Susceptibility and dilution effects of the kagomé bi-layer geometrically frustrated network. A Ga-NMR study of SrCr$_{9p}$Ga$_{12-9p}$O$_{19}$.

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The archetype of geometrically frustrated compounds SrCr$_{9p}$Ga$_{12-9p}$O$_{19}$ is a kagomé bi-layer of Heisenberg Cr$^{3+}$ ions (S = 3/2) with antiferromagnetic interactions. We present an extensive gallium NMR study over a broad Cr-concentration range (0.72 ≤ p ≤ 0.95). This allows us to probe locally the susceptibility of the kagomé bi-layer and separate the intrinsic properties due to geometric frustration from those related to site dilution. Compared to the partial study on one sample, p = 0.90, presented in Phys. Rev. Lett. 85, 3496 (2000), we perform here a refined study of the evolution of all the magnetic properties with dilution, with a large emphasis on the lowest diluted p = 0.95 sample synthesized for this study.

Our major findings are: 1) The intrinsic kagomé bi-layer susceptibility reaches a maximum at a temperature of ≈ 40 – 50 K, which we show here to be robust to a dilution as high as ≈ 20%. This maximum is the signature of the development of short range antiferromagnetic correlations in the kagomé bi-layer; 2) At low-T, a highly dynamical state induces a strong wipe-out of the NMR intensity, regardless of dilution; 3) The low-T upturn of the macroscopic susceptibility is associated to paramagnetic defects which stem from the dilution of the kagomé bi-layer. The low-T analysis of the p = 0.95 NMR lineshape coupled with a more accurate determination of the nuclear hamiltonian at high-T, allows us to discuss in detail the nature of the defect. Our analysis suggests that the defect can be associated with a staggered spin-response to the vacancies of the kagomé bi-layer. This, altogether with the maximum in the kagomé bi-layer susceptibility, is very similar to what is observed in most low-dimensional antiferromagnetic correlated systems, even those with a short spin-spin correlation length; 4) The spin glass-like freezing observed at $T_g$ ≈ 2 – 4 K is not driven by the dilution-induced defects.

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I. INTRODUCTION

Under certain circumstances, it is impossible for magnetic systems to minimize simultaneously all the interactions between the spins. The system is then frustrated. This is known to occur in the spin glass (SG) compounds where the disorder on the magnetic network induces a competition between the interactions. In a vast variety of systems, the frustration can arise from the geometry of the lattice itself, without disorder,

as in the case of the triangular-based antiferromagnetic (AF) networks. The kagomé (d = 2) and the pyrochlore (d = 3) networks with AF interactions are a particular class of geometrically frustrated networks where the triangles (for the kagomé lattice) and the tetrahedras (for the pyrochlore lattice) share corners instead of sides as for the familiar triangular network.

Within a classical theory, the ground state is built on triangles and/or tetrahedras with a zero total magnetic moment. Remarkably, the corner-sharing geometry gives rise to a macroscopic degeneracy of the ground state. By macroscopic, we mean that the energy of the kagomé or of the pyrochlore ground state is invariant under a rotation of a finite number of spins. Through these rotations, the system can explore all the spin configurations making up the ground energy level. The energy spectrum is therefore characterized by the existence of zero energy excitations, the so-called soft modes. In particular, the soft modes associated to a small number of spins are extremely efficient in destroying a long range magnetic order. A non magnetic ground state is predicted at $T \rightarrow 0$ K, with a spin-spin correlation function $\langle S_i S_j \rangle \sim \exp(-r_{ij}/\xi)$, where the correlation length $\xi$ does not exceed twice the lattice parameter. The huge
reservoir of soft modes leads also to a low energy shift of the excitation spectrum, so that an unusually highly dynamical state is predicted at low-\(T\). This peculiar ground state is commonly called a cooperative paramagnetic state or a “spin liquid state”.

Quite remarkably, a different description of quantum nature for \(S = 1/2\) geometrically frustrated AF networks yields similar results. As first elaborated by Anderson and validated through numerical calculations, the ground state can be constructed on spin singlet pairs and not on non magnetic triangles (or tetrahedras)\[19\] In particular, numerical studies point at the existence of a “gap” in the magnetic excitation spectrum of the kagomé \(S = 1/2\) network\[19\] and maybe in the pyrochlore \(S = 1/2\) network\[19\] The term gap is actually inappropriate as a continuum of singlet states is imbedded between the singlet ground state and the first excited triplet state. These singlet excitations are in some regards the analog of the classical soft modes. A spin liquid ground state is again favored, with unusual thermodynamic properties such as a high entropy at low-\(T\)\[19\]

The discovery of the kagomé-based insulator \(\text{SrCr}_9\text{Ga}_{12-9p}\text{O}_{19}\) in 1988,\[19\] brought considerable attention on geometric frustration. Since then, an intense mapping of the low-\(T\) physics of the kagomé \(\text{Cr}^{3+}\) and of the pyrochlore compounds has been carried out.\[19\] Original properties have been uncovered, encompassing anomalous SG states,\[19\] and ice-like ground states.\[19\] However, nowadays, only a few compounds are good candidates for a spin liquid ground state. Following Villain’s early work,\[19\] the discrepancy between experience and theory is to be found in the perturbations to the ideal AF Heisenberg Hamiltonian with nearest neighbor spin-spin interactions. The dilution of the network,\[19\] the interactions other than nearest neighbor,\[19\] the dipolar interaction,\[19\] the anisotropy,\[19\] etc. are perturbations which differentiate the geometrically frustrated compounds and make them deviate from the ideal spin liquid behavior. Each deviation can potentially induce a long range order, usually quite complex. In all experimental studies, one must therefore discriminate between the properties related to geometric frustration and those related to these perturbations, that we may label by the general term of disorder.\[19\]

However, even in the presence of these limiting parameters, spin liquid-like compounds do exist.\[19\] More than in any other compound, spin liquid-like properties are observed in \(\text{SrCr}_9\text{Ga}_{12-9p}\text{O}_{19}\) \(\text{SCGO(p), } 0 \leq p < 1\). The geometric frustration in SCGO arises from a kagomé bi-layer of Heisenberg \(\text{Cr}^{3+}\) ions \((S=3/2)\), a quasi-\(d = 2\) network of two kagomé layers connected by a triangular lattice linking layer (Fig. 1). The disorder in SCGO stems from the dilution of the \(\text{Cr}-\text{network by non magnetic } \text{Ga}^{3+}\) ions. To date, all SCGO crystals reported in literature are non stoichiometric \((p < 1)\).

Although an anomaly is observed at low-\(T\) \((T_g \approx 2 - 4\) K for \(0.6 \leq p < 1\)) in the macroscopic susceptibility suggesting the occurrence of a SG state\[19\] all the other experimental data available on SCGO point at the existence of a spin liquid-like ground state. The neutron diffraction pattern at \(T < T_g\) is characterized by a broad peak, from which is extracted a spin-spin correlation length of twice the \(\text{Cr}-\text{Cr}\) distance \((\xi \approx 2d_{\text{Cr-Cr}})\)\[22\] A more refined neutron experiment showed that the diffraction pattern is in agreement with the existence of subgroups of spins (singlets, triangles or tetrahedras) of zero magnetic moment\[22\] Neutrons also revealed that only a fraction of the \(\text{Cr}^{3+}\) moment is frozen and \(\mu SR\) experiments revealed the existence of a strongly fluctuating ground state.\[23\] A picture further supported by recent specific heat measurements that indicate that only \(\sim 50\%\) of the total entropy is removed below 100 K.\[23\]

From the macroscopic susceptibility \((\chi_{\text{macro}})\), one can extract that a strong AF interaction couples the neighboring spins with a characteristic Curie-Weiss temperature \(\Theta_{\text{macro}} \approx 500 - 600\) K. The Curie-Weiss behavior of \(\chi_{\text{macro}}\) extends to temperatures \(T \ll \Theta_{\text{macro}}\), which is recognized as the most typical signature of frustration.\[23\] Puzzlingly, at very low-\(T\), \(\chi_{\text{ macro}}\) progressively deviates from Curie-Weiss behavior and exhibits a behavior closer to a simple Curie law. This property of SCGO is actually encountered in the majority of the geometrically frustrated magnets. This is in deep contrast with the non magnetic ground state predicted for a spin liquid. It was conjectured that this Curie upturn might originate from the dilution, i.e. may not be an intrinsic property of the kagomé bi-layer susceptibility.\[23\] If this is indeed the case, what is then the susceptibility of the kagomé bi-layer? And what is the underlying mechanism which triggers the Curie upturn?

These are the main topics addressed in this work through the NMR of gallium nuclei of SCGO. The \(^{69}\text{Ga}\) and \(^{71}\text{Ga}\) nuclei \((I = 3/2)\) are local probes coupled to the \(\text{Cr}^{3+}\) ions. The gallium nuclei labeled \(\text{Ga}(4f)\) are at the heart of frustrated physics, as they are exclusively

FIG. 1: The magnetic lattice of SCGO is a stacking of kagomé bi-layers of \(\text{Cr}^{3+}\) ions \((\approx 78\%\) of the \(\text{Cr}\) sites), separated by \(\text{Cr}-\text{Cr}\) isolated spin pairs \((\approx 22\%\) of the \(\text{Cr}\) sites).
coupled to the Cr$^{3+}$ ions of the kagomé bi-layer (Fig. 2). The present NMR study was carried out on different Cr-concentrations of SCGO ($0.72 \leq p \leq 0.95$). The comparative study of the samples shows that Ga($4f$)-NMR can discern between the geometric frustration related properties and the disorder related properties of SCGO: we are able to probe independently the kagomé bi-layer susceptibility and the effects related to dilution, and thus answer both questions on a firm experimental ground.

The general outline of this paper is the following. After a detailed presentation of the samples used in this work, their characterization and a description of their magnetic couplings (Sec. II), we focus on the specifics of the Ga-NMR spectrum of SCGO: the gallium sites in SCGO, the nuclear parameters of the Ga($4f$) resonance line and the optimization of its detection (Sec. III), with a special emphasis on the new features brought by the study of the least diluted sample $p = 0.95$. We also show that NMR is a very refined technique for characterizing the amount of Ga/Cr substitution, especially in the low dilution limit. The following sections address the main points relevant to the frustrated physics. Compared to Ref. [1], the study of the dilution effects is entirely new. After a brief overview of the raw NMR spectra and some experimental details (Sec. IV), we present in Sec. V the first part of our comparative study. By probing the susceptibility on a local stand through the NMR shift, we identify the intrinsic, i.e. dilution-independent, susceptibility typical of the SCGO family — the archetype of geometrically frustrated compounds. We then discuss our experimental results in the light of the existing models and calculations. The main topic of Sec. VI is the study of the dilution effects. Using the NMR width, we can track down in SCGO the effect associated with the dilution of the magnetic network and isolate its contribution to the macroscopic susceptibility. Moreover, we demonstrate that the impact of the site dilution is not an effect simply localized around the substitution site. As we discuss, this sets specific constraints on the theoretical models describing the dilution effects. We finally suggest an interpretation of our NMR results based on the general context of the AF correlated systems. A summary and the concluding remarks can be found in Sec. VII.

