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# Distributions of Conduction Electrons as Manifested in MAS NMR of Gallium Nitride

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Magic-angle spinning (MAS) NMR of crystalline inorganic solids provides invaluable information about local chemical structure and is useful in inorganic synthetic chemistry because of its sensitivity to potential impurities in the sample. Perturbations to the local environment of a nuclear site can arise from changes in the disposition or identity of nearby atoms, for example. The chemical shift is typically the source of such structural information, although for quadrupolar nuclei (nuclear spin > 1/2), the nuclear quadrupole coupling constant is similarly informative. Thus, large chemical shift changes in the $^{71}$Ga MAS NMR spectra of the important III−V wide band gap semiconductor GaN have previously been attributed to structural effects of nitrogen vacancies.[1] In this communication, we provide $^{71}$Ga MAS NMR experimental results for polycrystalline GaN samples made by different synthetic approaches, with both unintentional as well as intentional (Ge) dopants, that strongly support the conclusion recently advanced for different GaN samples[2] that the types of chemical shift changes observed are due instead to *electronic effects from conduction band electrons* (Knight shifts) rather than chemical structural effects. A new strategy is demonstrated for identifying such effects in a single semiconductor sample, based upon relating the observed (inhomogeneous) distribution of spectral frequencies to the measured spin−lattice relaxation times $T_1$. We then show how to quantitatively analyze the distribution of carrier (electron) concentrations, which can provide insight into the heterogeneous nature of synthesized samples. Since many simple inorganic compounds are semiconductors, including II−VI and III−V binary compounds, being able to recognize the existence of and quantify such effects in interpreting MAS NMR spectra is vital. We show that impurities present at levels that are relatively low from a chemical standpoint (0.1% or less) can have profound effects upon MAS NMR spectra of semiconductors.

Figure 1a shows the $^{71}$Ga ($I = 3/2$, 60% natural abundance) MAS NMR spectra at 11.7 T and 9.0 kHz spinning speed of three different polycrystalline samples of hexagonal-GaN (h-GaN), obtained under quantitative nonsaturating conditions with 90° pulses and recycle delays ≥20 s. Only the central transition ($1/2 \leftrightarrow -1/2$) region is shown. The full spectrum including $\pm 1/2 \leftrightarrow \pm 3/2$ satellite transitions of the sample prepared using a Na/K flux[3] has been given previously,[4] along with chemical shift referencing, assignments of a minor component from the cubic polytype and spinning sidebands (seen as minor bumps in all three spectra), and additional characterization. Two of the samples were prepared by a new synthetic procedure[5] reacting Ga metal with $NH_3$ in the presence of Bi catalyst in boats made of either quartz or BN. All samples,

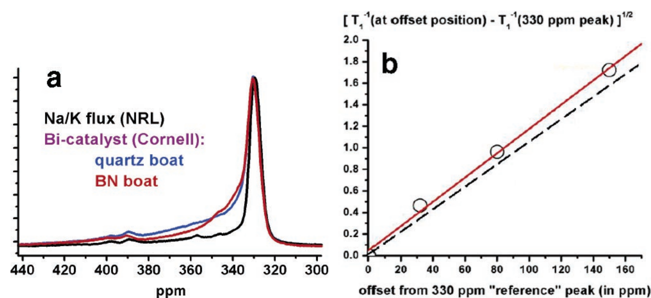


***Figure 1.*** (a) $^{71}$Ga fully relaxed central transition MAS NMR spectra of three h-GaN samples synthesized in different ways; (b) plot of the square root of the $^{71}$Ga spin−lattice relaxation rate $T_1^{-1}$ at 304 K corrected for the background rate versus the chemical shift offset at three positions in the high-frequency broad peak of the quartz boat sample in (a); dashed line corresponds to the theoretical slope for the degenerate electron case.

especially the two made with Bi catalyst, exhibit a broad structureless absorption on the high frequency (left) side of the main h-GaN peak.

