Ga NMR Study of the Local Susceptibility in Kagomé-Based $SrCr_8Ga_4O_{19}$: Pseudogap and Paramagnetic Defects

P. Mendels,[1] A. Keren,[1,2] L. Limot,[1] M. Mekata,[3] G. Collin,[4] and M. Horvatić[5]

[1]*Laboratoire de Physique des Solides, UMR 8502, Université Paris-Sud, 91405 Orsay, France*
[2]*Department of Physics, Technion, Israël Institute of Technology, Haïfa 32000, Israël*
[3]*Department of Applied Physics, Fukui University, Fukui 910, Japan*
[4]*Laboratoire Léon Brillouin, CE Saclay, CEA-CNRS, 91191 Gif-sur-Yvette, France*
[5]*Grenoble High Magnetic Field Laboratory, CNRS and MPI-FKF, BP 166, 38042 Grenoble Cedex 9, France*

(Received 6 December 1999)

We present the first Ga($4f$) NMR study of the Cr susceptibility in the archetype of kagomé-based frustrated antiferromagnets, $SrCr_8Ga_4O_{19}$. Our major finding is that the susceptibility of the frustrated lattice goes through a maximum around 50 K. Our data also support 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.

PACS numbers: 75.30.Cr, 75.50.Lk, 76.60.–k

The interest in triangular-based antiferromagnets (AF) was raised long ago by Anderson's suggestion for a resonating valence bond state (RVB) as an alternative to the classical Néel state [1]. After a decade of work on 2D geometrically frustrated AF, there is now a growing theoretical consensus that the $S = \frac{1}{2}$ kagomé Heisenberg AF is a good 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 coordinance. From a classical point of view [2,3], this generates a very high degeneracy of the ground state, translating into a huge density of low energy excitations, no long range order at $T = 0$, and a very short magnetic correlation length characteristic of a "spin liquid state." Quantum approaches for $S = 1/2$ suggest that a singlet ground state is favored [4,5].

Only some of these theoretical features were demonstrated experimentally on the archetypal kagomé-based AF $SrCr_{9p}Ga_{12-9p}O_{19}$ (SCGO:p). Susceptibility (χ) measurements [6,7] revealed the strong AF interactions through the occurrence of a Curie-Weiss (CW) susceptibility, $\chi = C/(T + \theta)$, with a Weiss temperature θ as high as 500–600 K (for $p \simeq 0.9$). The unusual extension of the CW law well below θ and the smallness of the ordering temperature, T_g, into a spin glasslike state, as detected by a peak in χ ($T_g \simeq 4$ K $\ll \theta$) are taken as convincing signatures of the high frustration. In addition, neutron [8] and low T muon spin relaxation (μSR) [9,10] studies prove that the freezing is quite marginal and involves only a 20%–30% fraction of the moment(s). The magnetic correlation length for $T < T_g$ is also found of the order of the inter-Cr spacing.

However, due to a *pure Curie* upturn which *dominates* the macroscopic susceptibility, χ_{macro}, below 60 K [6,7], there is *no* experimental determination of the $T \ll \theta$ kagomé-based lattice susceptibility. The Curie upturn and the subsequent spin glasslike ordering received many interpretations still highly debated. Whether geometric frustration generates an original ordering [6] or magnetic disorder due to nonmagnetic substitutions in the kagomé plane [11,12] is driving the spin glass ordering are still pending questions about the interplay of geometric frustration and frustration induced by random defects.

In this Letter, we present the first NMR study of *local* susceptibility in SCGO, where we can discriminate between the kagomé-based susceptibility, χ_{frust}, and the paramagnetic Curie one revealed at low T, χ_{def}, most likely induced by Ga/Cr substitutions (defects). Strikingly, we find a gaplike downturn of χ_{frust} below T as high as 50 K. This sets a novel energy scale, between θ and T_g for the relevant physics of SCGO.

From χ_{macro}, our SCGO:$p = 0.9$ sample proves to be typical [7] ($\theta = 560$ K, high-T Curie constant $C = 2.2$ emu/mol). A previous NMR spectrum analysis [13] showed that three different Ga NMR sites can 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. These sites represent 78% of the Cr moments and are arranged to form a kagomé bilayer (Fig. 1), proposed as a more correct description of the frustrated unit than pure kagomé plane [14].