## II. SAMPLES AND MAGNETIC COUPLINGS

The Cr$^{3+}$ ions of SCGO occupy three distinct sites which are denoted $12k$, $2a$ and $4_{vi}$ (Fig. 2). The Cr($12k$) sites represent 2/3 of the total number of Cr$^{3+}$ ions and are arranged to form a kagomé lattice. The two kagomé planes are separated by a Cr($2a$) triangular layer (1/9 of the Cr$^{3+}$ ions). The remaining 2/9 of the Cr$^{3+}$ ions occupy the Cr($4_{vi}$) sites. A realistic description of the Cr-Cr magnetic couplings in SCGO showed that this compound has couplings similar to Cr$_2$O$_3$. As was evidenced in Ref. [1], SCGO is made up of only two magnetic entities. 1) The kagomé bi-layer, i.e. the kagomé-Cr($2a$)-kagomé structure, with an average AF coupling of $J_{bi-layer} \approx 80$ K as we establish in Sec. V. 2) The Cr($4_{vi}$)-Cr($4_{vi}$) spin pairs with an AF coupling of $J_{pair} = 216(2)$ K, each pair being isolated from the others. The full structure is obtained by the stacking: spin pairs/kagomé bi-layer/spin pairs/kagomé bi-layer etc. The interaction between the kagomé bi-layer and the spin pairs is small ($\sim 1$ K). Since all the Cr($4_{vi}$) spin-pairs form non magnetic singlets at low-$T$ ($T \ll J_{pair}$, see Appendix), the low-$T$ properties of SCGO are expected to reflect those of the kagomé bi-layer network only.

From the previous considerations, it is quite clear that the kagomé bi-layer structure is more complex to model than a pure kagomé system. However, SCGO is ideal in many regards. As mentioned in the introduction, the interactions in the magnetic hamiltonian other than a nearest neighbor interaction, are likely to modify the spin liquid nature of the ground state. These interactions are here extremely small compared to the Cr-Cr interaction in the kagomé bi-layer. The anisotropy of Cr$^{3+}$ is $\approx 0.08$ K (spins are therefore Heisenberg), the dipolar interaction is $\approx 0.1$ K, and the next nearest neighbor interac-

| $p$   | $\mu_{eff}(\mu_B)$ | $\Theta_{macro}$ (K) | $T_g$ (K) |
|-------|---------------------|----------------------|-----------|
| 0.72  | 3.85(5)             | 356(11)              | 2.3       |
| 0.81  | 4.00(2)             | 439(7)               | 3.3       |
| 0.89  | 4.05(2)             | 501(7)               | 3.5       |
| 0.90  | 4.21(1)             | 560(5)               | 3.2       |
| 0.95  | 4.23(2)             | 608(7)               | 3.6       |
ations $J_{n,n'}$ are most likely $|J_{n,n'}| \approx 4$ K, as in Cr$_2$O$_3$. These microscopical details might not be totally uncorrelated to the spin liquid-like behavior observed in SCGO.

The present study was performed on a series of seven Cr-contents, corresponding to concentrations of $p = 0.72, 0.81, 0.89, 0.90, 0.91, 0.93, 0.95$. All the samples are ceramics and were synthesized by a solid state reaction of SrCO$_3$, Cr$_2$O$_3$ and Ga$_2$O$_3$ in air at 1350° C, typical for SCGO. The reaction products were checked by X-ray diffraction and by macroscopic susceptibility measurements. The physical parameters for $\chi_{\text{macc}}$ yielded results in agreement with literature (Tab. I). More refined characterizations were also performed. The $p = 0.81, 0.89, 0.95$ samples were investigated by high resolution neutron diffraction with the D2B spectrometer of the Institut Laue-Langevinin in order to estimate the occupation of the three Cr sites of SCGO, respectively $p_{12k}$, $p_{2a}$ and $p_{4f_{vi}}$, otherwise non measurable by X-ray diffraction. The results are presented in Fig. 3. The $p = 0.72$ and 0.90 samples were the object of $\mu$SR studies. Finally, the Cr-concentration of the samples was also checked directly by Ga-NMR (detailed in Sec. III).

The synthesis of samples with higher Cr-content than $p = 0.95$ failed. The X-ray diffraction showed a Cr$_2$O$_3$ parasitical presence of $\geq 0.5\%$ (our detection threshold) in the final product of $p = 0.95$ and all the additional Cr$_2$O$_3$ introduced in the solid state reaction to reach higher concentrations than $p = 0.95$ simply did not react. This sets the limit of this synthesis method to the $p = 0.95$ concentration. Interestingly, this limit may be related to the fact that the Ga/Cr substitution in SCGO is not uniform, i.e. the Cr-concentration is not equal to $p$ on all the sites. As shown in Fig. 3, the Ga/Cr substitution on the Cr(12k) sites corresponds to stoichiometry ($p \approx p_{12k}$), whereas in contrast the Cr(2a) sites are robust to substitution ($p_{2a} > p$), the non-stoichiometric gallium occupying preferentially the Cr(4f$_{vi}$) sites ($p_{4f_{vi}} < p$). We note that no gallium is present on the Cr(2a) sites of the $p = 0.95$ sample and that concomitantly the parasitical Cr$_2$O$_3$ problem occurs at this same Cr-concentration, an indication that the two phenomena may be related to the same chemical constraint.

A last point we would like to address, is the influence of the Ga/Cr substitution on the crystal parameters $a$ and $c$. The largest structural change we observed is a $\approx 0.004$ Å elongation of the Cr(12k)-Cr(2a) distance in the $p = 0.72$ sample (2.975 Å) compared to the $p = 0.95$ sample (2.971 Å). A study on a series of chromium-based oxides with Cr-O-Cr bonding angles $\approx 90°$ (as in SCGO) showed that the Cr-Cr exchange constant decreases linearly with increasing Cr-Cr distance (Fig. 3), with a slope of $\Delta J/\Delta d_{\text{Cr-Cr}} \approx 450$ K/Å from which we extract a negligible variation of the SCGO exchange constants at most of $\Delta J \approx 3$ K. We therefore expect the sizeable variation of the magnetic properties of SCGO with $p$ to reflect only the effect of the lattice dilation.

### III. GA-NMR SPECTRUM

The present NMR study was performed on the $^{69}$Ga ($^{69\gamma} = 10.219$ MHz/T, $^{69}Q = 0.178 \times 10^{-24}$ cm$^2$) and the $^{71}$Ga ($^{71\gamma} = 12.982$ MHz/T, $^{71}Q = 0.112 \times 10^{-24}$ cm$^2$) nuclei of SCGO powder samples ($\gamma$ and $Q$ are respectively the gyromagnetic ratio and the quadrupolar moment of the nucleus). The gallium ions are present on two distinct crystallographic sites, which are designated by Ga(4f) and Ga(4e) (Fig. 2). A previous spectral analysis carried out on the $p = 0.90$ sample in a sweep field set up at a radio-frequency of $\nu_{rf} = 131$ MHz, successfully assigned each site to the corresponding peak in the

![FIG. 3: The relative Cr-concentration on the 12k, 2a and 4f$_{vi}$ sites determined by the neutron measurements ($p_{12k}, p_{2a}, p_{4f_{vi}}$) versus the overall Cr-concentration ($p$) of our $p = 0.81, 0.89, 0.95$ samples (open squares) and of other samples in the literature (closed circles). The Cr-concentration of the three sites follows stoichiometry when the symbols fall on the solid line.](image)

![FIG. 4: The Cr-Cr couplings as a function of the Cr-O-Cr angle (left) and the Cr-Cr distance (right) for: the average Cr-Cr coupling of the SCGO kagomé bi-layer (see Sec. V B), the SCGO Cr(4f$_{vi}$)-Cr(4f$_{vi}$) pairs, Cr$_2$O$_3$ and a series of Cr-oxides. The stars stand for the Cr(12k)-Cr(12k) and the Cr(12k)-Cr(2a) couplings of SCGO’s kagomé bi-layer which we determined in a previous publication via a refined analysis of the NMR shift.](image)
NMR spectrum. There, it was shown that the Ga-NMR spectrum of both isotopes is actually the sum of three contributions: Ga(4f), Ga(4e) and an extra contribution related to the presence of non-stoichiometric gallium on the Cr sites, which we label by Ga(sub).

As was pointed out in Ref. 38, the interest of Ga-NMR resides in the fact that the gallium nuclei are coupled to the neighboring magnetic Cr$^{3+}$ ions through a Ga-O-Cr hyperfine bridge (Fig. 2). In particular, the $^{69,71}$Ga(4f) nuclei are exclusively coupled to the kagomé bi-layer, 9 from the 2 kagomé adjacent Cr(12k)-layers and 3 from the intermediate Cr(2a)-sites. Through Ga(4f)-NMR we are then able to probe locally the magnetic properties of the kagomé bi-layer. The present NMR study is therefore devoted to Ga(4f)-NMR.

Along with the hyperfine interaction mentioned above, the nuclear Hamiltonian of gallium in SCGO also bears an additional quadrupole interaction due to the electric field gradient (EFG) on the gallium sites. Following the usual notations, the nuclear Hamiltonian may be expressed as

$$\mathcal{H} = -\hbar \gamma \vec{I} \cdot \left( \vec{I} + \vec{K} \right) \cdot \vec{H} + \frac{\hbar \nu_Q}{6} \left[ 3I_z^2 - I^2 + \eta (I_x^2 - I_y^2) \right]$$

where $\vec{H}$ is the applied field, the principal axes of the magnetic shift tensor $\vec{K}$ are collinear with the direction of the nuclear spin operators $I_x$, $I_y$, and $I_z$, $\nu_Q$ is the quadrupole frequency and $0 \leq \eta \leq 1$ is the quadrupole asymmetry parameter. The main focus of the spectral analysis presented in this section is to complete the study of Ref. 38 by determining the quadrupole contribution to the nuclear Hamiltonian of Ga(4f), working in a frequency range ($\nu_{rf} = 40.454$ MHz) more appropriate for the observation of the $^{69,71}$Ga(4f) resonance lines. We study here the spectrum of the $p = 0.95$ sample which yields sharper quadrupole features than the $p = 0.90$ sample (or of any of the other samples studied). The knowledge of the quadrupole parameters reported in Tab. II allows us, in the following section, to separate the magnetic and the quadrupole contributions to the Ga(4f) spectrum and, hence, to safely evaluate the magnetic properties of the kagomé bi-layer.

In the second part of this section we focus on Ga(sub). We identify the contribution of Ga(sub) to the spectrum acquired at $\nu_{rf} = 40.454$ MHz and, on the basis of this contribution, provide a new method to evaluate the Cr-concentration of the SCGO samples through Ga-NMR, especially well suited for the very low dilutions.

### A. Spectral analysis of Ga(4f)

Neglecting the Ga-substituted sites, the Ga-NMR spectrum displays four sets of lines corresponding to the two isotopes distributed on both Ga(4e) and Ga(4f) sites. In a powder, for a given site and a given isotope, the lineshape results from the distribution of the angles between the field and the EFG principal axis. This yields singularities rather than well defined peaks – the so-called powder lineshape.

