

Crystal Structure Studies on the Garnet $Y_3Al_5O_{12}$ by ^{27}Al Single-Crystal NMR Spectroscopy

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Abstract: The capability of single-crystal NMR to extract crystal structure information is demonstrated by a ^{27}Al single-crystal NMR study of the garnet $Y_3Al_5O_{12}$ (YAG). By rotation of a YAG single crystal about three perpendicular axes 93 ^{27}Al spectra have been acquired, resulting in the observation of 3132 resonance frequencies. These have been assigned to three tetrahedral and four octahedral aluminum sites. A thorough analysis of the magnitudes and relative orientations of the quadrupole coupling tensors for these seven aluminum sites indicates the presence of a combination of symmetry elements that is unique to cubic crystal structures. Upper limits for the magnitudes of the anisotropic chemical shielding interaction are also determined for the seven aluminum sites and show that the geometrical arrangements of oxygen ions in the first coordination sphere of all aluminum sites must be nearly regular tetrahedra and octahedra, respectively.

Introduction

Crystals of the garnet $Y_3Al_5O_{12}$ (YAG) have recently attracted considerable interest in a variety of studies among chemists and physicists due to its properties as a laser host material. Previous solid-state NMR investigations of this material involve ^{27}Al single-crystal¹ and magic-angle spinning (MAS)^{2–4} NMR. The early ^{27}Al single-crystal work¹ took advantage of the YAG crystal structure (XRD)⁵ in the setup of the crystal orientation to reduce the complexity of the experimental spectra used for determination of the quadrupole coupling constant for the two different crystallographic aluminum sites (one tetrahedral, Al_{IV} , and one octahedral, Al_{VI}). On the other hand, the ^{27}Al MAS studies aimed at a determination of the relative populations for the two aluminum sites.^{2–4}

Generally, single-crystal NMR is known to provide not only the magnitudes of the tensors for the anisotropic NMR interactions but also their orientation in the crystal structure when the method is combined with XRD. However, considering the high performance of today's single-crystal NMR techniques⁶ it appears to us that information on crystal structures should be available for certain crystal symmetries from "state-of-the-art" single-crystal NMR, e.g., from ^{27}Al single-crystal NMR of YAG.

A recent ^{71}Ga single-crystal NMR study of YGG ($Y_3Ga_5O_{12}$),⁷ the gallium analogue of YAG, has shown that single-crystal

NMR provides information partly complementary to that obtained by XRD on the YGG crystal structure. Thus, it seems possible, but still appears a challenge, to perform a quite detailed description of the crystal structure of YAG solely by ^{27}Al single-crystal NMR. Furthermore, in the light of our recent observation on the first clear-cut existence of an ^{27}Al chemical shielding anisotropy (CSA) from ^{27}Al single-crystal NMR of sapphire,⁸ it would be of interest to investigate the possible presence of ^{27}Al CSA's for the two aluminum sites in YAG, especially since they exhibit higher local symmetry than the single Al_{VI} site in sapphire.

In this work we describe the acquisition and results of a complete analysis of the ^{27}Al single-crystal NMR spectra of YAG. Probably this task represents one of the most complex single-crystal NMR studies undertaken so far with respect to the number of observed resonances and their assignments. These resonances arise from the five ^{27}Al single-quantum transitions of seven magnetically nonequivalent Al atoms, resulting in a total of 3255 resonances for the 93 experimental spectra acquired. Within the spectral window used, 3132 of these resonances have been observed and assigned. The assignment and analysis have been carried out employing the software package ASICS (Analysis of Single-Crystal Spectra) recently described and developed in our laboratory.⁶

Experimental Section

The YAG crystal investigated in this work was grown by the Czochralski method with a MSR-3 Malvern type device and the radiofrequency heated iridium crucible in a N_2 atmosphere. The crucible loading was prepared with stoichiometric amounts of high-purity (99.999%) oxides. A single crystal of YAG (size $4 \times 4 \times 4$

