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Spin dynamics in frustrated magnets: from edge- to corner-sharing geometries

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Abstract

Our work in the past few years has been focused on local NMR (nuclear magnetic resonance) and μSR (muon spin resonance) studies of pure Heisenberg isotropic triangular lattices with nearest neighbour couplings, a prerequisite for reaching the ideal spin liquid case. In the case of chromates, although $S = 3/2$, the combination of the weakness of the Cr^{3+} single-ion anisotropy and that of an exchange interaction resulting from a direct overlap of the Cr^{3+} orbitals allows us to tackle these properties. We were recently able to single out, in the triangular compound $NaCrO_2$, an original dynamical crossover regime in a broad range of T between the peak in specific heat and a low T static ground state. Moving to the corner-sharing geometry of Kagome bilayers ($Ba_2Sn_2ZnGa_{10-7p}Cr_{7p}O_{22}$ and $SrCr_{9p}Ga_{12-9p}O_{19}$), we illustrate all the potential of local studies (NMR and μSR) for revealing some key aspects of the physics of these compounds, namely $T \to 0$ fluctuations, susceptibility, the impact of dilution defects which generate an extended response of the spin lattice as well as their puzzling spin glass state. These results are compared to the case of volborthite which features $S = 1/2$ spins on a corner-sharing, probably anisotropic, antiferromagnetic Kagome lattice.

(Some figures in this article are in colour only in the electronic version)

1. Frustration: one route to spin liquids

The fundamental interest in triangular-based antiferromagnets (AF) was raised long ago by Anderson's famous proposal for a resonating valence bond (RVB) state as an alternative to the classical 120° three-sublattice Néel state [1]. Although there is now a theoretical consensus

that the $S = 1/2$ Kagome or pyrochlore Heisenberg AF (HAF) are good candidates for showing such an RVB state at low T [2–4], no satisfactory experimental realization has yet been made available for checking these theoretical predictions. From a classical point of view, the corner-sharing geometry generates a macroscopic degeneracy of the ground state, branches of zero-energy excitation modes, no long range order at $T = 0$ and a very short magnetic correlation length characteristic of a 'spin liquid state'. One of the most striking results from exact diagonalizations of the $S = 1/2$ Kagome HAF is the existence of a continuum of low lying singlet excitations, in between the ground state and the first excited triplet, at variance with the case for the triangular HAF [2]. Despite the absence of an ideal case, many of the unusual features expected in the RVB scenario are revealed in various corner-sharing AF experimental systems. One can expect a fluctuating ground state for Heisenberg spins, provided the following conditions are fulfilled:

- a corner-sharing geometry such as that featured in a simple manner in the Kagome or pyrochlore lattices: this is a central condition as mentioned above;
- no disorder: disorder must be taken as a generic term for any deviation from the pure case of a Heisenberg Hamiltonian on a corner-sharing lattice; this disorder term therefore encompasses anisotropy, dipolar interaction, next nearest neighbour interactions as well as site and bond disorder or distorted triangles;
- $1/2$ spins: although this is not mandatory, one expects quantum fluctuations to be enhanced for $S = 1/2$ spins.

It is worth noting that, to our knowledge, no $S = 1/2$ material fulfils the above conditions. In $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$, second-and third-neighbour interactions play a dominant role [5, 6]. Volborthite is perhaps the first reported example of a $S = 1/2$ Kagome lattice [7] although one suspects spatially anisotropic nn interactions. Inspecting the other limit of large S, pure Kagome geometries are best represented by jarosites. Most of them have an AF order at low T with conventional spin wave excitations. Only in the case of hydronium jarosite do unconventional excitations seem to be observed in the $T = 0$ spin glass phase [8]. However, the nature of the 3D couplings and the role of the anisotropy need further clarifications to understand the physics at work in these systems. The Cr^{3+} ($S = 3/2$) bilayers of the magnetoplumbite family have long been considered as the archetypes of highly frustrated magnets. The direct Cr–Cr exchange and the $3d^3$ electronic configuration of the Cr^{3+} yield an ideal Heisenberg Hamiltonian. Unfortunately, as will be recalled in section 3, one cannot neglect the dilution of the magnetic lattice. As for 3D structures, rare earth pyrochlores have up to now been recognized as perfect corner-sharing lattices, but most of the fascinating properties of this family are governed by the delicate balance between magnetocrystalline anisotropy, dipolar interaction and exchange interaction. In the Ti series, only $Tb_2Ti_2O_7$ seems to reproduce the essential features of a spin liquid state [9] with no transition down to very low T. This absence of a transition might prove to be accidental if one refers to the ordered spin ice behaviour found in the parent $Tb_2Sn_2O_7$ compound [10, 11].

