the galNAc ( $\alpha$ -1 $\rightarrow$ 3) linkage is strong, that for the Fuc ( $\alpha$ -1 $\rightarrow$ 2) is less so and there must be some oligosaccharides, especially those with internal  $(1\rightarrow 6)$  linkages which show substantially greater flexibility. The Man ( $\alpha$ -1 $\rightarrow$ 6) linkage in the asparagine linked glycopeptides has been extensively studied and, although the evidence has received conflicting interpretations, it is generally agreed that conformational isomerism of the  $(\alpha - 1 \rightarrow 6)$  linkage is important.8,11 Furthermore, some other oligosaccharides such as maltose and cellobiose have been studied by methods similar to those used in this work, and different conclusions regarding conformational flexibility were reached.<sup>19-22</sup> It is not clear whether the different conclusions reached by these workers arise solely from differing assumptions in the interpretation of the data or whether there are real differences in the nature of the conformational flexibility between maltose and cellobiose and the blood group oligosaccharides. Furthermore, the extent of rigidity or lack of flexibility which we wish to imply for oligosaccharides and polysaccharides is not so great as that for globular proteins which are stabilized by interactions among residues separated by many chemical bonds. Since the nonbonded interactions responsible for the conformations of blood group oligosaccharides are mostly between atoms separated by only a few chemical bonds, there must be some small amount of relative motion between adjacent carbohydrate residues. For a polysaccharide this motion propagated over many residues leads to the observation of a stiff random coil in which segmental motion is readily observed. Thus, for high molecular weight polysaccharides, well-resolved NMR spectra are generally observed in which the line widths do not depend on molecular weight above a certain value. It is the local stiffness rather than the segmental motion which is the subject of this paper.

While the conformations of blood group oligosaccharides do not depend strongly on solvent and temperature, the observed NOE's of oligosaccharides do vary as a result of the change in the rotational correlation time. The simplest interpretation of the dependence of rotational correlation time on temperature and solvent is that it is determined by the bulk viscosity. Since  $\tau_c$  of a rigid sphere is linearly related to the ratio  $\eta/T$ , plots of  $\tau_c$  values obtained from the NOE data for both blood group oligosaccharides should be linear if this interpretation is correct. Such plots for the three solvents, D<sub>2</sub>O, Me<sub>2</sub>SO, and pyridine, at various temperatures give reasonably straight lines, implying that the NOE dependence of the rotational correlation time can be explained by the bulk viscosity of the solvent.

Acknowledgment. We thank Dr. Anthony J. Duben for helpful discussions on the computational aspects of this work.

## Solid-State Gallium-69 and Gallium-71 Nuclear Magnetic Resonance Spectroscopic Studies of Gallium Analogue Zeolites and Related Systems<sup>†</sup>

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Abstract: We have obtained solid-state 11.7-T <sup>69</sup>Ga and <sup>71</sup>Ga nuclear magnetic resonance (NMR) spectra of a series of gallosilicates (gallium analogues of zeolites Na-X, Na-Y, Na-sodalite, and Na-natrolite). From the apparent <sup>69</sup>Ga and <sup>71</sup>Ga chemical shifts, values of the nuclear quadrupole coupling constants  $(e^2 q Q/h)$  and the true, isotropic chemical shifts  $(\delta_i)$  have been deduced for the framework, tetrahedral, Ga(OSi)<sub>4</sub> sites. The  $e^2 qQ/h$  values are in the range 1.9–2.7 MHz for  $^{69}$ Ga and 1.2–1.7 MHz for <sup>71</sup>Ga. The isotropic chemical shifts are all in the range 171-186 ppm downfield from an external standard of 1 M Ga(NO<sub>3</sub>)<sub>3</sub>. Our results indicate that measurement of the apparent (second-order shifted) chemical shifts for pairs of isotopes of nonintegral spin quadrupolar nuclei in solids at one magnetic field strength is a useful new approach for determination of both isotropic chemical shifts and nuclear quadrupole coupling constant values.

