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^{29}Si NMR and ^{69,71}Ga NMR/NQR study of the kagomé compound $Nd_3Ga_5SiO_{14}$

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Abstract. We report a comprehensive ^{29}Si NMR and ^{69,71}Ga NMR/NQR study of the large-spin magnetically anisotropic kagomé compound $Nd_3Ga_5SiO_{14}$. We find a sizable transferred hyperfine coupling between the nuclear and electron moments, proving that these nuclei can be utilized as local probes which provide useful information about the magnetic Nd^{3+} ions. Our results give evidence of unexpectedly broad distributions of local environments on all nuclear sites under investigation, implying also exchange disorder.

1. Introduction

In recent past, a geometrical frustration of a spin lattice with frustrated exchange interactions has been an intensively studied subject due to a plethora of cooperative phenomena that it may lead to. The prototype example is a kagomé lattice with antiferromagnetic exchange, characterized by cooperative paramagnetic behavior due to its extensive degeneracy of a classical ground-state. Theoretically, it should exhibit a spin-liquid behavior in the classical and quantum case [1]. On the other hand, magnetic instabilities are usually experimentally observed at lower temperatures. However, these are absent at least down to 50 mK in the recently discovered spin-1/2 kagomé compound $ZnCu_3(OH)_6Cl_2$ [2] and the large-spin kagomé compound $Nd_3Ga_5SiO_{14}$ [3, 4].

The latter compound is the first example of a classical-spin kagomé lattice, which shows anisotropic magnetic behavior of the rare-earth Nd^{3+} $J = 9/2$ magnetic moments [5]. These reside on a network of corner-sharing equilateral triangles, topologically equivalent to the perfect kagomé lattice if nearest-neighbor exchange is considered [inset to Fig. 1(*b*)]. The spins were initially reported to be strongly antiferromagnetically coupled [5], however, this coupling could be in a sub-Kelvin range according to the more recent study [6]. Although the spin fluctuations slow down considerably with decreasing temperatures, they exhibit a plateau below 10 K and remain present at least down to 60 mK [4], proving a paramagnetic behavior of the compound.

2. Experimental results

Our ^{69,71}Ga NMR/NQR and ^{29}Si NMR measurements were performed on a single crystal of cylindrical shape (2 mm in diameter and 8 mm in length), which was grown by a floating zone technique [5]. Its crystal structure ($P321$ space group) and its purity were verified by X-ray diffraction and SQUID magnetization measurements. NMR was done at various fixed frequencies

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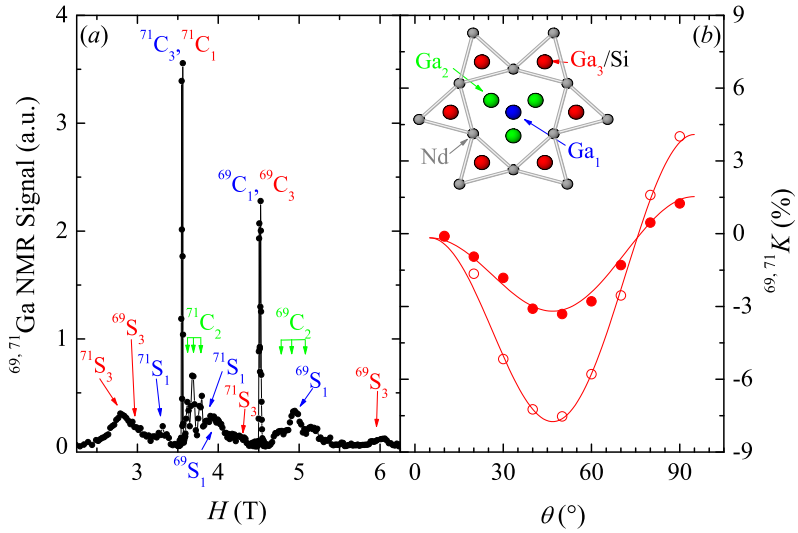

Figure 1. (a) ^{69,71}Ga NMR spectrum of $Nd_3Ga_5SiO_{14}$, recorded at 46.01 MHz and 80 K with $\mathbf{H}||\mathbf{c}$. Central and satellite transitions are labeled with C_i and S_i, respectively, where i denotes different Ga sites. (b) Angular dependence of the $^{69}C_3$ (○) and $^{71}C_3$ (●) NMR shift at 80 K and the corresponding fits (——) to Eq. **??**. Inset: the distorted kagomé network of Nd^{3+} magnetic moments and the location of the three crystallographically non-equivalent Ga and the Si site.

in the temperature range between 300 K and 20 K, using both a Fourier transform and a field-sweep technique when necessary. NQR spectrum was recorded with the same spectrometer by sweeping the frequency in zero magnetic field.

