^{71}Ga Chemical Shielding and Quadrupole Coupling Tensors of the Garnet $Y_3Ga_5O_{12}$ from Single-Crystal ^{71}Ga NMR

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A single-crystal ^{71}Ga NMR study of the garnet $Y_3Ga_5O_{12}$ (YGG) has resulted in the determination of the first chemical shielding tensors reported for the ^{71}Ga quadrupole. The single-crystal spectra are analyzed in terms of the combined effect of quadrupole coupling and chemical shielding anisotropy (CSA). ^{71}Ga quadrupole coupling and CSA parameters for the two (tetrahedrally and octahedrally coordinated) gallium sites with axial symmetry in YGG (Ga_{IV}, $C_Q = 13.1 \pm 0.2$ MHz and $\delta_\sigma = 54 \pm 50$ ppm; Ga_{VI}, $C_Q = 4.10 \pm 0.06$ MHz and $\delta_\sigma = 24 \pm 3$ ppm) are fully consistent with its cubic crystal structure which supports the reliability of the experimental data. In addition, the ^{71}Ga and ^{27}Al isotropic chemical shifts for YGG and YAG give further support to the linear correlation observed earlier between ^{71}Ga and ^{27}Al isotropic chemical shifts.

Introduction

^{71}Ga (spin $I = {}^3/_2$, 39.6% natural abundance) has a fairly large quadrupole moment ($Q = 1.1 \times 10^{-29}$ m^2) which gives rise to quite broad NMR lines for the central transition in powders because of the second-order term of the quadrupolar interaction. In spite of this, solid-state ^{71}Ga NMR is becoming an important tool for structural investigations of inorganic gallium compounds.[1−8] In particular solid-state ^{71}Ga NMR has been applied to studies of the isomorphous substitution of aluminum by gallium in zeolites,[1−6] a replacement of particular interest since it changes the acidity and thereby the catalytic properties of the zeolite.[9−11] Garnets of type $Y_3Al_{5-x}Ga_xO_{12}$ ($0 \le x \le 5$) are of special industrial interest, due to their application as laser hosts, and have recently been characterized by ^{27}Al MAS and static ^{71}Ga NMR.[7] However, the ^{71}Ga spectra, which were analyzed using the quadrupolar interaction only, showed some unexpected features which were interpreted as an additional gallium site.

Single-crystal[12−17] along with powder (static[18−25] and MAS[26−31]) NMR studies of quadrupolar nuclei have demonstrated that for certain heavier nuclei (e.g., ^{51}V, ^{59}Co, ^{87}Rb, ^{95}Mo, ^{133}Cs) the chemical shielding anisotropy (CSA) interaction cannot be neglected but must be considered in addition to the quadrupolar interaction in the spectral interpretation. Because of the increased interest in the application of ^{71}Ga solid-state NMR to materials science, it is imperative to know whether the CSA can or cannot be neglected for this nucleus. This is of special interest in the light of recent determinations of CSA's for ^{27}Al.[32,33] Furthermore, with today's magnetic field strengths up to 18.8 T it has been shown that NMR spectra of even lighter quadrupolar nuclei (e.g. ^{23}Na and ^{27}Al) are also influenced by the CSA.[33]

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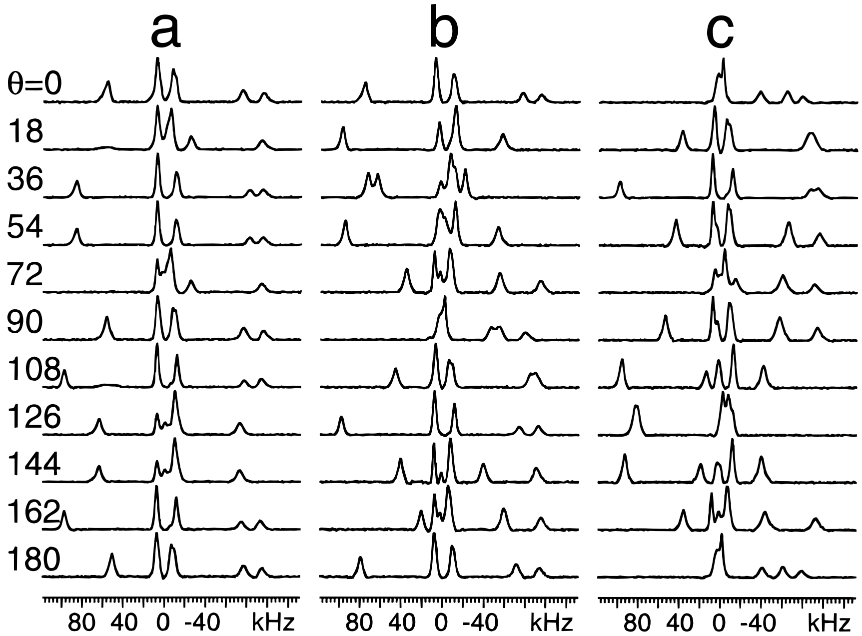