There has recently been considerable interest in the isomorphous replacement of Al in the framework structure of zeolites.<sup>1-4</sup> For example, gallium-replaced zeolites possess chemical properties different from their aluminum analogues, and offer the possibility of new catalytic activity.<sup>3,4</sup> Among the framework nuclei of gallosilicates (Si, Ga, and O), only the <sup>29</sup>Si nucleus has been extensively studied using nuclear magnetic resonance (NMR) methods.<sup>5,6</sup> The <sup>29</sup>Si "magic-angle" sample-spinning (MASS) NMR spectra of these systems can exhibit up to five resonances, depending on the number of next-nearest-neighbor galliums.<sup>5</sup> As a result,  $^{\bar{29}}Si$  MASS NMR techniques can be used to determine the composition of the gallosilicate framework,5 in much the same manner as with (aluminum-containing) zeolites, and other framework aluminosilicates. More recently, <sup>17</sup>O NMR studies of a few gallosilicates have identified the two chemically distinct oxygen sites, Ga-O-Si and Si-O-Si, and have made some interpretation of the bonding of these oxygens.<sup>7</sup>

Expansion of NMR methods to investigation of gallium nuclei in gallosilicates is in a much earlier stage of development.<sup>4,8</sup> However, a fully multinuclear NMR approach should provide useful structural information, as has already been obtained with the case of <sup>17</sup>O NMR.<sup>7</sup> In this paper, we report the first com-

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This work was supported in part by the U.S. National Science Foundation Solid-State Chemistry Program (Grant DMR 86-15206).

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Table I. Chemical Compositions of Ga Analogue Zeolites

	atom	ic absorpt	Si/Ga			
system	Na <sub>2</sub> O	Ga <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	H <sub>2</sub> O	AA <sup>b</sup>	<sup>29</sup> Si NMR <sup>c</sup>
Na-GaX	0.997	1.00	3.04	6.70	1.52	1.57
Na-GaY	1.05	1.00	4.17	8.75	2.09	2.04
Ga-sodalite	1.02	1.00	3.06	3.04	1.53	1.54
Ga-natrolite	1.06	1.00	3.40	2.60	1.70	1.72
Ga-sodalite <sup>d</sup>	1.10	1.00	2.20	3.50	1.10	1.054
Ga-sodalite <sup>d</sup>	1.09	1.00	2.07	3.09	1.04	1.003

<sup>a</sup>Chemical compositions determined by atomic absorption (AA) analyses, computed as the molar ratio of oxide to Ga<sub>2</sub>O<sub>3</sub>. <sup>b</sup>Si/Ga ratio from AA analysis results. 'Si/Ga ratio from <sup>29</sup>Si MASS NMR simulations using a Nicolet curve-fitting routine (NMRCAP). <sup>d</sup>Samples provided by Dr. K. Suzuki.

prehensive Ga NMR investigation of the gallium analogues of zeolites X, Y, sodalite, and natrolite, by means of MASS NMR techniques. We have been able to obtain isotropic chemical shifts  $(\delta_i)$  and nuclear quadrupole coupling constants  $(e^2 q Q/h)$  for the framework Ga nuclei, in essence by carrying out a "frequency dependence" study at one magnetic field strength, by observing the different apparent chemical shifts of <sup>69</sup>Ga (at 120 MHz) and <sup>71</sup>Ga (152.47 MHz). Our results indicate that Loewenstein's rule<sup>9</sup> holds for gallosilicates as well as aluminosilicates; i.e., no Ga-O-Ga linkages are observed. The abnormal composition of the gallo-sodalite claimed by Suzuki,  $^{10,11}$  4Na<sub>2</sub>O·5Ga<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·10H<sub>2</sub>O, is not supported by our Ga or Si NMR results, or by microchemical analyses of materials prepared using their recipes.

## Experimental Section

Synthesis of Sodium Zeolite Ga-X and Sodium Gallosodalite. The gallium analogues of Na-X and sodalite were synthesized by published methods<sup>5,7</sup> using a slurry of composition 2.1Na<sub>2</sub>O·Ga<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub>·60H<sub>2</sub>O. Sodium hydroxide (1.68 g) was dissolved in 6.81 g of water, and to this solution was added 1.874 g of gallium oxide. The mixture was stirred to dissolution. Next, Ludox HS-40 (6.01 g) and 0.12 g of aluminosilicate seed (13-X) were added, with stirring. Two equal portions of the resulting gel were transferred into two 25-mL Parr bombs, and "aged" for 24 h. One bomb was autoclaved at 100 °C for 8 h, and yielded Ga-X. The other was autoclaved for 24 h and yielded Ga-sodalite. The samples were washed, then dried for 3 h at 110 °C, yielding 1.57 and 1.54 g of crystalline Ga-X and Ga-sodalite, respectively

Synthesis of Sodium Zeolite Ga-Y and Ga-Natrolite. A slurry of composition 3Na<sub>2</sub>O·Ga<sub>2</sub>O<sub>3</sub>·8SiO<sub>2</sub>·140H<sub>2</sub>O was used to synthesize the gallium analogues of Na-Y<sup>5</sup> and natrolite. Ga-Y zeolite was synthesized as follows: 1.20 g of sodium hydroxide and 0.94 g of gallium oxide were first dissolved in 8.72 g of water. Next, 6.01 g of Ludox HS-40 and aluminosilicate seed material (Union Carbide SK 40, 1% Al relative to gallium) were added, with vigorous stirring. Two equal portions of the resultant gel were transferred into Parr bombs, aged for 96 h, then autoclaved at 100 °C for 20 and 25 h, respectively. Both samples yielded 1.30 g of gallium analogue Na-Y zeolite.

