INVESTIGATING LANTHANIDE DOPANT DISTRIBUTIONS IN YTTRIUM ALUMINUM GARNET (YAG) USING SOLID STATE PARAMAGNETIC NMR

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Graphical abstract

Abstract

This paper demonstrates the approach of using paramagnetic effects observed in NMR spectra to investigate the distribution of lanthanide dopant cations in YAG (yttrium aluminum garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}$) optical materials, as a complimentary technique to optical spectroscopy and other standard methods of characterization. We investigate the effects of Ce^{3+} , Nd^{3+} , Yb^{3+} , Tm^{3+} , and $\text{Tm}^{3+}\text{-Cr}^{3+}$ on ^{27}Al and ^{89}Y NMR spectra. We note shifted resonances for both AlO_4 and AlO_6 sites. In some cases, multiple shifted peaks are observable, and some of these can be empirically assigned to dopant cations in known configurations to the observed nuclides. In many cases, AlO_6 peaks shifted by more than one magnetic neighbor can be detected. In general, we observe that the measured intensities of shifted resonances, when spinning sidebands are included, are consistent with predictions from models with dopant cations that are randomly distributed throughout the lattice. In at least one set of ^{27}Al spectra, we identify two sub-peaks possibly resulting from two paramagnetic cations with magnetically coupled spin states neighboring the observed nucleus. We identify systematic changes in the spectra related to known parameters describing the magnetic effects of lanthanide cations, such as larger shift distances when the expectation value of electron spins is greater. We lastly comment on the promise of this technique in future analyses of laser and other crystalline oxide materials.

Key Words: Laser materials, Fermi contact shift, ^{27}Al , ^{89}Y

Introduction

Yttrium Aluminum Garnet (YAG) is a widely used material for solid-state lasers and other optical components. Since YAG's invention over 50 years ago, spectroscopic studies on it and similarly-structured crystals have contributed to the development of laser, scintillator, and phosphor materials [1,2]. The garnet structure is attractive for optical materials, offering great flexibility with respect to major and dopant compositions while often maintaining the desirable cubic symmetry [3,4]. Single crystals dominate applications of crystalline solid state laser materials. However, driven in part by a greater compositional flexibility and potential cost savings, researchers have developed polycrystalline ceramic laser materials that are rivaling the performance of single crystal counterparts [4,5]. Advancements in and/or additional spectroscopic techniques, which can clarify relationships between the atomic structure and optical properties, play a key role in further development. Also, given the widespread interest in geochemistry and mineralogy in the distributions and concentrations of lanthanides in silicate garnets as archival records of crystal growth environments, a better understanding of local cation order/disorder is potentially quite significant.

This paper details the application of Nuclear Magnetic Resonance (NMR) to a widely-used group of crystalline optical materials: YAG doped with optically active lanthanide (Ln^{3+}) ions. We present spectra with very high signal-to-noise ratios, which allow the detection and analysis of rarely identified spectral features—paramagnetically shifted resonances—that result from interactions between the unpaired electron spins of the dopant cations and the observed nucleus. We report well resolved, shifted peaks in

^{27}Al and ^{89}Y NMR spectra of YAG doped with low concentrations of Ce^{3+} , Nd^{3+} , Tm^{3+} or Yb^{3+} , and comment on the promise of using this technique to analyze future optical materials. An in-depth analysis of the ^{27}Al spectra illustrates the technique's ability to investigate cation distribution and assess effects of doped cations on the local structure. ^{27}Al spectra of YAG co-doped with high concentrations of Tm^{3+} and Cr^{3+} indicate some limits of this technique as spectral resolution is lost. The relative values of the observed paramagnetic shifts for the different dopants are compared to approximate theoretical expectations, which in some cases appear to agree well, and in other cases do not. The work presents a new application of paramagnetic NMR to studying such materials from 'viewpoint' of the non-lasing cations.

Background

Paramagnetic NMR

The interactions of an NMR-observed nuclide with the unpaired electron spins from a neighboring ion can result in spectra that can give quantitative insight into local environments. Often termed 'paramagnetic NMR', this approach has been applied to a variety of systems, including battery materials, fuel cell materials, natural and synthetic minerals, and simple oxides doped with transition metals, lanthanides, and even actinides [6–9]. There are two primary mechanisms that describe such interactions: the pseudocontact shift, in which the effective dipolar magnetic field produced by the unpaired electrons (necessarily in low-symmetry environments) affects the observed nucleus directly through space, and the Fermi contact shift, where unpaired electron density interacts directly or indirectly with s shells of the observed nucleus via interatomic bonds [10]. Both interactions are highly dependent on the spatial

arrangement of the ion and the observed nuclide, resulting in a frequency shift that corresponds to the magnitude of the effect, and a peak area proportionally equal to the abundance of each different spatial and/or bonding configuration of nuclear and electronic spins. Paramagnetic shifts are approximately additive, such that an observed nuclide with two neighboring paramagnetic cations in symmetry-equivalent sites will produce a shift twice as distant as one with a single neighboring paramagnetic cation; this phenomenon can be exploited to estimate cation distributions from resulting peak areas [7]. For simple systems, paramagnetic interactions are well described theoretically, and computational chemistry approaches to predicting these interactions can be accurate enough to assign shifts to specific bond paths or configurations [6,10,11]. In more complex systems, such as oxides doped with lanthanides, current theory and approximations do not always fully describe the observations [12]. Despite these limitations, paramagnetic shifts can, in many cases, provide enough constraints so that pseudocontact and/or Fermi contact parameters can be back calculated [13,14].

Garnet structure and previous investigations with paramagnetic NMR

Garnet compositions and structural sites can be labeled in various ways depending on the discipline. In this paper we are primarily concerned with YAG, $\text{Y}_3\text{Al}_2\text{Al}_3\text{O}_{12}$. We refer to the dodecahedral cation site with local D_2 symmetry that is primarily occupied by Y^{3+} cations as the YO_8 -site, which also contains the dopant lanthanides. The octahedral cation site with C_{3i} symmetry is occupied by Al^{3+} and referred to as the AlO_6 site. The tetrahedral site with S_4 symmetry, also occupied by Al^{3+} , is referred to as the AlO_4 site. In silicate garnets (well studied in several previous publications), the latter corresponds to the SiO_4 site [9,15].

Paramagnetic shifts are controlled by the configurations of NMR-observed nuclides and cations with unpaired electron spins. Both connecting bond paths and through-space distances are relevant. These configurations, relating the dodecahedral sites hosting the paramagnetic cations to the tetrahedral and octahedral sites in silicate garnets, were recently described in detail out to about 9 Å and are listed for these and as well as the YO₈ sites in YAG in Table S1 [15,16]. To label these configurations, we use a notation based on the NMR-observed site and the distance to the paramagnetic center, e.g. “*AlO₆-5.4*” for the second dodecahedral neighbor at 5.416 Å from the octahedral site. It is important to note (especially for discussions of pseudocontact shifts) that in some cases, crystallographically equivalent sites can potentially lead to magnetically inequivalent configurations, depending on the asymmetry of the site hosting the unpaired electron spin. In Table S1 these are further denoted as “*AlO₆-6.8i*”, “*AlO₆-6.8ii*”, etc.