The strategy for showing that these inhomogeneously broadened[2b] high-frequency absorptions are due to Knight shifts rather than chemical structural effects relies upon the ability of conduction electrons to relax nuclei and shorten spin−lattice relaxation times $T_1$. A Knight shift $K$ in the simplest case arises from electrons at the bottom of the conduction band having s-orbital character and thus finite probability of being at the nucleus and producing an electron−nucleus hyperfine interaction.[6] Such an interaction also serves to relax the nuclear spins, leading to the Korringa relationship $K^2T_1 = constant$, at constant temperature.[6] Knight shifts in metals are much larger than in semiconductors generally and hence have been much more extensively studied.

To measure the $^{71}$Ga spin−lattice relaxation induced by conduction band electrons, a train of 90° pulses asynchronous with the spinning is applied in order to saturate both central and satellite transitions as recently described,[7] and a rotor-synchronized Hahn spin−echo signal is obtained after a variable recovery time. Single-exponential magnetization recovery curves were obtained by monitoring the intensity at different frequency offsets from the main unperturbed h-GaN peak at 330 ppm (333 ppm corrected chemical shift[4]). Although a precise description of $T_1$ relaxation due to combined quadrupolar and magnetic (electron hyperfine) interactions in the four-level $I = 3/2$ system is quite involved, a recent study[7] justifies obtaining the rate $T_1^{-1}$ due to conduction electron relaxation by a simple procedure: subtract the "background" rate measured for the unperturbed 330 ppm h-GaN peak from the rate measured at a given frequency offset from 330 ppm (this offset is thus defined to be the absolute Knight shift). The former rate is determined almost entirely by a quadrupolar relaxation mechanism[7,8] (in these samples and at 304 K).

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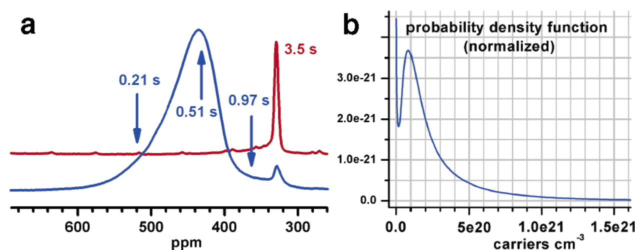


***Figure 2.*** (a) $^{71}$Ga MAS NMR (rotor-synchronized Hahn spin−echo) at 9.0 kHz spinning speed and 304 K of 0.13% Ge-doped h-GaN (blue) and Na/K flux reference from Figure 1a (red), with $T_1$ values measured at positions shown; (b) distribution of electron carrier concentrations calculated from Knight shift distribution in (a) according to theory for degenerate electron case and calibrated by independent measurements.

The resultant data points for one particular sample (Bi catalyst quartz boat h-GaN) are plotted in Figure 1b; the linearity of the plot agrees with Korringa-type relaxation, and the (forced) zero intercept substantiates the assumption of the 330 ppm peak as an unperturbed reference lacking significant Korringa relaxation. Moreover, if the conduction band electrons form a degenerate electron gas (yielding metallic conductivity above the Mott transition), then a straight line through the origin is predicted,[6] with a slope (at temperature $T$) = $(\gamma_n/\gamma_e)(4\pi kT/\hbar)^{1/2}$, involving fundamental physical constants (the magnetogyric ratios of the nucleus and electron, Boltzmann, and Planck constants).

Such a theoretical plot is represented by the dashed line in Figure 1b, which agrees surprisingly well with the experimental data. Thus, we can conclude that the sample has metallic conductivity and a carrier concentration above the Mott transition, which for GaN is around $(1.6-7) \times 10^{18}/\text{cm}^3$.[9] This is also consistent with the complete Li−U elemental analysis of the sample by glow discharge mass spectrometry, which identifies the only major impurities as O (650 wt ppm) and Si (380 wt ppm), presumably contaminants from the quartz boat container. Both elements are known shallow donors[10] in GaN that together would yield a carrier concentration of $2 \times 10^{20}/\text{cm}^3$ in the absence of any compensation.