Ga-natrolite was synthesized as follows: sodium hydroxide (0.40 g) and 0.312 g of gallium oxide were dissolved in 2.91 g of water. To this solution, 2.00 g of Ludox HS-40 and 0.026 g of Na-Y were added, with stirring. The resultant gel was aged for 24 h, then autoclaved at 100 °C for 24 h. The sample was washed and dried, yielding 0.85 g of crystalline Ga-natrolite.

Reagents used in the gallosilicate preparations were DuPont (Wilmington, DE) Ludox HS-40 colloidal silica (40 wt % SiO<sub>2</sub>), 99.99% gallium oxide (Aldrich, Milwaukee, WI), and Aldrich reagent grade sodium hydroxide.

Two samples of Ga-sodalite synthesized by published methods<sup>10</sup> were also kindly provided by Dr. K. Suzuki of National Chemical Laboratory for Industry, Tsukuba, Japan.

To characterize the samples, X-ray powder diffraction patterns were obtained. The powder patterns of the Ga-analogue zeolites were compared with published data on the same compound (Ga-sodalite<sup>12</sup>), or with that of the aluminum analogues  $(Na-X,^{12-14} Na-Y)^{14}$  sodalite,<sup>15</sup> and

Table II. NMR Properties of Aluminum and Gallium Isotopes

isotope	spin (I)	abundance (%) <sup>a</sup>	Larmor freq $\nu_0$ (MHz) <sup>b</sup>	quadrupole moment $Q$ $(10^{-24} \text{ cm}^2)^a$	rel line width W <sup>e</sup>
<sup>27</sup> Al	5/2	100	130.28	0.149	1.00
<sup>69</sup> Ga	$\frac{3}{2}$	60.4	120.00	0.178	6.46
<sup>71</sup> Ga	$\frac{3}{2}$	39.6	152.47	0.112	2.01

<sup>a</sup> From the Bruker NMR Table and CRC Handbook of Chemistry and Physics. <sup>b</sup>Larmor frequency, in MHz, for an 11.7-T magnetic field strength (<sup>1</sup>H resonance frequency of 500 MHz). <sup>c</sup>Computed as the ratio of the values taken by the function  $(e^2 q Q)^2 \{I(I + 1) - \frac{3}{4}\}$  ${h\nu_0 I^2(2I-1)^2}$  for the isotope and for <sup>27</sup>Al (central transition only), assuming the second-order quadrupole interaction is the dominant line-broadening mechanism, identical EFG tensors, and a zero asymmetry parameter,  $\eta$ .

natrolite<sup>16</sup>). All diffraction patterns for the Ga-analogue zeolites were in good agreement with the corresponding aluminosilicates. Chemical compositions of all samples were measured by atomic absorption analysis, and the results are given in Table I. The Si/Ga ratios were also obtained from <sup>29</sup>Si MASS NMR spectra and show good agreement with those obtained from the atomic absorption analysis (Table I). The gallosilicates studied have a broad range of Si/Ga ratios, ranging from 1.003 to 2.04. X-ray powder diffraction patterns were obtained with the use of a Norelco (Philips Electronics Instruments Inc., Mahwah, NJ) powder diffractometer, equipped with a copper X-ray tube and a graphite monochromator. Microchemical analyses were performed either by Galbraith Laboratories (Knoxville, TN) or by the University of Illinois Microanalysis Laboratory.

Two model compounds were also used in our Ga NMR study: NH<sub>4</sub>Ga(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O and KGa(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O. The gallium "alums" were synthesized using a published method,<sup>17</sup> and were characterized by microchemical analysis.