Paramagnetic effects have been previously investigated in flux grown polycrystalline YAG with ranges of Tb³⁺ or Ce³⁺ concentrations [17,18]. In both cases, the authors observed paramagnetic effects in the ²⁷Al and ⁸⁹Y spectra, and made predictions of the pseudocontact contributions. The more recent Ce:YAG study combined very high field NMR data with the latest understanding for predicting the pseudocontact shift [18]. Work on silicate garnets with paramagnetic shifts produced by transition metals observed such peaks in both ²⁹Si and ²⁷Al spectra [9,15,19]. For both silicate garnets and YAG, peaks were assigned to the (Al,Si)O₄ sites with both edge- and corner-shared dodecahedral sites (here, *AlO₄-3.0* and *AlO₄-3.7*), and to *AlO₆-3.4* (first neighbor, corner-shared) sites. The Ce:YAG study additionally identified shoulders

on the AlO_6 primary (unshifted) peak that were assigned to paramagnetic resonances due to the $\text{AlO}_6\text{-}5.4$ and either $\text{AlO}_6\text{-}6.8i$ or $\text{AlO}_6\text{-}6.8ii$ configurations. We note that the AlO_6 resonances in YAG are much narrower than those in the silicate garnets because of smaller quadrupolar coupling, often allowing more paramagnetic features to be resolved. In contrast, the SiO_4 resonances in the silicate garnets (at least at lower concentrations of transition metal cations) are generally narrower than the AlO_4 peaks in aluminate garnets such as YAG, as the quadrupolar coupling for the latter is relatively large and ^{29}Si has nuclear spin=1/2.

Numerous other methods, which in most cases are more familiar to the optical materials community, have been used to study YAG, including optical absorption and emission spectroscopy, XRD, EXAFS, and EPR [18,20–22]. For example, crystal chemical findings for Nd:YAG have been reviewed in detail [21]. In general, research has indicated that dopant cations are randomly distributed and that in crystals formed at high melting temperatures, small amounts of excess Y^{3+} can be found to occupy AlO_6 sites.

NMR Spectra of YAG

YAG is notable as all three elemental components have NMR active nuclides, and pure YAG has been investigated extensively as both a powder and single crystal [23–25]. An especially useful paper characterized the magic angle spinning NMR spectra of phases encountered across the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ pseudo-binary phase diagram [25]. In spectra for ^{27}Al (100% abundance, relatively high gyromagnetic ratio, nuclear spin $I=5/2$), two peaks representing the $\text{AlO}_6\text{-}$ and $\text{AlO}_4\text{-}$ sites are generally well resolved. The quadrupolar coupling frequency ($\nu_Q = C_Q \times 3/20$ for $I=5/2$), which controls the width

and shape of the peak, is especially low ($\approx 170 \pm 10$ kHz) for the AlO_6 -site, resulting in a narrow peak centered close to 1.5 ppm at high magnetic fields [25]. The isotropic chemical shift is only slightly higher, 2.1 ppm [25]. In contrast, the AlO_4 -site has a relatively large ν_Q (923 kHz) and near-zero quadrupolar asymmetry parameter ($\eta = 0.05$), resulting in a well-defined quadrupolar peak shape that is shifted significantly below the isotropic chemical shift of 77.5 ppm, depending on field [25].

Collecting NMR spectra of ^{89}Y (100% abundance, $I=1/2$) is not as straightforward as for ^{27}Al . Although ^{89}Y line shapes are not broadened by quadrupolar effects, its low gyromagnetic ratio and typically very long spin-lattice relaxation times make collecting high-quality spectra significantly more difficult. Fortunately, paramagnetic cations often decrease relaxation times, allowing for somewhat faster spectra collection. The isotropic chemical shift of ^{89}Y in YAG has been measured as 222 ppm, as well as its chemical shift anisotropy [25].

Experimental Methods

Samples

Samples of single crystal YAG were acquired from various commercial sources and are listed in Table 1. Two samples were produced by the laser heated pedestal growth (LHPG) method, 0.7%NdLHPG:YAG and 1.1%YbLHPG:YAG. All other samples are either described as produced by the Czochralski ('crystal-pulling') growth method, or presumed to be produced by this method due to their size. All samples were manufactured at quality levels intended for use as solid-state lasers.

Table 1. Sample composition and name.

Sample name	Dopant	% Y ³⁺ replaced with dopant ^a
0.3%Ce:YAG	Ce	0.30 ± 0.03
0.7%NdLHPG:YAG	Nd	0.74 ± 0.07
0.7%Nd:YAG	Nd	0.68 ± 0.07
1.0%Nd:YAG	Nd	0.97 ± 0.03
24%Er:YAG	Er	23.6 ± 0.01
0.9%Tm:YAG	Tm	0.93 ± 0.03
5.7%Tm0.4%Cr:YAG	Tm-Cr	5.73 ± 0.06, 0.37 ± 0.03
5.6%Tm0.9%Cr:YAG	Tm-Cr	5.56 ± 0.06, 0.90 ± 0.10
1.1%YbLHPG:YAG	Yb	1.06 ± 0.03

^aFor Tm-Cr doped samples, the Tm concentration is listed first.

A JEOL JXA-8230 electron microprobe, operated at 15 kV, 30 nA Faraday cup current and 3 μ m beam size, was used to determine sample compositions. Standards of kyanite (Al), corundum (Al), undoped single crystal YAG assumed to be stoichiometric (Al and Y), Y metal (Y), chromite (Cr), Ce₂O₃ (Ce), NdSi₂ (Nd), Er metal (Er), TmSi₂ (Tm), and Yb metal (Yb), were used. Reported average sample compositions are based on 10 EPMA points with uncertainties indicated as one sample standard deviation. No significant variations in stoichiometry were noted.

NMR data collection

NMR data were acquired using Varian/Chemagnetics “T3” probes with a Varian Unity/Inova 600 spectrometer at 14.1 Tesla (156.3 MHz for ²⁷Al and 29.5 MHz for ⁸⁹Y), and a Varian 800 spectrometer at 18.8 Tesla (208.4 MHz for ²⁷Al). An external “low gamma” box was used to tune the probe down in frequency for ⁸⁹Y experiments. 3.2 mm low Al background zirconia rotors were packed with 50-60 mg of powdered

samples. Sample temperature was changed slightly by increasing or decreasing the spinning speed (which caused a change in air frictional heating) in order to detect temperature effects on paramagnetic resonances. Temperatures are estimated, based on ^{207}Pb shifts in $\text{Pb}(\text{NO}_3)_2$, as $28 \pm 2^\circ\text{C}$ at 9 kHz, $54 \pm 3^\circ\text{C}$ at 18 kHz, $57 \pm 3^\circ\text{C}$ at 20 kHz and $60 \pm 3^\circ\text{C}$ at 21.5 kHz.

For ^{27}Al experiments, 0 ppm was referenced to 0.1 M $\text{Al}(\text{NO}_3)_3$. An effective radiofrequency power based on the liquid reference 360° pulse width was 95 kHz; for solids experiments a pulse width of 0.28 μs (28° tip angle) was generally used to assure quantitative observation of intensities for sites with widely varying ν_Q . Spectral windows of 2500 kHz (about 12000 ppm) on the 18.8 T spectrometer and 400 kHz (about 2500 ppm) on the 14.1 T spectrometer were used. Due to rapid spin-lattice relaxation of the paramagnetic features, short pulse delays of 0.05 s were used for spectra shown in the figures (unless otherwise noted) to emphasize the fast relaxing (but low intensity) paramagnetic features over those of the bulk. The unshifted “primary” resonances relaxed much more slowly; much longer pulse delays were used to quantify their intensities for comparison with those of the fast-relaxing components.

An exception to the typical 0.28 μs pulse width was used to better investigate the peak areas of paramagnetically shifted AlO_6 peaks in the ^{27}Al spectra of the Nd:YAG. By using long pulses of 9.5 μs , but the typical short pulse delay times of 0.05 s, the slow-relaxing, unshifted resonances (and, most importantly, their spinning sidebands) were even more effectively saturated, essentially filtering out these components from the spectra.