The quadrupole interaction of gallium nuclei in SCGO is a consequence of the coupling of the nucleus to the EFG produced by the surrounding electronic charges, here mainly the oxygen ions. As shown in Fig. 4, Ga(4e) is surrounded by a bi-pyramid of 5 oxygen ions. This environment has no local cubic symmetry and results

| Isotope | $\nu_Q^{71}$ (MHz) | $\nu_Q^{69}$ (MHz) | $\eta$ |
|---------|------------------|------------------|--------|
| Ga(4e)$^a$ | 20.5(3) | 32.6(5) | 0.050(35) |
| Ga(4f)$^b$ | 2.9(2) | 4.6(2) | 0.005(6) |

$^a$ From Ref. 38
$^b$ This work.
into a strong quadrupole frequency as was evidenced in Ref. [8] (Tab. II). In contrast with Ga(4e), Ga(4f) is surrounded by a nearly ideal tetrahedron of oxygens ions, only slightly elongated along the crystalline c-axis. Since a regular tetrahedron has a local cubic symmetry, we expect the quadrupole frequency of Ga(4f) to be \( \nu_Q(4f) \approx \nu_Q(4e) \). This agrees with Ref. [8] where the Ga(4f) quadrupolar effects were not detected at a frequency of \( \nu_r = 131 \text{ MHz} \). The asymmetry parameter \( \eta \), that quantifies the deviation of the EFG from axial symmetry, is in principle close to zero for both sites as they share a rotation axis along \( \hat{c} \).

We present in the top panel of Fig. 5 a field sweep spectrum, obtained at \( \nu_r = 40.454 \text{ MHz} \) and \( T = 80 \text{ K} \) for the \( p = 0.95 \) sample. The sweep, from 2.65 T to 4.80 T, covers the spectrum of both isotopes and yields the expected features. We first focus on the \( 69,71 \text{Ga}(4e) \) line. A powder sample simulation of the 4e-line is presented in the bottom panel of Fig. 5 to emphasize its contribution to the spectrum. Each 4e-isotope, i.e. \( 71 \text{Ga}(4e) \) and \( 69 \text{Ga}(4e) \), exhibits a resonance in a wide range of fields, with multiple quadrupole peaks and steps associated to the three nuclear Zeeman transitions 3/2 \( \rightarrow \) 1/2, 1/2 \( \rightarrow \) −1/2 and −1/2 \( \leftrightarrow \) −3/2. As evidenced in Fig. 5, in this field window only the 1/2 \( \leftrightarrow \) −1/2 resonance transition is resolved yielding for each 4e-isotope two singularities known as the central line singularities (labeled respectively by \( CL- \) and \( CL+ \) in Fig. 5). These two singularities are the boundaries of the central line splitting of width \( \approx \nu_Q^2/2\gamma \nu_r \). Compared to the working frequency of \( \nu_r = 131 \text{ MHz} \) used in Ref. [8], the much lower frequency of \( \nu_r = 40.454 \text{ MHz} \) allows here to spread the 4e line over a wider field-range. The \( 69,71 \text{Ga}(4e) \) contribution to the spectrum is a nearly constant background of small amplitude compared to the \( 69 \text{Ga}(4f) \) and \( 71 \text{Ga}(4f) \) lines — the two prominent peaks of Fig. 5 — hence there is a better contrast between the sites. Furthermore, overlap between the Ga(4e) and the Ga(4f) lines is also minimized at this radio-frequency.

We now focus on the \( 69,71 \text{Ga}(4f) \) line of Fig. 5. In these favorable experimental conditions, it can be seen that both 4f peaks are flanked by two shoulders, the so-called satellite singularities (labeled respectively by \( Sat- \) and \( Sat+ \) in the middle panel of Fig. 5), associated with the 3/2 \( \leftrightarrow \) 1/2 (\( Sat- \)) and the −1/2 \( \leftrightarrow \) −3/2 (\( Sat+ \)) nuclear transitions. The detection of the satellite singularities is a clear indication of the existence of quadrupole effects in the \( 69,71 \text{Ga}(4f) \) spectrum, implying also a central line splitting for Ga(4f). To emphasize this central line splitting, we present in Fig. 6 narrow field sweeps of both isotopes at \( T = 150 \text{ K} \). The sweep ranging from 3.820 T to 3.960 T covers the \( 69 \text{Ga}(4f) \) line (bottom abscissa) whereas the sweep ranging from 3.026 T to 3.069 T covers the \( 71 \text{Ga}(4f) \) line (top abscissa). As shown, the two central lines match since we expanded the field window of \( 71 \text{Ga}(4f) \) by a factor \( 69(Q^2/\gamma)^{71}(Q^2/\gamma) = 3.209 \), i.e. by the ratio of the central line quadrupolar widths expected for the two isotopes. Fig. 6 also indicates that the structure observed in the 4f line is dominated, at these temperatures, by quadrupole effects. In particular, the anisotropy in the shift \( K \), which could in principle yield additional structure to the line, is small, i.e. the shift is isotropic (\( K = K \)). This conclusion is further supported by a calculation, presented below, of all the field singularities.

We now turn to the evaluation of the quadrupole parameters of \( 69,71 \text{Ga}(4f) \). This was carried out using the field positions \( H_{sing} \) of the quadrupole singularities determined from Fig. 5 and reported in Tab. I which depend only on the three parameters \( \nu_Q(4f), \eta(4f) \) and \( K \), provided the shift is isotropic: \( H_{sing} = H(\nu_Q, \eta, K) \).

We evaluated the 4f quadrupole parameters from the singularity positions of \( 69 \text{Ga}(4f)Sat-, 69 \text{Ga}(4f)CL+ \) and \( 69 \text{Ga}(4f)Sat+ \). At \( T = 80 \text{ K} \), the shift is \( K = 0.0285(5) \). The extracted quadrupole parameters are presented in Tab. II and are found in agreement with expectations. To confirm the isotropic nature of the shift, we performed a self-consistency test by calculating the field positions of all the quadrupole singularities in Fig. 5. This is readily done using the three parameters \( \nu_Q(4f), \eta(4f) \) and \( K \), determined previously and the set of equations of Ref. [5].

Table III: The field positions of the 4f quadrupole singularities in Fig. 5. \( H_{sing} \) are the fields where each singularity was found experimentally and \( H_{calc} \) the calculated fields where the singularities are expected. The missing \( H_{calc} \) correspond to the field singularities used to perform the calculation.

| Sing. | \( 71H_{sing} \) (T) | \( 69H_{sing} \) (T) | \( 71H_{calc} \) (T) | \( 69H_{calc} \) (T) |
|-------|----------------------|----------------------|----------------------|----------------------|
| 4fCL- | 3.025(2)             | 3.838(1)             | 3.026(2)             | 3.838(2)             |
| 4fCL+ | 3.036(1)             | 3.865(1)             | 3.035(2)             |                     |
| 4fSat-| 2.924(9)             | 3.628(8)             | 2.921(9)             |                     |
| 4fSat+| 3.137(7)             | 4.066(8)             | 3.138(7)             |                     |

![FIG. 6: Field sweeps of the \( 69 \text{Ga}(4f) \) and the \( 71 \text{Ga}(4f) \) lines at \( T = 150 \text{ K} \). The closed (open) symbols represent \( 69 \text{Ga} \) (\( 71 \text{Ga} \)). The top abscissa is scaled to the bottom by a factor \( 69(Q^2/\gamma)^{71}(Q^2/\gamma) = 3.209 \) to evidence the quadrupole structure in the lines. The hump at \( \approx 3.065 \text{ T} \) is \( 71 \text{Ga}(sub) \).](image-url)
As shown in Tab. III, the calculated positions are in excellent agreement with the experimental ones.

Finally, concerning the quadrupole interaction in all the other SCGO samples studied, no appreciable change was evidenced in \( \nu_Q(4f) \) and \( \eta(4f) \). In conclusion, the Ga\((4f)\) central line is narrow enough in all the samples to allow to follow accurately the \( T \)-variation of the shift and of the linewidth.

B. Gallium substituted on the Cr sites

In Fig. 6 we compare the \( ^{71}\text{Ga} \) spectra obtained for the \( p = 0.81, 0.89, 0.95 \) samples at \( T = 150 \) K and \( \nu_{rf} = 40.454 \) MHz. Care was taken to ensure the same experimental conditions. The field sweeps of Fig. 7 cover a narrow field window \( \delta H \) (from 3.00 T to 3.15 T) centered on the central line of \( ^{71}\text{Ga}(4f) \) (\( H \approx 3.05 \)T). Two features differ between the samples. 1) The line at \( H \approx 3.065 \)T whose integrated area decreases with increasing \( p \), which is therefore \( ^{71}\text{Ga}(\text{sub}) \). 2) The constant background \( b(p) \) which decreases with increasing \( p \). \( ^{71}\text{Ga}(\text{sub}) \) and part of \( b(p) \) are therefore all the contribution of the non-stoichiometric gallium to the \( ^{71}\text{Ga} \) spectrum.

Since the non-stoichiometric gallium is present on the three Cr sites of SCGO, one would expect to detect three gallium lines and not a unique Ga\((\text{sub})\) line. To gain insight into this problem, we studied the spectrum of the parent and non magnetic compound SrGa\(_2\)O\(_{19}\) (\( p = 0 \)). The spectrum allows to evidence sizeable quadrupole effects on the 12\( k \) (\( ^{71}\nu_Q = 5.1(1) \) MHz and \( \eta = 0.47(3) \)) and on the 4\( f_{sv} \) (\( ^{71}\nu_Q = 1.6(1) \) MHz and \( \eta = 0.03(5) \)) substituted sites, otherwise non measurable in the magnetic compounds (\( p \neq 0 \)).

The quadrupole effects on the 2\( a \) site are negligible (\( ^{71}\nu_Q \approx 0.3 \) MHz and \( \eta \approx 0 \)). Turning back to the spectra of Fig. 6, the \( ^{71}\text{Ga}(\text{sub}) \) line is the unresolved sum of the 2\( a \) line and of the 12\( k \) and 4\( f_{sv} \) quadrupole central lines of substituted gallium, whereas the background \( b(p) \), in addition to the Ga\((4e)\) and Ga\((4f)\) satellites contributions mentioned in Sec. III A, contains the sum of the satellite contributions of the substituted gallium.