Nuclear Magnetic Resonance Spectroscopy. Gallium-69 and gallium-71 NMR spectra were obtained on a "home-built" Fourier transform NMR spectrometer, at 120.00 and 152.47 MHz, respectively, using an Oxford Instruments (Osney Mead, Oxford, U.K.) 11.7-T, 52-mm bore superconducting solenoid magnet, a Nicolet Instrument Corp. (Madison, WI) Model 1280 computer for data acquisition, and an Amplifier Research (Souderton, PA) Model 200L amplifier for final rf pulse generation. MASS NMR spectra were obtained using a "home-built" probe, the spinner design of which was modified from that provided by Dr. R. Wind.<sup>18</sup> The sample rotor has a 5.5-mm outer diameter and a  $\sim$ 70- $\mu$ L sample volume, and routinely spins at up to  $\sim 8$  kHz with air as the driving gas. The spinning frequency is monitored by measuring the ac voltage induced in a pick-up loop.<sup>19</sup> Static spectra were obtained using a "home-built" horizontal solenoid-type sample probe. Chemical shifts are reported in parts per million (ppm) from an external standard of 1 M Ga(NO<sub>3</sub>)<sub>3</sub> solution, where more positive values correspond to low-field, high-frequency, paramagnetic or deshielded values (IUPAC  $\delta$  scale). Line broadenings due to exponential multiplication were 50 to 500 Hz, depending on the line widths.

## **Results and Discussion**

By way of introduction to our results, we will first consider the magnetic resonance properties of the  $^{69}\mbox{Ga}$  and  $^{71}\mbox{Ga}$  isotopes, and compare them with those for <sup>27</sup>Al, as shown in Table II. Even though the nuclear quadrupole moments and the gyromagnetic ratios (or Larmor frequencies) are similar for all three isotopes, the smaller nuclear spin quantum number  $(I = \frac{3}{2})$  of Ga results in much broader line widths for Ga relative to Al (I = 5/2), when the second-order quadrupolar interaction is dominant. At the same magnetic field strength, the relative ratio of the line widths for <sup>27</sup>Al, <sup>69</sup>Ga, and <sup>71</sup>Ga is ~1:6.46:2.01, respectively (for detailed calculation, see footnote c in Table II).<sup>20</sup> This indicates that

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Table III. Solid-State "Magic-Angle" Sample-Spinning Ga NMR Chemical Shifts and Quadrupole Coupling Constants for Gallium Analogue Zeolites

		<sup>69</sup> (	Ga	71	Ga			
system	Si/Ga <sup>a</sup> ratio	$\delta_{obsd}^{b}$ (ppm)	fwhh <sup>c</sup> (kHz)	$\frac{\delta_{obsd}^{b}}{(ppm)}$	fwhh <sup>c</sup> (kHz)	$\delta_i^d$ (ppm)	e <sup>2</sup> qq <sup>69</sup> Ga	$\frac{Q/h^e}{^{71}\mathrm{Ga}}$
Ga-X <sup>f</sup>	1.57			174	6.41			
Ga-Y	2.04	162	6.91	172	5.52	175	2.7	1.7
Ga-sodalite	1.54	168	5.46	176	5.28	179	2.5	1.6
Ga-natrolite	1.72	161	5.82	169	5.10	171	2.3	1.5
Ga-sodalite	1.054	178	4.82	182	4.32	184	1.9	1.2
Ga-sodalite	1.003	178	4.93	184	3.55	186	2.1	1.3

<sup>a</sup>Calculated Si/Ga ratio from <sup>29</sup>Si MASS NMR spectrum. <sup>b</sup>Observed chemical shift, in ppm from an external 1 M Ga(NO<sub>3</sub>)<sub>3</sub> standard. <sup>c</sup>Full-width at half-height, in kHz. <sup>d</sup>Isotropic chemical shift, in ppm from an external 1 M Ga(NO<sub>3</sub>)<sub>3</sub> standard, calculated as described in the text. <sup>e</sup>Nuclear quadrupole coupling constant, in MHz. <sup>f</sup>We were not able to spin the Ga-X sample fast enough to obtain  $\delta_{obsd}$  for <sup>69</sup>Ga MASS.



Ga-Sodalite, 11.7 T

Figure 1. 11.7-T <sup>71</sup>Ga NMR spectra of sodium gallosodalite (Ga-sodalite) with Si/Ga = 1.54: (A) static, 3600 scans, recycle time = 1 s; (B) 3.8-kHz MASS, 2800 scans, recycle time = 200 ms; (C) 7.6-kHz MASS, 2500 scans, recycle time = 300 ms.

solid-state Ga NMR is expected to be much more difficult than Al NMR, because it requires severe experimental conditions, such as much higher spinning speeds for MASS, and/or shorter 90° pulses to excite the broader spectral widths expected. Of the two Ga isotopes, <sup>71</sup>Ga is more attractive because of its smaller quadrupole moment and larger gyromagnetic ratio, which help compensate for its lower natural abundance. However, as we show below, NMR of *both* <sup>69</sup>Ga and <sup>71</sup>Ga at the highest magnetic field strengths possible appears to be the method of choice for Ga NMR studies of zeolites, since it can provide *both* isotropic chemical shift data (corrected for second-order effects) and  $e^2qQ/h$  information.