Figure 1. Single-crystal ^{71}Ga NMR spectra (9.4 T) for the central transition of the garnet YGG each recorded following an 18° increment in the rotation about the axes (a) $-x^T$, (b) y^T, and (c) $-z^T$.

This work reports the succesful determination of parameters describing the combined effect of ^{71}Ga CSA and quadrupole coupling required for the interpretation of single-crystal ^{71}Ga NMR spectra of the garnet $Y_3Ga_5O_{12}$ (YGG). The results clearly demonstrate that even at ordinary magnetic field strengths (e.g., 9.4 T used in this study) the ^{71}Ga CSA needs to be taken into account. In contrast to the recent study[7] it is shown that YGG has two crystallographically distinct Ga^{3+} sites, one tetrahedrally and the other octahedrally coordinated, and not three different sites. This is in accordance with the crystal structure determined by X-ray diffraction.[34,35]

Experimental Section

The garnet $Y_3Ga_5O_{12}$ single crystal was grown by the Czochralski technique.[36] For the NMR investigation a piece of size approximately equal to $1 \times 5 \times 3$ mm^3 was cut from a much larger crystal. The ^{71}Ga single-crystal NMR experiments were performed at 121.99 MHz (9.4 T) on a Varian UNITY-400 spectrometer equipped with a home-built single-crystal NMR probe described elsewhere.[37] The goniometer of the single-crystal probe has three dovetail mortises into which a tenon (with the crystal glued onto its surface) is mounted. Mounting the tenon (T) in the three mortises results in rotation about the $-x^T$, y^T, and $-z^T$ axes, respectively.[37] Eleven spectra, each for an angular increment of 18°, were recorded for each rotation axis with an accuracy of ±0.4° for the angular adjustment. The NMR experiments employed a spectral width of 500 kHz, single-pulse excitation with a pulse width $\tau_p = 2\ \mu s$ for $\gamma B_1/2\pi \approx 55$ kHz ($\tau_p = 4.5\ \mu s$ for a 90° solution flip angle), and 512 scans with a relaxation delay of 2 s. Isotropic chemical shifts (ppm) and the frequency scales (kHz) in all figures are relative to an external solution of 1.0 M $Ga(NO_3)_3$.

The quadrupole coupling and CSA interactions are defined by the parameters

$$C_Q = \frac{eQ}{h}V_{zz} \qquad \eta_Q = \frac{V_{yy} - V_{xx}}{V_{zz}} \tag{1}$$

$$\delta_{iso} = {}^1/_3(\delta_{xx} + \delta_{yy} + \delta_{zz}) \qquad \delta_\sigma = \delta_{iso} - \delta_{zz} \qquad \eta_\sigma = \frac{\delta_{xx} - \delta_{yy}}{\delta_\sigma} \tag{2}$$

where the principal elements $\lambda_{\alpha\alpha}$ ($=V_{\alpha\alpha}$, $\delta_{\alpha\alpha}$) are defined as

$$|\lambda_{zz} - {}^1/_3(\lambda_{xx} + \lambda_{yy} + \lambda_{zz})| \geq |\lambda_{xx} - {}^1/_3(\lambda_{xx} + \lambda_{yy} + \lambda_{zz})| \geq |\lambda_{yy} - {}^1/_3(\lambda_{xx} + \lambda_{yy} + \lambda_{zz})| \tag{3}$$

