Crystal Structure Studies by Single-Crystal NMR Spectroscopy. ^{71}Ga and ^{69}Ga Single-Crystal NMR of β-Ga_2O_3 Twins

Thomas Vosegaard,[†] Inger P. Byriel,[†] Laurent Binet,[‡] Dominique Massiot,[§] and Hans J. Jakobsen*[,†]

Contribution from the Instrument Centre for Solid-State NMR Spectroscopy, Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark, Laboratoire de Chimie Appliquée de l'Etat Solide, ENSCP, 11 rue P&M Curie, 75231 Paris Cedex 05, France, and Centre de Recherches sur la Physique des Hautes Températures, 1D Ave de la Recherche Scientifique, 45071 Orléans Cedex 2, France

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Abstract: ^{71}Ga and ^{69}Ga single-crystal NMR spectra of a β-Ga_2O_3 twin have been analyzed in terms of the ^{71}Ga/^{69}Ga quadrupole coupling and chemical shielding anisotropy (CSA) interactions. Analyses of the magnitudes and orientations of the interaction tensors for the two distinct crystallographic gallium sites in the two twin crystals resulted in accurate values for the parameters describing the quadrupole coupling and CSA tensors. Moreover, it has been possible to determine the actual twin-law of our sample crystal. Along with a recent ^{71}Ga single-crystal NMR investigation of YGG, this work shows that gallium CSA generally has to be taken into account in addition to the dominant quadrupole coupling interaction.

Introduction

Solid-state gallium (^{71}Ga/^{69}Ga) NMR is becoming an increasingly important tool in structural studies related to gallium chemistry, e.g., of gallium-containing zeolites and minerals.[1] In particular ^{71}Ga MAS and static NMR of powder samples have been used since the ^{71}Ga isotope is easier to approach than its ^{69}Ga partner because of the higher Larmor frequency and smaller quadrupole moment for ^{71}Ga. From these studies ^{71}Ga isotropic chemical shifts and in some cases also ^{71}Ga quadrupole coupling parameters have been determined. Furthermore, a recent ^{71}Ga single-crystal NMR study of the garnet $Y_3Ga_5O_{12}$ (YGG)[2] has demonstrated that ^{71}Ga may generally exhibit the tensorial interactions from not only the quadrupole coupling but also the anisotropic chemical shielding. Obviously this adds to the complexity of the experimental spectra and their analysis but also to the avaliable potential information characterizing the gallium sites.

β-Ga_2O_3 is a transparent conducting oxide, and its potential applications in optoelectronic devices have recently been investigated.[3] Moreover, this material exhibits a free electron memory effect that results in a hysteresis of the conduction electron spin resonance depending on the magnetic field sweep direction.[4] A polycrystalline sample of β-Ga_2O_3 has recently been investigated by ^{71}Ga/^{69}Ga MAS and static NMR of the central ($m = {}^1/_2 \leftrightarrow -{}^1/_2$) transitions.[5] This material has tetrahedral (Ga_{IV}) and octahedral (Ga_{VI}) sites, and quadrupole coupling constants (C_Q's) ranging from 8 to 18 MHz were determined for the two isotopes ($^{71}Ga_{VI}$: $C_Q = 8.3$ MHz and $^{69}Ga_{IV}$: $C_Q = 17.5$ MHz). In the presence of such large quadrupole coupling interactions it becomes difficult to record spectra of polycrystalline samples without severe intensity distortions of the broad powder pattern resulting from the second-order broadening of the central transition (width of ∼1 MHz at 7.1 T). To overcome this problem the static ^{69}Ga spectrum was obtained by summation of several subspectra acquired by using different carrier frequencies.[5]

In the presence of large anisotropic interactions single-crystal NMR spectroscopy has recently proven of great advantage in studies of quadrupolar nuclei.[6] The reason is that single-crystal NMR is not sensitive at all to the intensity distortions caused by imperfect excitation because the technique relies only on the frequencies and not intensities for the discrete narrow resonances. This is in contrast to the undistorted line shape required for analysis of the normally quite featureless static powder spectra. The excellent performance of single-crystal NMR in such cases has been demonstrated in a recent ^{87}Rb single-crystal NMR study of the two rubidium sites for Rb_2CrO_4,[6] a material investigated as a powder by a variety of solid-state NMR techniques. However, all the powder methods were only able to successfully characterize one of the two rubidium sites.[6]

This work describes a ^{71}Ga and ^{69}Ga single-crystal NMR investigation of β-Ga_2O_3. The spectra are analyzed in terms of the magnitudes and orientations of the quadrupole coupling and chemical shielding anisotropy (CSA) tensors yielding accurate values for the parameters describing these two interac-

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* Address correspondence to this author.