For ^{89}Y experiments, 0 ppm was referenced to 1 M YCl_3 , as previously done for YAG [25]. Effective radiofrequency power of 14 kHz was determined from the 360° pulse width for the ^{89}Y YO_8 -site peak of 0.7%Nd-LHPG:YAG. A 26° tip angle, single pulse of 5 μs was used for all spectra shown here. Spin-lattice relaxation of the primary (unshifted) resonance was extremely slow even in doped samples of YAG, resulting in low signal to noise ratios and experiments that lasted between 4 hours to 4 days. Significant probe ringing was present, which was removed by back predicting over the first 75 μs of the FID. This may have obscured very broad spectral components, but these were likely not observable at obtainable signal to noise levels in any case.

NMR peak area analysis

In the analysis of peak areas in ^{27}Al NMR spectra of oxide materials collected at high fields with relatively fast MAS, spinning sidebands often can be assumed to contain little or no intensity from the central $\pm\frac{1}{2} - \frac{1}{2}$ transition (chemical shift anisotropy is small). In such cases, accurate relative areas of peaks for different sites can be obtained from the central peaks by simply correcting for any intensity of the satellite transition sideband beneath the central peaks. This can be easily done by calculation if quadrupolar parameters are known, or empirically by subtracting an area based on one or more observed satellite transition sidebands [26]. However, for systems with paramagnetic dopants, both procedures may be highly inaccurate because there can be significant spinning sideband intensity from the central transition signals, especially those of paramagnetically shifted resonances, caused by strong nuclear-electronic dipolar coupling. This problem can often be readily recognized by comparison of

sideband manifold shapes for doped vs. undoped samples or for shifted vs. unshifted resonances in a single doped sample. This was clearly the case for sideband patterns of the Ln:YAG samples studied here, which not only had enhanced intensity in the innermost sidebands but sometimes highly asymmetrical manifolds suggesting strong perturbation by the paramagnetic cations (see Figure S1).

In some cases, the amount of 'extra' $\pm \frac{1}{2} - \frac{1}{2}$ transition intensity in the sidebands can be estimated by direct comparison with an undoped sample (assuming that the quadrupolar parameters are approximately the same), as was done for several transition-metal doped silicate garnets [9,15,16,19]. If ν_Q is relatively large, sidebands for the central and at least the $\pm 1/2 - 3/2$ transitions may be separated in frequency and have distinctly different line shapes, allowing their contributions to be assessed directly. In such a case, though, as for the AlO_4 peaks in YAG (see below), relatively broad peaks can make resolution and accurate measurement of small, shifted features difficult. In contrast, in the case of a relatively small value of ν_Q , sidebands from different transitions may overlap completely but their manifold may be narrow enough to allow observation of all sideband intensity within a normal spectral window. The high signal-to-noise ratios obtained for the Ln:YAG spectra allowed integration of all of the significant spinning sideband intensities for the unshifted and shifted AlO_6 peaks, providing a more accurate view of their correct relative intensities than methods limited to corrections of the central peak. This typically involved the measurement of areas out to 9 or even 12 sidebands. Extreme care was taken in determining the integrated values, and their associated uncertainties. Uncertainty values were determined following the Guide to the Expression of Uncertainty in Measurement, and include

analyses of multiple spectra and estimated contributions from noise, imperfect baseline corrections, and small variations in phase corrections [27]. When overlapping AlO_6 peaks were fitted to estimate areas, the DMFit software package was used with Gaussian line shapes [26].

Results and Discussion

^{27}Al NMR spectra: general features

The ^{27}Al NMR spectra of Ce^{3+} , Nd^{3+} , and Yb^{3+} doped YAG resemble those of the undoped phase, and are dominated by AlO_4 and AlO_6 primary features reasonably well described by the parameters previously reported for undoped YAG [25]. The spectra for the Ln:YAG samples all have additional peak broadening and multiple smaller peaks that show systematic changes in position with temperature—characteristics that identify these features as products of paramagnetic interactions [10,15]. As a typical example, Figure 1 features a wide spectral window (1200 ppm) for the 0.7%Nd:YAG, where the central AlO_6 and AlO_4 primary peaks are labeled. These peaks are surrounded by their associated spinning sidebands (SSB). The feature labeled “A” is an AlO_6 peak shifted to a new position by a paramagnetic interaction. The Tm and Tm-Cr doped YAG spectra have, in contrast, much broader AlO_6 peaks (FWHM ca. 20 - 50 ppm, see below).

Figure 1. ^{27}Al NMR spectrum of 0.7%Nd:YAG. The unshifted AlO_6 and AlO_4 peaks, the paramagnetically shifted “A” peak, and two representative spinning sidebands (SSB) are labeled. The intensities of the peaks that are not paramagnetically shifted (i.e. AlO_4 and AlO_6) are reduced in these spectra because pulse delays were too short for complete relaxation (“unrelaxed”) (14.1 T, 17.7 kHz spinning speed).

Nd:YAG ^{27}Al NMR spectra

In addition to the primary peaks in the ^{27}Al spectra of the Nd:YAG, there are three obvious paramagnetically shifted resonances: AlO_4 -B, A, and E, labeled in Figure 2. Note that because most of the detailed discussion here concerns AlO_6 resonances, we use simple letter labels for these features, e.g. “A” and “AA”. These features are similar to those previously reported in Ce:YAG phosphors, except that the Nd:YAG peaks have proportionally larger shifts [18]. This results in less overlap between the shifted and unshifted features, resulting in distinct and resolvable AlO_4 -B and E peaks. This enhanced separation allows easier identification of contributions to the spinning sideband manifolds of the shifted peaks with respect to the unshifted peak. An example of this is presented in Figure 2, where the AlO_4 -B peak has a notable component of its central transition ($\pm\frac{1}{2} - \frac{1}{2}$) quadrupolar peak shape and intensity distributed into the spinning sidebands, while the unshifted AlO_4 peak does not. This has significant implications with respect to peak area integrations, as introduced in the experimental

section. We also identify two shoulders on the AlO_6 primary peak, labeled D and C (Fig. 3), as well as shoulders on the shifted A peak that are probably related to two Nd^{3+} cations neighboring the observed nucleus, such as peaks EE, AE, AC, and AA (labels correspond to additive shifts from neighbors in both of the corresponding configurations). The AA peak is comprised of two sub-peaks possibly resulting from magnetically coupled electronic spin states in adjacent paramagnetic cations, which we describe in a following section. We could not identify an AlO_4 -A peak (first neighbor edge-shared dodecahedral site, AlO_4 -3.0 in Table S1) corresponding to the one previously identified in Ce:YAG phosphors (as well as the analogous SiO_4 sites in Fe^{2+} containing silicate garnets); it is expected to be present but possibly difficult to resolve [15,18].

Figure 2. ^{27}Al NMR spectrum of 1.0%Nd:YAG. Signal from the central transition of the shifted, AlO_4 -B peak (with quadrupolar splitting) is clearly observable in the spinning sidebands (SSB). The vertical scales of the upper segments are increased 40 times (14.1 T, 20 kHz spinning speed).

Figure 3. ^{27}Al NMR spectra of 0.7%NdLHPG:YAG at 18.8 T (a,b) and 0.7%Nd:YAG at 14.1 T (c). In (a), the AlO_6 primary peak is surrounded by the one-neighbor shifted peaks C, D, and E. In (b), the one-neighbor A peak is surrounded by associated two-neighbor shifted peaks AE and AC, and the higher frequency shoulder of peak A is expected to have contributions from the AD two-neighbor shift. In (c), peak AA is detectable as two peaks bracketing the expected additive peak position. The position shifts with the small temperature changes caused by varying the spinning speed, faster=warmer. A 9.5 μs observe pulse was used to collect (c) to fully saturate overlapping, unshifted resonances. Here and elsewhere, “vs” is a vertical scale multiplier.

