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^{69,71}Ga solid state static, MAS and DAS NMR study of β–Ga_2O_3

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Abstract

We report solid state NMR results using both ^{69}Ga and ^{71}Ga in crystalline β-Ga_2O_3. In the β-Ga_2O_3 structure Gallium occupies both octahedral and tetrahedral sites which can be distinguished by analyzing the central transition lineshape of both nuclei. These static lineshapes extend over more than one MHz. A procedure to acquire such a wide linshape as a Variable Offset Cumulative Spectrum using full echo acquisition and without going to a point by point acquisition is described. In addition to static experiments, two dimensional ^{71}Ga dynamic-angle spinning results resolving both tetrahedral and octahedral sites in the isotropic dimension are obtained.

Résumé

Nous présentons les spectres RMN du ^{69}Ga et du ^{71}Ga dans β-Ga_2O_3. Dans cette structure le Gallium occupe des positions octahèdriques et tétrahèdriques qui peuvent être séparées dans l'analyse des transitions centrales observées sur échantillon statique pour chacun des deux isotopes. Les spectres s'étendent sur plus d'un MHz de large et ont été acquis avec un protocol particulier (Variable Offset Cumulative Sspectrum) sans recourir à l'acquisition point par point. De plus nous montrons qu'il est possible d'obtenir des spectres résolus sur ce composé par la technique de « Dynamic Angle Spinning ».

Key words : NMR, Gallium, Quadrupolar Interaction, DAS.

The chemistry of Gallium in the solid state is very similar to that of Aluminum. Gallium can be substituted for Aluminum in similar crystal structures of material science interest. Gallium oxide, β-Ga_2O_3, has monoclinic symmetry with two crystallographically distinct sites (four and six fold oxygen coordination) for Gallium. It is a model system for further solid state Gallium NMR studies[1,2].

Gallium has two stable NMR observable isotopes : ^{69}Ga (60%) and ^{71}Ga (40%). Both are quadrupolar nuclei with I=3/2 spin and both have reasonable sensitivities (ν_0 at 7.0 T of 72.1 and 91.6 MHz and nuclear quadrupole moments of 1.68 and 1.06 10^{-29} m^2 respectively). It is well known that their NMR spectra are dominated by the quadrupolar interaction which often results in significant second-order broadening of the central transition in polycrystalline samples. The width of second-order broadenings is on the order of Q^2/ν_0 (expressed in frequency, with Q the nuclear quadrupolar moment and ν_0 the Larmor frequency), and are a factor of 3.2 times larger for ^{69}Ga (larger Q and lower frequency) than for ^{71}Ga.

All the spectra presented below are broad and have been acquired using a Hahn-Echo ($\pi/2$-τ-π-acquire) excitation sequence, synchronized to the spinning rate in the case of the MAS spectra. The typical selective $\pi/2$ pulse lengths were between 1 and 2 μ. In the case of ^{69}Ga, even

with the maximum power available it was not possible to fully irradiate the whole central transition extending over more than one MHz and the observed spectrum was a distorted wide line that was impossible to phase properly. Since the time domain signal decays rapidly due to the large inhomogeneous anisotropic broadening it is possible to shift the echo far enough into the acquisition window to acquire the whole echo without significant loss of intensity. This allows us to improve the signal to noise by a factor $2^{1/2}$ and by taking the Fourier transform from $-\infty$ to $+\infty$, as proposed for the shifted echo Dynamic Angle Spinning (DAS) experiments[3], to obtain an absorption mode only lineshape. With this processing, as illustrated in Figure 1 (top), the dispersion part of the spectrum is null and a magnitude computation thus gives the pure absorption mode lineshape. The whole processing of those full echo can thus be done automatically independently from the acquisition conditions and it becomes possible to sum the spectra acquired for different irradiation offsets to reconstruct the wide static line. In the present case the ^{69}Ga VOCS spectrum presented in Figure 1 (bottom) has been reconstructed as the sum of a series of 9 spectra (bottom of the figure) acquired at offset incremented by 125 kHz on both sides. The inset gives an approximation of the obtained bandwidth.