[†] University of Aarhus.

[‡] Laboratoire de Chimie Appliquée de l'Etat Solide.

[§] Centre de Recherches sur la Physique des Hautes Températures.

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tions for the two crystallographic gallium sites. During the course of the investigation we discovered that our β-Ga$_2$O$_3$ crystal is a twin. While twinning usually leads to problems in X-ray diffraction we demonstrate that twin crystals may in certain cases be taken into advantage in single-crystal NMR studies. All ^{71}Ga and ^{69}Ga resonances from the two twins are observed. These resonances result not only in two independent sets of data but more importantly, from the data it has been possible to derive the orientation of the β-Ga$_2$O$_3$ unit cell (relative to the frame of the goniometer) and also the actual twin-law from the relative orientation of the NMR tensors for the two twins.

Experimental Section

A centimeter size colorless transparent crystal of β-Ga$_2$O$_3$ was grown by melting and recrystallization according to the Verneuil method.[7] The starting powder, purchased from Metal-Europe, was 99.99% pure. From the original crystal, a smaller sample (size $\sim 2 \times 2 \times 7$ mm^3) was cut out and glued onto a dovetail tenon (T) that fits into the goniometer of our home-built single-crystal NMR probe.[8] This design allows rotation of the crystal about the following three orthogonal axes: $-x^{\mathrm{T}}$, y^{T}, and $-z^{\mathrm{T}}$. The rotation about a particular axis is fully automated and is controlled by the SUN Sparc 10/30 host computer of the spectrometer via a home-built interface that ensures a high accuracy ($\pm 0.1°$) for the angular setting.[9] The ^{71}Ga and ^{69}Ga single-crystal NMR experiments were all performed on a Varian INOVA-400 spectrometer at 121.94 and 95.95 MHz, respectively. Single-pulse excitation ($\tau_{\mathrm{p}} = 2\ \mu$s for $\gamma B_1/2\pi = 55$ kHz) was employed for both isotopes along with an optimized relaxation delay of 2 s, 512/1024 scans, and a spectral width of 500 kHz/2 MHz for ^{71}Ga/^{69}Ga. For both isotopes 21 spectra were recorded for each rotation axis following an incrementation in the rotation angle (θ) of 9°. Isotropic chemical shifts (δ_{iso}) are in ppm relative to an external 1.0 M solution of Ga(NO$_3$)$_3$.