In order to evaluate the Cr-concentration of our samples using Ga-NMR (\( p_{\text{NMR}} \)), we determine the intensities \( I_{4f} \) and \( I_{\text{sub}}(p) \) of respectively the \( ^{71}\text{Ga}(4f) \) central line and the \( ^{71}\text{Ga}(\text{sub}) \) line of Fig. 6. To do so, we evaluate the integrated area of both lines corrected for the transverse exponential relaxation (\( T_2(\text{sub}) = 78(2) \)\( \mu \)s and \( T_2(4f) = 50(1) \)\( \mu \)s). \( I_{\text{sub}}(p) \) and \( I_{4f} \) are respectively proportional to the amount of gallium present on the three substitution sites and on the 4\( f \) site. The lines are well separated in the \( p = 0.95 \) sample, so that \( I_{\text{sub}}(p) \) and \( I_{4f} \) are evaluated separately. For the more diluted samples, the intensity \( I_{4f} \) is fixed to the \( p = 0.95 \) value as the amount of gallium on the 4\( f \) site is independent on Cr-concentration. \( I_{\text{sub}}(p) \) was then evaluated either by direct integration of the spectrum over the field window \( \delta H \) and subsequent subtraction of both \( b(p)\delta H \) and \( I_{4f} \), or by reproducing all the lines with a minimal 3 gaussian fit and an additional constant background \( b(p) \) (one gaussian for the \( ^{71}\text{Ga}(4f) \) line with an intensity fixed to the \( p = 0.95 \) value, and two gaussians for \( ^{71}\text{Ga}(\text{sub}) \), the area of which yields \( I_{\text{sub}} \)). From the ratio \( I_{\text{sub}}/I_{4f} \), we can extract \( p_{\text{NMR}} \). In the inset of Fig. 6 we show the variation of \( p_{\text{NMR}} \) with the concentration \( p \) determined by X-ray and neutron diffraction. Whatever the method employed (integration or multiple gaussian fits), we notice a perfect agreement between the different characterization methods. Since \( p_{\text{NMR}} \) is equal to \( p \), we conclude that the actual chemical content corresponds to the nominal concentration.

Incidentally, Ga-NMR proves to be a quite accurate tool for determining the Cr-concentration in SCGO, especially for dilutions as low as 5% or less where the other techniques are beyond their sensitivity limit. For the samples with \( p > 0.95 \), we did not find any further decrease of the \( I_{\text{sub}} \) value which confirms locally that it is impossible to synthesize samples beyond the \( p = 0.95 \) limit found through X-ray diffraction.

IV. DILUTION AND \( T \)-DEPENDENCE OF THE \( ^{71}\text{Ga}(4f) \) SPECTRUM

To appreciate the experimental evidence of the properties we discuss in the next sections, we present here the dilution and the \( T \)-dependence of the raw \( ^{71}\text{Ga}(4f) \)-NMR spectra. The main relevant physical parameters of interest are the shift of the line, which as we establish allows us to probe directly the susceptibility of the kagomé bi-layer, and the linewidth which in contrast yields information on the distribution of the internal local fields in...
the kagomé bi-layer. We also briefly describe the analysis performed to extract these spectral parameters.

A. Experimental data

The Ga(4f) spectra were recorded in a wide T-range, from 5 K to 410 K. Up to 200 K, the spectra were obtained in a sweep field set up with a working frequency of $\nu_{rf} = 40.454$ MHz. For $150 \, K \leq T \leq 410 \, K$, the spectra were recorded in a static field of $\approx 7 \, T$ by a swept frequency variant of the field step spectroscopy method. Our data can be sorted in two distinct temperature domains, typically $T \geq 100 \, K$ and $T < 100 \, K$.

A typical series of high-T spectra ($100 \, K \leq T \leq 180 \, K$) is presented in Fig. 8 for the $p = 0.95$ sample. The field window (from 3.00 T to 3.08 T) covers the central line of $^{71}\text{Ga}(4f)$. Fig. 8 is representative of the evolution of Ga(4f) at $T \geq 100 \, K$ for all the samples studied. The line shape is nearly constant with temperature, as dominated by $T$-independent quadrupole effects, and shifts towards the low fields with decreasing temperature. The shift, which is experimentally measured by the position of the $^{71}\text{Ga}(4f)^{CL+}$ singularity and performing minor quadrupole corrections (see Sec. III), therefore increases when the temperature is lowered.

The $T$-dependence of both $K$ and the width changes at low-T. We present in Fig. 8 spectra ranging from 5 K to 50 K for the $p = 0.95$ sample (top) and the $p = 0.81$ sample (bottom). The field window covers the $^{71}\text{Ga}(4f)$ line, but is larger than in Fig. 8 from 2.90 T to 3.15 T. Three important features should be noticed.

1. The line now shifts toward the high fields and hence $K$ is decreasing with the temperature. However $K$ does not reach the zero value, i.e. the $^{71}\text{Ga}(4f)$ line is never centered at the reference value $^{71}H_{ref} = \nu_{rf}/^{71}\gamma = 3.116 \, T$. The comparison of the two series of spectra establishes that the change in the shift direction is not affected by the dilution.

2. The width increases with decreasing temperature. The quadrupole structure that can still be noticed on the $T = 50 \, K$ spectrum of the $p = 0.95$ sample, is progressively washed away as temperature is lowered. At $T = 20 \, K$, the line is marked by a smooth symmetric broadening of gaussian nature. This broadening is more important for the $p = 0.81$ sample than for the $p = 0.95$ sample, i.e. the width is sensitive to the dilution. The $^{71}\text{Ga}(sub)$ line is no longer resolved in this T-domain.

3. A last feature we would like to underline is the abrupt decrease of the detected $^{69,71}\text{Ga}(4f)$ nuclear population at $T < 15 \, K$ in both samples. The nuclear population, proportional to the integrated area of the $4f$ line, actually decreases in the same way in all the samples studied (Fig. 9). It therefore originates from a dilution-independent mechanism. The present result confirms the conclusions of the previous $\mu$SR-$^{71}$Ga(4f)-NMR study on the $p = 0.90$ sample. There, the wipe-out of the intensity was assigned to originate from the intrinsic high dynamics of the kagomé bi-layer spin system when $T \rightarrow 0 \, K$. This effect, explicitly evidenced in SCGO by $\mu$SR measurements, is taken to be the signature of a spin liquid-like ground state. Because of this abrupt decrease of the NMR signal,
The $^{69,71}$Ga($4f$) population detected by NMR. For each sample, the integrated area of the $4f$ line is normalized by the integrated area measured in the $20-50$ K temperature range, where it is found constant in temperature. The Ga($4e$) contribution, constant in temperature, was subtracted. $T_2$ corrections were found quite small and do not affect estimates below 50 K.

$^{69,71}$Ga($4f$) is not a suitable probe for $T < 10-15$ K.

The comparison of the spectra of all the samples enables us in the next sections to easily separate the properties related to the dilution from the intrinsic properties independent on the dilution.

B. NMR line analysis

Compared to Ref. [32], we employed here a different method to evaluate the shift $K$ and the width $\Delta H$ of the spectra of Fig. 10. (i) For all the samples, we choose a $^{69,71}$Ga($4f$) high-$T$ reference spectrum dominated by $T$-independent quadrupole effects ($S_Q(H)$) (ii) In order to recover the low-$T$ broadening of gaussian nature, $S_Q(H)$ is convoluted by a normalized gaussian function $G(H)$ of width $\Delta H$. Since it is impossible to fit separately the substituted and non-substituted sites, we explicitly assume that for the highly diluted samples both sites broaden identically. This is likely the case in view of the hyperfine coupling paths. The low-$T$ spectrum, $S_M(H)$, is therefore simply reproduced by

$$S_M(H) = a \left[ y_0 + \int_{-\infty}^{+\infty} G(H - H')S_Q(H' + H_s) dH' \right]$$

where $H_s$ is the field-shift of $S_Q(H)$, from which we extract $K$. Since the $^{69,71}$Ga($4f$) line lies on a constant background that results mainly from the contribution of the second gallium site Ga($4e$) (see Fig. 7), the amplitude $a$ and the constant background $y_0$ are employed to readjust the relative spectral weights of the $4e$ and of the $4f$ lines when the transverse relaxation corrections varies differently on the two gallium sites. We also restricted our fits to the left side of the line, very sharp at high-$T$ and which has the major advantage of not being affected by the Ga/Cr substitutions. Concerning the values of $K$, we did not find any significant difference with the method employed in Ref. [32].

C. Magnetic contribution to the Ga($4f$)-NMR line: shift and width

We briefly recall here the relationship between the contribution of each gallium nucleus to the Ga($4f$)-NMR line and its local magnetic environment in order to underline what can be exactly probed through Ga($4f$)-NMR (more details can be found in Ref. [32]).

Each Ga($4f$) nucleus is coupled to its Cr(12k) and Cr(2a) nearest neighbors (n.n.) through a Ga-O-Cr hyperfine interaction with an hyperfine constant $A$. We suppose that the susceptibility in the kagomé bi-layer varies from Cr site to Cr site and label it, in a generic manner, by $\chi$. A Ga($4f$) at site $i$ will contribute to the NMR spectrum at a position depending upon the number of the n.n. occupied Cr sites and their susceptibility $\chi$. This corresponds to the shift $K^{(i)}$ in the NMR spectrum for a gallium at site $i$

$$K^{(i)} = \sum_{\text{occupied n.n.Cr(12k,2a)}} A \chi$$

(the chemical shift is negligible). The average shift of the NMR line, that we label by $K$ in the following sections, is simply related to the average susceptibility $\bar{\chi}$ over all the Cr sites. As we establish, the shift corresponds to the frustrated susceptibility $\chi_{\text{frustr}}$, so that $K \propto \chi_{\text{frustr}}$. Instead, the spatial distribution of $K^{(i)}$ around $K$ defines the magnetic width of the Ga-NMR spectrum and reflects the existence of a spatial distribution of $\chi$ (as we detail in Sec. [10]), a spatial distribution of the hyperfine constant or a distribution related to the presence of Cr-vacancies in the nuclear environment is negligible and cannot justify the low-$T$ broadening observed.

V. KAGOMÉ BI-LAYER SUSCEPTIBILITY: EVIDENCE FOR CORRELATIONS EFFECTS

As mentioned in the previous section, the shift $K$ measures the average kagomé bi-layer susceptibility that proves to be unobservable at low-$T$ through the macroscopic susceptibility measurements. We show here that the $T$-dependence of $K$ gives a sharp evidence for a maximum in the susceptibility $\chi_{\text{frustr}}$ around 50 K, whatever the amount of dilution. The comparison of our results on the SCGO compound with the different models existing in the literature, does not allow us to totally validate or invalidate them. Our observations rather favor an image,
FIG. 11: Top panel. $K$ versus $T$ down to 15 K. A minor second-order quadrupole correction has been performed. Inset. $K^{-1}$ versus $T$ for $p = 0.95$. Bottom panel. $K$ plotted using reduced units. $C_{CW}$ and $\Theta_{NMR}$ are respectively the Curie-Weiss constant and temperature extracted from the high-$T$ Curie-Weiss fit to $K^{-1}$ described in the text.

supported by recent neutron diffraction data, where the short range magnetic correlations play a central role.