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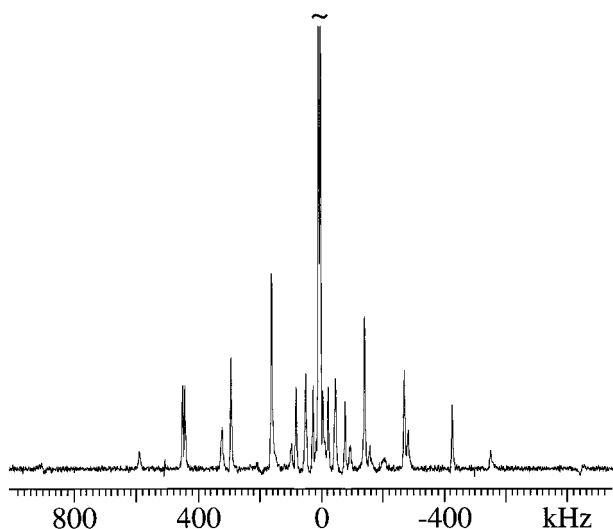


Figure 1. Typical ^{27}Al NMR spectrum of a single crystal of YAG. The spectrum results from rotation about the $-z^T$ axis ($\theta = 54^\circ$) and shows 25 resolved resonances within the spectral window of 2 MHz. The central resonance has been cut off at about $1/6$ of its height.

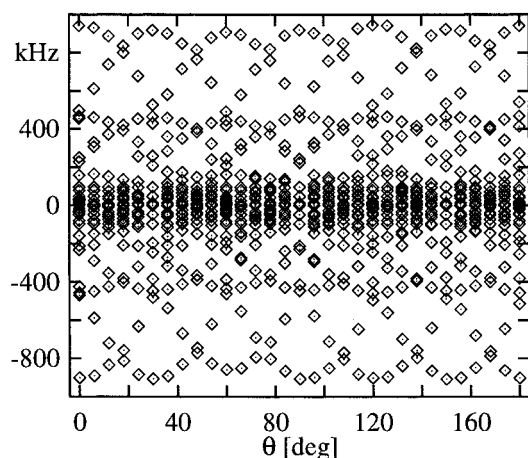


Figure 2. Plot of the 802 resonance frequencies (before their assignment) observed from rotation about the $-z^T$ axis versus the rotation angle (θ).

mm^3) was cut from an optically homogeneous crystal and used for recording the ^{27}Al single-crystal NMR spectra on a Varian UNITY-400 spectrometer at 104.19 MHz. The experiments were performed with use of a home-built single-crystal NMR probe equipped with a new goniometer design.^{6,9} With an arbitrary orientation the crystal is glued onto the surface of a dovetail tenon (T) that fits into three mortises of the goniometer, a design that allows rotation of the crystal around the three perpendicular axes, $-x^T$, y^T , and $-z^T$, respectively.⁹ The rotation of the goniometer is fully automated and is controlled by the SUN Sparc 10/54 workstation of the spectrometer via a home-built interface.⁶ This results in a very high accuracy ($\pm 0.1^\circ$) for the angular setting. For each axis 31 spectra were recorded following an incrementation of 6° for the rotation angle (θ). All experiments employed single-pulse excitation ($\tau_p = 0.3 \mu\text{s}$ for $\gamma B_1/2\pi = 55 \text{ kHz}$), an optimized relaxation delay of 1 s, 128 scans, and a spectral width of 2 MHz. The total acquisition time for all 93 spectra was 4 h. ^{27}Al isotropic chemical shifts (δ_{iso}) are in ppm relative to an external 1.0 M solution of $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$).

Results and Discussion

A typical ^{27}Al NMR spectrum of the YAG single crystal is shown in Figure 1. The spectrum displays 25 resolved reso-

Table 1. ^{27}Al Quadrupole Coupling Parameters (C_Q , η_Q) and Isotropic Chemical Shifts (δ_{iso}) for the Three Al_{VI} and Four Al_{IV} Sites in YAG