Results and Discussion

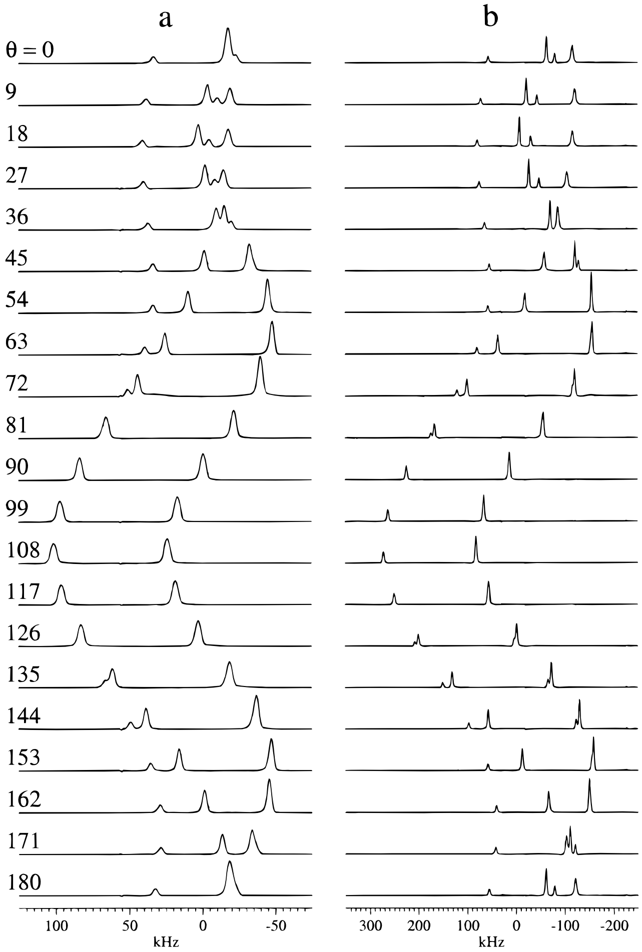

Figure 1. ^{71}Ga (a) and ^{69}Ga (b) single-crystal NMR spectra showing the region of the central transitions for the twin β-Ga$_2$O$_3$ crystal. Both sets of spectra are recorded for rotation about the $-x^{\mathrm{T}}$ axis.

Figure 1 shows the ^{71}Ga and ^{69}Ga single-crystal NMR spectra of the central transitions recorded for rotation about the $-x^{\mathrm{T}}$ axis. The spectra for each isotope exhibit almost the same dependence on the rotation angle (θ). However, the ^{71}Ga resonances span $\sim$250 kHz while the ^{69}Ga resonances span $\sim$750 kHz because of the larger quadrupole moment for this isotope. The typical line widths are 2.5−4 and 3−5 kHz for the ^{71}Ga and ^{69}Ga resonances, respectively. For each spectrum a maximum of four resolved central transition resonances with relative intensities of approximately 1:1:2:2 are observed. The assignment of these resonances to four different gallium sites is accomplished by the software package *ASICS* (*A*nalysis of *S*ingle-*C*rystal *S*pectra) recently developed in our laboratory.[9] In the high-field and secular approximations the resonance frequency for the central transition, influenced by the combined effect of second-order quadrupolar shift and CSA, is given by the equation

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

where α ($=-x^{\mathrm{T}}$, y^{T}, or $-z^{\mathrm{T}}$) is the axis of rotation. Explicit expressions for the coefficients M^{α} are given elsewhere.[10] The quadrupole coupling and CSA tensors are described by the parameters

$$C_{\mathrm{Q}} = \frac{eQV_{zz}}{h}, \qquad \eta_{\mathrm{Q}} = \frac{V_{yy} - V_{xx}}{V_{zz}} \quad (2)$$

$$\delta_{\mathrm{iso}} = {}^{1}\!/_{3}(\delta_{xx} + \delta_{yy} + \delta_{zz}), \qquad \delta_{\sigma} = \delta_{\mathrm{iso}} - \delta_{zz}, \qquad \eta_{\sigma} = \frac{\delta_{xx} - \delta_{yy}}{\delta_{\sigma}} \quad (3)$$

where the principal axis elements $A^{\sigma,\mathrm{P}_\sigma}_{\alpha\alpha} = -\delta_{\alpha\alpha}$ and $A^{\mathrm{Q},\mathrm{P}_\mathrm{Q}}_{\alpha\alpha} = eQ/(2I(2I-1)h)V_{\alpha\alpha}$ are defined in the order

$$|A^{\lambda,\mathrm{P}_\lambda}_{zz} - \frac{1}{3}\mathrm{Tr}(\mathbf{A}^{\lambda})| \geq |A^{\lambda,\mathrm{P}_\lambda}_{xx} - \frac{1}{3}\mathrm{Tr}(\mathbf{A}^{\lambda})| \geq |A^{\lambda,\mathrm{P}_\lambda}_{yy} - \frac{1}{3}\mathrm{Tr}(\mathbf{A}^{\lambda})| \quad (4)$$

with P$_\lambda$ denoting the principal axis frame for the interaction λ. The relative orientation of P$_\sigma$ and P$_\mathrm{Q}$ is described by the Euler angles (ψ, χ, ξ) according to the previous definition.[10]