In Fig. 1(a) we show a typical ^{69,71}Ga NMR spectrum. Its complexity is due to many factors, some general to Ga NMR and others specific to $Nd_3Ga_5SiO_{14}$. Starting with the latter, there are three crystallographically non-equivalent Ga sites, Ga_i ($i = 1 - 3$) [inset to Fig. 1(b)]. Second, three magnetically non-equivalent Ga_2 and two Ga_3 sites are present in the crystal unit cell, thus defining six sets of lines for a general direction of the applied magnetic field. Turning to general characteristics, both isotopes (^{69}Ga and ^{71}Ga) have similar sensitivity and possess nuclear spin $I = 3/2$. The letter leads to quadrupolar splitting of the central (C) and the two satellite (S) lines in electric field gradient (EFG) of the crystal. All together, these results in 36 lines, which may ultimately be resolved in the Ga NMR spectrum of $Nd_3Ga_5SiO_{14}$. When assigning the experimentally observed peaks we took advantage of the know ratio of the quadrupolar moments $^{69}Q/^{71}Q = 1.583$ and qyromagnetic ratios $^{69}\gamma/^{71}\gamma = 0.7871$. We performed angular dependent measurements and frequency dependence for special high-symmetry directions of the applied field H – when H is perpendicular to the kagomé planes ($\mathbf{H}||\mathbf{c}$) all the magnetically non-equivalent sites give the same set of peaks. We were able to assign all the peaks in the ^{69,71} NMR spectrum [Fig. 1(a)] – all of the expected C and S peaks were observed for sites $Ga_{1,3}$, while only C peaks were resolved for the Ga_2 site. Surprisingly, the Ga_2 site yields three distinctive central lines even for $\mathbf{H}||\mathbf{c}$ when all the three non-equivalent Ga_2 site within the unit cell yield the same spectra. This is due to local distortions, as further discussed later on.

From the Ga NMR spectra, we can first determine the quadrupolar frequencies ν_Q for $Ga_{1,3}$ sites. With their sizable quadrupolar moments, Ga nuclei are coupled to electron charge distribution. Because of the local three-fold rotational axes (c direction) the asymmetry parameter η is zero for the $Ga_{1,3}$ sites, yielding the first order quadrupolar shift of the satellites and the second order quadrupolar shift of the central lines of the simplest possible form [7],

$$\Delta\nu_q^{(1)} = \nu_Q(3\cos^2\theta - 1), \Delta\nu_q^{(2)} = -\frac{\nu_Q^2}{16\nu_0}(I(I+1) - 3/4)(9\cos^2\theta - 1)(1 - \cos^2\theta). \quad (1)$$

Here θ denotes the angle between H and the eigenvector of the largest EFG principal value (c direction), while $\nu_0 = \gamma H/h$ is the Larmor frequency. The first order shift of the S and the second order shift of the C lines simultaneously yield values of ν_Q, which are summarized in table 1. As an example, in Fig. 1(b) we show the fit of the $^{69,71}C_3$ shifts to $\Delta\nu_q^{(2)}$ in Eq. (1).

Table 1. Quadrupolar frequencies ν_Q (in MHz) for $Ga_{1,2,3}$ sites. The 1, 3-site values are obtained from the shift of C and S peaks and the 2-site values from the NQR peaks at $\nu_Q\sqrt{1+\eta^2/3}$, which yields three distinctive groups (a, b, and c) of the Ga_2 sites [see Fig. 4(b)].

Site	1	2a	2b	2c	3
^{69}Ga	4.6	25.0	26.5	30.9	15.1
^{71}Ga	2.9	16.2	16.7	19.1	9.6

Next, we highlight magnetic coupling between Ga nuclei and Nd^{3+} moments. This is responsible for the shift and broadening of the Ga peaks with decreasing temperature, as shown for the $^{71}C_{1,3}$ lines in Fig. 2(a). If the spectra were solely determined by the quadrupolar (q) interaction and chemical shift (cs) they would be temperature independent in the investigated temperature range below 80 K. With additional magnetic coupling, the relative shift

$$K = \frac{\nu - \nu_0}{\nu_0} = A\chi_l + \frac{\Delta\nu_{cs}}{\nu_0} + \frac{\Delta\nu_q}{\nu_0} \quad (2)$$

