Ga NMR study of the local susceptibility in SrCr$_5$Ga$_{19}$O$_{19}$: pseudogap and paramagnetic defects

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We present the first Ga(4f) NMR study of the Cr susceptibility in the archetype of Kagomé based frustrated antiferromagnets, SrCr$_5$Ga$_{19}$O$_{19}$. Our major finding is that the susceptibility of the frustrated lattice goes through a maximum around 50 K. Our data also supports the existence of paramagnetic “clusters” of spins, responsible for the Curie behavior observed in the macroscopic susceptibility at low $T$. These results set novel features for the constantly debated physics of geometrically frustrated magnets.

The interest in triangular-based antiferromagnets (AF) was raised long ago by Anderson’s suggestion for a resonating valence bond state (R.V.B) as an open alternative to the classical Néel state. After a decade of extensive work on 2D geometrically frustrated AF, there is now a growing theoretical consensus that the $S = 1/2$ Kagomé Heisenberg AF is a very promising candidate for such an RVB state at low $T$. Instead of sharing bonds, as in a triangular lattice, the frustrated triangles share sites with a smaller coordination. From a classical point of view, this generates a very high degeneracy of the ground state, which translates into a huge density of low energy excitations, an absence of long range order at $T = 0$ and a very short magnetic correlation length characteristic of a so-called "spin liquid state". Quantum approaches for $S = 1/2$ spins suggest that a singlet ground state is energetically favoured.

Only some of these theoretical features were demonstrated experimentally on the archetypal system SrCr$_9$Ga$_2$O$_{19}$ (SCGO-$p$) Kagomé-based AF. Susceptibility measurements showed the strong AF character of the interactions through the occurrence of a Curie-Weiss (CW) temperature as high as $\theta \approx 500 - 600$ K (for $p \approx 0.9$). The extension of the CW law well below $\theta$ and the smallness of the spin glass like ordering detected in susceptibility only at low $T \ll \theta$, ($T_g = 3 - 5$ K) are taken as convincing signatures of the high frustration. In addition, neutron data and low $T \mu$SR studies altogether prove that the freezing is quite marginal and involves only a 20-30% fraction of the moment(s). The magnetic correlation length is also found of the order of the inter-Cr spacing.

However, due to a Curie upturn which dominates the macroscopic susceptibility, $\chi_{macro}$, below 60 K there is no experimental determination of the $T \ll \theta$ Kagomé-based lattice susceptibility. The Curie upturn received many interpretations still highly debated, encompassing magnetic disorder due to non magnetic substitutions in the Kagomé plane or original geometrically frustrated spin glass like order.

In this Letter, we present the first NMR study of local susceptibility in SCGO, where we can discriminate between the susceptibility associated with the Kagomé based frustrated magnetism, $\chi_{frust}$, and the purely paramagnetic susceptibility, $\chi_{def}$, most likely induced by Ga/Cr substitutions (defects). Strikingly, we find a gap-like downturn of $\chi_{frust}$ below $T$ as high as 50 K. This sets a novel energy scale, between $\theta$ and $T_g$ for the relevant physics of SCGO.

From $\chi_{macro}$ measurements, the SCGO-$p = 0.9$ sample was found to be typical for such a Cr content, with $\theta = 560$ K and a high-$T$ Curie constant, $C = 2.2$ emu/mol. An extended NMR analysis of the spectrum was presented in a previous paper. There, it was clearly established that 3 different Ga NMR sites could be resolved, Ga(4e), Ga(4f) and Ga substituted on Cr sites, Ga(sub). We focus here on the Ga(4f) site, whose line shift probes both the Cr(12k) Kagomé and Cr(2a) triangular planes susceptibility through the neighboring O. Interestingly, these sites form the so-called pyrochlore slab (fig.1).

Below $T = 200$ K the $^{71}$Ga spectra were recorded by sweeping the field, using a conventional $\pi/2 - \tau$ spin echo sequence to detect the $^{71}$Ga(4f) and $^{69}$Ga(4f) nuclear transitions. Compared to Ref. [13], a much lower NMR frequency $\nu_0 \approx 40$ MHz was used to ensure a better suppression of the Ga (4e) contribution. This is achieved by taking advantage of the quadrupole line broadening ($\approx \nu_0^2/\nu_0$) which is strongly different for the two sites which have a different local charge environment ($^{71}Q_{4f,4e} \approx 2.9, 20.5$ MHz). For $220 < T < 450$ K, the NMR spectra were taken by sweeping the frequency in a fixed 7.5 T field.

