experimental observations. The measured chemical shift of the AlO$_4$ site also agrees within error with the value reported by Florian et al.[61] However, there is disagreement in the shift reported in the single-crystal study of Vosegaard et al.[62] compared with both our study and that of Florian et al.[61]

4.2 | Ln:YAG

The Y$_{2.91}$Ln$_{0.09}$Al$_5$O$_{12}$ materials present a more challenging test of the TOP-STMAS/MQMAS method. This is caused by an increased number of resonances due to Al that is in close proximity to the Ln ion and which therefore experiences a paramagnetic shift, large paramagnetic relaxation enhancement, and the presence of inhomogeneous BMS, which further complicate the extraction and analysis of the quadrupolar lineshapes. Moreover, the paramagnetically shifted resonances have lower intensity, due to the low level of doping.

DFT calculations predict that introduction of lanthanide dopants in the structure causes small changes in lattice parameters, which results in variations in the unit cell volume. The unit cell volume varies approximately linearly with the ionic radius of the lanthanide (Figure 7). In Figure 5, the first Ln–Y coordination shell of the Ln:Yag structures is represented. The substitution of Y with Ln effectively breaks the symmetry of the structure and creates three distinct local aluminum environments, one six-coordinated AlO$_6$ and two four-coordinated AlO$_4$, all with distinct distances to the lanthanide ion. DFT calculations suggest that these distances, however, are barely affected by the substitution of Y with the Ln ions (Figure 7) indicating that the local lattice around an Ln ion is only very slightly distorted and that the lanthanide ions are significantly compressed in the rigid YAG lattice, which is in agreement with previous experimental observations.[10]

The $^{27}$Al spectra of the Ln-doped YAGs are related to that of the undoped phase because they are primarily dominated by the features of the AlO$_4$ and AlO$_6$ sites that are remote from the Ln ion, with additional broadening but with multiple lower intensity peaks that result from Al closer to Ln experiencing paramagnetic interactions (Figures 8a, b and 9a, b), which have been previously identified.[10,63] Considering that the contributions to the shift from the paramagnetic Ln ions are additive, it is possible to identify two shifted AlO$_6$, which exhibit a narrower lineshape and hence lower $C_Q$, because the distance between the two shifted AlO$_6$ sites and the bulk AlO$_6$ and the closest shifted site is approximately the same. These sites arise from the presence of one and two lanthanide ions in the first Ln–Y coordination shell. In the Nd and Yb:YAG spectra (Figures 8a and 9a) the presence of shoulders around the AlO$_6$ is quite pronounced and have...
been previously attributed to dopants from the second or further away Ln–Y coordination shells.\textsuperscript{[63]} The shifted resonances are broadened by BMS, which blurs the features typical of second-order quadrupolar broadening and perturbs the extraction of $C_q$ and $\eta^q$. We therefore turned to TOP-STMAS to separate these effects.

The experimental TOP-STMAS spectra are shown in Figures 8c,d and 9c,d. In the Nd, Eu, and Yb:YAG spectra, we were able to identify and assign one shifted $\text{AlO}_4$, with quadrupolar parameters similar to the bulk four-coordinated site. The quadrupolar parameters and chemical shift of the $\text{AlO}_4$ are extracted from the
FIGURE 9  (a) Tb:yttrium aluminum garnet (YAG) and (b) Yb:YAG $^{27}$Al nuclear magnetic resonance spectrum. The spectra with the full spinning sideband manifolds in view are shown in the supporting information. (c,d) z-Filtered two-dimensional one-pulse satellite-transition magic-angle spinning $^{27}$Al spectra together with extracted slices and best fits of the quadrupolar dimension (e,f) of Tb and Yb, respectively. Horizontal dotted line in (c) and (d) correspond to slices extracted of the shift. The shifted Tb:YAG was fit with an additional Gaussian lineshape to account for the contributions from the CT autocorrelation that affects the quadrupolar lineshape. All spectra were acquired at 14.1 T, 60 kHz spinning speed.

TOP-STMAS experiments and are shown in Table 3. The best fits of the quadrupolar dimension are represented in Figures 8e,f and 9e,f. The quadrupolar coupling parameters of both bulk and shifted sites do not vary significantly, within error, as we progress along the lanthanide series and are all similar to the quadrupolar parameters of the AlO$_4$ site of pristine YAG (Figure 6). It is important, however, to note that distributions of quadrupolar parameters may affect the accuracy of the experimental results, which is reflected in the increase of experimental error, particularly in the Tb and Yb:YAG systems, where the spectra are significantly broader. 