A. An intermediate temperature scale

The $T$-dependence of $K$ for the $p = 0.81, 0.89, 0.95$ samples is presented in Fig. 11. The figure is the quantitative evaluation of the line shift of Fig. 8 and Fig. 9. $K$ increases following a Curie-Weiss law (see below) up to a temperature of $T_{max} = 40–50$ K, where it reaches a maximum. Below $T_{max}$, $K$ decreases, but does not reach 0 for the observed temperatures ($T \geq 15$ K). The decrease in $K$ is slightly more pronounced with increasing dilution. For the $p = 0.81$ sample $K(T = 15$ K$)/K(T_{max}) \approx 0.86$, instead of 0.92 for the $p = 0.95$ sample. Although for $T < 15$ K the measurement of $K$ is less significative since a wipe out of the intensity occurs, we observed in the $p = 0.90$ sample only a decrease of $K(T = 7$ K$)/K(T_{max}) \approx 0.77.$

The typical $T$-variation of $K^{-1}$ is presented in the inset of Fig. 11 for the $p = 0.95$ sample. The high-$T$ variation of $K^{-1} (T \geq 100$ K$)$ is linear for all the samples, suggesting a Curie-Weiss behavior. A linear extrapolation to $K^{-1} = 0$ yields the Curie-Weiss temperature as determined by NMR ($\Theta_{NMR}$). The values of $\Theta_{NMR}$ are 453(30), 469(27), and 484(25) K for the $p = 0.81, 0.89, 0.95$ sample respectively. We find here in $K$ a well known property of the susceptibility of the geometrically frustrated compounds: the Curie-Weiss behavior continues to subsist at temperatures $T \ll \Theta_{NMR}$.

Assuming the Curie-Weiss value of the kagomé bi-layer to be $(\chi_{macro} S(S + 1)/3k_B)$, where $(\chi_{macro}) = 5.14$ is the average number of nearest neighbors for a Cr site of the kagomé bi-layer as the Cr-environments of the Cr($2a$) and the Cr($12k$) sites differ, we find an average exchange constant of $J_{bi-layer} \approx 80$ K. As shown in Fig. 3, this value is close to the exchange constant $J = 76(3)$ K observed in Cr$_3$O$_3$ where the Cr$^{3+}$ ions have a local octahedral environment similar to Cr($12k$). We also gained more insight on the couplings of the kagomé bi-layer through a mean-field analysis of the high-$T$ shifted, detailed in Ref. 15 that allowed us to evaluate the Cr($12k$)-Cr($2a$) and the Cr($12k$)-Cr($12k$) couplings (their values are reported on Fig. 4). Turning back to the NMR Curie-Weiss temperature, $\Theta_{NMR}$ is of the same order as the macroscopic Curie-Weiss temperature, although smaller with an increasing difference at higher Cr-concentrations. This difference is related to the fact that the susceptibility of Cr($4f_{vi}$)-Cr($4f_{vi}$) isolated spin pairs also contributes to $\chi_{macro}$, but is absent in $K$ since the Ga($4f$) nuclei probe only the susceptibility of the kagomé bi-layer (Sec. V B).

The linear behavior of $K$ for $T \ll \Theta_{NMR}$ and the deviation from this behavior that results in a maximum in $K$ versus temperature, is a common feature of the three samples. It then stems from a physics robust on dilution, therefore related to an intrinsic property of the kagomé bi-layer. $T_{max}$ is a new temperature scale for SCGO since it differs substantially from the two known characteristic temperatures, the freezing temperature $T_g (T_{max}/T_g \approx 10)$ and the Curie-Weiss temperature ($T_{max}/\Theta_{NMR} \approx 0.1$).

B. Evidence for a two component macroscopic susceptibility

We compare in Fig. 11 the $T$-dependence of $K$ (left y-axis) and of $\chi_{macro}$ (right y-axis) for the $p = 0.95$ sample. The discrepancy between the low-$T$ behavior of $K$ and $\chi_{macro}$ is quite clear since instead of a maximum in the susceptibility, $\chi_{macro}$ exhibits a Curie-like law at low-$T$. The difference between $K$ and $\chi_{macro}$ is also perceptible directly on the spectra of Fig. 4 where an arrow indicates the approximate position where the maximum of the $^{71}$Ga($4f$) line should occur if $K \propto \chi_{macro}$. Instead of a model where $\chi_{macro}$ has a single component, our results establish that $\chi_{macro}$ yields at least two distinct contributions. The first one is $\chi_{frus}$, spatially uniform over the kagomé bi-layer and that is reflected in $K$ (Sec. V C). A second one, non-uniform over the Cr sites, that is necessary to explain the Curie-like upturn observed at low-$T$. We label this contribution by $\chi_{def}$, since in Sec. V we establish that $\chi_{def}$ is the susceptibility of the magnetic defects generated by the dilution of the
kagomé bi-layer. The comparison of Fig. 12 establishes on an experimental ground the conjecture by Schiffer et al. of a two component macroscopic susceptibility.

The macroscopic susceptibility probes both contributions at low-T. If we also take into account the susceptibility of the Cr(4f
vi) isolated spin pairs (χpair), the three contributions to χmacro are

\[ χ_{macro} = χ_{frustr} + χ_{pair} + χ_{def} \] (1)

The dominant Curie susceptibility of the defects χdef at low-T prevents to probe χfrustr through macroscopic measurements.

Using Eq. (1), we can fit the T-dependence of χmacro given some simple remarks and minor assumptions. The T-dependence of χfrustr is known through K, and for this reason the fit was performed in the 15 K ≤ T ≤ 350 K range, where we have a full intensity in the NMR signal. This T-range of the fit leads to an inaccuracy in the determination of a possible low-T Curie-Weiss temperature of χmacro, hence we assume a pure Curie component χdef = Cdef/T to fit the low-T upturn. The susceptibility χpair is quantitatively derived analytically (see Appendix). The only unknown parameters of Eq. (1) are the effective moment µ_eff(4f
vi) of the Cr^{3+} ions of χpair, the Curie constant Cdef of the defects and the hyperfine constant A.

The fit to χmacro for the p = 0.95 sample is presented in Fig. 13 and reproduces correctly the evolution of the experimental macroscopic susceptibility in the T > 15 K range. In Tab. IV we have reported the fitting parameters extracted from the three samples p = 0.81, 0.89, 0.95. The effective moment is close to the 3.87µB value expected for a Cr^{3+} ion, and the Curie contribution Cdef is found to decrease with increasing p. The values of Cdef presented here, even if extracted from a fit which does not cover the 5 K ≤ T ≤ 15 K range where χdef dominates, nevertheless are in good agreement with those of

![Fig. 12: K (left) and χmacro (right) for the p=0.95 sample. K and χmacro do not follow exactly the same law at high-T, since χmacro probes also the susceptibility of the Cr(4f
vi)-Cr(4f
vi) spin pairs.](image)

![Fig. 13: The three contributions to χmacro obtained through the fit described in the text: the kagomé bi-layer susceptibility (χfrustr), the Cr(4f
vi)-Cr(4f
vi) spin pairs susceptibility (χpair) and the Curie susceptibility induced by dilution (χdef = Cdef/T).](image)

| p   | µ_eff(4f
vi)(µB) | Cdef (emu K/mol) | A × 10^3 (Oe/µB) |
|-----|----------------|------------------|-------------------|
| 0.81| 4.0(6)         | 0.51(12)         | 3.4(4)            |
| 0.89| 4.5(4)         | 0.45(10)         | 3.4(4)            |
| 0.95| 4.3(2)         | 0.25(5)          | 3.9(2)            |

Tab. IV where the Cdef value is dominantly determined by the very low-T region fit of χmacro (Sec. VII). Finally, A is nearly constant with p, confirming the assumption of Sec. II that the site dilution does not alter in a significant way the couplings in SCGO, hence that the Ga-O-Cr hyperfine interaction is also constant with the dilution.

C. Discussion

We compare here our experimental data for the intrinsic susceptibility χfrustr of the frustrated lattice reflected in K to the calculations performed for the kagomé and the pyrochlore networks through different approaches.

Within a classical frame where the minimization of the Heisenberg hamiltonian is constructed on the basis of non magnetic triangles and tetrahedras, different authors have simulated the susceptibility of the kagomé and the pyrochlore network by Monte-Carlo calculations. All these models suggest a Curie-Weiss susceptibility which extends to low-T (T ≪ Θ), in agreement with the high-T behavior of K (T > 100 K). Although these models do not predict a maximum in the susceptibility versus temperature, all agree with our results on the absence of
a Curie upturn at low-$T$ as is detected in $\chi_{macro}$.

The susceptibility for the $S = 1/2$ kagomé network has been calculated by an exact diagonalization of the Heisenberg Hamiltonian.\cite{Mondelli} As mentioned in the introduction, the ground state is here constructed on non magnetic singlet spin in a triplet state. The calculated susceptibility hence varies as $\sim \exp(-\Delta/T)$ at low-$T$, with a maximum in the susceptibility occurring at $\Delta \approx 0.1J$. However, it seems difficult to reconcile this maximum with our results. First, we would expect to observe in $K$ a much sharper decrease in temperature than what is observed experimentally. Secondly, the energy scale of $\Delta$ itself does not agree with our data. In fact, taking $J \approx 80$ K, the maximum of $K$ falls at $T_{max} \approx 0.5J > \Delta$ (note that $\Delta$ should be weaker than $0.1J$ for $S = 3/2$ spins or even disappear).\cite{Mondelli}

The interpretation of the observed maximum for SCGO has to be researched elsewhere than in the gap predicted by this model. We stress that the Ga(4f)-NMR intensity loss does not allow us to probe deeply the predictions of this model which places the gap in the $T < 15$ K range. But, clearly, our data reveal that other parameters have to be taken into account for $T \gg \Delta$ to explain the origin of the maximum in $K$ vs $T$ at $\approx 0.1\Theta$.

In this context, it appears natural to seek an interpretation in more conventional terms. The maximum in $K$ versus temperature indicates an increasing magnetic rigidity of the kagomé bi-layer spin network. As in all the $d = 2$ AF systems, we suggest that the maximum is an experimental signature of a small reinforcement of the magnetic correlations. The quasi-constancy of $K$ for all $p$ below this maximum (only a slight decrease is observed) is therefore an indication that the correlations are short ranged and concomitantly do not depend on the dilution.

Let us recall the typical characteristics evidenced in the susceptibility of $d = 2$ AF networks with Heisenberg spins as reviewed in Ref.\cite{Mondelli}. At high-$T$, the $d = 2$ susceptibility follows a Curie-Weiss law, but exhibits a maximum in the susceptibility at a temperature $T_{max} \approx \Theta$, which is a consequence of the development of magnetic correlations. However, in contrast with $d = 3$ systems where a long range order is established at $T_c \approx \Theta$, a $d = 2$ system has a finite correlation length at $T_{max} \approx \Theta$ that eventually diverges when $T \rightarrow 0$ K. The low dimensionality of the lattice inhibits the full development of the critical fluctuations. In the case of the kagomé bi-layer of SCGO, we suggest that the geometric frustration is even more efficient in preventing correlations to develop, moving the maximum in $\chi_{frustr}$ down to $T_{max} \approx 0.1\Theta$.

On the experimental side, new neutron diffraction measurements further support this point of view. As mentioned in Sec. I, neutron studies on SCGO have established that the magnetic correlations in the SG phase ($T < T_g$) are short ranged. C. Mondelli et al. observed more recently the neutron diffraction spectrum in a wider temperature range than the previous experiments ($1.5 \leq T \leq 200$ K).\cite{Mondelli} As shown in Ref.\cite{Mondelli}, the characteristic diffuse peak typical for short range correlations ($\xi \approx 2 \times d_{Cr-Cr}$) develops at $T \leq 60$ K, precisely in the same temperature range where the maximum in $\chi_{frustr}$ occurs. This maximum is therefore the signature of the development of these short range correlations. The feeble decrease in $\chi_{frustr}$ we observe simply reflects the finite value of $\xi$ at $T < T_{max}$.