The observation of four distinct resonances in the experimental spectra is inconsistent with the monoclinic crystal symmetry of β-Ga$_2$O$_3$ (space group *C*2/*m*, No. 12).[11] According to the crystal structure there should be only two (equally populated) gallium sites, namely the Ga$_{\mathrm{IV}}$ and the Ga$_{\mathrm{VI}}$ sites, each resulting in one resonance in the single-crystal spectra. The results of a preliminary analysis of the spectra in terms of

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Table 1. ^{71}Ga/^{69}Ga Quadrupole Coupling Parameters (C_Q, η_Q), Isotropic Chemical Shifts (δ_{iso}), and Relative Intensities for the Four Magnetically Nonequivalent Gallium Sites in the Twin β-Ga_2O_3 Crystal

isotope	site	C_Q (MHz)	η_Q	δ_{iso} (ppm)	intensity
^{71}Ga	Ga_{IV}	11.05 ± 0.04	0.884 ± 0.009	199 ± 3	1
		11.05 ± 0.05	0.878 ± 0.010	196 ± 4	2
	Ga_{VI}	8.13 ± 0.07	0.148 ± 0.017	25 ± 4	1
		8.08 ± 0.08	0.158 ± 0.019	20 ± 4	2
^{69}Ga	Ga_{IV}	17.58 ± 0.16	0.854 ± 0.020	244 ± 33	1
		17.69 ± 0.11	0.843 ± 0.015	238 ± 24	2
	Ga_{VI}	13.11 ± 0.13	0.139 ± 0.019	32 ± 19	1
		13.13 ± 0.12	0.133 ± 0.019	37 ± 17	2

the ^{71}Ga and ^{69}Ga quadrupole coupling parameters and the isotropic chemical shifts for the four sites are listed in Table 1. Error limits are calculated as 95% confidence intervals for the individual parameters[12] according to the procedure described elsewhere.[9] The quadrupole coupling parameters indicate the presence of only two crystallographically different gallium sites, since the parameters for the four sites are pairwise identical within error limits. The crystallographically equivalent but magnetically nonequivalent sites show relative intensities of approximately 1:2 in the spectra, suggesting that our sample crystal actually consists of two single crystals with relative volumes of 1:2.

The orientations of the principal elements, $V_{\alpha\alpha}$, with respect to the tenon frame are readily determined from diagonalization of the quadrupole coupling tensors. We note that the V_{yy} element for the Ga_{IV} site and the V_{xx} element for the Ga_{VI} site within each crystal are parallel. This is good agreement with the monoclinic β-Ga_2O_3 crystal structure in which the Ga_{IV} and Ga_{VI} positions are located on a mirror plane perpendicular to the *b* axis.[11] As usual, this implies that one of the principal elements of the NMR tensors should be perpendicular to the mirror plane, i.e., parallel to the *b* axis in this case.[13] Thereby we have verified the local mirror-plane symmetry of the two gallium sites, and moreover, the orientation of the crystallographic *b* axis with respect to the tenon frame has been determined for each of the two crystals, i.e., the *b* axis is aligned along the V_{yy} (Ga_{IV}) and V_{xx} (Ga_{VI}) elements. It is noted that the V_{yy} (Ga_{IV}) and V_{xx} (Ga_{VI}) elements for the two crystals of relative volume 1:2 are parallel, and therefore the crystallographic *b* axes for the two crystals are also parallel.