A typical set of the field sweep spectra, recorded around 3T, is reported in Fig. 2. The high $T$ part (upper panel), show that upon cooling the NMR lines shift to the right (lower $H$), without any appreciable broadening. In contrast, the low $T$ part (lower panel), shows that upon further cooling the lines shift to the left (higher $H$), and
broaden. This crossover (taking place at \( \sim 50 \text{K} \)) in the \( T \) - dependence of the shift, reflecting the local magnetic susceptibility, is the major finding of this letter.

Another feature seen in Fig. 2 is a wipe-out of the intensity due to fast nuclear relaxation when the dynamics of electronic spins slows down. This is common in various systems ranging from spin glasses to AF correlated systems [15,16]. From Ref. [15] and the \( \mu \)SR relaxation data reported on the same compound [16], one would naively expect this effect to occur in SCGO only in the vicinity of \( T_g \). Carefully measured integrated intensity of the \( ^{69,71} \text{Ga} \) spectra shows no variation above 15 K (fig.3), clearly demonstrating that our data very reliably reflects the behavior of all the electronic spins in the system, including the \( T \)-range 15-50 K where the shift direction changes. On the contrary, it is worth noticing that below \( T = 10 \text{K} \sim 3T_g \), more than 50% of the sites are wiped out of our experimental window, indicating the occurrence of an inhomogeneous dynamics of the spin system [17] in an unusually high \( T \)-range as compared to \( T_g \).

The shift \( K \) and the width \( \Delta H \) are extracted from the NMR line at all \( T \). \( K \) is related to the average field at the Ga(4f) site, and directly probes the (homogeneous) susceptibility of the Cr(12k) and Cr(2a) ions. \( \Delta H \) originates from a distribution of internal fields on the nuclear Ga(4f) site, which is naturally associated with an inhomogeneous susceptibility of the Cr spin system. For \( T > 120 \text{K} \), the line broadening is small enough that, for practical purpose, we extract \( K \) from the shift of the line edges. This method is not adequate at lower \( T \). Below 120 K, the line is symmetrically broadened, and to deduce \( K \), we used either the centre of gravity or a partial Gaussian fit of the Ga(4f) contribution. Independently of the type of analysis, \( K \) was found to decrease at low \( T \). \( \Delta H \) was extracted from Gaussian fits [15].

First we discuss the temperature dependence of \( K \) which is presented in fig. 4, where we also include results taken at various applied fields. From the high \( T \)-data (inset), we can extract a Néel temperature \( \theta_{\text{NMR}} \approx 470 \text{K} \) of the same order as \( \theta_{\text{macro}} = 560 \text{K} \). This confirms that \( K \) reflects the physics of the frustrated unit. As mentioned before, \( K \) first increases with decreasing \( T \) down to 50 K, but below, \( K \) flattens and even decreases by 20%. The sharp contrast between the temperature dependence of \( K \) and \( \chi_{\text{macro}} \), below 50 K, is emphasized by the dashed arrow in the figure. It reveals that 2 different types of Cr have to be considered. In other words, our shift data rule out models which attempt to associate the low-\( T \) macroscopic susceptibility only with a generic - therefore homogeneous- property of the frustrated lattice. Further investigations, to be detailed elsewhere [16], clearly confirm that the shift variation reported for this sample is an intrinsic feature of the frustrated network as it is very little dependent on the Cr/Ga substitution (at variance with the width).

Next we discuss the variation of \( \Delta H \) at low \( T \). The results, taken for various frequencies, are summarized in fig.5. At low \( T \), the broadening scales remarkably with the applied field for both isotopes. This clearly confirms the magnetic origin of the width at low \( T \) [3]. A Curie-like behavior is found for \( \Delta H(T) \), as shown by the solid line. We therefore plot in the inset \( \Delta H/H_0 \) versus \( \chi_{\text{macro}} \) measured for the same \( H_0 \sim 3 \text{Tesla} \) field, using \( T \) as an implicit parameter. The linearity of the relationship between \( \Delta H \) and \( \chi_{\text{macro}} \) strongly suggests that the Curie upturn, which dominates \( \chi_{\text{macro}} \) at low \( T \), and the linewidth have a common origin of inhomogeneous magnetism. The deviation between \( \chi_{\text{macro}} \) and \( K < T = 50 \text{K} \) is also straightforwardly explained by this viewpoint.

In summary, our NMR results are consistent with a picture where \( \chi_{\text{macro}} \) is a sum of two distinguished components \( \chi_{\text{frust}} \) and \( \chi_{\text{def}} \). \( \chi_{\text{frust}} \) is the homogeneous susceptibility reflected in \( K \) and representing the physics of the kagomé-based lattice. It has a Curie-Weiss like behavior at high \( T \) and displays a crossover at 50 K to a pseudogap behavior. \( \chi_{\text{def}} \) is the inhomogeneous contribution to the susceptibility reflected in \( \Delta H \) and originating from defects of the frustrated block. This component has a pure Curie low-\( T \) contribution and it dominates \( \chi_{\text{macro}} \) at \( T \rightarrow T_g^+ \).