A recent quantum mean field theory study also points at this direction.\cite{Garcia-Adeva} The basic idea here is to explicitly account for the magnetic correlations by constructing the ground state not on interacting spins, but on interacting triangles or tetrahedras of spins. Within this framework, García-Adeva et al. calculated the susceptibility of the kagomé and the pyrochlore networks for various spin values, providing a reference for comparisons to our Ga-NMR shift $K$ (their mean-field theory does not account for the existence of a spatially non uniform susceptibility responsible for the NMR linewidth broadening, see Sec.\cite{Garcia-Adeva}). In a recent paper\cite{Mondelli} they also studied the influence of the lattice dilution on the susceptibility of these networks. This theory seems to capture most of the main features of our data: the calculated susceptibility for the diluted kagomé and pyrochlore networks exhibits a maximum at $T_{max} \approx 0.15\Theta$ followed by a feeble decrease of the susceptibility in the $0.05\Theta$ temperature range. Although the order of magnitudes found are very encouraging, as we underline in the bottom panel of Fig.\cite{Garcia-Adeva}, more experimental and theoretical studies are needed here to completely validate this model. Indeed, García-Adeva et al. predict that the susceptibility’s maximum should be progressively washed out with increasing dilution and eventually disappear (in a $S = 5/2$ kagomé lattice for a $\sim 10 - 15\%$ dilution and in a $S = 3/2$ pyrochlore lattice for a $\sim 20 - 30\%$ dilution), a feature that somewhat contradicts our observations. Furthermore, as evidenced in the bottom panel of Fig.\cite{Garcia-Adeva}, the $T$-dependence of $K$ for $T > T_{max}$ is dilution-independent. This would only agree with the susceptibility calculated for a diluted pyrochlore lattice, but for $T < T_{max}$ the more pronounced decrease in $K$ we observe is opposite to what is predicted for the pyrochlore lattice. Unfortunately the Ga-NMR intensity loss at $T < 15$ K (Sec.\cite{Mondelli}) does not enable us to further verify their model, in particular to verify whether there is a Curie-like upturn in the susceptibility for $T \ll 0.05\Theta$. We conclude then that for an adequate comparison between data and theory, the influence of the kagomé bi-layer structure should be taken into account in the calculations. Also, the non random distribution of the non magnetic vacancies in SCGO’s kagomé bi-layer might induce quantitative differences between the calculated and experimental susceptibilities, as pointed out in Ref.\cite{Mondelli}.

The general picture drawn by our overview of the experimental and theoretical data is that even short range spin-spin correlations clearly play a major role in SCGO, or more generally in all geometrically frustrated compounds. Future studies are required in this direction to further uncover the low-$T$ properties of these systems.
VI. DILUTION EFFECTS

In this section, we focus on the dilution-dependent susceptibility revealed by the NMR linewidth at low-\(T\). We show that the low-\(T\) paramagnetic behavior observed in \(\chi_{macro}\) originates from the dilution of the kagomé bilayer. This feature is observed in nearly all the geometrically frustrated AF compounds and appears as a generic behavior of this class of materials.\(^{13}\)

Naturally, the macroscopic susceptibility could allow, in some way, to appreciate the dilution effects through its low-\(T\) behavior. Though, the multiplicity of the Cr sites in SCGO complicates the analysis. The Ga(4\(f\))-NMR width not only enables to evidence that the vacancy of a spin on the network, i.e. the dilution, generates a paramagnetic defect, but also allows to shed light on the more fundamental question concerning the nature of the defect.

A. Low-\(T\) macroscopic susceptibility

In Fig. 14 we present the low-\(T\) macroscopic susceptibility of most of the samples studied. The low-\(T\) paramagnetic upturn of \(\chi_{macro}\) is observed at all the concentrations, increasing in an appreciable way with growing dilution. This establishes that the origin of this contribution is related to the Ga/Cr substitution. The non-magnetic gallium vacancy on the network must therefore induce a perturbation which affects the neighboring magnetic Cr\(^{3+}\) ions. A paramagnetic defect is then generated, whose susceptibility \(\chi_{def}\) is reflected in the low-\(T\) behavior of \(\chi_{macro}\).

In order to determine the exact low-\(T\) dependence of the susceptibility associated with the defects, the contribution to \(\chi_{macro}\) of both \(\chi_{frustr}\) and \(\chi_{pair}\) should in principle not be neglected. Since \(\chi_{frustr}\) cannot be determined through NMR below 15 K, we follow Ref. \(^{22}\) and conveniently fit \(\chi_{macro}\) by a two component expression

\[
\chi_{macro} = \frac{C}{T + \Theta} + \frac{C_{def}}{T + \Theta_{def}}
\]

Anyhow, the corrections from \(\chi_{frustr}\) and \(\chi_{pair}\) are small at low-\(T\) compared to \(\chi_{def}\) and do not affect significantly the analysis. The first Curie-Weiss term roughly takes into account the contribution from \(\chi_{frustr}\) and \(\chi_{pair}\), which dominate at high-\(T\). The second term, the more relevant for this section, also Curie-Weiss, quantifies the contribution of \(\chi_{def}\).

The fits, shown by a solid line in Fig. 14 for the \(p = 0.90\) sample, were performed in the 5 K \(< T \leq 350\) K range for all the samples and reproduce correctly the low-\(T\) behavior of \(\chi_{macro}\). The fitting parameters are presented in Tab. V and are in agreement with Ref. \(^{31}\). The values of \(C\) and \(\Theta\) yield an overestimate of \(\approx 10 - 20\%\) compared to those of Tab. III. The values of \(C_{def}\) are in agreement with the analysis of Sec. V. As expected, \(C_{def}\) decreases with the dilution and most importantly is found to be only a weak fraction of the constant \(C\), \(C_{def}/C \approx 1\%\) (Tab III). Finally, the Curie-Weiss temperature \(\Theta_{def}\), which is an indication of the average interaction between the defects, is negligibly small within error bars except for the \(p = 0.72\) sample for which it is at most 2 K.

Strictly speaking, it should be finally noticed that \(\chi_{macro}\) is not sufficient on its own to establish experimentally whether the defects stem from the dilution of the kagomé bi-layer. Indeed, the Ga/Cr substitution on a Cr(4\(f_{vi}\)) site can in principle break a spin pair and free a paramagnetic spin, that can then contribute to the paramagnetic upturn of \(\chi_{macro}\). In contrast with \(\chi_{macro}\), Ga(4\(f\))-NMR is not sensitive to Cr(4\(f_{vi}\)) and, as

| \(p\) | \(C\) (emu K/mol) | \(\Theta\) (K) | \(C_{def}\) (emu K/mol) | \(\Theta_{def}\) (K) | \(C_{def}/C\) (%) |
|------|------------------|--------------|-------------------------|-------------------|-----------------|
| 0.72 | 14.0(2)          | 467(19)      | 0.53(3)                 | 2.3(1.0)          | 3.8(2)          |
| 0.81 | 17.6(3)          | 650(15)      | 0.39(3)                 | 0.9(1.0)          | 2.2(2)          |
| 0.89 | 20.5(4)          | 752(17)      | 0.34(3)                 | 0.6(1.0)          | 1.7(2)          |
| 0.90 | 22.0(6)          | 792(25)      | 0.24(3)                 | 0.5(2.0)          | 1.0(2)          |
| 0.95 | 23.5(7)          | 826(22)      | 0.15(3)                 | 0.2(2.0)          | 0.6(2)          |

TABLE V: The parameters of the two component fit to \(\chi_{macro}\) described in the text. At low dilution, the fit yields a stronger error.
presented in the next subsection, allows a better understanding of the dilution effects in SCGO.

B. Dilution effects through the Ga(4f)-NMR width

In Fig. 15 we present the $T$-dependence (10 K $\leq T \leq$ 60 K) of the low-$T$ width of $^{69,71}$Ga(4f) ($^{69,71}\Delta H$) for five of the seven samples studied. We recover here the properties mentioned about the raw spectra: $^{69,71}\Delta H$ increases as the temperature drops and is very sensitive to the dilution, in contrast with $K$. The low-$T$ behavior of $^{69,71}\Delta H$ bears strong similarities to the one of $\chi_{\text{macro}}$. The perfect scaling of the two isotopes widths $^{69,71}\Delta H$ normalized by the reference field $^{69,71}H_{\text{ref}}$ ($= \nu_{r,f}/^{69,71}\gamma$) – explicitly shown for the $p = 0.95$ sample in Fig. 13 – underlines the magnetic origin of the low-$T$ broadening ($^{69,71}\Delta H \propto ^{69,71}H_{\text{ref}}$), in agreement with the prior study on the $p = 0.90$ sample.

The fact that the $^{69,71}$Ga(4f) linewidth increases rapidly at low-$T$ and with the dilution, whereas the shift varies little, establishes the existence of a susceptibility that is spatially inhomogeneous over the kagomé bi-layer, due to the defects associated with the Ga/Cr substitution. Since the Ga(4f) nuclei are only coupled to the kagomé bi-layer, the defects probed by Ga-NMR are necessarily localized in the kagomé bi-layer.

The effect associated to the dilution is not reduced to a mere suppression of a Cr site without any magnetic signature over the neighboring spins (i.e. a magnetic defect) as indicated by the large modification of the $^{69,71}$Ga(4f) lineshape at low-$T$. Indeed, in the opposite case, one would expect a lineshape which results from the gallium nuclear spins coupled to various Cr-environments all bearing the same susceptibility. One would therefore expect the linewidth to scale with the susceptibility, then $K$, which varies only by 20% from 60 K to 15 K, whereas the linewidth increases by one order of magnitude. For this very same reason, a spatial distribution of the hyperfine constant, which yields also a width $\propto K$, cannot justify the broadening observed and also has to be ruled out.

The $T$-dependence of $^{69,71}\Delta H$ is correctly reproduced by a Curie-Weiss law of the form $C_{\text{def/NMR}}/(T + \Theta_{\text{def/NMR}})$, where $C_{\text{def/NMR}}$ is a constant and $\Theta_{\text{def/NMR}}$ a Curie-Weiss temperature. The fits are presented in Fig. 15 as solid lines. The values of $\Theta_{\text{def/NMR}}$ are extremely low, at maximum of $\approx 4$ K and vary randomly with dilution. Although we cannot exclude completely a Curie-Weiss behavior, especially at high dilution, we may consider the evolution in temperature of $^{69,71}\Delta H$ as very close to a Curie law. The values of $C_{\text{def/NMR}}$ are plotted as a function of $(1-p)$ in the top panel of Fig. 16 (right y-axis) along with the value of $C_{\text{def}}$ extracted from $\chi_{\text{macro}}$ by Eq. (4) (left y-axis).