Results and Discussion

The garnet YGG represents a challenging material for ^{71}Ga NMR because its large quadrupole couplings[7] make it extremely difficult to obtain high-resolution spectra of a powder sample. Although of higher resolution, single-crystal ^{71}Ga NMR spectra of YGG may, following the crystal structure,[34,35] be complicated by the presence of three magnetically nonequivalent but crystallographically equivalent Ga^{3+} ions with tetrahedral coordination to oxygen (Ga_{IV}). In addition, there are four magnetically nonequivalent Ga^{3+} ions of octahedral coordination (Ga_{VI}) within one crystallographic site.[34,35] Thus, altogether a maximum of seven gallium sites may be distinguishable in the single-crystal ^{71}Ga spectra.

Figure 1 shows the YGG single-crystal ^{71}Ga NMR spectra resulting from rotation about the $-x^T$ (a), y^T (b), and $-z^T$ (c) axes. Within the chosen spectral window of 500 kHz only the central ($m = -{}^1/_2 \leftrightarrow {}^1/_2$) transitions are observed. Three of the resonances in the spectra make excursions over a range of 200 kHz and are assigned to the three magnetically nonequivalent Ga_{IV} ions. Four overlapping lines are observed in the central region of all spectra, and for clarification Figure 2 shows an expansion of the spectrum resulting from rotation about the y^T axis for $\theta = 108°$ along with a deconvolution of the four lines assigned to the four magnetically nonequivalent Ga_{VI} ions. A preliminary analysis of the seven individual gallium resonances gave $C_Q = 13.1$ MHz, $\eta_Q = 0$, and $\delta_{iso} = 219$ ppm for three of the resonances showing these to originate from the tetrahedral (Ga_{IV}) sites.[8] The four remaining resonances gave $C_Q = 4.1$ MHz, $\eta_Q = 0$, and $\delta_{iso} = 6$ ppm in agreement with the assignment of these resonances to the crystalographically equivalent Ga_{VI} sites.

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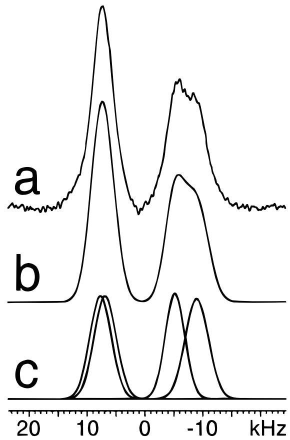

Figure 2. (a) Expansion of the experimental single-crystal ^{71}Ga NMR spectrum recorded following rotation about the y^T axis by $\theta = 108°$. (b) Complete deconvolution of the experimental spectrum in (a) clearly demonstrating the presence of four distinct and equally intense resonances in (c).

The analysis of the single-crystal spectra is carried out in terms of the combination of the quadrupole coupling (Q) and CSA (σ) interactions as recently done in the case of ^{39}K and ^{87}Rb NMR.[14,16,17] The resonance frequency for the central transition is given by

$$\nu^{(\alpha)}_{-1/2\leftrightarrow 1/2}(\theta) = A^{(\alpha)}_{Q,\sigma} + B^{(\alpha)}_{Q,\sigma}\cos 2\theta + C^{(\alpha)}_{Q,\sigma}\sin 2\theta + D^{(\alpha)}_{Q}\cos 4\theta + E^{(\alpha)}_{Q}\sin 4\theta \quad (4)$$

where α $(=-x^T, y^T, \text{ or } -z^T)$ is the rotation axis and the coefficients $M^{(\alpha)}_{Q,\sigma}$ are functions of the quadrupole coupling and CSA tensors in the tenon (T) frame according to the expressions and definitions of Euler angles given elsewhere.[17] The rotation plots of the experimental resonance frequencies are shown in Figures 3 and 4 for the three magnetically nonequivalent Ga_{IV} and four magnetically nonequivalent Ga_{VI} ions, respectively. The full curves are given by eq 4 and employ the optimized parameters for the quadrupole coupling and CSA. These parameters are summarized in Table 1 along with their error limits that are calculated as 95% confidence intervals for the optimized parameters.[38]