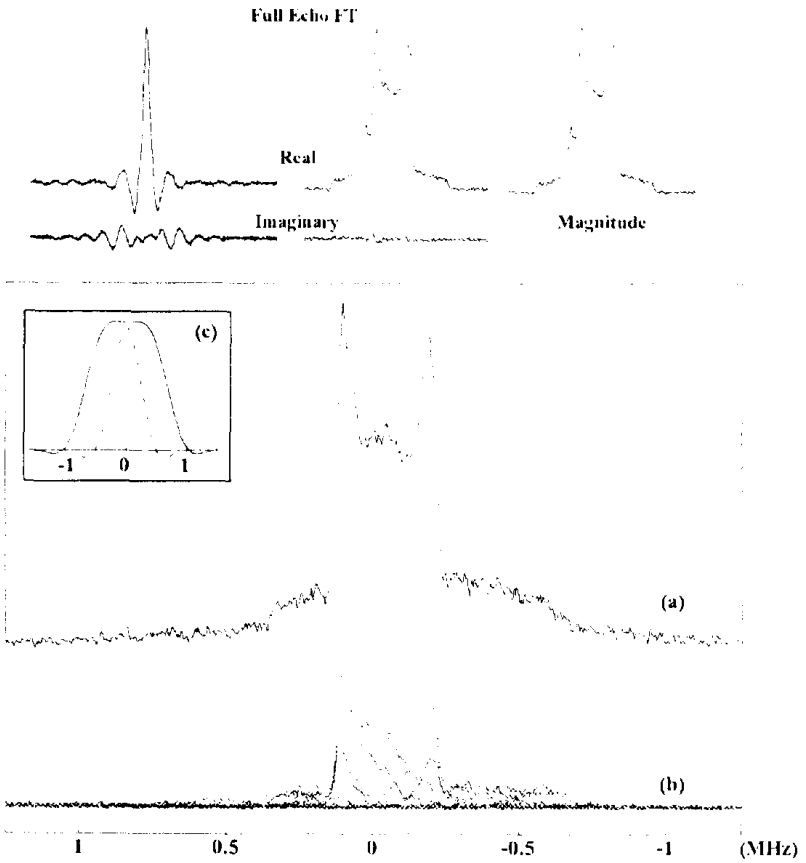

Figure 1 ^{69}Ga spectrum of β-Ga_2O_3. The upper part (a) shows an example of the acquisition of a full echo spectrum and its processing (^{71}Ga at 11.7 T). note that the shape of the magnitude spectrum is not modified. The lower part (b) shows the 9 acquired spectra and the reconstructed VOCS spectrum with the rebuilt irradiation profile (c).

A convenient way to retrieve the NMR parameters (isotropic chemical shift and electric field gradient tensor) of the two sites from all the different spectra (^{69}Ga, ^{71}Ga at 7.0 and 11.7 T)

is to report the positions of the principal spectral discontinuities in a comprehensive graphic diagram (Figure 2) where each site plot as a straight line according to the following equation :

$$\delta_x = \delta_{iso} + V_{zz}^2 \; f_x(\eta) \frac{1}{6} \left[\frac{3\,eQ}{2I(2I-1)\,h\,\nu_0} \right]^2 10^6 \left[I(I+1) - 3/4 \right] = \delta_{iso} + V_{zz}^2 \; X_x \left(\frac{eQ}{\nu_0}, \eta \right)$$

with $f_1(\eta) = +(3+\eta)^2/24$ and $f_6(\eta) = -2(1+\eta)/3$ for the outermost discontinuities which are the easiest to locate. Each point is placed according to its X_x value and η is optimized to the best linear fit for each site. The intercept at X=0 gives the isotropic chemical shift and the slope the principal value of the Electric Field Gradient (V_{zz}=|eq|).

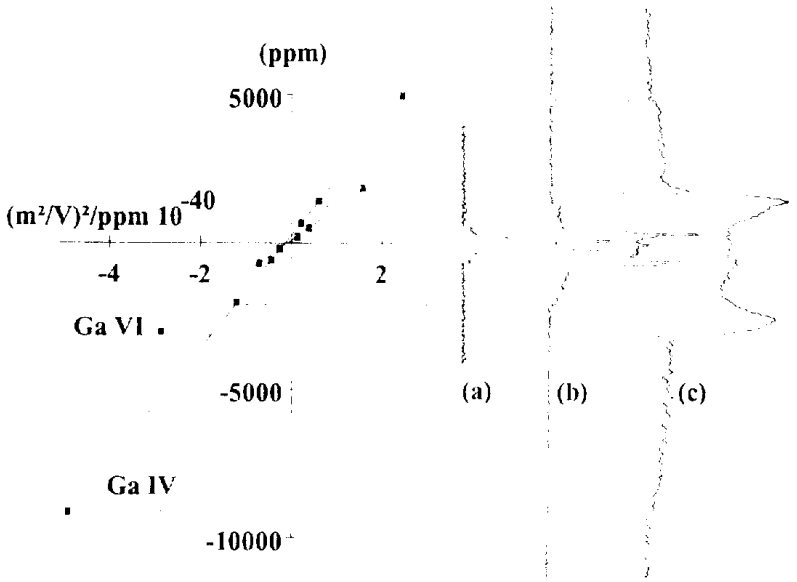

Figure 2 Discontinuity Multifield Graph reporting the positions observed for (a) ^{69}Ga at 7.0 T, (b) ^{71}Ga at 7.0 T and (c) ^{71}Ga at 11.7 T. Each site plots as a straight line.

DAS can provide isotropic spectra for quadrupolar nuclei like ^{87}Rb or ^{17}O by implementing a matched evolution of the magnetization at two complemental angles[3-6] that completely refocus all anisotropic broadening. It was an interesting goal to test whether DAS was able to resolve the two sites. The following spectrum has been obtained with a single hop shifted echo DAS experiment (SEDAS[3]) with the (37.38°/79.19°) pair of DAS angles at 9.4 T, 11.8 kHz spinning rate, over a spectral width of 200 kHz. The isotropic projection shows (Figure 3) the presence of two spinning sideband manifold, one intense corresponding to the six fold Ga site and a second one of much smaller intensity corresponding to the four fold coordinated site which have the greatest quadrupolar coupling constant.