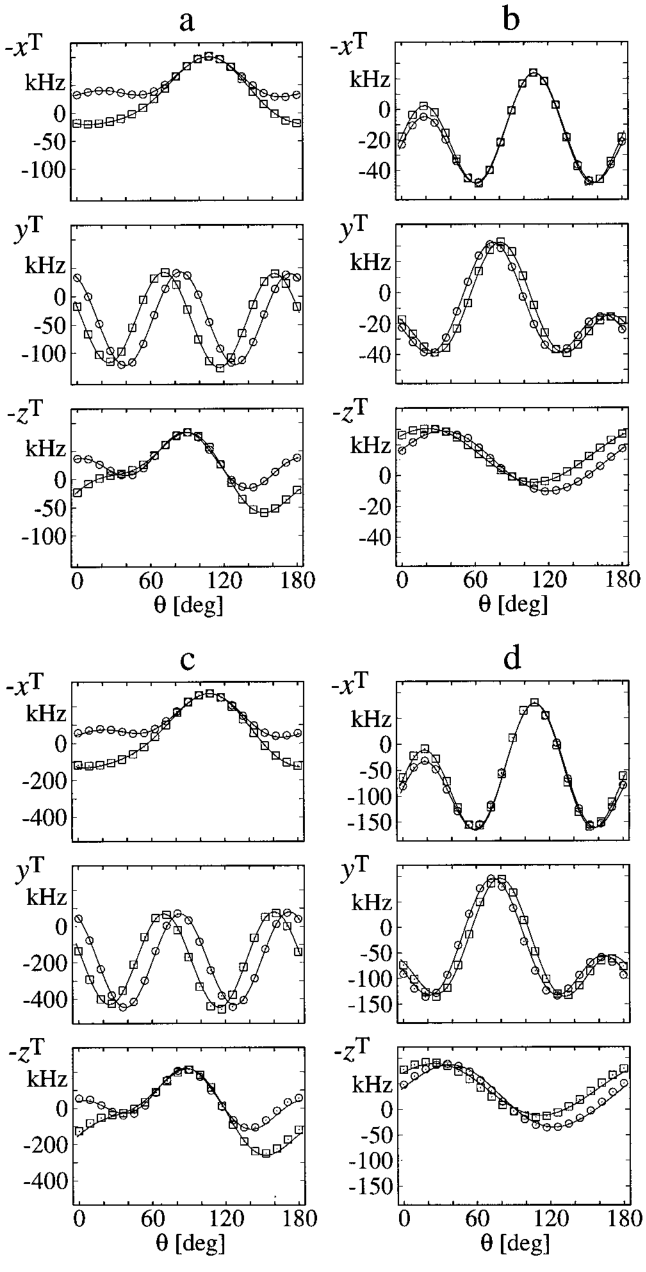

Figure 2. Rotation plots of the ^{71}Ga (a, b) and ^{69}Ga (c, d) resonances observed and assigned to the Ga_{IV} (a, c) and Ga_{VI} (b, d) sites. The solid lines represent curves calculated by eqs 1 and 4 with use of the optimized parameters in Table 2. Squares/circles indicate the resonances that originate from the larger/smaller of the two twins.

In the early X-ray structure study of β-Ga_2O_3 it was mentioned that this material is likely to grow twin crystals.[11] A detailed investigation of the twinning and morphology of β-Ga_2O_3 describing all possible twin-laws was performed by Wolten and Chase,[14] who, however, claimed the crystal symmetry to be triclinic (space group *P1*) rather than monoclinic. Most importantly, the β-Ga_2O_3 morphology study[14] showed the presence of type {001} faces in all of more than 100 crystals investigated, and the size of the these faces was always larger than all other faces of the crystals.[14] Our β-Ga_2O_3 crystal has the shape of an irregular polyhedron, however, with one face being considerably larger than all other faces. Using the results of the morphology study[14] we assume that this face is of type {001}. This assumption is fully supported by the observation that the [001] axis (i.e., the axis normal to the (001) plane) is approximately perpendicular to the V_{yy} (Ga_{IV}) and V_{xx} (Ga_{VI}) elements and thereby to the *b* axis in accordance with the crystal structure.

If the two crystals in our sample are twins they should somehow be related to each other by symmetry.[14] By investigation of the orientation of the V_{zz} elements (which are determined with the highest accuracy) for the Ga_{IV} and Ga_{VI} sites in the two crystals we find that the *same* symmetry axis (e.g., C_2 axis or an axis normal to a mirror plane) relates the V_{zz} elements from the two crystals for both the Ga_{IV} and Ga_{VI} sites. This symmetry axis is perpendicular to the *b* axis and, most importantly, also perpendicular to the (001) face and thereby parallel to the *c** axis. This shows that the two crystals are related by a C_2 axis along the crystallographic *c** axis or by a mirror plane perpendicular to this axis. A very common twin-law in β-Ga_2O_3 crystals matches this requirement. This is the

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[14] Wolten, G. M.; Chase, A. B. *J. Solid State Chem.* **1976**, *16*, 377. For simplicity we use the unit cell and nomenclature of Geller[11] and have translated the face and twin-law assignment given in the triclinic unit cell accordingly.