The relatively large ν_Q for the AlO_4 sites in YAG leads to an obvious quadrupolar splitting in the central peak and in any sideband containing intensity for the central $\pm\frac{1}{2} - \frac{1}{2}$ transition. In undoped YAG, and for the unshifted AlO_4 peak of the Ln-YAG samples, these contributions are negligible and sidebands are clearly dominated by the much narrower line shape of the $\pm\frac{1}{2} - \frac{3}{2}$ transition ($\pm\frac{3}{2} - \frac{5}{2}$ sidebands are much broader and, although detectable, are not clearly seen in most of the spectra shown here) [25,28]. However, in contrast, for the $\text{AlO}_4\text{-B}$ peak this $\pm\frac{1}{2} - \frac{1}{2}$ transition lineshape is visible in an asymmetric distribution extending to the +3 SSB and the -2 SSB, probably due to strong nuclear-electronic dipolar coupling or possibly, to an enhanced chemical (or paramagnetic) shift anisotropy. This distinction is not apparent for the AlO_6 features

because of the much smaller ν_Q , and sidebands for all transitions are practically overlapping. However, the distribution of the AlO_4 -B central transition sidebands looks qualitatively similar to that of AlO_6 sidebands, and it is reasonable to assume that the AlO_6 shifted features are similarly affected by the same mechanism. We attempted to quantify the shifted peak sideband manifold asymmetry, but could not determine a unique model to describe this.

As described in the experimental section, the low ν_Q for the AlO_6 sites meant that all significant spinning sidebands could be observed and integrated, avoiding the problem of distinguishing contributions from different transitions. The peak areas for the AlO_6 features of the 0.7%NdLHPG:YAG and 0.7%Nd:YAG are listed in Table 2. The unshifted peak, and the neighboring peaks/shoulders E, D, and C are difficult to integrate individually, and so an integration window that includes all of these features was chosen. Similarly, an integration window including the A peak and the nearby two-neighbor shifted resonances was chosen.

As noted above and in a previous study of Ce:YAG, the clearly resolved A peak (largest paramagnetic shift for AlO_6 sites) is most likely assignable to a single Ln^{3+} in the first cation shell, denoted AlO_6 -3.4; E, D, and C are likely the result of dopant ions in the second or even farther shells [18]. In principle, modeling the effects of varying distributions of dopants cations on the spectra would require more complete assignments, as the number of equivalent occupancies for each given configuration could be different and calculated peak intensities would vary. Fortunately in the YAG structure, each magnetically inequivalent configuration out to six bonds away has six equivalent sites, so that some modeling of the dopant distribution can be done without

complete assignments of shifted resonances to configurations. We have thus made a simple probabilistic model based on known dopant concentration and assuming random distribution over all YO_8 sites (see supplementary material for details). In this model we account for the effects of multiple neighbors, which shift intensity out of the single neighbor resonances: this correction is small for low dopant concentrations but can become quite significant above about 1%.

Results of this calculation are given in Table 2. The close agreement between the integrated peak areas and expected peak areas, particularly that of the observed AA peak, indicates that Nd^{3+} is randomly distributed in YAG produced at high temperatures. AlO_4 peak parameters, are reported and discussed minimally in Table S3.

Table 2. 0.7%NdLHPG:YAG AlO_6 -site peak positions and areas.

AlO_6 -site peaks	δ^a (ppm) ± 0.2	δ_{shift} (ppm) ± 0.2	FWH $M \pm 0.1$	0.7%NdLHPG:YAG % peak area		0.7%Nd:YAG % peak area	
				Integrated ^b	Expected	Integrated ^c	Expected
E	5.6	4.1	1.5	95.1 ± 5.8	95.6 ± 0.4	94.4 ± 5.7	96.0 ± 0.4
Shoulder (D)	3.8 ± 0.4	2.3 ± 0.4	1.4				
Unshifted peak	1.5	0	2.5				
Shoulder (C)	-1.1 ± 0.5	-2.6 ± 0.5	1.6				
A	-65.2	-66.7	2.2	4.7 ± 0.3	4.1 ± 0.4	5.5 ± 0.4	3.9 ± 0.4
AA	-130.4	-131.9	2.4	0.087 ± 0.011	0.076 ± 0.014	0.068 ± 0.014	0.065 ± 0.013

^aPeak center; " δ_{shift} " in this and following tables is the offset from the unshifted resonance; determined from 20 kHz spinning speed spectra.

^bFrom integration of ± 9 SSB in 14.1 T, 19 kHz, 9.5 μs pulse length spectrum.

^cFrom integration of ± 9 SSB, 14.1 T, 18 kHz, 9.5 μs pulse length spectrum

Ce:YAG ^{27}Al NMR spectra

Our ^{27}Al NMR results on Ce:YAG laser material confirm many of the findings previously reported for Ce:YAG phosphors, and add several new details [18]. In

comparison to the previously described Ce:YAG phosphor, our material has a lower Ce^{3+} concentration and was produced at high temperature using the Czochralski technique. This could result in minor differences in Ce^{3+} cation distribution or to minor amounts of Y^{3+} occupying the AlO_6 site; however we do not detect any such effects [2]. In agreement with the previous report, we identify the same five shifted peaks or shoulders which we label A, E, C, $\text{AlO}_4\text{-A}$, and $\text{AlO}_4\text{-B}$ [18]. All of these features are visible in Figure 4, with the exception of $\text{AlO}_4\text{-A}$, which has some components detectable at a frequency higher than the range displayed despite overlapping with sidebands from other resonances.

As noted above for Nd:YAG, the spinning sideband manifold for the paramagnetic, AlO_6 A peak in Ce:YAG contains “extra”, $\pm 1/2$ – $1/2$ intensity and is asymmetric in shape (Fig. S4-1), suggesting that a complete analysis and integration of the sidebands will give a more accurate estimation of the peak area than the approximation made previously [18]. We also detect an additional shoulder on the high frequency side of the AlO_6 primary peak (labeled D in Figure 5) that was confirmed by a comparison with the line shape observed in an undoped YAG. The latter indicates negligible peak broadening due to increased relaxation rate and confirms that the shifted features are independent of any residual quadrupolar peak shape. The narrowness of the peak is likely the result of the very low Ce^{3+} concentration of our sample, resulting in minimal contributions from multi-neighbor resonances. Using a long observe pulse (to more effectively saturate the unshifted resonance and sidebands) as demonstrated on the AA peak of Nd:YAG we observed the Ce:YAG AA peak previously reported for Ce:YAG phosphors. The size of this feature was very small (as expected on

the basis of random Ce distribution and our Ce concentration) and overlapping with AlO_4 sidebands.

Figure 4. ^{27}Al NMR spectra of the AlO_4 and AlO_6 regions for 0.3%Ce:YAG. Upper spectra are experimental (14.1 T, 20 kHz spinning speed), lower traces show fitted components.

Figure 5. ^{27}Al NMR spectrum of 0.3%Ce:YAG compared with an undoped YAG. Only the regions near the main AlO_6 peaks are shown. (14.1 T, 20 KHz spinning speed).

The integrated peak areas of the A peak and the primary peak, including its shoulders added by small paramagnetic shifts and all significant sidebands, are reported in Table 3. The resulting peak areas corresponds remarkably well to those

expected from a random model as described above. In this case, for example, a hypothetical strong clustering of Ce^{3+} ions would produce a greater-than-random intensity for doubly shifted peaks. Even if these were not directly observable, their presence would correspondingly reduce the area of the A peak below that which is observed. Shifted peak parameters for the AlO_4 peaks are reported in Table S3.

The peak positions of the shifted AlO_6 shoulders were determined using Gaussian fits and constraining their widths to the observed A peak values. At 14.1 T field, and with the known ν_Q , isotropic chemical shifts are expected to be only about 0.3 ppm higher.