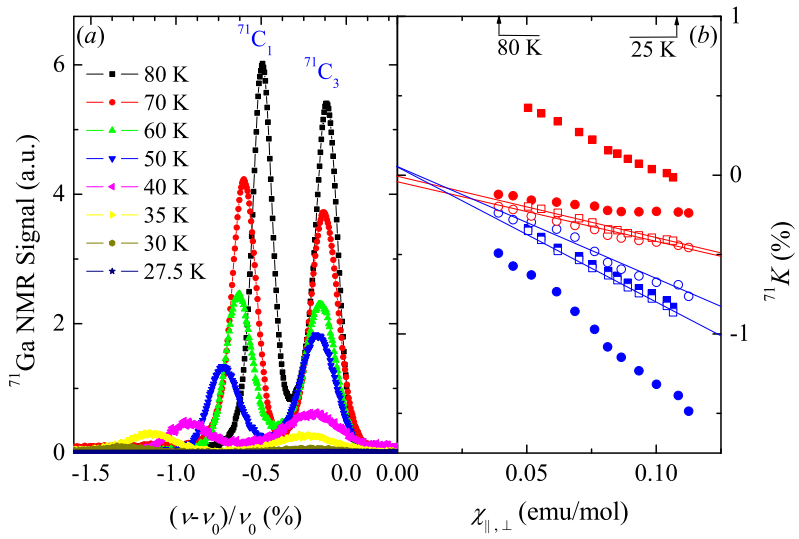

Figure 2. (a) Temperature evolution of the $^{71}C_{1,3}$ NMR lines at 46.01 MHz and **H**||**c**. (b) Scaling of $^{71}C_1$ (●, ■) and $^{71}C_3$ (●, ■) shift with susceptibility for **H**||**c** (●, ●) and for **H** ⊥ **c** (■, ■). Open symbols correspond to the shift due to transferred hyperfine interaction, which is obtained by subtracting the dipolar, the demagnetization and the quadrupolar contribution.

has an additional magnetic contribution, which is proportional to the local susceptibility χ_l. It has three different sources, $A = A_{hf} + A_{dd} + A_{dm}$; a hyperfine ($hf$) and a dipolar ($dd$) coupling between Nd^{3+} moments and Ga nuclei and a macroscopic demagnetization (dm) field.

In Fig. 2(b) the linear scaling of the relative NMR shift with bulk susceptibility is shown for $^{71}C_{1,3}$ peaks. We performed a dipolar-field calculation by taking account of all the Nd^{3+} moments around a particular site within a certain radius – fictitious Lorentzian sphere – so that the dipolar field would converge. This microscopic field was then combined with a continuum theory by adding the macroscopic Lorentzian field. Subtracting thus calculated dd contribution, the dm contribution and the q contribution from the measured NMR shift allows us to evaluate the hf coupling constants. Our calculations reveals that all the contributions to the shift are of a similar magnitude and that the hf coupling is close to being isotropic, therefore being mainly of the s-type. The values of the latter coupling are collected in table 2.

Table 2. Transferred hyperfine coupling constant A_{hf} of the $^{71}Ga_{1,3}/^{29}Si$ nuclei and Nd^{3+} magnetic moments (in kOe/μ_B).

Site	$^{71}Ga_1$	$^{71}Ga_3$	^{29}Si
H||**c**	-1.22	-0.60	-0.53
H $\perp$ **c**	-1.47	-0.69	-0.53

In Fig. 3(a) the ^{29}Si NMR spectra recorded between 300 K and 20 K are shown. ^{29}Si nuclei are spin-1/2 species and therefore do not exhibit quadrupolar effects. Very similar shifting and broadening to that of the $^{69,71}Ga$ signal is observed also for ^{29}Si. The analysis of the magnetic coupling constants with Nd^{3+} moments yields isotropic hf coupling $A_{hf} = -0.53$ kOe/μ_B.