Table 2. ^{71}Ga/^{69}Ga Quadrupole Couplings (C_Q, η_Q), Chemical Shielding Anisotropies (δ_σ, η_σ), Isotropic Chemical Shifts (δ_{Iso}), and Relative Orientations of the Quadrupole Coupling and CSA Tensors (Ψ, X, ξ) for the Ga_{IV} and Ga_{VI} Sites

isotope	site	C_Q (MHz)	η_Q	δ_{iso} (ppm)	δ_σ (ppm)	η_σ	ψ (deg)	χ (deg)	ξ (deg)	ref
^{71}Ga	Ga_{IV}	11.20 ± 0.03	0.844 ± 0.007	196.4 ± 1.6	−33 ± 5	0.1 ± 0.2	0[a]	4 ± 4	0[a]	this work
		11.0	0.85[b]	200[b]						5
	Ga_{VI}	8.34 ± 0.03	0.094 ± 0.008	25 ± 1	37 ± 3	0.73 ± 0.18	0 ± 20	88 ± 3	−2 ± 17	this work
		8.3	0.08[b]	40[b]						5
^{69}Ga	Ga_{IV}	17.71 ± 0.09	0.854 ± 0.013	240 ± 20[c]	−33[a]	0.1[a]	0[a]	4[a]	0[a]	this work[c]
		17.5	0.85[b]	200[b]						5
	Ga_{VI}	13.21 ± 0.08	0.123 ± 0.012	38 ± 12	37[a]	0.73[a]	0[a]	88[a]	−2[a]	this work
		13.4	0.08[b]	40[b]						5

[a] Parameter fixed during optimization (see text). [b] Parameters determined from a multifield (7.1 and 11.7 T) and multinuclear (^{71}Ga and ^{69}Ga) analysis. [c] Simulations of this site employ direct diagonalization of the effective Hamiltonian given in eq 4.

so-called $(001)_m$ law[14] which expresses that the two twins are related by a mirror plane perpendicular to the c^* ([001]) axis. This allows us to conclude that our β-Ga_2O_3 crystal is a twin where the two twins are related by the $(001)_m$ twin-law.

The postulate of Wolten and Chase[14] that β-Ga_2O_3 should be triclinic with space group *P1* is, however, inconsistent with the present NMR results. This reduction of the crystal symmetry implies the presence of two crystallographically inequivalent Ga_{VI} and Ga_{IV} sites of equal population and without any local mirror-plane symmetry, whereas the monoclinic crystal structure implies only one tetrahedral and one octahedral site. The latter is consistent with our observation in the single-crystal spectra of only one Ga_{IV} and one Ga_{VI} site within each twin crystal. This combined with our observation of local mirror-plane symmetry at the gallium sites makes it unlikely that the crystal has the triclinic crystal symmetry. It has also been pointed out by Geller[15] that the symmetry of β-Ga_2O_3 is most likely monoclinic with space group $C2/m$.

A combined analysis of all resonances originating from two crystallographically equivalent but magnetically nonequivalent gallium sites (i.e., one from each of the two crystals) results in the optimized ^{71}Ga and ^{69}Ga quadrupole coupling and CSA parameters in Table 2. Figure 2 shows rotation plots of the resonances from all four magnetically nonequivalent gallium sites for the ^{71}Ga and ^{69}Ga spectra (the squares/circles indicate the resonances originating from the larger/smaller crystal) along with the solid lines that are calculated by using the optimized parameters from Table 2. It is not possible to obtain accurate values for the ^{69}Ga CSA because of the very large ^{69}Ga quadrupole coupling constants. Therefore, the ^{71}Ga CSA parameters have been employed in the optimizations of the ^{69}Ga quadrupole coupling parameters. The requirement that the CSA tensors must have one principal element parallel to the *b* axis *(vide supra)* is fulfilled for the Ga_{VI} site by the Euler angles χ, $\xi = 90°, 0°$ which are within the error limits. On the other hand, the optimizations of ^{71}Ga quadrupole coupling and CSA parameters for the Ga_{IV} site are quite insensitive toward variation of the Euler angles ψ and ξ. However, the above requirement of the crystal structure may be fulfilled by $\psi = m\pi/2$ and $\xi = n\pi$ ($m, n = 0$ or 1). Individual simulations of all combinations for n and m gives the smaller root-mean-square value with $\psi = \xi = 0°$ for the Ga_{IV} site.