Table 3. 0.3%Ce:YAG AlO_6 -site peaks as determined at 20 kHz spinning speed.

AlO_6-site peaks	δ^a (ppm) ± 0.4	δ_{shift} (ppm) ± 0.4	FWHM ± 0.2	% Peak area^b	% Expected peak area
Shoulder (E)	3.8	2.3	1.4	98.3 $\pm$ 4.9	98.2 $\pm$ 0.2
Shoulder (D)	2.9	1.4	1.4 $\pm$ 0.5		
Unshifted peak	1.5 $\pm$ 0.2	0	1.8		
Shoulder (C)	-1.1	-2.6	1.4 $\pm$ 0.4		
A	-15.9 $\pm$ 0.2	-17.4 $\pm$ 0.2	1.4	1.7 $\pm$ 0.2	1.8 $\pm$ 0.2

^apeak center position

^bIncludes integration of ± 8 SSB.

Yb:YAG ^{27}Al NMR spectra

In spectra for 1.1% Yb:YAG spectra (Fig. 6), the primary resonances for AlO_4 and AlO_6 resemble those for Ce- and Nd-YAG discussed above, but are broader due at least in part due to higher dopant concentration. Overlapping the AlO_4 unshifted peak is

a small feature at 68 ppm, which is most likely part of a shifted AlO_4 peak; however, we could not resolve its entire quadrupolar peak shape. The pattern of shifted AlO_6 resonances appears to be analogous to but inverted from those seen for the other dopants, with one having a relatively large shift to higher frequency (A), one with a smaller shift to lower frequency (E), and several shoulders on the unshifted resonance (B, C, D). Between peak B and the unshifted AlO_6 peak is additional intensity which we label peak C, a distinction based on expectations from systematic, relative effects of the different dopants as discussed below. Two-neighbor shifts related to the A, B and E peaks (i.e., AB, BB, AE, DE, and EE) can be easily identified with magnified vertical scale. However, peak AA is not observable as it overlaps with the primary AlO_4 peak.

Figure 6. ^{27}Al NMR spectrum for 1.1%Yb:YAG center peaks (14.1 T, 20 kHz spinning speed).

Figure 7. ^{27}Al NMR spectrum for 1.1%Yb:YAG, showing the region around the +4 spinning sideband (a). (b) shows the sum of modeled one- and two-neighbor shifted peaks; (c) the one-neighbor components only; (d) the two neighbor components. 514 ppm is 4 times the rotor frequency offset from 0 ppm for the center peak. Peaks marked by * were added to help the model converge.

For comparison with model predictions, areas were integrated for the AlO_6 primary and associated peaks within the +15 and -24 ppm of its position, for the A peak and all features within ± 6 ppm, and for the AE two-neighbor peak that in most cases appeared distinct from the A peak. A similar approach was taken for the spinning sidebands.

To better interpret the AlO_6 features in the 1.1%Yb:YAG spectra we used a constrained fitting routine to estimate individual peak areas. To develop the constraints, we determined that five single-neighbor peaks were necessary to best describe the overall observable shapes of the spectra, and estimated their positions and widths. Then, two-neighbor peak widths and positions were determined by iteratively adjusting the ideal (additive) values to match details of the spectra. To optimize the fitting algorithm, overlapped peaks were represented using only one peak, such as peak E-

DD. Three tiny excess peaks were also added to help the fitting algorithm converge, and are marked by asterisks in both the figures and tables, and we do not suspect they are pertinent to the AlO_6 analysis. The resulting 18 peak model with defined peak positions and widths was then used to estimate amplitudes for the center band and 16 nearest sidebands (± 8 sidebands) and is presented in Table 4. An example of one such fit, for the +4 spinning sideband, is illustrated in Figure 7.

Both the peak areas from the fits and those predicted from a random model have been grouped together as in the integrations of the experimental spectra and summed to allow comparison. The grouped fitted values and the integrated values correspond nicely, implying that over wider ppm windows the fitting is an accurate representation of the experimental data, and that the random model is again a good approximation. Interestingly, the B peak has a larger area relative to the other one-neighbor peaks. Because of this, we suspect that the B peak is due to two configurations with nearly identical shifts, and therefore adjusted our predicted peak area model to reflect twice as many equivalent sites for this peak.

Due to incomplete knowledge of one-neighbor peak locations and peak widths, the results of our peak areas estimated by fitting are approximate and incomplete. For future work, determining peak positions in low dopant concentration materials where peaks are even better resolved should increase the accuracy and therefore effectiveness of this approach.

Table 4. Summary of integrations and parameters determined from peak fitting of spectra for 1.1%YbLHPG:YAG.

AlO ₆ - site peaks	δ^a (ppm) ± 0.3	δ_{shift} (ppm) ± 0.3	Peak area determined by integration	% peak area estimated by fitting	Summarized fit	Predicted % peak area	Summarized Prediction	Equivalent sites
AB	47.2	45.6	4.2% $\pm$ 0.5	0.2 $\pm$ 0.0	4.3% $\pm$ 0.6	0.6	5.70%	-
AC	44.4	42.8		0.3 $\pm$ 0.1		0.3		-
A	40.6	39		3.3 $\pm$ 0.7		4.8		6
AD	35.3	33.7		0.5 $\pm$ 0.1		0.4		-
AE	29.6	28	0.2% $\pm$ 0.1	0.2 $\pm$ 0.1	0.2% $\pm$ 0.1	0.3	0.30%	-
BB	14.1	12.5	95.6% $\pm$ 6.7	0.5 $\pm$ 0.1	95.5% $\pm$ 4.4	0.6	94.30%	-
BC	11.1	9.5		1.1 $\pm$ 0.2		0.6		-
B	7.6	6		7.2 $\pm$ 1.4		9.7		12 ?
C	4.9	3.3		5.1 $\pm$ 1.0		4.8		6 ?
Prime	1.6	0		71.9 $\pm$ 14.4		75.3		-
*	-1.5	-3.1		0.5 $\pm$ 0.1		-		-
D	-3.9	-5.5		3.3 $\pm$ 0.7		4.9		6
EC	-7	-8.6		0.6 $\pm$ 0.1		0.3		-
E - DD	-9.7	-11.3		3.7 $\pm$ 0.7		4.9		6
*	-12.5	-14.1		0.4 $\pm$ 0.1		-		-
DE	-15.1	-16.7		0.7 $\pm$ 0.1		0.3		-
EE	-21.4	-23		0.4 $\pm$ 0.1		0.1		-
* (AlO ₄ - satellite)	-28.2	-		0.2 $\pm$ 0.0		-		-

Tm:YAG ²⁷Al NMR spectra

The spectra for 0.9%Tm:YAG contain peaks that are much broader than those for the Nd:YAG, Ce:YAG and Yb:YAG described above, which complicated analysis. The AlO₄ and AlO₆ primary peaks are located where expected from data on other samples, and there appear to be shoulders on both sides of the latter (Fig. 8). Other features are visible, but distinguishing them from one another by varying spinning speed and temperature was difficult and ultimately unconvincing. However, the very different ν_Q values for the AlO₄ and AlO₆ resonances lead to substantially different 180 ° (null) pulse widths of about 3 and 4.5 μ s respectively. Collecting sets of spectra with pulse widths across these values greatly facilitated identification of spectral components (both

with and without paramagnetic shifts) corresponding to each of the two sites. Combining this approach with variation of temperature/spinning speed allowed the separation of AlO_6 paramagnetic features from the AlO_4 contributions to the spectra. However, due primarily to the larger widths of the AlO_4 peaks, this approach to finding AlO_4 paramagnetic features was not useful. Examples are presented in Figure 9.

Figure 8. ^{27}Al NMR spectra for Tm-containing YAG. Note the severe broadening for the higher Tm content samples (14.1 T, 20 kHz spinning speed).