	C_Q (MHz)	η_Q	δ_{iso} (ppm)
tetrahedral			
1	6.113 ± 0.016	0.010 ± 0.003	82.1 ± 0.7
2	6.086 ± 0.015	0.004 ± 0.003	81.6 ± 0.8
3	6.103 ± 0.016	0.004 ± 0.004	80.6 ± 0.4
“average” ^a	6.103 ± 0.009	0.006 ± 0.002	81.5 ± 0.4
Brog <i>et al.</i> ¹	6.017 ± 0.017	0 ^b	c
octahedral			
1	0.6359 ± 0.0017	0.004 ± 0.008	2.0 ± 0.4
2	0.6368 ± 0.0019	0.010 ± 0.005	2.1 ± 0.5
3	0.641 ± 0.003	0.009 ± 0.009	2.3 ± 0.5
4	0.638 ± 0.004	0.018 ± 0.009	2.2 ± 0.5
“average” ^a	0.6371 ± 0.0012	0.010 ± 0.004	2.1 ± 0.2
Brog <i>et al.</i> ¹	0.632 ± 0.005	0 ^b	c

^a Parameters are determined from simultaneous fitting of the resonances from all the magnetically equivalent but crystallographically nonequivalent sites (see text). ^b Axial symmetry assumed due to the YAG crystal symmetry. ^c Isotropic chemical shift not reported.

nances of varying intensity within the spectral window of 2 MHz. The assignment of these resonances to the different transitions (central and satellite) and magnetically nonequivalent aluminum nuclei is performed by using a plot of the resonance frequencies versus the rotation angle for each of the three rotation axes. Figure 2 shows this plot for the spectra recorded for rotation about the $-z^T$ axis. Although the plot appears very complex, it is possible to assign all resonances to 32 curves with use of our software package ASICS. These curves can immediately be assigned to seven distinct aluminum sites and they include seven pairs of outer ($m = \pm 5/2 \leftrightarrow \pm 3/2$) and inner ($m = \pm 3/2 \leftrightarrow \pm 1/2$) satellite transitions. The resonances for these transitions are observed to fit the function⁹

$$\nu_{m \leftrightarrow m-1}^{(\alpha)}(\theta) = A_m^{(\alpha)} + B_m^{(\alpha)} \cos 2\theta + C_m^{(\alpha)} \sin 2\theta \quad (1)$$

However, of the total of seven central transitions ($m = 1/2 \leftrightarrow -1/2$) it was only possible to observe four of these according to the function¹⁰

$$\nu_{1/2 \leftrightarrow -1/2}^{(\alpha)}(\theta) = A_{1/2}^{(\alpha)} + B_{1/2}^{(\alpha)} \cos 2\theta + C_{1/2}^{(\alpha)} \sin 2\theta + D_{1/2}^{(\alpha)} \cos 4\theta + E_{1/2}^{(\alpha)} \sin 4\theta \quad (2)$$

The lack of the observation for three of the curves for the central transitions is caused by overlap of the experimental resonances (*vide infra*). The satellite transitions are dominated by the first-order quadrupolar interaction while the central transition will be influenced by the combined effect of the second-order quadrupolar shift and CSA. Explicit expressions for the coefficients ($\alpha = -x^T$, y^T , or $-z^T$) in eqs 1 and 2 are given elsewhere.^{9,10} The parameters describing the quadrupole coupling tensor are defined as

$$C_Q = \frac{eQV_{zz}}{h}, \quad \eta_Q = \frac{V_{yy} - V_{xx}}{V_{zz}} \quad (3)$$

where the $V_{\alpha\alpha}$ terms are the principal axis elements of the electric field gradient (EFG) tensor, defined in the order

$$|V_{zz}| \geq |V_{xx}| \geq |V_{yy}| \quad (4)$$

The ^{27}Al quadrupole coupling parameters and isotropic chemical shifts for the seven aluminum sites are listed in Table