We show in Figure 1A the static 152.47-MHz (11.7-T) <sup>71</sup>Ga NMR spectrum of a sample of gallium analogue sodium sodalite (Ga-sodalite) having a Si/Ga ratio of 1.54. The static spectrum has a  $\sim 15$ -kHz line width at half-height, but does not show a second-order quadrupole-broadened line shape, presumably due to dipolar interactions, and perhaps, in addition to a small distribution of chemical shifts and quadrupole coupling constants, from crystallographically nonequivalent sites. A 3.8-kHz MASS NMR spectrum of the same sample (Figure 1B) also yields a broad peak, with no resolved spinning sidebands. This MASS result indicates that this spinning speed is not fast enough to overcome the static line-broadening interactions present and that much faster spinning speeds are needed in order to study this system. For such broad and featureless spectra, obtaining accurate chemical shifts is quite difficult, because the base line is not well defined and phase adjustments are difficult. The importance of



Figure 2. 11.7-T<sup>71</sup>Ga MASS NMR spectra of a series of gallium analogue zeolites: (a) gallium analogue Na-X (Ga-X), at 7.8 kHz, 5000 scans; (B) gallium analogue Na-Y (Ga-Y), at 7.1 kHz, 2500 scans; (C) Ga-sodalite with Si/Ga = 1.54, at 7.6 kHz, 2500 scans; (D) gallium analogue natrolite (Ga-natrolite), at 7.4 kHz, 3600 scans; (E) Ga-sodalite with Si/Ga = 1.054, at 6.2 kHz, 3500 scans; (F) Ga-sodalite with Si/Ga = 1.03, at 7.0 kHz, 1100 scans. A typical recycle time was 300 ms.

spinning speed is clearly seen in the 7.6-kHz spectrum shown in Figure 1C, in which the spinning sidebands are now clearly resolved from the central peak, and phase adjustments and accurate chemical shift measurements are more readily performed.

We show in Figure 2 the 152.47-MHz <sup>71</sup>Ga MASS NMR spectra of a series of gallium analogue zeolites. All of the spectra show only single peaks with *observed* chemical shifts,  $\delta_{obsd}$ , in the range of 169 to 184 ppm. The silicon-to-gallium ratio, observed chemical shift, and line width at half-height for each zeolite are given in Table III. In each case, we assign the single peak to tetrahedral framework Ga, Ga(OSi)<sub>4</sub>.

None of the gallium analogue zeolites studied show any resonance near  $\sim 0$  ppm, where hexahydrated octahedral gallium,  $Ga(H_2O)_6^{3+}$ , is expected, based on our studies of model compounds (Figure 3 and Table III). From this observation, we suggest that any extra-lattice Ga present in our gallosilicates is unlikely to be present as  $Ga(H_2O)_6^{3+}$ . In zeolites, extra-lattice Al,  $Al(H_2O)_6^{3+}$ , appears as a sharp resonance near  $\sim 0$  ppm.<sup>21</sup>

In order to better characterize the solid-state NMR of octahedral Ga, we have studied a number of model compounds. The 11.7-T <sup>71</sup>Ga MASS NMR spectrum of NH<sub>4</sub>Ga(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (NH<sub>4</sub>-Ga-alum) is shown in Figure 3A. Both the 11.7-T <sup>69</sup>Ga (data not shown) and <sup>71</sup>Ga NMR spectra consist of sharp, single peaks, corresponding to Ga(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>, with observed chemical shifts

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Figure 3. Gallium NMR spectra of octahedrally coordinated galliumcontaining compounds: (A) 11.7-T <sup>71</sup>Ga, NH<sub>4</sub>Ga(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, 5.8-kHz MASS, 2000 scans; (B) 11.7-T <sup>71</sup>Ga, KGa(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, 5.8-kHz MASS, 2000 scans; (C) 8.45-T <sup>69</sup>Ga, NH<sub>4</sub>Ga(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, 6.3-kHz MASS, 4000 scans; (D) spectral simulation of C. A typical recycle time was 300 ms.

at -2.7 and -1.2 ppm, respectively. From the different  $\delta_{obsd}$  for the two isotopes (see discussion for Figure 4), we obtain nuclear quadrupole coupling constants  $(e^2 q Q/h)$  of 1.1 and 0.7 MHz for <sup>69</sup>Ga and <sup>71</sup>Ga, respectively, and an isotropic chemical shift  $(\delta_i)$  of -0.7 ppm.