Figure 9. ^{27}Al NMR spectra for 0.9%Tm:YAG. The upper “Spin speed” group of spectra was collected with a pulse width ($2\ \mu\text{s}$) that minimized AlO_4 spectral contributions, with spinning speed varied from 18.0 (upper) to 20.0 kHz (lower) to distinguish sidebands. In the lower “Pulse length” spectra, the spinning speed is kept constant at 20.0 kHz, with the pulse width varied from 3 (upper) to $6\ \mu\text{s}$ (lower), across the 180° tip angle of the AlO_6 peak to help isolate AlO_6 peaks from AlO_4 components.

The furthest shifted AlO_6 feature was assigned as peak A by analogy with data from other compositions. The pattern of the remaining peaks—B, C, D, and E—resembles that in the Yb:YAG, with the same sign of the shifts, which again appears opposite to that observed for Nd:YAG and Ce:YAG. These shifts for Tm:YAG are the largest identified for any of the YAG samples studied here. Future work could take advantage of these large shifts but use a lower concentration of Tm to increase spectral resolution and detect more paramagnetic features.

High dopant concentrations and limitations of paramagnetic NMR

We have also investigated some laser materials with higher dopant concentrations that indicate some potential limits of this technique. In an extreme

example, we attempted to investigate a 24%Er:YAG, and although the sample was seemingly unaffected by a powerful hand-held magnet, at 14.1 T the magnetic effects were strong enough to remove the packed rotor from spinning module when inserting the probe into the magnet. In another example presented in Figure 8 the spectra of two co-doped TmCr:YAG samples with approximately 6% dopant may indicate the upper limits of paramagnetic NMR on such materials, although much faster sample spinning speeds could be beneficial. The peaks are considerably broadened, resulting in poor quality spectra with low information content. Relative to the already broad 0.9%Tm:YAG spectra, there is little surprise that increased Tm concentration continues to result in significant peak broadening as relaxation time is decreased and the areas of two or more-neighbor peaks increases.

Contrary to the success of arrayed pulse width experiments for the 0.9%Tm:YAG, this approach could only identify the two main features corresponding to the AlO_4 and AlO_6 peaks for the higher Tm samples. We note that the AlO_6 180° pulse width for the Tm-Cr samples was approximately 4 μs , close to that for the 0.9%Tm:YAG sample, indicating that the quadrupolar coupling was not significantly altered by increased dopant concentrations. Fitted peak widths and Tm^{3+} concentrations are positively correlated, but Cr^{3+} content appears to have a minimal additional effect at higher Tm^{3+} concentrations (Table 5).

Table 5. Effect of Tm^{3+} concentration on AlO_6 peak width.

Sample	% Tm^{3+}	FWHM (ppm)
Undoped YAG	0	2
0.9% Tm :YAG	0.97 ± 0.03	12 ± 2
TmCr :YAG	5.73 ± 0.06	50 ± 10
TmCr :YAG	5.56 ± 0.06	50 ± 10

These two samples also clearly indicate that high lanthanide concentrations or dopants with comparable or larger expected magnetic effects relative to Tm^{3+} may be difficult to study using NMR. The opposite is however also likely, such that lanthanides with weaker magnetic effects may yield informative NMR spectra at higher dopant concentrations, and lanthanides with stronger couplings can likely still allow good data at lower dopant concentrations. Magnetic effects on spectra for each lanthanide can be estimated from two well-studied physical parameters introduced in the following section.

Theoretical expectations and assignments of shifts to dopant configurations

The relative magnitudes of the paramagnetic shifts identified in Ce^{3+} , Nd^{3+} , Tm^{3+} and Yb^{3+} YAG samples correspond fairly well both with values expected from previous observations in pyrochlores, phosphates, and organic systems and from theoretical considerations [14,29,30]. Two physical parameters that are unique to each lanthanide, the expectation value of electronic spin $\langle S_z \rangle$ and the Bleaney's constant C^D , have been shown in some molecular systems with axial symmetry to approximate the relative proportions of the Fermi contact and pseudocontact components of a paramagnetic shift respectively [14]. Bleaney's constant is an estimation of paramagnetic susceptibility calculated on the basis of each lanthanide's electronic structure [12,14,31]. Although applying this approach in full to crystalline solids is inappropriate, these parameters do

offer a convenient starting approximation for the expected relative paramagnetic interactions for the different lanthanides. Values for $\langle S_z \rangle$ and C_D taken from the literature are reported in Table 6 for the cations studied here.

Table 6. Comparison of AlO_6 peak shifts in YAG for various Ln^{3+} dopants, and published parameters for expectation values of electronic spins $\langle S_z \rangle$ and Bleaney's constants C^D . Ratios for various dopant pairs are also shown.

Peak or variable ^a	Determined values				Ratios					
	Ce^{3+}	Nd^{3+}	Tm^{3+}	Yb^{3+}	Ce:Nd	Ce:T _m	Ce:Yb	Nd:T _m	Nd:Yb	Tm:Y _b
C^D	-6.3	-4.2	52.4	21.5	0.7	-8.4	-3.4	-12.6	-5.2	0.4
$\langle S_z \rangle$	1	4.5	-8.2	-2.6	4.6	-8.4	-2.6	-1.8	-0.6	0.3
A	-15.4	-66.7	128.5	39.2	4.3	-8.3	-2.5	-1.9	-0.6	0.3
B ^b	(-1.2)	(-2.6)	39.5	6.1	(2.2)	(-32.9)	(-5.1)	(-15.2)	(-2.3)	0.2
C	-1.2	-2.6	9.5	3.4	2.2	-7.9	-2.8	-3.7	-1.3	0.4
D	3.1	2.3	-18.5	-5.4	0.7	-6	-1.7	-8	-2.3	0.3
E	4.2	4.1	-43.5	-11.3	1	-10.4	-2.7	-10.6	-2.8	0.3

^aCommonly used $\langle S_z \rangle$ values are listed, which are calculated based on experimental values for shifts identified in aqueous lanthanide complexes [32]. Of the various C^D values reported in the literature, we chose those which give the closest agreement to Bleaney's original experiments [31].

^bValues in parenthesis are an alternative assignment of the C peak for the Ce^{3+} and Nd^{3+} YAG. Due to the closer agreement of the ratios for the C assignment with the mean values of the column we believe a B peak assignment is incorrect.

Table 6 also shows the shifted distances for the identified paramagnetic resonances. As noted above, peak A was assigned to the furthest shifted peak regardless of sign, peak E assigned to the second furthest shift, which is consistently opposite that for A, and peak D is assigned to the feature between the unshifted peak and E. The assignment of B and C (distinguishable only for Yb:YAG and Tm:YAG) depends on less certain arguments discussed below. The ratios of these shifts for the different dopants, which are listed in the right half of the table, are most informative.

Theoretically, the signs of the appropriate $\langle S_z \rangle$ and C^D parameters should dictate the signs of the paramagnetic shifts, and therefore the signs of the parameter ratios from one lanthanide to another should show a consistent relationship to the signs of the ratios of the observed shifts. As Table 6 shows, the sign of the ratios in each column consistently match as expected. Furthermore, under the assumption that the $\langle S_z \rangle$ and C^D values control the Fermi contact and pseudocontact interactions respectively, shifts with larger Fermi contact contributions should have ratios for different dopants that are closer to the corresponding $\langle S_z \rangle$ ratios, and shifts that are primarily caused by the pseudocontact interactions should have ratios closer to those for C^D .