Below $T = 200$ K, the ^{71,69}Ga($4f$) spin echo spectra were recorded by sweeping the field. A much lower frequency $\nu_0 \simeq 40$ MHz than in [13] was used to minimize the Ga($4e$) contribution. Indeed, due to local charge environments, the quadrupole line broadening ($\simeq \nu_Q^2/\nu_0$) is quite different for the two sites ($\nu_Q[^{71}\mathrm{Ga}(4f)] \simeq$ 2.9 MHz; $\nu_Q[^{71}\mathrm{Ga}(4e)] \simeq 20.5$ MHz). For 220 K $< T <$ 450 K, a frequency sweep in a fixed $H_0 = 7.5$ T field was used.

A typical set of the field sweep spectra, recorded around 3 T, is reported in Fig. 2. The high-T part (upper panel) shows that upon cooling the NMR lines shift to the right (lower H), without any appreciable broadening. In contrast, upon further cooling (lower panel), the lines shift

 0031-9007/00/85(16)/3496(4)$15.00

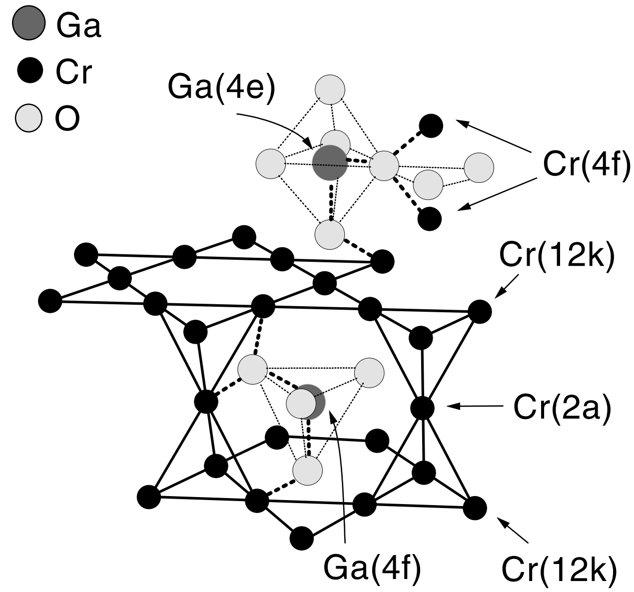

FIG. 1. Structure of ideal $SrCr_9Ga_3O_{19}$. The thick dashed lines show the hyperfine coupling paths of the Ga nucleus to various Cr sites. Cr($2a$) and Cr($12k$) are coupled and form a kagomé bilayer. The site labels are conventional and numbers reflect the density of each plane in the elementary cell.

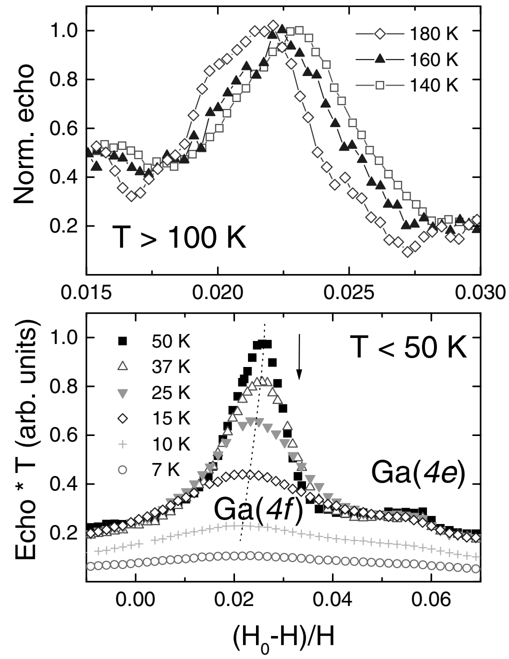

FIG. 2. Typical ^{71}Ga($4f$) field sweep spectra ($\nu_0 =$ 40.454 MHz). H_0 is the nonshifted value of the resonance field and H is the applied field. Upper panel: $T > 100$ K, expanded scale. Bottom panel: $T < 50$ K; the arrow is indicative of the position of the line expected at 25 K in a one-component model of χ_{macro} (with K and χ_{macro} scaled at high T).

to the left (higher H) and broaden. This crossover (at $T \sim 50$ K) in the T dependence of the shift, reflecting χ_{frust}, is the major finding of this Letter.