Spectroscopic properties calculations of systems containing lanthanide ions with unpaired electrons with
DFT is a crude approximation due to their challenging electronic structure. For this reason, the quadrupolar parameters obtained with plane-wave GGA-DFT GIPAW method were unrealistic, whereas at the hybrid-DFT level with CRYSTAL code convergence could not be achieved at all. Therefore, the paramagnetic lanthanide ions in the respective Ln:YAG structures were replaced by diamagnetic counterparts, lanthanum and lutetium, to obtain trustworthy $^{27}$Al quadrupolar parameters. As the quadrupolar coupling is a property that depends on the local molecular geometry, this represents a reasonable approximation to study local effects of lanthanide insertion into YAG structure, given that structures were optimized with appropriate chemical composition. We also note that no significant differences were observed between the quadrupolar parameters calculated with either La or Lu inserted into the given structure. The DFT calculated quadrupolar parameters of the bulk and of the furthest four-coordinated AlO$_4$ (Figure 5) are not significantly affected by the presence of an Ln ion (Table 3). The AlO$_4$ closest to Ln ion exhibits a trend of a small increase in $C_Q$ as we progress along the lanthanide series (Table 3), which is likely a consequence of the steric effects. Both the experimental and calculated quadrupolar coupling parameters indicate that the local environments around the lanthanide ions are not extensively affected by introduction of the lanthanide ion, which further evidences the rigidity of the YAG lattice. The stiffness of nearest neighbor bonds results in high-phosphor quantum efficiency, as shown in George et al.$^{[10]}$ due to the inaccessibility of phonon modes, and a large crystal-field splitting if the lanthanide ion has bigger ionic radius than the yttrium ion it replaces. The quadrupolar coupling parameters calculated for all structures are presented in the supporting information.

### Table 3

Extracted experimental shift and quadrupolar interaction parameters, and computed (CRYSTAL) quadrupolar interaction parameters of the four-coordinated $^{27}$Al sites. To calculate the quadrupolar parameters, the paramagnetic lanthanide ion was replaced with La after structure optimization. See text for details.

| Shift (ppm) | $C_Q$ (MHz) | $\eta$ |
|-------------|-------------|-------|
| **Bulk sites** | | |
| TOP-STMAS | Nd:YAG | 78 ± 1 | 5.8 ± 0.6 | 0.3 ± 0.1 |
| Eu:YAG | 78 ± 2 | 6.0 ± 0.6 | 0.2 ± 0.1 |
| Tb:YAG | 78 ± 2 | 6.6 ± 0.7 | 0.6 ± 0.2 |
| Yb:YAG | 78 ± 3 | 7.0 ± 0.8 | 0.2 ± 0.1 |
| **CRYSTAL** | | | |
| Nd:YAG | 51 ± 2 | 6.2 ± 0.6 | 0.3 ± 0.1 |
| Eu:YAG | 123 ± 4 | 6.3 ± 0.5 | 0.1 ± 0.2 |
| Tb:YAG | 132 ± 3 | 7.0 ± 0.8 | 0.3 ± 0.1 |
| Yb:YAG | | | |
| **Shifted sites** | | | |
| TOP-STMAS | Nd:YAG | 51 ± 2 | 6.2 ± 0.6 | 0.3 ± 0.1 |
| Eu:YAG | 123 ± 4 | 6.3 ± 0.5 | 0.1 ± 0.2 |
| Tb:YAG | 132 ± 3 | 7.0 ± 0.8 | 0.3 ± 0.1 |
| Yb:YAG | | | |
| CRYSTAL $r_{Ln-Al} = 3.4$ Å | Nd:YAG | 5.1 | 0.1 |
| Eu:YAG | 5.5 | 0.1 |
| Tb:YAG | 5.7 | 0.1 |
| Yb:YAG | 6.1 | 0.1 |
| CRYSTAL $r_{Ln-Al} = 3.7$ Å | Nd:YAG | 6.0 | 0.2 |
| Eu:YAG | 6.0 | 0.1 |
| Tb:YAG | 6.0 | 0.1 |
| Yb:YAG | 6.0 | 0.0 |

Abbreviations: STMAS, satellite-transition magic-angle spinning; TOP, two-dimensional one pulse; YAG, yttrium aluminum garnet.

### 5 | CONCLUSIONS

We have presented a new approach to process STMAS and MQMAS spectra by applying a double shear transformation based on TOP processing. This method permits the separation of isotropic shift and quadrupolar anisotropy into orthogonal dimensions and consequentially removes the broadening induced by the BMS and a second-order quadrupolar anisotropy. This method, which we refer to as the TOP-STMAS/MQMAS, is shown to greatly facilitate the extraction of quadrupolar parameters in paramagnetic systems affected by distributions of chemical shifts. Furthermore, it overcomes the limitation of spectral width in the $\omega_1$ dimension, due to rotor synchronization, which can be crucial in paramagnetic systems with large shift dispersion.

We acquired TOP-STMAS $^{27}$Al spectra of a series of Ln-doped YAG systems, which are a widely used class of materials in solid-state science. Using this methodology, we were able to identify the shifted four coordinate sites and extract the quadrupolar parameters of both bulk and shifted sites. The quadrupolar coupling parameters of both paramagnetically shifted and bulk unshifted sites do not vary significantly with the introduction of different lanthanide ions and are all similar to the quadrupolar...
parameters of the pristine material. This result suggests that local environments are not highly distorted and further corroborates the rigidity of the YAG host lattice, crucial to its optical properties, also evidenced by DFT calculations.

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CONFLICT OF INTEREST

The authors have no conflict of interest to declare.

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SUPPORTING INFORMATION

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