Rather remarkably, the observed A peak shift ratios in Table 6 nearly match the $\langle S_z \rangle$ ratios, which implies that the Fermi contact interaction is primarily responsible for the paramagnetic shift resulting from this configuration of nuclear and unpaired electron spins. Indication of a strong Fermi contact interaction further supports the conclusions of previous studies of Ce:YAG and Fe-containing silicate garnets, which assigned the A peak to the $A/O_6-3.4$, (first neighbor cation) configuration [18,33]. Additionally, this agreement should be useful in predicting the location of the A peak in future work on other garnets, e.g., the A peak would be expected at ca. +500 ppm in Tb:YAG, and around -50 ppm in Pr:YAG.

The ratios of the observed shifts for B, C, D and E typically have values in between those of the $\langle S_z \rangle$ and the C^D ratios, when the latter are significantly different, e.g. as for Ce:Nd or Nd:Tm. Such intermediate values are expected because the significance of the pseudocontact shift probably increases relative to that of the Fermi contact shift as the number of intervening bonds increases. With this understanding,

peaks B and C were labeled as such by determining which assignment produced the most reasonable ratios. For comparison, in Table 6, the alternative assignment of labeling the Nd^{3+} and Ce^{3+} C peaks as B peaks are those listed with a parentheses. Note how the values in the C row are much closer to the column average than the B row values. We suspect that the B peak is not visible in the Ce:YAG and Nd:YAG spectra due to the low C^D values of these cations, resulting in B peaks that are indistinguishable from the unshifted peak.

Previous work on Ce:YAG concluded that peak E is related to the $A/O_6-5.4$ configuration (closest second cation neighbor), which our data on additional compositions support. Peak E is always the second furthest shifted peak, which implies a relatively close spatial relationship between the observed nuclide and the paramagnetic cation. It also relaxes quickly relative to paramagnetic features with smaller shifts.

The remaining peaks B, C, and D therefore probably result from more distant configurations, but at this time we cannot make specific assignments. In the previous Ce:YAG investigation, peak C was assigned to an $A/O_6-6.8$ configuration, but which of the two possible magnetically inequivalent configurations (i and ii in Table 1) was not deduced. Most challenging is determining an assignment for the B peak, especially since it is not detected in the Ce:YAG and Nd:YAG. Future work that studies relaxation in low concentration Yb:YAG and Tb:YAG could potentially assign these peaks.

The constrained peak fitting of our 1.1%YbLHPG:YAG spectra (Table 4) indicates that most one-neighbor shifted resonances appear to have roughly equal area, consistent with the equal numbers of equivalent sites for many or most of the closest

neighbor configurations (Table S1). Peak B, however, has a larger intensity, which possibly indicates that it is composed of overlapping signals from two closely related configurations, such as AlO_6 -6.8i, ii or AlO_6 -8.1i,ii.

We find no evidence that would contradict the assignments of the AlO_4 -A and AlO_4 -B peaks to AlO_4 -3.0 (edge-shared) and AlO_4 -3.7 (corner-shared) as previously determined in both silicate garnet and Ce:YAG [18,33]. However, it is somewhat surprising that more AlO_4 features for configurations beyond 3.7 Å are not observed in YAG, especially since AlO_6 paramagnetic shifts are produced from at least 8.1 Å in YAG and a third tetrahedral paramagnetic shift is observed in Fe^{2+} -containing silicate garnet [15]. The broad quadrupolar peak shape for AlO_4 sites, and fewer equivalent sites for each AlO_4 configuration are likely explanations.

Dopant cation distributions

Paramagnetic NMR offers an ability to investigate the distribution of dopant cations, and potentially identify deviations from a random distribution. In a fully disordered distribution, the areas of the paramagnetically shifted peaks should be equal to values modeled using a binomial distribution, the dopant concentration, and the number of equivalent sites, taking into account the effects of multiple magnetic cation neighbors (see also supplementary material). In systems where dopant cations “avoid” other dopant cations, for example to minimize local lattice strain when there is a significant size mismatch, the areas of multi-neighbor peaks would be smaller than those predicted by the random model. If, in contrast, there is clustering of dopant cations on adjacent YO_8 sites, areas of multi-neighbor peaks would be larger than modeled, and first-neighbor peaks smaller. In YAG, the NMR signals from the AlO_6 site

are particularly well suited for investigating dopant distributions due to its narrow peak width (small ν_Q) and simple configurations with neighboring YO_8 sites. Furthermore, when the two-neighbor AA peak is detectable, it presents an ideal window on localized distributions, due to the short distances and limited number of AlO_6 -3.4 (first cation neighbor) configurations.

As noted in the Ce:YAG section, the integrated peak areas (including analysis of spinning sidebands) support a random distribution of Ce^{3+} cations on YO_8 sites (Table 3). However, the spectra that we were able to collect on this sample could not completely characterize the identified AA peak. In our investigation of dopant cation distribution in Nd:YAG, greatly simplified spectra were collected using longer pulse lengths to suppress slow relaxing components. Here, the observed areas for AlO_6 sites with both single and two dopant neighbors are close to those predicted by a random distribution, placing our NMR results in good agreement with previous findings from optical spectroscopy [2]. Further studies at even higher magnetic fields and with faster sample spinning could yield even better quantitation [18]. For Yb:YAG, uncertainties are somewhat larger, but do not deviate substantially from the random model. Investigation of samples with lower dopant concentrations could improve resolution in cases where stronger coupling leads to more broadening of spectra.

Splitting of two-neighbor peaks: magnetic coupling of electronic spins?

If two cations with unpaired electron spins occur in nearby YO_8 sites in YAG, magnetic coupling of their spin systems may be expected, e.g. to yield ferromagnetic $+1/2 +1/2$, or antiferromagnetic $+1/2 -1/2$ states [34]. If the energy difference of these

states is small relative to Boltzmann's constant multiplied by the temperature (kT), then their populations will be nearly equal and strictly additive effects on paramagnetic shifts are expected. However, as the energy difference and the corresponding state population difference increases, the magnetic susceptibility of the coupled system can be increased in the ferromagnetic case, or decreased in the antiferromagnetic case, resulting in a shift that varies from additivity. The strength of the magnetic coupling, and thus the perturbation in the observed shift, is likely to depend strongly on the distance between the two dopant neighbors. Two Ln^{3+} neighbors with the same configuration with respect to the observed nuclear spin (e.g. AlO_6 -3.4 in the case of the "A" peak) may indeed have very different Ln^{3+} - Ln^{3+} distances, for example for cations in YO_8 sites sharing adjacent (3.7 Å) vs. opposite corners of an AlO_6 octahedron (5.6 to 6.7 Å). In this case, a splitting of the doubly-shifted resonance may be expected, as observed for the AA resonance in Nd:YAG (Fig. 3). A previous ultra-high field NMR study of Ce:YAG also identified two partially overlapped peaks comprising the two-neighbor peak labeled as AA here, although the specific origin of this splitting was not discussed [18]. Other mechanisms for such splitting could involve site distortion (and thus lowering of local symmetry) caused by cation size mismatch, leading to changes in bond distances and angles, which again might be expected to vary depending on the relative locations of two neighboring dopants. A related symmetry-reduction mechanism can play a role in peak splitting, even in the case of a single paramagnetic cation neighbor, as hypothesized for the "D" peak in Nd-doped YPO_4 [30]. In our own recent study of paramagnetic shifts observed in ^{25}Mg spectra of Ni^{2+} doped MgO, we identified two nearly equal area peaks close to the expected additive peak location of a single

neighbor shift (Fig. 7, O and P, from that paper), but did not deduce a source of this apparent splitting [7]. We suggest here that this might also be related to magnetic coupling of adjacent unpaired electron spins.