Another feature seen in Fig. 2 is a wipeout of the intensity due to fast nuclear relaxation when electron spin dynamics slows down. This is common in systems ranging from spin glasses to AF correlated systems [15,16]. From Ref. [15] and the μSR data reported on the same sample [9], one would expect this to occur in SCGO only in the vicinity of T_g. The integrated intensity of the ^{69,71}Ga spectra shows no variation above 15 K (Fig. 3), so that our data very reliably reflect 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, below $T = 10\text{ K} \sim 3T_g$, more than 50% of the sites are wiped out of our experimental window, indicating an inhomogeneous dynamics of the spin system [15] in an unusually high-T range as compared to T_g.

The shift K and the width ΔH 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 (average) susceptibility of the Cr($12k$) and Cr($2a$) ions. At low T, it was proven that ΔH has a magnetic origin [13], i.e., reveals a distribution of internal fields on the nuclear Ga($4f$) site, which is naturally associated with a spatially *inhomogeneous* susceptibility of the Cr spins. For $T > 120$ K, the line shape is due to quadrupole effects and the broadening is small enough (Fig. 2) that, for practical purposes, 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 K is deduced from either the center of gravity or a partial Gaussian fit of the Ga($4f$) contribution which also yields ΔH [17]. Independently of the analysis, K was found to *decrease* at low T.

First we discuss the T dependence of K presented in Fig. 4, where we also include results for various applied fields. From the high-T data (inset), we extract a Néel temperature $\theta_{\text{NMR}} \simeq 470$ K of the same order as $\theta_{\text{macro}} = 560$ K [18]. This confirms that K reflects the physics of the frustrated unit. As mentioned before, K

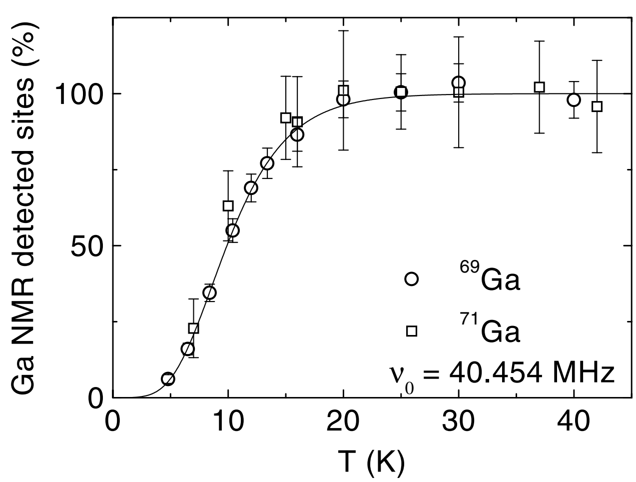

FIG. 3. Number of Ga($4f$) sites detected by NMR for both isotopes. T_2 corrections are quite small and do not affect the estimates below 50 K.

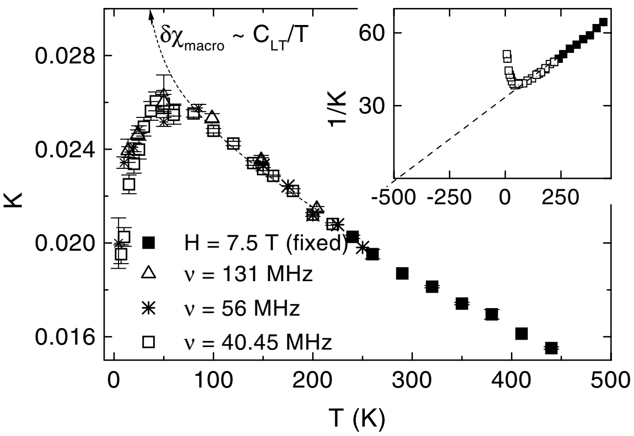

FIG. 4. K versus T down to 10 K, for various fields/frequencies. Minor second-order quadrupole corrections have been performed. The spread in the low-T values taken in various conditions is due to the sizable line broadening; see Fig. 2. The dashed line figures K variation expected from χ_{macro} within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

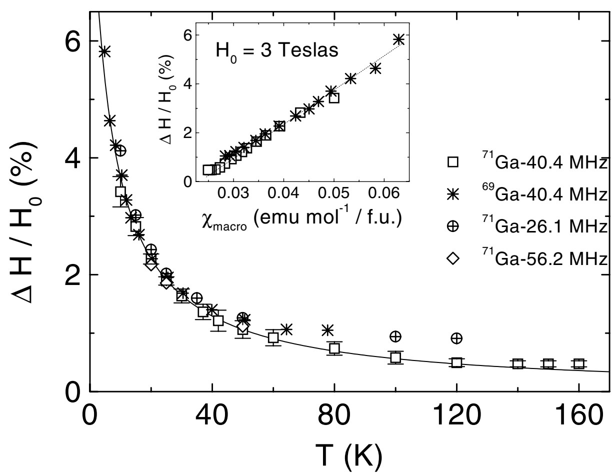

FIG. 5. Relative full width at half maximum plotted versus T for the two isotopes at various fields. At high T, T-independent quadrupole effects dominate ΔH and are larger for ^{69}Ga and low fields. Inset: Plot of $\Delta H/H_0$ versus χ_{macro}.