We now turn to discuss our experimental results in light of existing theories. Susceptibility of the pure Kagomé network has been numerically simulated using various models. In many of them, such as e.g. the case of singlets formation [4], a gap \( \Delta \) appears in \( \chi_{\text{frust}} \) and \( \chi_{\text{frust}} \sim e^{-\Delta/T} \) at low \( T \). Using for \( \Delta \) the temperature \( T_{\text{max}} = 50 \text{K} \) where \( K \) peaks, one would expect a much sharper decrease of \( \chi_{\text{frust}} \) than the 20% decrease observed at 20 K. The discrepancy between the theoretically expected and measured decrease of \( K \) might be solved using a more realistic model of pyrochlore slab [1]. In this model spins from the triangular Cr(2a) layer combine with the Kagomé Cr(12k) to generate a basic unit with an uncompensated moment. This moment is expected to add a 1/\( T \) homogeneous contribution to \( \chi_{\text{frust}} \), which should weaken the drop of \( K \) below \( \Delta \). Whether such a term somewhat counterbalances the effect of the gap on the measured \( K \) is still speculative as, unfortunately, an experimental confirmation is prevented by the loss of NMR intensity below 15 K. Therefore, we cannot definitely conclude on the full opening of a gap at the present stage, hence the name pseudogap.

Regardless of the nature of the gap, the value of \( T_{\text{max}} \) is very surprising. In most models \( T_{\text{max}} < 0.1J \) where \( J \sim 100K \) [14] is the exchange interaction. Here \( T_{\text{max}} \sim J/2 \), which is much bigger than expected and obviously further theories are required to explain in detail our results. To our knowledge, only a chiral model features a peak in \( \chi \) at \( T \) as high as 0.4J [5]. From the absence of neutron signature, one does not expect any real magnetic order to occur around 50K. Our shift data would rather indicate an increase of the magnetic correlations peaked at the chiral wave-vector. This scenario resembles the case of the pseudogap in High \( T_c \) cuprates. An even sim-
pler interpretation to the high value of $T_{\text{max}}$ relies on the fact that for any low dimensional AF correlated system, one expects the susceptibility to decrease at low $T$. The crossover usually occurs in non-frustrated 2D AF for $T \sim \theta$ [22], however, because of frustration, it could occur at lower temperatures, here 10 times smaller than $\theta$. The ratio $\theta/T_{\text{max}}$ might, finally, prove to be a better characterization of the degree of frustration than using $\theta/T_S$ since the origin of the spin glass freezing might be associated with defects, as discussed below.

We now propose an interpretation for the origin of the line width in the light of the model developed in [11]. There, the origin of the $1/T$ paramagnetic behavior of $\chi_{\text{macro}}$ is assigned to the existence of triangles of the Kagomé lattice non fully occupied by Cr$^{3+}$ moments. The substitution of two adjacent Cr$^{3+}$ sites by Ga seems necessary to generate a paramagnetic-like “defect” at low $T$. A priori such a paramagnetic defect could lead to a well defined feature in the spectrum and a broadening, depending on the response of the electronic spin system to this defect. The number of Ga sites directly coupled to these $\sim (1-p)^2 = 1\%$ triangles is small and the corresponding signal is thus likely unobservable. On the contrary, a staggered response (sign oscillation of the field generated by the defect as a function of distance) over few lattice constants, is expected to lead to a symmetric line broadening of the full line. This phenomenon is observed in a large number of systems such as High $T_c$ cuprates, or 1D spin chains and ladders, where a similar low-$T$ increase of the NMR linewidth [21] is reported. Therefore, we conclude that the defects in SCGO must be coupled to the surrounding correlated spins, in agreement with the idea of Ref. [11] [22].