^{89}Y NMR spectra

In fully relaxed ^{89}Y spectra of 0.3%Ce:YAG, 0.7%Nd-LHPG:YAG, 0.9%Tm:YAG and 1.1%Yb-LHPG:YAG samples, a single peak corresponding to eight coordinated Y^{3+} is visible within 1 ppm of the previously reported position of 222 ppm [25]. In the single pulse experiments used here, we estimate that pulse delays of between 1 and 4 hours were needed for full relaxation. In contrast, spectra with pulse delays smaller than 5 s are dominated by fast relaxing paramagnetic features and contain almost no contributions from the principal peak. Figure 10 displays the 1 s pulse delay spectra for 0.3%Ce:YAG, 0.7%Nd-LHPG:YAG, and 1.1%Yb:YAG.; peak locations are reported in the supporting information.

Figure 10. ^{89}Y spectra of Ln:YAG. Only fast relaxing features are visible. The unshifted peak position as observed in more fully relaxed spectra is indicated with a dashed line. Absolute vertical scale is the same for all spectra (14.1 T, 1 s pulse delays).

Qualitatively, the spectra of the Yb^{3+} and Tm^{3+} doped samples have similar shapes. The peaks shifted to the highest frequency are probably products of the same nuclear-electronic spin configuration, because they are both relatively large, have the greatest shifts up in frequency, and are the only peaks with identifiable sidebands, the latter probably implying strong dipolar coupling and a nearby magnetic neighbor. We label these peak α in both spectra. Comparisons of 0.9%Tm:YAG spectra with pulse delay times of 0.05, 1, and 2 s also indicate that the α peak is the first peak to be fully relaxed. The α peak for Yb:YAG has three total visible sideband peaks that comprise

28% of its total intensity; that for Tm:YAG has one pair of visible sidebands that comprise 46% of its intensity. Both sideband manifolds are asymmetric with the first lower frequency sideband larger than the first higher frequency sideband. We identified no other spinning sidebands in any of our ^{89}Y spectra, an observation that, given our signal-to-noise levels, agrees with the previously reported CSA parameters for the pure material [25]. All of the features unique to this α peak indicate that it is most likely caused by the $\text{YO}_8\text{-}3.7$ configuration, i.e. the first dodecahedral cation neighbor. The relative magnitudes of the shifts for this resonance ($\text{Tm} > \text{Yb}$) seem to roughly correspond with the relative values of $\langle S_z \rangle$ and C^D for these cations (Table 6) as well as with the observed effects on ^{27}Al spectra where Tm shifts were also correspondingly larger. The ^{89}Y spectra for these two compositions also show a second major peak shifted only slightly up in frequency from the primary chemical shift, a resolved peak at lower frequency, and at least one shoulder with a smaller shift, Table S4. These might all result from more distant configurations. However, despite these apparent similarities, we are hesitant to make more specific assignments without a more complete understanding of the relaxation and/or higher signal to noise ratios. The magnitude of these shifts is worth considering with respect to other lanthanides, which may help guide future research. For example, the C^D value for Er^{3+} is between Tm^{3+} and Yb^{3+} values, however the $\text{Er}^{3+} \langle S_z \rangle$ value is approximately twice as large as for Tm^{3+} , thus ^{89}Y spectra of Er:YAG could help estimate the size of the Fermi contact interaction relative to the Tm^{3+} and Yb^{3+} spectra. This may even indicate that early NMR work on Tb:YAG may not have analyzed data over large enough spectral window [17]. For example, a noisy feature visible at ca. 900 ppm in the static spectra may have been a

paramagnetically shifted resonance; this would not be unreasonable given the large values of both $\langle S_z \rangle$ and C^D for Tb^{3+} .

In the 0.3%Ce:YAG spectra, we identified three peaks, two of which are shifted to higher frequencies and the third of which is residual intensity at the unshifted peak location. In the 0.7%NdLHPG:YAG spectra, we identified five peaks. Two are shifted to higher frequencies and two are shifted to lower frequencies. Peak locations are again given in Table S4.

We attempted to determine the intensities of the shifted peaks in the 1 s pulse delay spectra relative to the fully relaxed spectra, which could help constrain peak assignments. However, the low signal-to-noise ratios of the latter resulted in large uncertainties, and we could not reasonably use peak area constraints to make peak assignments.

For the Ce:YAG spectra, we label the most-shifted peak as “ β ”, which was also reported in a previous study of a similar material and assigned to the first-neighbor cation configuration $YO_8-3.7$ [18]. We agree with the criteria used to make this assignment, which would then suggest that peaks α (Yb:YAG and Tm:YAG) and β (Ce:YAG) are the result of the same configuration. This conclusion is somewhat troubling since the sign of Ce^{3+} shifts are therefore not opposite in sign to those of the Yb^{3+} and Tm^{3+} shifts as observed in the ^{27}Al spectra and expected from $\langle S_z \rangle$ and C^D values. One possible explanation could be different relative contributions from the Fermi contact shifts and the pseudocontact shifts for the different dopants for even the first neighbor shifts for ^{89}Y . Finally, we note that the overall shapes of the spectra for Nd:YAG, as well as the number of observable shifted resonances, are different from

those of the samples. We thus hesitate to speculate about peak assignments for this composition.

Conclusions

This paper presents new work analyzing paramagnetic shifts in solid-state NMR spectra of YAG laser materials. Temperature effects on paramagnetic shifts enabled swift identification of these resonances in most cases. For systems with broadening and peak overlap, we present approaches to identifying shifted peak positions that take advantage of differential relaxation or varying nutation frequencies for different sites. Collecting fully relaxed spectra, which are necessary for quantitative analysis, is aided by paramagnetic cations, but can still be challenging for ^{89}Y .

In the ^{27}Al spectra, our results on the octahedral AlO_6 paramagnetic shifts indicate that trends in the lanthanide series can be approximately explained by the expectation value of electronic spin and the Bleaney's constant. Peak areas for single-neighbor shifts can be described well by random dopant cation distributions in the low concentration Ce^{3+} and Yb^{3+} materials studied. In a 0.7%Nd:YAG grown using laser heated pedestal growth, additional data for two-neighbor shifts confirm this conclusion. Tm-Cr samples studied here serve as examples of dopant concentrations and/or coupling strengths that compromise resolution and should likely be avoided for future work. For ^{27}Al spectra, a general trend of a dominant Fermi contact shift for dopants within the first cation shell was identified. However, for ^{89}Y spectra, we observe shifts that apparently do not simply follow the anticipated trends for the four lanthanides studied. More theoretical work needs to be done to predict these interactions with accuracy.

In ^{27}Al spectra for Ce, Nd, Tm, and Yb doped samples, as well as ^{89}Y data for Tm and Yb doped samples, spinning sideband manifolds for strongly-shifted resonances (near neighbor configurations) showed clear asymmetry. Significant central transition intensity observable in the asymmetric spinning sideband manifold suggests dipolar coupling and/or chemical or paramagnetic shift anisotropy. Quadrupolar coupling frequency appears, however, to be minimally affected by neighboring paramagnetic cations. Future work investigating this asymmetry may provide additional insight into the local environment surrounding dopant cations.

Future work on YAG could pursue many promising directions that would further the capabilities of this technique, as solid state NMR is well suited for investigating ceramic laser materials for both trace impurity phases and magnetic dopant distributions. The presence of unpaired spins could be further utilized with Dynamic Nuclear Polarization NMR which has been shown for ^{89}Y in solids to increase the observable signal considerably [35]. ^{17}O NMR investigation of doped YAG is possible, which may be simplified by the single oxygen site. The cubic symmetry of YAG may lend itself to MAS NMR susceptibility matching, which could help resolve the broad peaks in the Tm doped YAG [36]. In systems with two different dopants, twice shifted peaks may provide insight into clustering or avoidance of the two species. Further work at additional dopant concentrations and with other lanthanide dopants may additionally contribute to the understanding of paramagnetic interactions in inorganic solids and the development of future laser materials.

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