As shown, the dependencies of both $C_{\text{def}}$ and $C_{\text{def/NMR}}$ on $(1-p)$ perfectly match, suggesting that $^{69,71}\Delta H$ and $\chi_{\text{macro}}$ probe the same susceptibility at low-$T$, i.e. $\chi_{\text{def}}$. This is further underlined in Fig. 17 by the linear re-

FIG. 15: $^{69,71}\Delta H$ versus $T$ for some samples studied. $^{69,71}\Delta H$ is extracted from the $\nu_{r,f} = 40.454$ MHz spectra following the fit described in Sec. V B. $^{69,71}\Delta H$ is normalized by the reference field $^{69,71}H_{\text{ref}}$ to superimpose results from the two isotopes (as explicitly shown for $p = 0.95$). The solid lines are the Curie-Weiss fits $C_{\text{def/NMR}}/(T + \Theta_{\text{def/NMR}})$.

FIG. 16: Top panel: $C_{\text{def}}$ extracted from $\chi_{\text{macro}}$ (left) and $C_{\text{def/NMR}}$ (right) extracted from the NMR width $^{69,71}\Delta H$ versus dilution $(1-p)$. The dashed line is a guide to the eye. Bottom panel: The SG temperature $T_g$ of our SCGO samples versus dilution.
relationship between $\Delta H/H_{ref}$ and $\chi_{macro}$ at low-$T$. Since the defects probed by Ga-NMR are located in the kagomé bi-layer, Fig. 16 and Fig. 17 indicate that the defects on the Cr(4f) sites yield a contribution scaling with the one from the kagomé bi-layer or little contribute to $\chi_{macro}$. In view of the quantitative analysis of $C_{def}$ presented in Ref. \cite{54}, the latter explanation is the more plausible. Finally, we note in Fig. 16 that $C_{def/NMR}$ and $C_{def}$ are linear with $(1 - p)$ at low dilutions ($p > 0.90$), and become progressively sub-linear with $(1 - p)$ at higher dilutions. This deviation is directly perceptible on the spectra of Fig. 1, where the FWHM of the $p = 0.81$ sample is clearly not $\approx 4$ times that of the $p = 0.95$ sample.

C. Discussion on the nature of the defect

1. Models for the localized defects

To our knowledge, two models describe the dilution effects in a geometrically frustrated system. Both are constructed in a classical approach where the ground state corresponds to a minimization of the exchange energies on triangles (or tetrahedras) of spins.

The most recent model was proposed by Moessner et al.\cite{47}. The basic idea here is that a paramagnetic moment in the kagomé network is generated when two vacancies are adjacent on a triangle (3 adjacent vacancies are needed for the pyrochlore network). The defect corresponds in this case to a unique spin of the network, and at low dilution the defect’s susceptibility is $\chi_{def} \sim (1-p)^2/T$ for the kagomé network ($\sim (1-p)^3/T$ for the pyrochlore network). This prediction is in striking contrast with the linear variation of the NMR width on dilution reported in Fig. 14. To reconcile our data to the theory of Ref. \cite{47}, it was suggested in Ref. \cite{55} that the magnetic broadening of the width may reflect a distribution of random local fields ($\propto \chi_{def}$), due to the coupling of each gallium nucleus to the 12 neighboring Cr sites of the kagomé bi-layer. Basically, the NMR width $\Delta H$ would then probe the mean deviation of the susceptibility on these 12 sites (and not simply $\chi_{def}$), thus $\Delta H \propto \sqrt{(1-p)^2}/T$. Although appealing, this scenario is quite unlikely since the macroscopic susceptibility measurements which are insensitive to the effect of a local summation of fields, do not yield a quadratic $(1-p)^2$ variation on dilution.

The second model – purely empirical – was proposed in Ref. \cite{71}. There, a defect is generated by a vacancy which perturbs the neighboring spins, uncorrelating them from the rest of the spin network. These uncorrelated spins were baptized “orphan” spins. Two distinct spin populations then coexist: the orphan spins with a paramagnetic behavior making up the defect, and the frustrated spins outside the defect with a susceptibility equal to $\chi_{frustr}$. In order to examine the implications of the orphan model on the Ga(4f)-NMR low-$T$ spectrum, we assume, as a starting point, that the defect is built only on the orphan spins nearest neighbors (n.n.) of the vacancy (Fig. 18). We consider the important case of the $p = 0.95$ sample where the dilution is weak enough to allow refined conclusions and where the Ga/Cr substitution occurs only on the kagomé layers (the Cr(2a) site is not substituted, see Fig. 6). A simulation allows us to model the expected lineshape. To do so, we start by randomly suppressing 5% of the spins on the kagomé network to account for the existence of non magnetic vacancies.

![FIG. 17: $^{69,71}\Delta H$ versus $\chi_{macro}$ for some of the samples studied ($T$ is an implicit parameter).](image)

![FIG. 18: The simulated sweep field central line of $^{71}$Ga(4f) at $T = 20$ K and $T = 10$ K ($\nu_{ref} = 40.4544 MHz$) if orphan spins n.n. to the vacancy were present in the kagomé bi-layer of the $p = 0.95$ sample. Also shown is the experimental central line of $^{19}$Ga(4f) recorded for $p = 0.95$ at 20 K (open circles). The area of the experimental and of the simulated lines are normalized.](image)
The n.n. spins of the vacancies are given a susceptibility \( \propto \mu_{eff}(d, f) / T \) where \( \mu_{eff}(d, f) \approx 1.5 \mu_B \) (evaluated later in the section) to account for the orphan spins, whereas the remaining Cr sites a susceptibility \( \chi_{frustr} \). Next, we classify the various nuclear populations along their Cr-environments. To construct the spectrum, each population is associated to a quadrupole line simulated with the parameters of Tab. I, with a shift reflecting their Cr-environment and an intensity weighted by the population size. Finally, the Ga(4f)-NMR simulated line is obtained by summing the spectra associated to all the nuclear populations. The line simulation for \( T = 20 \text{ K} \) and \( T = 10 \text{ K} \) is presented in Fig. 18. As shown, neither the broadening, nor the simulated lineshape agree with our \(^{71}\text{Ga}(4f)\) low-T experimental spectrum. Indeed, in the \( p = 0.95 \) sample, \( \approx 35\% \) of the gallium nuclei do not probe an orphan spin, hence \( \approx 35\% \) of the spectral weight yields a shift \( \propto \chi_{frustr} \) (short dashed line in Fig. 18). The majority of the gallium nuclei probe at least one orphan spin, so that \( \approx 65\% \) of the spectral weight yields a shift dominated by a 1/T contribution at low-T (dashed line in Fig. 18). Independently on the value of \( \mu_{eff} \), one would therefore expect to observe \( \approx 65\% \) of the spectral weight to shift toward the low fields with decreasing temperature whereas the remaining part is little shifted. This would yield a non-observed asymmetric broadening of the NMR line with decreasing temperature.

Clearly, a model built on orphan spins n.n. of the vacancy is unsatisfactory and the perturbation generated by the vacancy must be extended in space. Can we then imagine the defect to be made up of orphan spins which are first, second, third etc. neighbors of the vacancy? Since the spin-spin interaction is AF this situation is very unlikely to occur. As we show below, an extended staggered perturbation constructed on an AF interaction is conceivable.

2. A defect built on AF correlations

In Sec. 5 we showed via the observed NMR shift that \( \chi_{frustr} \) exhibits a maximum in temperature, a common feature for the AF correlated systems. It is therefore natural to seek an interpretation for the origin of the paramagnetic defect also in the general context of the AF correlated systems. Indeed in the AF systems such as the \( d = 1 \) spin chains, the quasi-\( d = 2 \) spin ladders and the \( d = 2 \) cuprates, it is now well established that a vacancy (or a magnetic impurity) generates a long range oscillating magnetic perturbation and creates a paramagnetic component in the macroscopic susceptibility. The symmetric broadening of the NMR line observed in these systems is to be related to the oscillating character of the perturbation. We propose that the dilution effects of the SdCGO kagomé bi-layer can be described by the same physics of these correlated systems.

We recall first some basics concerning this model. The presence of a vacancy in the AF correlated network of spins develops a magnetic perturbation, which, in a general fashion, affects a spin at the lattice position \( \vec{r} \) by

\[
m(\vec{r}) \sim \chi'(\vec{r}) H_{ref}
\]

where \( m(\vec{r}) \), \( \chi'(\vec{r}) \) and \( H_{ref} \) are the magnetization, the susceptibility and the applied magnetic field (constant over \( \vec{r} \)). For an AF system, \( \chi'(\vec{r}) \) is peaked at a given vector \( \vec{Q} \). As an example, we choose \( \chi'(\vec{r}) \) to have a gaussian shape

\[
\chi'(\vec{r}) = \chi' G((\vec{r} - \vec{Q}) \exp(-r^2/4\xi^2)
\]

where the function \( G((\vec{r} - \vec{Q}) \) is oscillating and periodic in \( \vec{r} \) with a period related to \( \vec{Q} \). \( \xi \) is the spin-spin correlation length and \( \chi' \) the amplitude of \( \chi'(\vec{r}) \). This translates into an oscillating polarization of the spin network with a periodicity of \( \sim Q^{-1} \) and damped over \( \sim \xi \).

In Fig. 19 we illustrate this with a polarization calculated for the kagomé network. In the absence of low diluted single crystals necessary to determine the exact form of \( \chi'(\vec{r}) \) and the nature of the vector \( \vec{Q} \) through neutron diffraction experiments, we assume a gaussian shape for \( \chi'(\vec{r}) \) and take the reciprocal vector \( \vec{Q} = (1/3, 1/3) \) of the so-called kagomé \( \sqrt{3} \times \sqrt{3} \) spin configuration. By selecting this vector, we partially account for the effects related to frustration.

The staggered shape of the polarization ensures that the NMR line of the nuclei probing the spins of the lattice is broadened on both sides, i.e. that the broadening

![FIG. 19: A gaussian staggered polarization of arbitrary intensity generated by a vacancy (center of the figure) on a 50 site kagomé lattice. \( \xi \) is twice the spin-spin distance and the staggered vector is \( \vec{Q} = (1/3, 1/3) \), i.e. the vector of the \( \sqrt{3} \times \sqrt{3} \) kagomé spin configuration.]
is symmetric and scales with the applied field, in agreement with our data. A non staggered polarization would generate only local fields pointing in the same direction and the NMR line would then be only broadened on one side, i.e. the broadening would be asymmetric (as in the orphan spin model). The actual shape of the broadening (gaussian, lorentzian etc.) depends on \(\chi'(T)\), on the vector \(\vec{Q}\) and on the geometrical details of the nucleus-spin coupling.

On the macroscopic stand, the vacancy generates a paramagnetic defect with a macroscopic susceptibility

\[
\chi_{\text{def}} = \frac{(1-p)\mu_{\text{eff}}^2(\text{def})}{3k_B T}
\]

(3)

where \(\mu_{\text{eff}}(\text{def})\) is the effective moment of a defect. Although the exact nature of the defect is not well established and is still the object of theoretical studies [5], two scenarios may be conceived. 1) The defect is the sum of all the polarizations, in other words the magnetization \(M = \sum_p m(\vec{r})\), whose susceptibility is paramagnetic. The \(1/T\) variation of the overall moment has then no intuitive explanation. 2) The vacancy generates a localized paramagnetic moment on the n.n. spins, which generates the staggered response \(\chi'(T)\) in the spin network. In this case, one needs to understand microscopically why a paramagnetic moment is created.