Figure 3 shows the orientation of the quadrupole coupling and CSA tensors with respect to the molecular frame. The assignment of the two pairs of tensor orientations to each of the two twins cannot be determined by analysis of the NMR parameters. Therefore, this assignment has been performed on the basis of the orientation of the electric field gradient (EFG) tensor as calculated by an electrostatic point-monopole model.[16] This calculation only includes oxygen atoms in the first coordination sphere using effective oxygen charges determined from the Ga−O bond valences.[17,18]

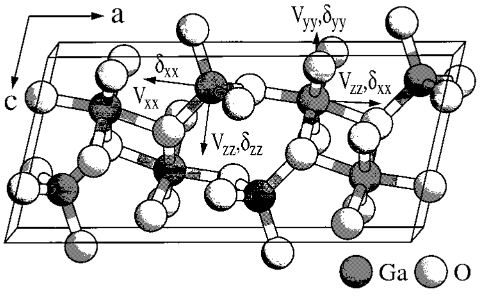

Figure 3. Projection of the monoclinic β-Ga_2O_3 unit cell ($Z = 2$) onto the *ac* plane, i.e., the mirror plane in which the Ga_{IV} and Ga_{VI} sites are located is the plane of the paper. The orientations of the quadrupole coupling and CSA principal elements with respect to the crystal frame are shown for the two sites.

With the large ^{69}Ga quadrupole coupling constant of Ga_{IV} ($C_Q = 17.6$ MHz) it is questionable if the high-field approximation ($H_Z \gg H_Q$, H_σ) is valid. Therefore, the analysis of this site has been carried directly by diagonalization of the effective Hamiltonian, $H_{eff} = H_Z + H_Q + H_\sigma$, which may be expressed in the $|m\rangle$ basis according to the matrix

$$\begin{pmatrix}
\frac{3}{4}\left(A_{xx}^{Q,L}+A_{yy}^{Q,L}+3A_{zz}^{Q,L}-2\upsilon_0\left[1-A_{zz}^{\sigma,L}\right]\right) & \frac{\sqrt{3}}{2}\left(2\left[A_{xz}^{Q,L}-iA_{yz}^{Q,L}\right]+\upsilon_0\left[A_{xz}^{\sigma,L}-iA_{yz}^{\sigma,L}\right]\right) & \frac{\sqrt{3}}{2}\left(A_{xx}^{Q,L}-A_{yy}^{Q,L}-i2A_{xy}^{Q,L}\right) & 0 \\
\frac{\sqrt{3}}{2}\left(2\left[A_{xz}^{Q,L}+iA_{yz}^{Q,L}\right]+\upsilon_0\left[A_{xz}^{\sigma,L}+iA_{yz}^{\sigma,L}\right]\right) & \frac{1}{4}\left(7\left[A_{xx}^{Q,L}+A_{yy}^{Q,L}\right]+A_{zz}^{Q,L}-2\upsilon_0\left[1-A_{zz}^{\sigma,L}\right]\right) & \upsilon_0\left[A_{xz}^{\sigma,L}-iA_{yz}^{\sigma,L}\right] & \frac{\sqrt{3}}{2}\left(A_{xx}^{Q,L}-A_{yy}^{Q,L}-i2A_{xy}^{Q,L}\right) \\
\frac{\sqrt{3}}{2}\left(A_{xx}^{Q,L}-A_{yy}^{Q,L}+i2A_{xy}^{Q,L}\right) & \upsilon_0\left[A_{xz}^{\sigma,L}+iA_{yz}^{\sigma,L}\right] & \frac{1}{4}\left(7\left[A_{xx}^{Q,L}+A_{yy}^{Q,L}\right]+A_{zz}^{Q,L}+2\upsilon_0\left[1-A_{zz}^{\sigma,L}\right]\right) & \frac{\sqrt{3}}{2}\left(2\left[-A_{xz}^{Q,L}+iA_{yz}^{Q,L}\right]+\upsilon_0\left[A_{xz}^{\sigma,L}-iA_{yz}^{\sigma,L}\right]\right) \\
0 & \frac{\sqrt{3}}{2}\left(A_{xx}^{Q,L}-A_{yy}^{Q,L}+i2A_{xy}^{Q,L}\right) & \frac{\sqrt{3}}{2}\left(-2\left[A_{xz}^{Q,L}+iA_{yz}^{Q,L}\right]+\upsilon_0\left[A_{xz}^{\sigma,L}+iA_{yz}^{\sigma,L}\right]\right) & \frac{3}{4}\left(A_{xx}^{Q,L}+A_{yy}^{Q,L}+3A_{zz}^{Q,L}+2\upsilon_0\left[1-A_{zz}^{\sigma,L}\right]\right)
\end{pmatrix}$$