In this paper we review the results on both static and dynamical aspects revealed by local techniques such as NMR and μSR. In the first part we summarize recent results on $NaCrO_2$ which features a good realization of the triangular HAF [12], a reference case worth reinvestigation. In the second part, we review the results obtained on Cr Kagome bilayers [13–15] which are compared in the last part to the volborthite case [16].

2. Triangular lattice: the case of $NaCrO_2$

In $NaCrO_2$, well separated Cr^{3+} planes alternate with an ABCABC stacking along the c-axis (figure 1). A detailed analysis of the NMR lineshape and the absence of a measurable lineshift clearly confirm that the Cr–Cr exchange is direct. This has two important consequences: the

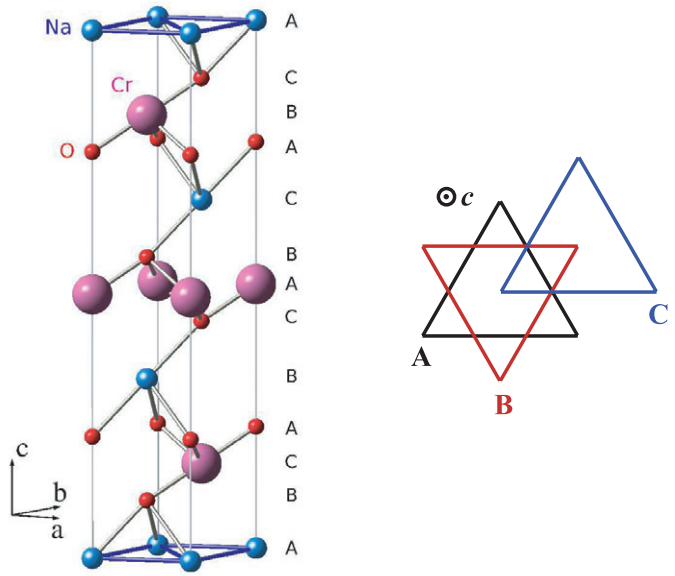

Figure 1. Left: unit cell of the $NaCrO_2$ phase. Right: projection on the *a*–*b* plane.

second-neighbour interaction is negligible and the coupling along the *c*-axis should be quite weak, which ensures a very pronounced 2D character. One should note that in the case of $LiCrO_2$, the smaller size of the Li^+ ion favours a more 3D coupling which might lie at the origin of the 3D transition around 64 K towards what has been reported to be an 18-sublattice Néel state [17]. $NaCrO_2$ therefore appears as a simple 2D model case for the THAF which has not been much studied experimentally.

Specific heat and susceptibility (χ) data are presented in figure 2. χ goes through a maximum around 46 K while the raw specific heat has a kink, which turns out to be a broad maximum in the magnetic contribution (figure 2, inset). While the maximum of χ at finite T is a common feature of 2D systems which reveals a growth of antiferromagnetic correlations, the well defined anomaly in the specific heat should rather be an indication of the onset of a transition.

The existence of a complete freezing is evident from NMR data taken at low T where a remarkable broadening of the NMR spectrum occurs (figure 3). The linewidth, which is found to be independent of T below 10 K, simply reflects the existence of a dipolar internal field due to spin freezing. The featureless lineshape can be associated with either a large disorder of the internal fields created at the Na site or, more likely, with a complex magnetic stacking perhaps even more complex than in the case of the 18 sublattices of $LiCrO_2$. The origin of this order is rather unclear at the present stage and one has still to dig out what the 3D coupling at work could possibly be.