Quantitatively, the expected NMR broadening is magnetic and related to \(\chi^*\) and \(\xi\) by

\[
\Delta H \propto A\chi^*\mathcal{F}(\xi, 1-p)\frac{H_{\text{ref}}}{T}
\]

(4)

where \(A\) is the hyperfine coupling constant between the spin and the nucleus. \(\mathcal{F}\) is a function of \(\xi\) and of the dilution \((1-p)\). The form of \(\mathcal{F}\) depends on the form of \(\chi'(T)\).

The NMR width is sensitive to all variation in \(T\) of \(\xi(T)\) and \(\chi^*(T)\) in contrast with the macroscopic measurements. The surprising simple \(1/T\) variation of \(\Delta H\) we observe by Ga-NMR in SCGO might indicate that once the correlations set in below 50 K, very little changes occur for \(\xi(T)\) and \(\chi^*(T)\) due to the high frustration. Concerning \(\xi(T)\), neutron measurements are very rewarding since they do infer that the spin-spin correlation is constant with temperature when \(T < 60\) K (Sec. [5]).

At low dilution, where the interaction between the defects can be neglected, \(\mathcal{F}(1-p) \propto (1-p)\). The evolution of \(C_{\text{def}/\text{NMR}}\) with the dilution reflects the one of \(\mathcal{F}(1-p)\). Fig. [6] indicates that \(C_{\text{def}/\text{NMR}}\) is linear with \((1-p)\) at low dilution, but deviates progressively from linearity at higher dilution. This deviation is indeed expected. It can be associated with an “interference” between the polarizations induced by the nearby vacancies. This phenomenon, known now for several years, was first evidenced in the case of the RRKY polarization in the dilute alloys [3]. It is very important to note that \(C_{\text{def}/\text{NMR}}\) likely extrapolates to 0 when \(p \rightarrow 1\) or in the worst case to a value lower than the observed values of \(C_{\text{def}/\text{NMR}}\) for \(p \leq 0.95\). Since the SG state occurs at nearly the same temperature in all the samples and \(T_g\) varies the opposite way of \(1-p\) (bottom panel of Fig. [6]), this clearly demonstrates that the origin of the SG state is not related to the dilution-induced defects. Whether a small residual \(p\)-independent Curie term associated with intrinsic (topological) defects might explain the freezing is still a matter of speculation as higher Cr-concentrations than \(p > 0.95\) would be necessary to conclude.

To summarize, our NMR and macroscopic susceptibility results agree perfectly with a picture of a defect built on the AF correlations of the frustrated network. In conclusion we now elaborate on the effective value of the paramagnetic moment detected in the low-\(T\) macroscopic susceptibility.

Following Eq. (3) and from the \(C_{\text{def}}\) constant of Tab. [5], we deduce a nearly \(p\)-independent value for the defect effective magnetic moment of \(\mu_{\text{eff}}(\text{def}) \approx 1.5 \mu_B\) smaller than the expected 3.87 \(\mu_B\) value for a free \(S = 3/2\) spin. The weak ratio \(C_{\text{def}}/C\) of Tab. [5] is then simply explained in this viewpoint since \(C_{\text{def}}/C = \frac{(1-p)\mu_{\text{eff}}^2(\text{def})}{p\mu_{\text{eff}}^2(\text{Cr}^{3+})} \approx 0.15(1-p)/p\). We can either speculate that the geometric frustration might diminish the efficiency of the polarization induced by the vacancy, indication that the nature of the defect is complex or the paramagnetic defect can be modeled into a \(S = 1/2\) spin quantum state. Also, in the case where \(\mu_{\text{eff}}(\text{def})\) results from the sum of the oscillating spin polarization there is no reason to find a 3/2 value. Further theoretical work in this direction is indeed required to model the defect and achieve a quantitative understanding of our data.

**VII. SUMMARY AND CONCLUDING REMARKS**

The SCGO kagomé bi-layer compound was studied for the first time through a local probe over a wide variety of Cr-concentrations. New and original properties were unravelled for the archetype of geometrically frustrated compounds. Ga(4f)-NMR allowed us to observe the kagomé bi-layer susceptibility \(\chi_{\text{frustr}}\), otherwise non-accessible by macroscopic measurements. A maximum in \(\chi_{\text{frustr}}\) occurs at a temperature \(T_{\text{max}} \approx 0.1\) \(\Theta\), robust to a dilution as high as \(\approx 20\%\). No gaped feature is evidenced. The maximum signals the appearance of short ranged magnetic correlations in the kagomé bi-layer, as observed in all the AF \(d = 2\) Heisenberg systems. \(T_{\text{max}}\) is a new energy scale for SCGO, which sets a new constraint on the theoretical models.

A close examination of the dilution effects by Ga(4f)-NMR allowed us to establish, on a firm experimental ground, that paramagnetic defects are present on the kagomé bi-layer. The defects stem from the vacancies in the spin network, i.e. from the substitution of magnetic \(\text{Cr}^{3+}\) ions with non magnetic \(\text{Ga}^{3+}\) ions. The defects are responsible for the low-\(T\) Curie upturn of \(\chi_{\text{macro}}\). The
macroscopic susceptibility therefore does not probe an intrinsic property of the kagomé bi-layer at low-\(T\), but mainly a property related to the dilution. Interestingly, the SG transition is detected precisely in the low-\(T\) upturn of \(\chi_{\text{macro}}\). As there are experimental signatures suggesting that this transition is an intrinsic feature of SCGO, this means that the defects do not trigger the freezing, but do freeze at \(T < T_g\). The origin of the SG transition remains to be elucidated.

Finally, we proposed a mechanism that justifies the existence of the paramagnetic defects, which, to our knowledge, is the only one that gives a consistent interpretation for both the Ga(4f)-NMR and the macroscopic susceptibility results. Our NMR data point at a defect which possesses strong analogies with the defects observed in most of the AF correlated systems — where the presence of a vacancy (or a magnetic impurity) generates a staggered response from the spin network. Up to now, the dilution in SCGO, or more generally in the frustrated systems, has been considered a parasitical effect to be minimized in order to measure the intrinsic properties related to the geometric frustration. In light of our results, it is interesting to reverse the problematic. The study of the response from the magnetic lattice to a non magnetic vacancy can be an indirect way of probing the intrinsic properties of the frustrated network such as \(\xi(T)\) or \(\chi^*(T)\). The experimental study and the theoretical models to describe this response are a new domain of investigation for the geometrically frustrated systems.

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APPENDIX: SUSCEPTIBILITY OF AN ISOLATED SPIN PAIR

We consider pairs of spins \(s\) with an AF exchange constant \(J\). Their states are labeled by their total spin quantum number, \(S = 0, 1, 2, ..., 2s\), and lie at energies \(E_S = JS(S+1)/2\) relative to the ground state. The partition function for \(N\) independent pairs (\(2N\) being the total number of spins involved in pair formation) is

\[
Z = \left[ \sum_{S=0,2s} g_S \exp(-\beta E_S) \right]^N
\]

where \(g_S\) is the degeneracy of each level and \(\beta = 1/k_B T\). The sum is taken over \(S = 0,1,2,3...2s\). We now apply an external field \(H\) to calculate the susceptibility. The degeneracy is lifted by a Zeeman splitting \(E_{m_S}(H) = g\mu_B H m_S\) so that

\[
Z(H) = \left[ \sum_{S=0,2s} \sum_{m_S=-S,S} \exp[-\beta(E_S + E_{m_S})] \right]^N
\]

where \(m_S = -2s, ..., 0, ..., 2s\) are the Zeeman levels for a spin \(S\). From the expression of \(Z(H)\) we then derive the susceptibility of \(N\) isolated spin pairs

\[
\chi = \frac{N g^2 \mu_B^2}{k_B T} \sum_{S=0,2s} \sum_{m_S=-S,S} m_S^2 \exp(-\beta E_S) \sum_{S=0,2s} g_S \exp(-\beta E_S)
\]

The susceptibility of a \(\text{Cr}(4f_{vi})\)-\(\text{Cr}(4f_{vi})\) spin pair (\(s = 3/2\)) per formula unit of SCGO is therefore

\[
\chi_{\text{pair}} = \frac{2}{p_{4f_{vi}}^2} \frac{\chi}{N} = \frac{p_{4f_{vi}}^2 \mu_{eff}^2}{s(s+1)k_BT} \times \frac{2\exp(-\beta J) + 10\exp(-3\beta J) + 28\exp(-6\beta J)}{1 + 3\exp(-\beta J) + 5\exp(-3\beta J) + 7\exp(-6\beta J)}
\]

where we have introduced the effective moment \(\mu_{eff} = \sqrt{\gamma^2 \mu_B^2 s(s+1)}\). The value of the AF exchange constant, i.e. of the singlet-triplet gap, is \(J = 18.6(1)\) meV. To account for the dilution effects, \(\chi_{\text{pair}}\) is weighted by \(p_{4f_{vi}}^2\), the statistical probability of having a pair of \(\text{Cr}(4f_{vi})\)-\(\text{Cr}(4f_{vi})\) per formula unit of SCGO. The value of \(p_{4f_{vi}}\) is known from neutron refinements (Fig. 8). Note that in the limit \(T \gg J/k_B\), we recover the sum of two \(s = 3/2\) paramagnetic susceptibilities: \(2p_{4f_{vi}}^2 \mu_{eff}^2 / 3k_BT\).

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Taking a binomial distribution for Ga/Cr substitutions, we do not take into account the non-random character of the Ga/Cr substitution. Since each Ga(4f) nucleus is coupled to 9 Cr(12f)-sites and only to 3 Cr(2a)-sites, which, moreover, are less substituted than the Cr(12f)-sites, it is safe to use an average hyperfine constant $A = (9A_{2a} + 3A_{12f})/12$. A calculation in Ref. 42 suggests $A_{12f}/A_{2a} \approx 2$.

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For clarity, we do not take into account the non-random character of the Ga/Cr substitution. Since each Ga(4f) nucleus is coupled to 9 Cr(12f)-sites and only to 3 Cr(2a)-sites, which, moreover, are less substituted than the Cr(12f)-sites, it is safe to use an average $p$ equal to the nominal concentration.

Taking a binomial distribution for Ga/Cr substitutions on the $4f_{15}$ site, the paramagnetic susceptibility resulting from the broken spin-pairs would yield a Curie constant of $\approx 0.36$ emu K/mol for $p = 0.95$ sample, more than twice the experimental value of Tab. 3. The substitutions on the $4f_{15}$ site are therefore sub-stoichiometric. Some chemical constraint must favor substitutions by pairs of gallium ions, minimizing the number of paramagnetic spins resulting from the broken spin-pairs.
Furthermore, if this were the case, the gallium nuclei in the highly diluted samples would be only coupled to paramagnetic orphan spins. The gallium line would then shift as $1/T$ at low-$T$, in contrast with our observations.

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