where ν_0 is the Larmor frequency and L refers to a laboratory fixed frame in which the magnetic field is aligned along the z axis. Performing the calculation with this approach, however, yields only small changes (a few percent) to the ^{69}Ga quadrupole coupling parameters compared to those obtained with the high-field approximation (eq 1).

Since the ^{71}Ga and ^{69}Ga isotopes reside in identical environments we predict that the two EFG tensors, determined from the ^{71}Ga and ^{69}Ga quadrupole coupling parameters, are identical. Table 3 shows the principal elements ($V_{\alpha\alpha}$) of the EFG tensors for the Ga_{IV} and Ga_{VI} sites, and indeed we observe a very good

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Table 3. Principal Elements of the Electric Field Gradient Tensors for the Ga_{IV} and Ga_{VI} Sites Determined from the ^{71}Ga and ^{69}Ga Quadrupole Coupling Parameters[a]

site	isotope	V_{zz} [10^{21} V/m^2]	V_{yy} [10^{21} V/m^2]	V_{xx} [10^{21} V/m^2]
Ga_{IV}	^{71}Ga	4.373 ± 0.012	-0.341 ± 0.016	-4.032 ± 0.016
	^{69}Ga	4.36 ± 0.02	-0.32 ± 0.03	-4.04 ± 0.03
Ga_{VI}	^{71}Ga	3.256 ± 0.012	-1.475 ± 0.014	-1.781 ± 0.014
	^{69}Ga	3.25 ± 0.02	-1.425 ± 0.02	-1.825 ± 0.02

[a] The EFG principal elements are calculated by eq 2 with use of the following values for the quadrupole moments: $Q = 1.06 \times 10^{-29}$ m^2 (^{71}Ga) and $Q = 1.68 \times 10^{-29}$ m^2 (^{69}Ga).

agreement between the EFG tensor determined from the ^{71}Ga and ^{69}Ga quadrupole coupling parameters.

A recent ^{71}Ga and ^{69}Ga spin−echo NMR investigation of a polycrystalline β-Ga_2O_3 sample reported the quadrupole coupling parameters and isotropic chemical shifts for the two isotopes as obtained from multifield analyses of the overlapping powder line shapes for the two sites from static and MAS spectra.[5] These parameters are listed in Table 2 for comparison with the present results. There is generally a good agreement between the present parameters determined from single-crystal NMR and those of the static/MAS investigation. However, the parameters of the present work appear to be determined with a higher degree of accuracy.

Conclusion

Investigations of a β-Ga_2O_3 crystal by ^{71}Ga and ^{69}Ga single-crystal NMR spectroscopy have resulted in accurate ^{71}Ga and ^{69}Ga quadrupole coupling and CSA parameters and have demonstrated that our β-Ga_2O_3 crystal is a twin. For each twin two crystallographically distinct gallium sites, each with local mirror plane symmetry, are observed. The twinning yields two pairs of interaction tensors which allow a determination of the relevant twin-law for our β-Ga_2O_3 crystal. Our results support the monoclinic crystal symmetry of β-Ga_2O_3 while the proposed triclinic symmetry is inconsistent with our observation of only one Ga_{IV} and one Ga_{VI} site. The gallium CSA parameters determined here and the ^{71}Ga CSA parameters for YGG demonstrate that spectral effects caused by the CSA interaction are generally present in ^{71}Ga NMR.

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