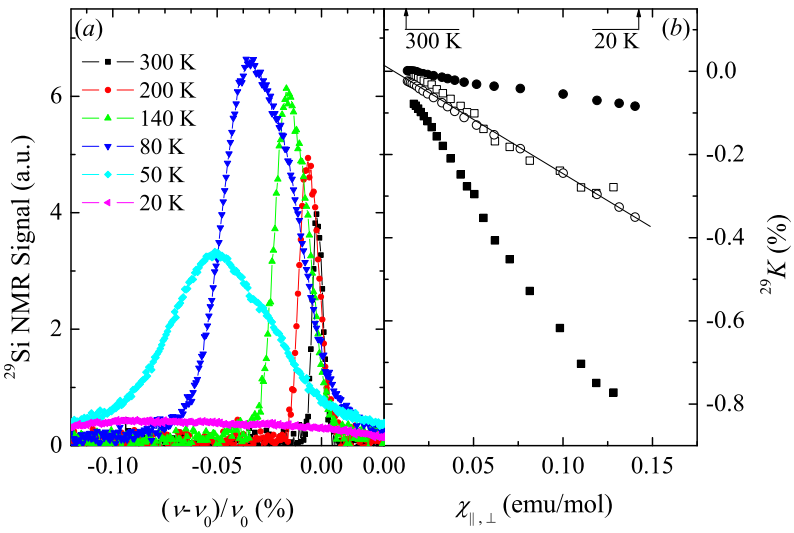

Figure 3. (a) Temperature evolution of the ^{29}Si NMR line at 59.17 MHz and **H**||**c**. (b) Scaling of the NMR shift with susceptibility for **H**||**c** (●) and for **H** $\perp$ **c** (■). Open symbols correspond to the shift due to transferred hyperfine interaction, which is obtained by subtracting the dipolar and the demagnetization contribution.

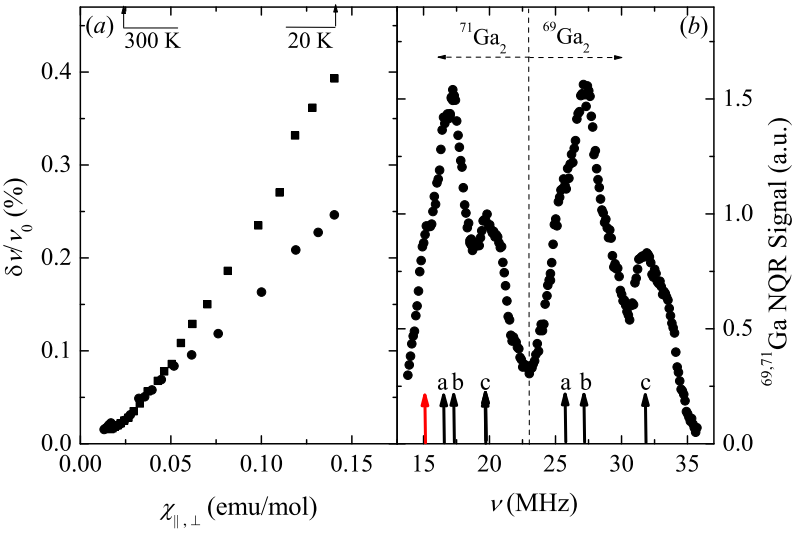

Figure 4. (a) Scaling of the relative line-width of the ^{29}Si NMR peak with susceptibility for $\mathbf{H}||\mathbf{c}$ (●) and for $\mathbf{H} \perp \mathbf{c}$ (■). (b) Ga NQR spectrum at 80 K, with thick black arrows indicating the position of three Ga_2 peaks (a, b, c) for each isotope and the red arrow the $^{69}Ga_3$ peak.

Next, we turn to the drastic broadening of both the ^{69,71}Ga [Fig. 2(a)] and the ^{29}Si [Fig. 3(a)] NMR lines, which is together with a significant enhancement of the spin-spin and spin-lattice NMR relaxation [4] responsible for the disappearance of these lines around 20-25 K. The NMR signal is recovered only below ∼2 K in high-enough magnetic field, which dramatically slows down Nd^{3+} spin fluctuations [4]. In Fig. 4(a) the broadening of the ^{29}Si NMR signal between 300 K and 20 K is displayed. The relative line-width $\delta\nu/\nu_0$ scales with susceptibility almost linearly and is noticeably more enhanced for $\mathbf{H} \perp \mathbf{c}$, in which direction also the line-shift is bigger. We calculated a distribution of the demagnetization field, whose width is around 3% of the average value. It is much to narrow to account for the experimental line-widths. The scaling with susceptibility implies that broad distributions of local environments exist in $Nd_3Ga_5SiO_{14}$.