The quadrupole coupling parameters (C_Q, η_Q) for both the Ga_{IV} and Ga_{VI} sites are determined with very small error limits. Moreover, the CSA parameters (δ_σ, η_σ, δ_{iso}) and the angle (χ) between the unique principal elements V_{zz} and δ_{zz} are determined with a good accuracy for the Ga_{VI} site. On the other hand, it turns out that the resonance frequencies for the Ga_{IV} site are rather insensitive toward variation of the CSA parameters because of the dominance of the quadrupole coupling for this site. Therefore, it has only been possible to determine the CSA (δ_σ) and the isotropic chemical shift (δ_{iso}) for this site whereas the η_σ and χ have been kept fixed at $\eta_\sigma = \chi = 0$ during the optimization as a consequence of the crystal symmetry *(vide infra)*.

The reliability of the parameters may also be discussed in the light of the crystal symmetry. Within the cubic crystal structure of YGG (space group I$a\bar{3}d$) the Ga_{IV} and Ga_{VI} sites are located in the symmetry positions 24(d) and 16(a), respectively.[34] Both of these sites have local $\bar{n}$-symmetry ($n = 4$ for Ga_{IV} and $n = 3$ for Ga_{VI}), implying that the quadrupole coupling and CSA tensors should be axial symmetric ($\eta_Q = \eta_\sigma = 0$) and

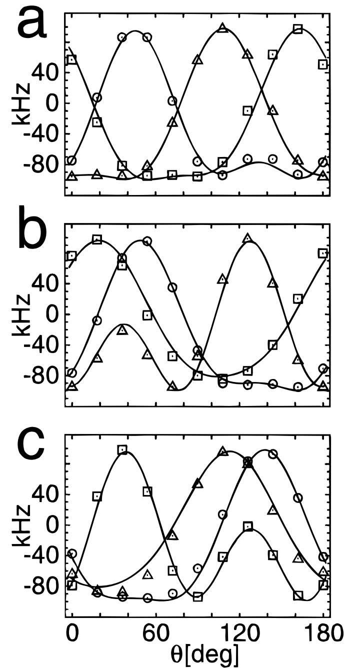

Figure 3. Rotation plots for the tetrahedral gallium site (Ga_{IV}) of YGG with the experimental resonance frequencies marked with dotted circles, boxes, and triangles for the three magnetically nonequivalent Ga^{3+} ions for rotation about the three axes (a) $-x^T$, (b) y^T, and (c) $-z^T$. The curves are calculated by employing the optimized parameters (Table 1) and eq 4.

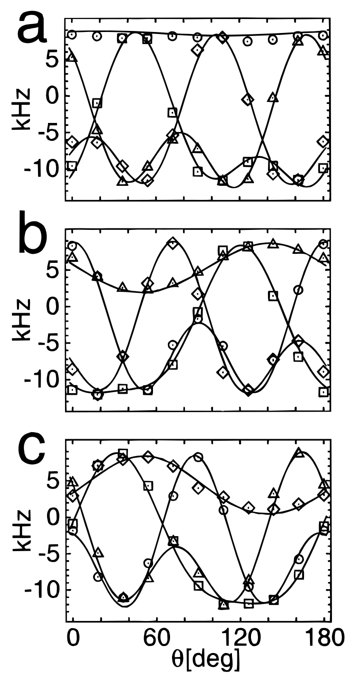

Figure 4. Rotation plots for the octahedral gallium site (Ga_{VI}) of YGG with the experimental resonance frequencies marked with dotted circles, boxes, traingles, and diamonds for the four magnetically nonequivalent Ga^{3+} ions for rotation about the three axes (a) $-x^T$, (b) y^T, and (c) $-z^T$. The full curves are calculated by employing the optimized parameters (Table 1) and eq 4.

that the unique principal elements (V_{zz} and δ_{zz}) should be aligned along the inversion axis.[39] The parameters in Table 1 demonstrate that from an experimental point of view the axial symmetry of the quadrupole coupling tensor ($\eta_Q = 0$) is fulfilled for both sites. Moreover, for the Ga_{VI} site it has been possible