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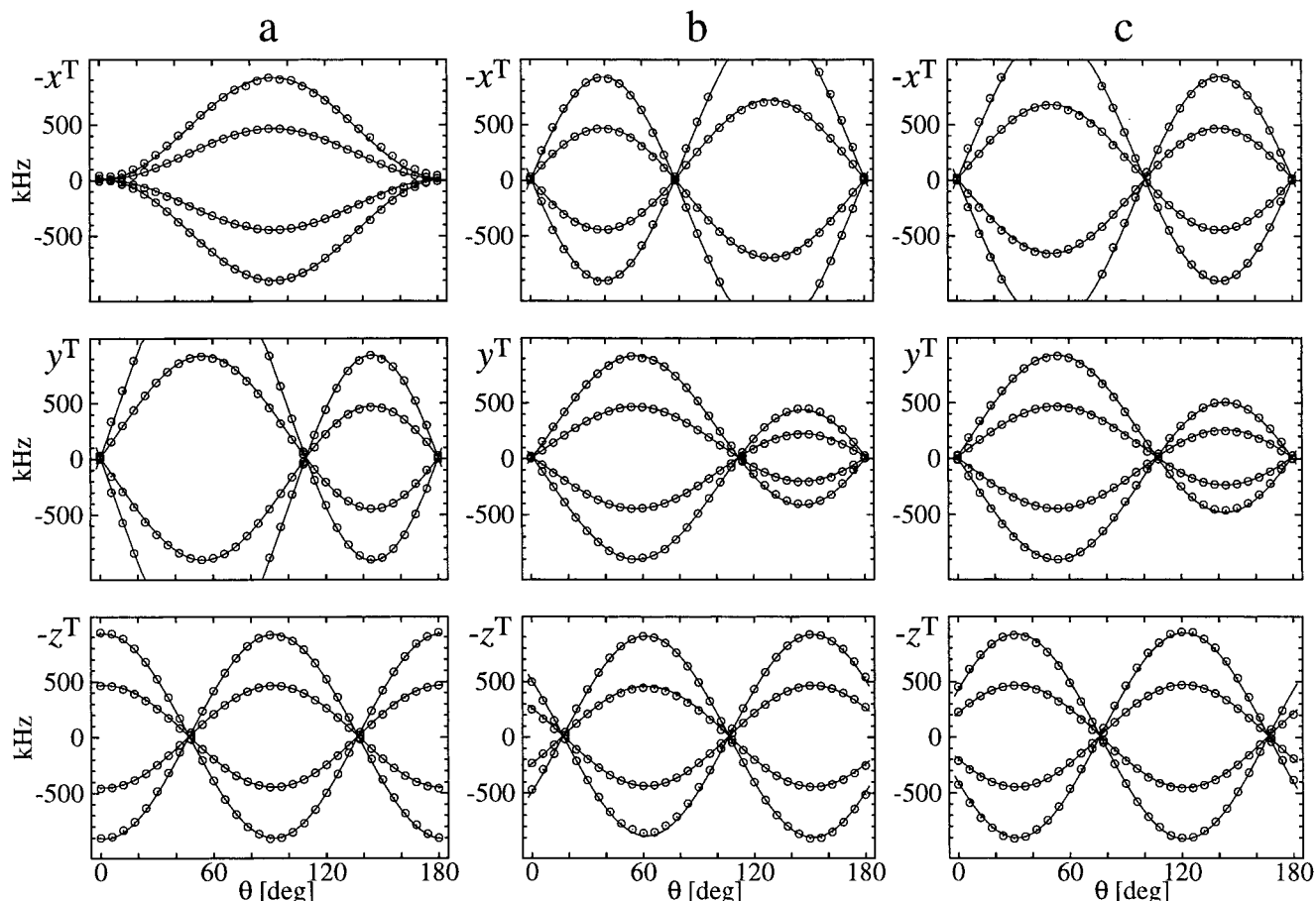


Figure 3. Rotation plots of the three Al_{IV} sites (a, b, and c) for all three rotation axes ($-x^T$, y^T , and $-z^T$ from top to bottom). The experimental resonance frequencies are marked as circles, while the solid lines represent curves calculated by eq 1 with use of the optimized parameters in Table 1.