Such distribution on the Ga_2 site is observable also in its NQR spectrum [Fig. 4(b)]. Because of our frequency limitation on the lower bound, the recorded NQR spectrum is solely due to the Ga_2 site (with the exception of the small kink at 15.1 MHz), where the EFG is the strongest. Even though the asymmetry parameter η is non-zero for this site, a single NQR line at $\nu_Q\sqrt{1+\eta^2/3}$ is expected for $I = 3/2$ spins [7]. On the contrary, at least three distinctive components corresponding to three different Ga_2 sites are experimentally observed in the NQR spectrum of each isotope, even though all the Ga_2 sites within the unit cell are equivalent in zero field. Assuming $\eta = 0.30$, calculated from the crystal structure, the ν_Q values, summarized in table 1, are obtained. The three Ga_2 NQR peaks also justify the triple splitting of the $^{69,71}C_2$ NMR lines for the highly symmetric direction $\mathbf{H}||\mathbf{c}$. The broad three-peak NQR spectrum of each isotope directly displays the distribution of the largest EFG eigenvalue on the Ga_2 site.

3. Discussion

The T-dependent ^{69,71}Ga and ^{29}Si NMR spectra prove that these nuclei can serve as local probes well coupled to the Nd^{3+} magnetic moments and can therefore detect the magnetism of the underlying kagomé lattice. The shift of the $^{71}C_{1,3}$ and ^{29}Si peaks scales linearly with the bulk susceptibility, proving that the bulk and the local magnetic responses are identical.

On the contrary, in 3*d*-metal kagomé compounds the intrinsic kagomé susceptibility in regularly overshadowed by impurity contribution in bulk measurements at low temperatures [8].

We find a significant hyperfine interaction of Ga and Si nuclei with Nd^{3+} moments. This interaction is due to an overlap of atomic orbitals and is most probably mediated through oxygen since the distance between Ga/Si and nearest-neighbor Nd sites is big (3.45 Å- 3.92 Å) while *f* electrons are well confined. Although we can not directly measure the Nd exchange coupling, the sizable transferred hyperfine interaction implies that exchange is not negligible, even if its effect on susceptibility is overshadowed by crystal-field effects at higher temperatures [6].

Next, we highlight the broadness of the recorded NMR(NQR) peaks. The NQR spectrum of the Ga_2 site and all the $Ga_{1,3}$ NMR peaks which are shifted in first order (satellite transition) or second order (central transition, except $C_{1,3}$ for $\mathbf{H}||\mathbf{c}$) are unexpectedly broad for a single crystal. They are broadened due to wide distributions of corresponding quadrupolar frequencies. We believe that the origin of such broad distributions of ν_Q on each site, arising from distribution of local environments, lies in the random Ga^{3+}/Si^{4+} occupation of the Ga_3 crystal site [5]. This "randomness of charge" then causes distribution in electric field gradients. Second, we argue that it is also responsible for distributions of the magnetic coupling constants between nuclei and Nd^{3+} moments and/or distributions of local susceptibilities. Namely, the peaks not affected by the quadrupolar interaction (the central $C_{1,3}$ peaks for $\mathbf{H}||\mathbf{c}$ and the ^{29}Si spectra) broaden significantly with lowering temperature, as the susceptibility monotonically increases. The observed linear scaling with bulk susceptibility then corresponds to a distributions of shifts. We note, that these distributions are very broad, since the line-widths and the line-shifts are of a similar magnitude. The presence of the distributions of the magnetic coupling constants and/or local susceptibilities proves that local structural deformations due to the Ga^{3+}/Si^{4+} randomness on the Ga_3 site are present. This implies randomness of magnetic exchange. It is then interesting, that no spin-glass behavior is observed in $Nd_3Ga_5SiO_{14}$ down to 60 mK [4] despite the exchanged disorder [9], especially since we expect a non-negligible magnetic exchange.

4. Conclusions

Our extensive NMR/NQR study has, first, established that the bulk magnetic response of $Nd_3Ga_5SiO_{14}$ is intrinsic to the system, since it doesn't differ from the local-probe response. Second, we detected a sizable hyperfine coupling of the Ga/Si nuclei and Nd^{3+} magnetic moments, which indirectly implicates a non-negligible exchange between the Nd^{3+} moments, since both are due to overlapping atomic orbitals. Last, our broad NMR and NQR spectra give direct evidence of broad distributions of local environments. We believe that these are due to the random occupation of the Ga_3 crystal sites by Ga^{3+} and Si^{4+}. This probably induces both the random charge distributions as well as local distortions of the crystal structure.

Acknowledgments

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