We show in Figure 3B the 11.7-T <sup>71</sup>Ga MASS NMR spectrum of KGa(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (K-Ga-alum). The <sup>69</sup>Ga and <sup>71</sup>Ga MASS NMR spectra of K-Ga-alum are similar to those of NH<sub>4</sub>-Gaalum, with  $\delta_{obsd}$  at -0.5 and 1.1 ppm, respectively. This result yields  $e^2qQ/h$  of 1.1 MHz for <sup>69</sup>Ga and 0.7 MHz for <sup>71</sup>Ga, and a  $\delta_i$  of 1.6 ppm, as described below in more detail.

These  $e^2 q Q/h$  values of the Ga-alums obtained from the different observed chemical shifts for the two isotopes are consistent with those obtained from line-shape simulations. For example, we show in Figure 3C the 8.45-T (86.4 MHz) <sup>69</sup>Ga MASS NMR spectrum of NH<sub>a</sub>-Ga-alum. Because of the larger nuclear quadrupole moment of <sup>69</sup>Ga, and operation at a lower magnetic field strength, second-order quadrupolar structure is apparent. The spectrum was simulated using the methods described previously.<sup>22</sup> The simulated spectrum (Figure 3D) yields  $e^2 q Q/h$ = 1.3 MHz, and an asymmetry parameter,  $\eta$ , of 0.3. The simulation of K-Ga-alum gives a similar result,  $e^2 q Q/h = 1.2$  MHz and  $\eta = 0.3$ . Both  $e^2 q Q/h$  values are in good agreement with the 1.1-MHz values determined at 11.7 T from the apparent chemical shifts of the two gallium isotopes. We note here that the aluminum-containing alums have much smaller <sup>27</sup>Al  $e^2qQ/h$  values, 395 and 441 kHz for K-alum and NH<sub>4</sub>-alum, respectively, and  $\eta$  of 0.0.<sup>23</sup> Presumably this effect is due to a larger distortion of the octahedron owing to the increased size of Ga<sup>3+</sup> over Al<sup>3+</sup>.

All of the gallosilicates we have examined show excellent agreement between Si/Ga ratios determined by <sup>29</sup>Si NMR, and by atomic absorption analyses (Table I). These results strongly suggest that Loewenstein's rule holds for gallosilicates as well as for aluminosilicates, and that accurate Si/Ga ratios can be obtained by <sup>29</sup>Si MASS NMR, as proposed by Vaughan et al.<sup>5</sup> In particular, we obtained <sup>71</sup>Ga and <sup>29</sup>Si MASS NMR spectra of gallium and analogue sodalites whose originally reported composition,<sup>10,11</sup> 4Na<sub>2</sub>O·5Ga<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·10H<sub>2</sub>O, appears to violate Loewenstein's rule (Si/Ga = 0.2). Gallium-71 NMR spectra of the two samples provided to us are shown in Figures 2E and 2F. From <sup>29</sup>Si NMR measurements on these samples (data not shown), we obtain Si/Ga ratios of 1.054 and 1.003, respectively. The <sup>71</sup>Ga NMR spectra show no evidence of the existence of either Ga-

Ga-Sodalite, 11.7 T



**Figure 4.** 11.7-T Ga MASS NMR spectra of Ga-sodalite with Si/Ga = 1.003: (A) <sup>71</sup>Ga at 7.0 kHz, 1100 scans; (B) <sup>69</sup>Ga at 7.6 kHz, 16000 scans. A 300-ms recycle time was used in both cases. Note the smaller second-order shift of the <sup>71</sup>Ga resonance ( $\delta_{obsd}$  183.<sub>8</sub> ppm, at 152.47 MHz) compared with that of the <sup>69</sup>Ga signal (178.<sub>2</sub> ppm, at 120.0 MHz), due to the larger  $\nu_0$  and smaller Q of <sup>71</sup>Ga (Table II).

O-Ga linkages, or of a gallium-rich extra-lattice phase. These results lead us to conclude that the original composition, derived from X-ray fluorescence experiments, was in error, and indeed, both our NMR results and microchemical analysis are consistent with the recently amended composition of  $Na_{6.7}[Ga_{5.9}Si_{6.1}O_{24}]$ . 9.8(H<sub>2</sub>O,OH), proposed by Suzuki et al.<sup>24</sup>

The Si/Ga ratio of 1.72 for Ga-natrolite is somewhat unusual, since natrolite (Al analogue) has a well-ordered structure (there are only two types of silicon atoms—those connected to three AlO<sub>4</sub> tetrahedra, Q<sup>4</sup>(3Al), and those connected to two AlO<sub>4</sub> tetrahedra, Q<sup>4</sup>(2Al), in a 2:1 ratio) and gives a Si/Al ratio of 1.50.<sup>25</sup> Further work is in progress to find the origin of the apparently anomalous Si/Ga ratio in the Ga-natrolite.