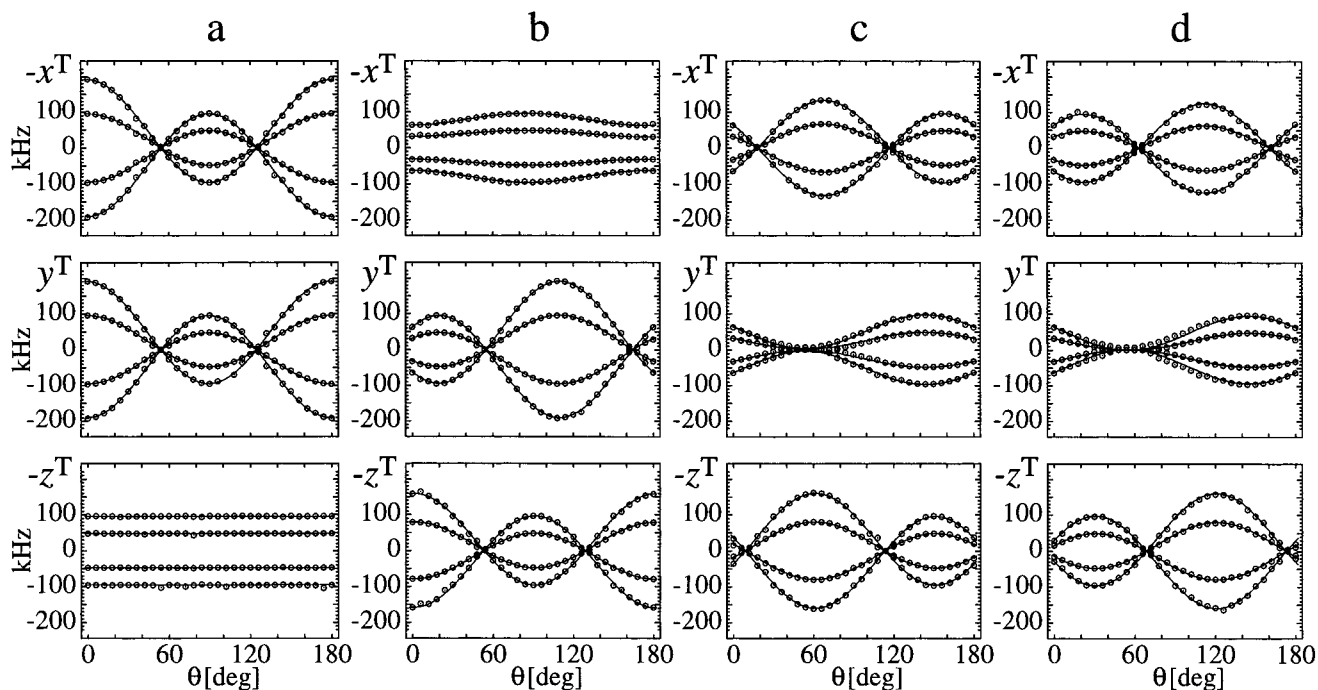


Figure 4. Rotation plots of the four Al_{VI} sites (a, b, c, and d) for all three rotation axes ($-x^T$, y^T , and $-z^T$ from top to bottom). The experimental resonance frequencies are marked as circles, while the solid lines represent curves calculated by eq 1 with use of the optimized parameters in Table 1.

1 along with their error limits evaluated as 95% confidence intervals for the individual parameters.¹¹ The isotropic chemical shifts indicate the presence of three tetrahedral and four

octahedral aluminum sites. The rotation plots for the satellite transitions are shown in Figures 3 and 4 for the Al_{IV} and Al_{VI} sites, respectively. In these figures the solid lines represent

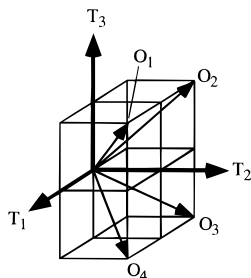


Figure 5. The orientation of the unique principal elements for the four octahedral aluminum sites (marked O_i , $i = 1, 2, 3$, and 4) with respect to the orthogonal frame expanded by the three principal V_{zz} elements for the three magnetically nonequivalent tetrahedral aluminum sites (marked T_i).