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Table 1. ^{71}Ga Quadrupole Coupling (C_Q, η_Q), Chemical Shielding Anisotropy (δ_σ, η_σ), Isotropic Chemical Shift (δ_{iso}), and the Angle χ between V_{zz} and δ_{zz} for Ga_{IV} and Ga_{VI} in YGG

site	C_Q (MHz)	η_Q	δ_{iso} (ppm)	δ_σ (ppm)	η_σ	χ (deg)	ref
Ga_{VI}	4.10 ± 0.06	0.03 ± 0.04	5.6 ± 1.2	24 ± 3	0.2 ± 0.3	2 ± 5	this work
	4.6	0	14				7
Ga_{IV}	13.1 ± 0.2	0.05 ± 0.03	219 ± 19	54 ± 50	0^a	0^a	this work
	13	0	245				7

^{a} Parameter fixed during optimization. See text.

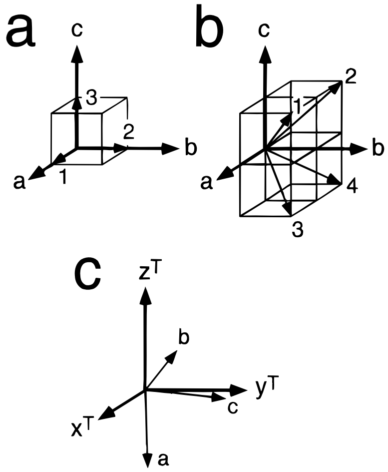

Figure 5. Orientation of the unique principal elements $V_{zz}^{(i)}$ within the crystal frame for (a) the three magnetically nonequivalent Ga_{IV} ions (marked 1, 2, and 3) and (b) the four magnetically nonequivalent Ga_{VI} ions (marked 1, 2, 3, and 4). The numbering used refers to the numbers used for the unique principal elements $V_{zz}^{(i)}$ in Table 2. Through the symbols dotted circles, boxes, triangles, and diamonds in Table 2 the $V_{zz}^{(i)}$ elements may be related to the rotation plots in Figures 3 and 4. (c) Orientation of the crystallographic axes with respect to the tenon (T) frame.

to experimentally verify the axial symmetry of the CSA tensor and the coincidence of the principal elements V_{zz} and δ_{zz}. From the crystal symmetry it can be concluded that the three (four) magnetically nonequivalent Ga_{IV} (Ga_{VI}) ions have the inversion axis aligned along the 100, 010, and 001 (111, $11\bar{1}$, $1\bar{1}1$, and $\bar{1}11$) axis, respectively, as depicted in Figure 5a,b. The orientation of the three principal elements ($V_{zz}^{(i)}$, $i = 1-3$) for the tetrahedral site is found from diagonalization of the quadrupole coupling tensors in the tenon frame. In accordance with the crystal structure these three principal elements are found to be mutually perpendicular (Figure 5a), which lead to the orientation depicted in Figure 5c for the crystal axes within the tenon frame. The direction cosines for the principal axes $V_{zz}^{(i)}$ of both Ga_{IV} and Ga_{VI} with respect to the crystal frame are then calculated in a straightforward manner, and the results are shown in Table 2. Most interesting, within a few degrees the direction cosines describing the orientation of the four Ga_{VI} principal elements ($V_{zz}^{(i)}$, $i = 1-4$) are oriented along the cubic diagonals of the crystal frame as expected from the crystal structure (Figure 5b).

For comparison with the present parameters the ^{71}Ga quadrupole coupling parameters recently determined from a static ^{71}Ga powder NMR study of YGG[7] are shown in Table 1. The parameters for Ga_{IV} are in good agreement with the parameters from the present single-crystal work. Furthermore, the problems encountered in the line shape analysis for the Ga_{VI} region of the powder spectrum[7] (i.e., requiring the introduction of an additional Ga site) have been clarified in the present work. Only one single octahedral site is necessary for the interpretation of the single-crystal spectra, in accordance with the crystal symmetry.