We show in Figure 4 the 11.7-T <sup>69</sup>Ga and <sup>71</sup>Ga MASS NMR spectra of Ga-sodalite. The observed chemical shifts,  $\delta_{obsd}$ , are at 178.<sub>2</sub> and 183.<sub>8</sub> ppm, for <sup>69</sup>Ga and <sup>71</sup>Ga, respectively. The differences in  $\delta_{obsd}$  are due to the different quadrupole moments and Larmor frequencies of the two isotopes, which cause different amounts of second-order quadrupole-induced shifts ( $\delta_{QS}$ ) from the isotropic chemical shift ( $\delta_i$ ). The quadrupole-induced shift from the isotropic chemical shift for the  $m \leftrightarrow m - 1$  transition of a power sample under MASS conditions is given by:<sup>26</sup>

$$\delta_{\rm QS}(m) = -\frac{3}{40} \left(\frac{e^2 q Q}{h \nu_0}\right)^2 \frac{I(I+1) - 9m(m-1) - 3}{I^2 (2I-1)^2} \left(1 + \frac{\eta^2}{3}\right)$$

where  $e^2 qQ/h$  is the nuclear quadrupole coupling constant,  $\nu_0$  is the Larmor frequency, and  $\eta$  is the asymmetry parameter of the electric field gradient tensor. For both <sup>69</sup>Ga and <sup>71</sup>Ga  $(I = 3/_2)$ , and for observation of only the central transition  $(m = 1/_2)$ , the second-order quadrupole-induced shift  $(\delta_{QS})$  from the isotropic value may thus be calculated (in ppm) as:<sup>26</sup>

$$\delta_{\rm QS} \ (\rm ppm) = -\frac{10^5}{4} \left( \frac{e^2 q Q}{h \nu_0} \right)^2 \left( 1 + \frac{\eta^2}{3} \right)$$

The nuclear quadrupole coupling constants  $(e^2qQ/h)$  for the two isotopes differ only by the ratio of the nuclear quadrupole moments (Q), because the electric field gradients (eq) felt by the two isotopes

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**Figure 5.** Plot of <sup>27</sup>Al  $e^2qQ/h$  value vs. <sup>71</sup>Ga  $e^2qQ/h$  values for the compounds studied in this paper. The solid lines through the origin are theoretical relations derived either from the ratio of nuclear quadrupole moments, which gives  $e^2qQ/h$  (<sup>27</sup>Al) = 1.33  $e^2qQ/h$  (<sup>71</sup>Ga), or from the ratio of  $e^2Qq_0$  values which gives  $e^2qQ/h$  (<sup>27</sup>Al) = 0.476  $e^2qQ/h$  (<sup>71</sup>Ga). The dashed line through the points is the least-squares fit to the data, and has a slope of 1.375.

are essentially identical. If we assume  $\eta = 0$ , we can readily determine that for Ga-sodalite the true isotropic chemical shift  $(\delta_i)$  is 185.6 ppm, and the nuclear quadrupole coupling constants  $(e^2 qQ/h)$  are 2.07 and 1.30 MHz for <sup>69</sup>Ga and <sup>71</sup>Ga, respectively, since there are two observables and only two unknowns. This procedure was alluded to above for the Ga-alums, and we believe it may have general utility for pairs of isotopes of nonintegral spin quadrupolar nuclei in solids. Calculated results for all zeolites investigated are shown in Table III. We note that although  $\eta$  is unknown, uncertainties in its value can cause at most a 15% error in determination of the quadrupole coupling constant, and cause no error in determination of the isotropic chemical shift,  $\delta_i$ .

An interesting trend can be seen between the isotropic chemical shift values and the Si/(Ga + Si) ratio for all of the gallosilicates studied. We find:

$$\delta_i (ppm) = -74.2[Si/(Ga + Si)] + 222.2$$

with a correlation coefficient of 0.91 (solid line). The correlation indicates that the isotropic chemical shifts generally become more deshielded with decreasing Si/Ga ratios. This trend becomes more evident if we drop the point corresponding to Ga-natrolite, which has a quite different framework morphology from that of the other five samples. The new correlation is

$$\delta_i (ppm) = -63.4[Si/(Ga + Si)] + 216.8$$

with a correlation coefficient of 0.98. These results imply that there are gradual structural changes upon changing Si/Ga (or Si/Al ratios), one possibility being that the mean (Si–O–Ga) bond angle may decrease with increasing Si/Ga ratios.