curves calculated by eq 1 employing the optimized parameters from Table 1. The fact that the three magnetically nonequivalent Al_{IV} sites have the same values for the quadrupole coupling parameters within experimental errors indicates that these sites belong to only one crystallographic Al_{IV} site. Likewise, the similar quadrupole coupling parameters for the four Al_{VI} sites indicate that these sites also originate from the same crystallographic Al_{VI} site. This supposition is further supported by the orientations for the unique principal elements ($i = 1, 2$, and 3) of the three EFG tensors for the three magnetically nonequivalent Al_{IV} sites with respect to the tenon frame. The three principal elements are mutually perpendicular and thereby define the axes of an orthogonal coordinate system (C) related to the crystal frame rather than the tenon frame. Most importantly, it also follows from the direction cosines that the unique principal elements ($i = 1, 2, 3$, and 4) for the four Al_{VI} sites are aligned along the $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}\bar{1}1]$, and $[\bar{1}1\bar{1}]$ orientations of this C coordinate system. As shown in Figure 5 this geometrical configuration indicates the presence of 3-fold rotation axes (e.g., C_3) along the $\langle 111 \rangle$ directions and 4-fold rotation axes (e.g., C_4) along the $\langle 100 \rangle$ directions. Since the quadrupole coupling tensors all exhibit axial symmetry ($\eta_Q = 0$) this suggests that the aluminum atoms are located *on* the symmetry axes with their unique element V_{zz} aligned along these axes, i.e., the crystallographic Al_{IV} and Al_{VI} sites exhibit local 4- and 3-fold symmetries, respectively. The presence of 4-fold symmetry along the axes of an orthogonal frame and additional 3-fold symmetry along the space diagonals of this frame represents a unique combination of symmetry elements of cubic crystal structures.¹² This thorough analysis of the ^{27}Al single-crystal NMR data leads us to conclude that YAG has a cubic crystal structure with two crystallographically distinct aluminum sites (one of tetrahedral and the other of octahedral coordination). The Al_{IV} site has a local 4-fold symmetry oriented along a $\langle 100 \rangle$ axis and the Al_{VI} site has a local 3-fold symmetry oriented along a $\langle 111 \rangle$ axis. These results are in excellent agreement with the YAG crystal structure obtained from XRD.⁵

Three of the four rotation plots obtained for the central transitions make excursions across a frequency range of approximately 11 kHz and are assigned to the three Al_{IV} sites. The fourth rotation plot displays essentially a constant frequency for all crystal orientations and originates from overlapping resonances of the four Al_{VI} sites. Figure 6 shows the rotation plots for the central transitions of the three Al_{IV} sites. The solid

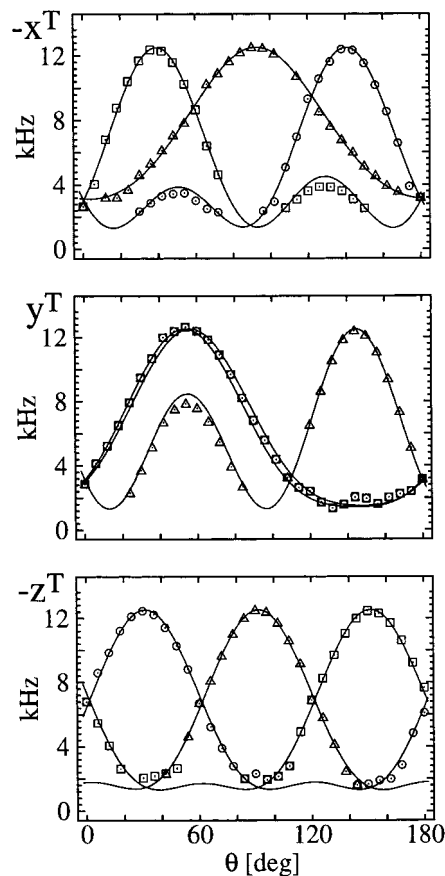


Figure 6. Rotation plots of the central transition frequencies for the three Al_{IV} sites for all three rotation axes ($-x^T$, y^T , and $-z^T$ from top to bottom). The experimental resonances are marked with triangles, squares, and circles and correspond to the Al_{IV} sites numbered 1, 2, and 3 in Table 1, respectively. It has not been possible to observe the resonances located between 0 and 1 kHz since in this region these resonances overlap with those of the four Al_{VI} sites.

lines correspond to simulations including the second-order quadrupolar shift as calculated from the quadrupole coupling parameters determined from the satellite transitions and employing the optimized value for the isotropic chemical shifts (Table 1). Inclusion of the CSA as an additional interaction in the simulations^{7,8,10} makes no significant improvement in the root-mean-square deviation between the experimental and simulated resonance frequency curves for either the Al_{IV} or the Al_{VI} sites but results in upper limits for the magnitude of the CSA (Al_{IV} : $\delta_\sigma = 0 \pm 3$ ppm and Al_{VI} : $\delta_\sigma = 0 \pm 2$ ppm).