Table 2. Direction Cosines Describing the Orientation of the Unique Principal Elements $V_{zz}^{(i)}$ of the ^{71}Ga Quadrupole Coupling Tensors for Ga_{IV} and Ga_{VI} in YGG

	a	*b*	*c*	Symbol^a
		Ga_{IV}		
$V_{zz}^{(1)}$	1.000	0.000	0.000	⊙
$V_{zz}^{(2)}$	0.000	1.000	0.000	⊡
$V_{zz}^{(3)}$	0.000	0.000	1.000	△
		Ga_{VI}		
$V_{zz}^{(1)}$	0.573	0.598	0.560	⊡
$V_{zz}^{(2)}$	−0.517	0.650	0.557	⊙
$V_{zz}^{(3)}$	0.578	0.598	−0.556	△
$V_{zz}^{(4)}$	−0.591	0.552	−0.558	◇

^{a}Symbols used in Figures 3 and 4.

A linear correlation between ^{27}Al and ^{71}Ga isotropic chemical shifts

$$\delta_{iso}(^{71}Ga) = (2.83 \pm 0.10)[\delta_{iso}(^{27}Al)] - (4.50 \pm 4.90) \quad (5)$$

has been observed for structurally analogous aluminum and gallium compounds for which only oxygen atoms occupy the first coordination sphere.[8] This correlation is fully supported by the present ^{71}Ga isotropic chemical shifts for YGG when compared to the ^{27}Al isotropic shifts recently determined for YAG ($Y_3Al_5O_{12}$) by ^{27}Al MAS NMR.[7,40] From the latter data and eq 5 we predict $\delta_{iso}(Ga_{IV}) = -2 \pm 5$ ppm and $\delta_{iso}(Ga_{IV}) = 211 \pm 9$ ppm in excellent agreement with the experimental results. Thus, considering the well-known linear correlation between ^{27}Al and ^{29}Si chemical shifts generally found in minerals,[41,42] it is expected that ^{71}Ga NMR may provide important information about the geometry of the gallium sites (e.g., bond lengths and bond angles), in a manner similar to applications of ^{29}Si and ^{27}Al isotropic chemical shifts.[41−51]

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The ^{71}Ga and ^{27}Al quadrupole couplings in YGG and YAG are expected to reflect the similarities/dissimilarities for the local environment of these nuclei in the two materials. However, the experimentally determined ^{27}Al quadrupole couplings in YAG ($C_Q(Al_{IV})$ = 9 MHz and $C_Q(Al_{VI})$ = 0.9 MHz)[40] are smaller than the corresponding ^{71}Ga values for YGG (Table 1), although the quadrupole moment for ^{27}Al ($Q = 1.5 \times 10^{-29}$ m^2) is larger than for ^{71}Ga ($Q = 1.1 \times 10^{-29}$ m^2). These unexpected results may be accounted for in the light of the local geometry of the gallium and aluminum nuclei. It has been shown[41,42] that electric field gradients are influenced by the mean deviation

$$\Theta = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\theta_i - \theta_{reg})^2} \qquad (6)$$

between the O−M−O bond angles (θ_i) measured from XRD[34,35,52] and the bond angles in a regular polygon (θ_{reg}). For YGG we find $\Theta(Ga_{IV})$ = 7.54° and $\Theta(Ga_{VI})$ = 6.04° whereas the corresponding ^{27}Al values for YAG (6.85 and 3.35°) are somewhat smaller. Thus, this may account for the difference observed for the ^{27}Al and ^{71}Ga quadrupole couplings in YAG and YGG and also the fact that the quadrupole couplings for the M_{VI} sites show larger discrepancies than those for the M_{IV} sites.

In conclusion, it has been shown that analysis of the ^{71}Ga single-crystal NMR spectra of YGG requires consideration of the combined effect of quadrupole coupling and CSA. Two distinct crystallographically nonequivalent gallium sites are found, in accordance with the crystal structure. Moreover, the orientation of the quadrupole coupling tensors with respect to the crystal frame have been determined from the NMR results and confirm the crystal symmetry. The ^{71}Ga CSA parameters determined for YGG indicate that the CSA must be considered in general as an additional interaction to the quadrupolar interaction in solid-state ^{71}Ga NMR. Finally, a linear correlation between ^{27}Al and ^{71}Ga isotropic chemical shifts is fully supported when comparing the present ^{71}Ga results with a recent ^{27}Al study of YAG.

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