Finally, we shall briefly comment on the relationship between the <sup>71</sup>Ga  $e^2qQ/h$  values found in this work with the <sup>27</sup>Al values found in the literature. The <sup>27</sup>Al  $e^2qQ/h$  values quoted are 0.93 MHz for sodalite,<sup>27</sup> 1.66 MHz for natrolite,<sup>28</sup> 2.0 MHz for Na-X

and Na-Y zeolites,<sup>29</sup> 0.441 MHz for NH<sub>4</sub>-alum,<sup>23</sup> and 0.395 MHz for K-alum.<sup>23</sup> Figure 5 shows a plot of <sup>27</sup>Al  $e^2 qQ/h$  vs. <sup>71</sup>Ga  $e^2 q Q/h$  values together with two predictions (solid lines). The first prediction is derived from the ratio of nuclear quadrupole moments (Q) of the two nuclei which gives a theoretical line with a slope of 1.33 which goes through the origin. If we assume that the two isostructural compounds have identical electric field gradients (eq), the experimental  $e^2 q Q/h$  values would follow this trend. The second prediction is derived from the ratio of nuclear quadrupole coupling constants for atoms produced by a single unbalanced p electron  $(e^2Qq_0)$ . The  $e^2Qq_0$  values are 37.52 MHz for <sup>27</sup>Al and 78.798 MHz for <sup>71</sup>Ga.<sup>30</sup> In both cases, the field gradient arises from a single electron, the 3p electron for <sup>27</sup>Al, and the 4p electron for <sup>71</sup>Ga. The ratio of the  $e^2Qq_0$  values gives a straight line with a slope of 0.476. Although there are only eight points, it is interesting to note a clear trend in that the <sup>71</sup>Ga  $e^2 qQ/h$ values are uniformly larger than would be predicted from the <sup>27</sup>Al results when corrected for the different quadrupole moments, and uniformly smaller than the predicted values when corrected for the different  $e^2Qq_0$ . The deviations from these predictions can be explained by the following three competing factors. The larger <sup>71</sup>Ga  $e^2 qQ/h$  values than predicted from the ratio of Q's may originate in part from the increased ionic radius of Ga<sup>3+</sup> over Al<sup>3+</sup> (0.62 Å vs. 0.50 Å) which induces structural changes and results in more distortion around gallium in these systems. Also the contribution of the inner closed-shell electrons to the electric field gradient at the nucleus (Sternheimer shielding term) is larger for Ga<sup>3+</sup>, which will lead to <sup>71</sup>Ga  $e^2 q Q/h$  values that are larger than predicted. Finally, the greater electronegativity of Ga compared to Al (1.81 vs. 1.61, Pauling electronegativity scale) will lead to increased p orbital contributions to the EFG, resulting in larger <sup>71</sup>Ga  $e^2 q Q/h$  values than predicted from the ratio of the Q values.

The method we have described above for determining  $e^2qQ/h$ and  $\delta_i$  values has, in suitable cases, advantages over the more conventional field-dependent approach.<sup>26</sup> First, only one magnet is required, although it should be of the highest field strength possible. This yields the narrowest line, at least for lines whose width is dominated by second-order quadrupolar effect. Thus, spectral signal-to-noise ratio is maximized. Second, because lines are narrower at high field, it is not necessary to spin as fast in the MASS experiment as at low field. Whatever the maximum spinning speed available, spectral signal-to-noise ratios and appearance (phasing) are improved at high field. We thus believe that the method may be of use in obtaining  $e^2qQ/h$  and  $\delta_i$  values for other isotope pairs, for example: <sup>35</sup>Cl and <sup>37</sup>Cl; <sup>39</sup>K and <sup>41</sup>K; <sup>63</sup>Cu and <sup>65</sup>Cu; <sup>79</sup>Br and <sup>81</sup>Br; <sup>85</sup>Rb and <sup>87</sup>Rb; <sup>95</sup>Mo and <sup>97</sup>Mo; <sup>185</sup>Re and <sup>187</sup>Re; and <sup>191</sup>Ir and <sup>193</sup>Ir.

Acknowledgment. We are grateful to Dr. R. Wind for providing us with drawings of his high-speed spinner, to Dr. K. Suzuki for providing us with samples of the sodium gallosodalites, and to Drs. K. D. Schmitt, S. E. Schramm, C. G. T. Knight and N. Janes for useful comments on the manuscript. The X-ray work was carried out in the center for Microanalysis of Materials, University of Illinois, which is supported by the U.S. Department of Energy under Contract DE-AC 02-76ER 01198.

Registry No. 69Ga, 14391-02-7; 71Ga, 14391-03-8.

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