first increases with decreasing T down to 50 K, but below, *K flattens* and *even decreases* by 20%. The sharp contrast between the T dependence of K and χ_{macro}, below 50 K (Fig. 4), is indeed evident in the raw data as emphasized by the arrow in Fig. 2 (see legend). It reveals that *two different types of Cr* must be considered, which rules out models associating the low-T macroscopic susceptibility only with a generic—therefore homogeneous—property of the frustrated lattice. Further investigations to be detailed in [19] clearly confirm that the shift variation reported for this sample is an intrinsic feature of the frustrated network as it depends very little on the Cr/Ga substitution (at variance with ΔH).

Next we discuss the variation of ΔH at low T. The results are summarized in Fig. 5. At low T, the broadening scales remarkably with the applied field for both isotopes. This confirms the magnetic origin of the width at low T [13]. A Curie-like behavior is found for $\Delta H(T)$ (solid line). We therefore plot in the inset $\Delta H/H_0$ versus χ_{macro} measured for the same $H_0 \sim 3$ Tesla field, using T as an implicit parameter. The linearity of the relationship between ΔH and χ_{macro} strongly suggests that the Curie upturn, which dominates χ_{macro} at low T, and the linewidth have a common origin of *inhomogeneous* magnetism. The deviation between χ_{macro} and K below $T = 50$ K is also well explained by this viewpoint.

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

We now turn to discuss our results in light of existing models where susceptibility for the pure kagomé network has been numerically calculated. In many of them, such as for spin singlets [4], a gap Δ appears in χ_{frust} and at low T, $\chi_{\mathrm{frust}} \sim e^{-\Delta/T}$. Using for Δ the temperature $T_{\max} = 50$ K where K peaks, one would expect a much sharper decrease of χ_{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 kagomé bilayer [12]. 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 χ_{frust}, which should weaken the drop of K below Δ. 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.

Regardless of the nature of the gap, the value of $T_{\max}$ is very surprising. In most models $T_{\max} < 0.1J$ where $J \sim 100K$ [14] is the exchange interaction. Here $T_{\max} \sim J/2$, 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 χ at T as high as $0.4J$ [3]. From the absence of neutron signature, one does not expect any real magnetic order to occur around 50 K. Our shift data would rather indicate an increase of the magnetic correlations. This scenario resembles the case of the pseudogap in high-T_c cuprates. An even simpler interpretation of $T_{\max}$ is that for any low dimensional AF correlated system, one expects χ to decrease at low T. The crossover occurs in nonfrustrated

2D AF for $T \sim \theta$ [20]; however, because of frustration, it could occur at lower temperatures, here 10 times smaller than θ. The ratio $\theta/T_{\max}$ might, finally, prove to be a better characterization of the degree of frustration than using θ/T_g since the origin of the spin glass freezing might be associated with defects, such as discussed below.

We now propose an interpretation for the origin of the width, in the light of [12]. There, the origin of the $1/T$ paramagnetic behavior of χ_{macro} is assigned to triangles of the kagomé lattice nonfully occupied by Cr^{3+} moments. The substitution of two adjacent Cr by Ga is necessary to generate a paramagneticlike "defect" at low T. *A priori,* this 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; thus the corresponding signal is 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 broadening. This is recognized as the explanation for a similar low-T increase of the NMR width reported in numerous systems such as high-T_c cuprates, spin chains, or ladders [21]. We therefore conclude that the defects in SCGO must be coupled to the surrounding correlated spins, as suggested in [12,22].