From all these measurement we can derive a single set of NMR parameters for the two crystallographic sites (table below). The measured isotropic chemical shifts lie in the expected domains from previous studies[7].

Tableau 1 : NMR parameters of the two Ga sites (in parenthesis the values derived from the graph).

Site	δ_{iso} (ppm)	$V_{zz}=\lvert eq_{zz}\rvert$ (10^{21} V m^{-2})	C_Q (^{69}Ga) (MHz)	C_Q (^{71}Ga) (MHz)	η
Ga VI	40 (50)	3.3 (3.4)	13.4	8.3	0.08 (0.0)
Ga IV	200 (220)	4.3 (4.4)	17.5	11.0	0.85 (0.8)

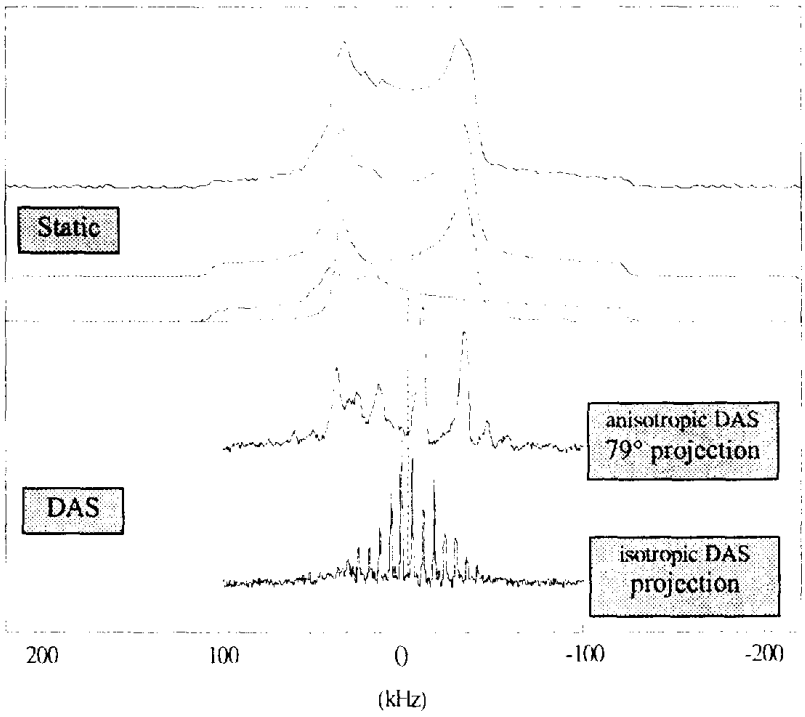

Figure 3 Stack plot of the DAS isotropic resolved spectrum, the unresolved anisotropic projection (79°) and the static spectrum with its model. The dashed lines indicate the isotropic positions.

By the use of the two NMR active Gallium isotopes at different fields it has been possible to acquire the wide or very wide static spectra and characterize the NMR parameters of the two structural sites (Ga_{IV} and Ga_{VI}) of β-Ga_2O_3. The DAS experimental technique applies to ^{71}Ga and provides isotropic resolution of the two structural sites where high speed MAS gave no further resolution compared to the static conditions. The study of this model compound opens the way for further investigation of Gallium solid state chemistry in systems of material science interest like zeolites, molecular sieves, or the garnet solid solutions[8].

1 D. Massiot, I. Farnan, N. Gautier, D. Trumeau, A. Trokiner and J.P. Coutures, *Solid State NMR* **4**, 241, (1995)

2 D. Massiot, I. Farnan, N. Gautier, D. Trumeau, P. Florian and P.J. Grandinetti, *26th ENC proceedings, Boston USA, March 1995.*

3 P.J. Grandinetti, J.H. Baltisberger, A. Llor, Y.K. Lee, U. Werner, M.A. Eastman and A. Pines, *J. Magn. Reson. A.* **103**, 72 (1993)

4 A. Llor, J. Virlet, *Chem. Phys. Lett.* **152**, 248 (1988).

5 B.F. Chmelka, K.T. Mueller, A. Pines, J. Stebbins, Y. Wu and J.W. Zwanziger, *Nature* **339**, 42 (1989).

6 P.J. Grandinetti, *Encyclopedia of Nuclear Magnetic Resonance, D.M. Grant and R.K. Harris editors*, John Wiley & Sons, (1995) *and references cited therein.*

7 S.M. Bradley, R.F. Howe and R.A. Kydd, *Magn. Reson. Chem.* **31**, 883 (1993)

8 N. Gautier, D. Massiot, I. Farnan, M. Gervais and J.P. Coutures, *J. Chim. Phys. proceeding GERM XIV this Issue*