For a quantitative analysis of the low-$T$ contribution of Ga/Cr substitutions to $\chi_{\text{macro}}$, one needs to subtract the contribution from an ideal pure sample, unfortunately not stable. Nevertheless, we use a simple (and consistent) viewpoint where $\chi_{\text{macro}}$ is dominated by the substitution defects at low $T$. From the value of the low temperature Curie constant $C_{LT}$ deduced from $\chi_{\text{macro}}$, we can deduce the value of the effective moment associated with one defect, $\mu_{\text{eff}}$, provided the number of defects, $N_{\text{defect}}$, is known. We follow [11] and write $N_{\text{defect}}/N_{\text{Cr}} = 3/2(1-p)^2$, where $N_{\text{Cr}}$ is the total number of Cr. From $C_{LT} = N_{\text{defect}}\mu_{\text{eff}}^2/3k_B = 0.03$ emu/mol [22], we find $\mu_{\text{eff}}(\text{defect}) \sim 4\mu_B$, typical of a spin 3/2. This reminds a similar case for $S = 1/2$ AF cuprates where the absence of spin in the square 2D network generates a staggered damped response of the surrounding spins with a total moment corresponding to a spin 1/2 [23]. The overall consistency with the model of Ref. [11] is encouraging, but, of course, more NMR and susceptibility experiments are needed for other low substitution rates, in order to further check the quadratic concentration dependence of $N_{\text{defect}}$.

In conclusion, we have demonstrated that the intrinsic Kagomé/pyrochlore slab susceptibility displays a broad maximum around $T \sim J/2$. For $T < 20K$, our data suggest that the macroscopic susceptibility is dominated by the contribution from defects which remain coupled to the frustrated network [11]. Finally, the occurrence of a slowing down of spin fluctuations is clearly evidenced below 15K. Our results definitely set new constraints on the theoretical models and are stimulating for other NMR studies in the broad class of frustrated systems.

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FIG. 1. Structure of ideal SrCr$_9$Ga$_3$O$_{19}$. The thick dashed
lines show the hyperfine coupling paths of Ga nucleus to
various Cr sites. Light grey circles are oxygens. Cr(2a) and
Cr(12k) are coupled and form a pyrochlore slab.

FIG. 2. Typical $^{71}$Ga(4f) field sweep spectra obtained for
$\nu_0 = 40.454$ MHz, plotted versus $(H_0 - H)/H$ ($H_0$ is the
non-shifted value of the resonance field and $H$ is the applied
field). Upper panel: $T > 100K$, expanded scale. Bottom
panel: $T < 50 K$: the arrow indicates approximately the po-
sition of the line expected at 25 K in a one-component model
of $\chi_{macro}$ (with $K$ and $\chi_{macro}$ scaled at high $T$).

FIG. 3. Number of Ga(4f) sites detected by NMR. The
$^{69}$Ga estimate is more accurate as the ratio of the (4e) contri-
bution (quadrupolar broadening) to the (4f) one (magnetic
broadening) is 2.5 smaller than for $^{71}$Ga. $T_2$ corrections were
found quite small and do not affect the estimates below 50 K.

FIG. 4. $K$ versus $T$ down to 10 K, for various fields / fre-
quencies. Minor second-order quadrupole corrections have
been performed. The spread in the low-$T$ values taken in var-
ious conditions is due to the sizeable line broadening, see fig.2.
The dashed line figures $K$ variation expected from $\chi_{macro}$
within a one-component model. Inset: $1/K$ versus $T$. The
straight line extrapolation to $1/K = 0$ yields $\theta_{NMR}$.

FIG. 5. Relative full width at half maximum plotted versus
$T$ for the 2 isotopes at various fields. At high $T$, $\Delta H$ is domi-
nated by $T$- independent quadrupole effects, more prominent
for $^{69}$Ga and low fields. Inset: Plot of $\Delta H/H_0$ versus $\chi_{macro}$
in the same $T$-range.
Ga($4f$) Ga($4e$)

P. Mendels et al., fig. 2

Norm. echo

$T > 100$ K

Echo * $T$ (arb. units)

$T < 50$ K

$(H_0 - H)/H$
Ga NMR detected sites (%) vs. T (K)

$\nu_0 = 40.454$ MHz

$^{69}$Ga and $^{71}$Ga

P. Mendels et al., fig.3
$\chi_{\text{macro}} \sim C_{LT}/T$

- $H = 7.5 \, T$ (fixed)
- $\nu = 131 \, \text{MHz}$
- $\nu = 56 \, \text{MHz}$
- $\nu = 40.45 \, \text{MHz}$

P. Mendels et al., fig. 4
\( \frac{\Delta H}{H_0} (\%) \) vs. \( T \) (K)

Inset: \( \chi_{\text{macro}} \) (emu mol\(^{-1}\) / f.u.) for different Ga isotopes at 3 Teslas.

- \( ^{71}\text{Ga}-40.4 \text{ MHz} \)
- \( ^{69}\text{Ga}-40.4 \text{ MHz} \)
- \( ^{71}\text{Ga}-26.1 \text{ MHz} \)
- \( ^{71}\text{Ga}-56.2 \text{ MHz} \)

P. Mendels et al., fig.5