A more dramatic illustration of how major Knight shift effects can arise from chemically rather minor substitution levels is illustrated in Figure 2a by the $^{71}$Ga MAS NMR spectrum of Ge-doped h-GaN prepared by a Na/K flux method[3] and shown from chemical analysis to contain 0.13 wt % Ge. Germanium is known to behave as a shallow donor in GaN.[10] Similar spectra greatly broadened by inhomogeneous interactions with only a minor component of unperturbed h-GaN have been recently reported for a h-GaN sample doped with both Ge and Mn, a magnetic dopant.[2b] The $^{71}$Ga $T_1$ values measured at various positions in the spectrum (as shown in Figure 2a) decrease with increasing offset from the unperturbed peak, and when plotted as in Figure 1b had a linear slope that agreed to better than 4% with that for the sample in Figure 1b. Therefore, we similarly conclude that a distribution of degenerate conduction electrons is responsible for the Knight shifts and relaxation effects in this sample.

We now use the fact that for degenerate electrons the Knight shift is proportional to $n^{1/3}$, where $n$ is the electron carrier concentration,[6] to quantitatively deduce the *distribution* of carrier concentrations in the sample. Although we do not yet have a calibration relating the $^{71}$Ga Knight shift to an absolute concentration of carriers, we can use the latter values measured by Corti et al. from Raman[8] for a conductive doped GaN film. By finding the Knight shift offset where their reported $^{71}$Ga $T_1$ is equal to our value at the same temperature, we can then assume the concentrations are equal at this Knight shift (see Supporting Information for details for here and below). The probability density function of carrier concentrations thus calculated from experimental data points is shown in Figure 2b; the transformation from a discrete uniform-interval Knight shift space to the carrier concentration space requires some care. The mean carrier concentration thus derived is $1.8 \times 10^{20}$ cm$^{-3}$, whereas the maximum value is only 0.47 times this value, reflecting a distribution skewed to higher values. If all Ge atoms were simple electrically active shallow donors with no compensation, the carrier concentration would be $6.6 \times 10^{19}$ cm$^{-3}$. This smaller value may indicate the presence of other $n$-type dopants, such as O, or else inaccuracies in the assumed calibration (which do *not* affect the shape of the distribution). Plotting the curve of Figure 2b with a logarithmic axis yields a Gaussian distribution as the predominant component. This so-called log-normal distribution serves to describe a wide variety of disparate phenomena. The Knight shift distributions for the Bi-catalyzed GaN samples observed in Figure 1a seem more likely to arise from gross inhomogeneities in the sample caused by the influx of impurities from the reaction vessel.

While this study reports results only for GaN, the observations and strategies adopted should be applicable to a wide variety of other inorganic (and organic) semiconductors. The main general conclusions include the following: (1) impurities at levels of 0.1% or less can completely alter the appearance of MAS NMR spectra of semiconductors through the effects of conduction band electrons rather than perturbations to the chemical structure; (2) inhomogeneously broadened peaks in a single sample can be shown to arise from such effects by the Korringa-type plot of Figure 1b if the sample contains an unperturbed peak providing a “zero” reference for Knight shifts and a “background” relaxation rate or if both values can be estimated from other samples or experiments; (3) for heavily doped semiconductors that exhibit metallic conductivity (still far below that of normal metals), one can use the Knight shift distribution to infer the distribution of carrier concentrations in the sample; (4) combined with other analytical and spectroscopic techniques, this approach could be used to investigate whether dopants are distributed randomly throughout all crystallites or unevenly from crystallite to crystallite, clustered within crystallites, or segregated to surfaces. Relating the distribution observed to the *spatial length scale* of dopant concentration fluctuations is an intriguing area for future exploration.

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**Supporting Information Available:** The procedures used for calculating the carrier probability density function and further experimental details are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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