For a quantitative analysis of the low-T contribution of Ga/Cr substitutions to χ_{macro}, one needs to subtract the contribution from an ideal pure sample, unfortunately not stable. Nevertheless, we use a simple (and consistent) viewpoint where χ_{macro} is dominated by the *substitution* defects at low T. From the low-T Curie constant C_{LT} extracted from χ_{macro}, we can deduce the value of the effective moment of one defect, μ_{eff}, provided we know the number of defects, N_{defect}. We follow [12] and write $N_{\text{defect}}/N_{\text{Cr}} = 3/2(1 - p)^2$, where N_{Cr} is the total number of Cr. From $C_{LT} = N_{\text{defect}}\mu_{\text{eff}}^2/3k_B = 0.03$ emu/mol, we find $\mu_{\text{eff}}(\text{defect}) \sim 4\mu_B$, typical of a spin 3/2. This reminds us of 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 [12] is encouraging, but, of course, more NMR and susceptibility experiments are needed for $p \to 1$ to further check the quadratic concentration dependence of N_{defect}.

In conclusion, we have demonstrated that the intrinsic kagomé (or kagomé bilayer) susceptibility displays a broad maximum around $T \sim J/2$. For $T < 20$ K, our data suggest that the macroscopic susceptibility is dominated by the contribution from defects which remain coupled to the frustrated network [12]. Finally, the occurrence of a slowing down of spin fluctuations is clearly evidenced below 15 K. Our results definitely set new constraints on the theoretical models and are stimulating for other NMR studies in the broad class of frustrated systems.

We acknowledge Y. J. Uemura who suggested this work and C. Lhuillier, F. Mila, H. Alloul, and J. Bobroff for fruitful discussions.

[1] P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).
[2] E. F. Schender and P. C. Holdsworth, in *Fluctuations and Order: The New Synthesis* (Springer-Verlag, Berlin, 1994), and references therein; A. Keren, Phys. Rev. Lett. **72**, 3254 (1994).
[3] J. N. Reimers and A. J. Berlinsky, Phys. Rev. B **48**, 9539 (1993).
[4] P. Sindzingre *et al.,* Phys. Rev. Lett. **84**, 2953 (2000).
[5] F. Mila, Phys. Rev. Lett. **81**, 2356 (1998).
[6] A. P. Ramirez, G. P. Espinosa, and A. S. Cooper, Phys. Rev. Lett. **64**, 2070 (1990).
[7] B. Martinez *et al.,* Phys. Rev. B **46**, 10 786 (1996).
[8] C. Broholm, G. Aeppli, G. P. Espinosa, and A. S. Cooper, Phys. Rev. Lett. **65**, 3173 (1990).
[9] Y. J. Uemura *et al.,* Phys. Rev. Lett. **73**, 3306 (1994).
[10] A. Keren *et al.,* Phys. Rev. Lett. **84**, 3450 (2000).
[11] P. Schiffer and I. Daruka, Phys. Rev. B **56**, 13 712 (1997).
[12] R. Moessner and A. J. Berlinsky, Phys. Rev. Lett. **83**, 3293 (1999).
[13] A. Keren *et al.,* Phys. Rev. B **57**, 10 745 (1997).
[14] S.-H. Lee *et al.,* Phys. Rev. Lett. **76**, 4424 (1996).
[15] D. E. MacLaughlin and H. Alloul, Phys. Rev. Lett. **36**, 1158 (1976).
[16] P. Mendels *et al.,* Physica (Amsterdam) **171C**, 429 (1990); T. Imai *et al.,* Phys. Rev. Lett. **82**, 4300 (1999); R. J. Curro *et al.,* Phys. Rev. Lett. **85**, 642 (2000).
[17] The broad Ga(4*e*) contribution appears as a pedestal (Fig. 2, bottom) and becomes more prominent below 50 K. It is taken into account in our fits of ΔH.
[18] The difference between θ_{NMR} and θ_{macro} can be assigned to the extra contribution of Cr(4*f*) to χ_{macro}; see L. Limot *et al.,* cond-mat/0007019.
[19] L. Limot *et al.* (to be published).
[20] L. J. de Jongh, *Magnetic Properties of Layered Transition Metal Compounds* (Kluwer Academic Publishers, Dordrecht, The Netherlands, 1990).
[21] J. Bobroff *et al.,* Phys. Rev. Lett. **79**, 2117 (1997); N. Fujiwara *et al.,* Phys. Rev. Lett. **80**, 604 (1998).
[22] Based on a two-component analysis of the susceptibility of various frustrated magnets, a similar picture of paramagnetic moments was conjectured by [11]. The moments are there uncorrelated to other Cr spins, then purely local, at variance with our findings.
[23] A. W. Sandvik, E. Dagotto, and D. J. Scalapino, Phys. Rev. B **56**, 11 701 (1997).