It has been reported that generally the CSA interaction is dominated by short-range effects such as bonding and charge distributions within the first coordination sphere.^{13,14} While this also holds for the quadrupole coupling interaction, experimental observations show that this interaction in addition appears to be more sensitive to long-range effects from the crystal lattice compared to the CSA. With these assumptions the CSA interaction seems a useful probe for investigating the symmetry of the first coordination sphere of the nucleus studied. A recent study reported an ^{27}Al CSA for the single Al_{VI} site in sapphire ($\delta_\sigma = -17.6 \pm 0.6$ ppm, $\eta_\sigma = 0$),⁸ where the Al^{3+} ions are located in slightly distorted octahedra, i.e., the octahedra are stretched along their 3-fold symmetry axis resulting in two

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different sets of Al–O bond lengths (1.852 and 1.971 Å), each observed for three of the six Al–O bonds.¹⁵ Therefore, the present values for the ²⁷Al CSA's in YAG ($\delta_\sigma = 0$) indicate that the oxygen atoms in the first coordination sphere of the Al_{IV} and Al_{VI} sites should be arranged as regular tetrahedra and octahedra, respectively. This is in excellent agreement with the XRD crystal structure of YAG which reports equal bond lengths for all Al–O bonds of the Al_{IV} (1.761 Å) and Al_{VI} (1.937 Å) sites and only small deviations from ideal tetrahedral and octahedral O–Al–O angles.⁵

Combined analyses of the total number of resonance frequencies for the satellite transitions of *all* three Al_{IV} sites (1060 frequencies) and for the four Al_{VI} sites (1483 frequencies), i.e., the crystallographically equivalent but magnetically nonequivalent sites are assumed to have the same magnitude but different orientation for their quadrupole coupling tensor, result in the “average” quadrupole coupling parameters summarized in Table 1. For comparison with parameters determined in this study, the data of the early ²⁷Al single-crystal study¹ are also included in Table 1. We note that there is a minor discrepancy for the quadrupole coupling constant for the Al_{IV} site while there is an excellent agreement for the Al_{VI} site. Comparison of the present results with a recent ⁷¹Ga single-crystal NMR study of YGG⁷ shows that the magnitudes of the two EFG tensors of YGG are larger than those for YAG. As discussed elsewhere⁷ this is ascribed to the somewhat more distorted environments of the gallium ions in YGG when compared to the aluminum ions in YAG. The determination of negligible ²⁷Al CSA's for YAG as compared to the observation of ⁷¹Ga CSA's for the two sites

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in YGG (Ga_{IV}: $\delta_\sigma = 54 \pm 50$ ppm, Ga_{VI}: $\delta_\sigma = 24 \pm 3$ ppm)⁷ may be justified by the more distorted environments of the gallium ions in YGG and/or the fact that anisotropic shieldings are more often encountered for heavy-metal nuclei than for the lighter elements.

Conclusion

In addition to representing probably one of the most challenging single-crystal NMR studies performed so far, this study demonstrates that information regarding crystal structures may in certain cases be obtained from single-crystal NMR spectroscopy as exemplified by the present ²⁷Al NMR investigation of YAG. The orientations and magnitudes of the EFG tensors for seven magnetically nonequivalent Al³⁺ ions (three tetrahedral and four octahedral) observed for YAG show the presence of a combination of symmetry elements in the YAG single crystal that is unique to cubic crystal structures. Moreover, the upper limits determined for the magnitude of the CSA interaction for these Al³⁺ ions indicate that the oxygen atoms located in their first coordination sphere are arranged in nearly perfect tetrahedral and octahedral geometries. Thus, this work seems to represent one of the most detailed examples on the application of single-crystal NMR for characterization of crystal structures.

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