The most striking and original result is the observation of a peak of the relaxation rate in μSR at a temperature much lower than that of the singularity in the specific heat. In NMR this translates into a wipe-out of the NMR intensity, meaning that the relaxation time is shorter than our observation window (figure 4). This is quite unusual in ordinary transitions where one would expect the relaxation rate and the specific heat to peak at the same temperature. The broad dynamical regime rather points to an original crossover scenario (40–10 K) where

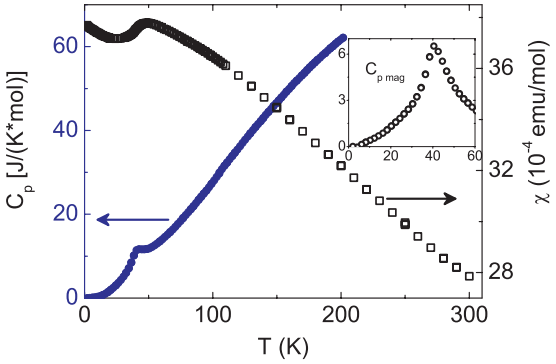

Figure 2. Specific heat and susceptibility data. Inset: magnetic contribution to the specific heat as obtained by subtracting the non-magnetic contribution estimated from data taken for $NaScO_2$.

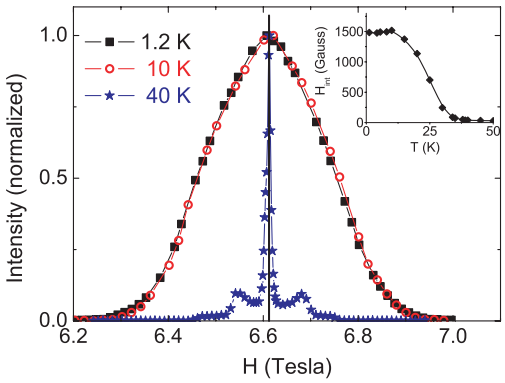

Figure 3. ^{23}Na NMR spectra at low T as compared to data at $T = 40$ K. The spectra are normalized to the maximum intensity. Inset: variation with T of the FWHM extracted from all the spectra.

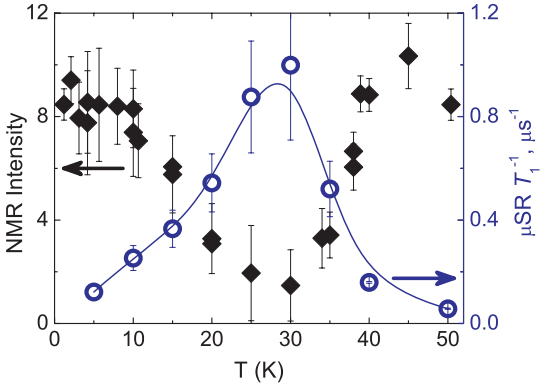

Figure 4. NMR wipe-out effect as evidenced from the loss of intensity and corresponding maximum of the relaxation rate observed in μSR.

fluctuations reflect the intrinsic physics of the 2D THAF extending in a broad range of T prior to a complete 3D ordering below 10 K. This is certainly related to the triangular nature of the

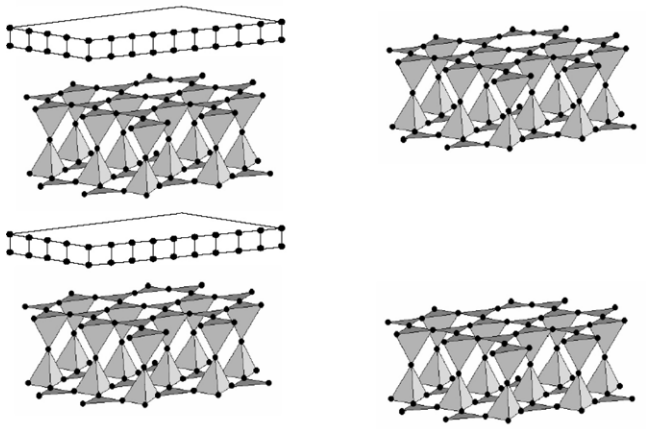

Figure 5. Kagome bilayers in SCGO (left) and BSZCGO (right). The magnetism for both compounds arises from the stacking of magnetically decoupled Kagome bilayers, ensured in SCGO by the presence of non-magnetic singlets and in BSZCGO by a large inter-bilayer distance.

lattice and to original excitation modes. Speculatively, one could think of Z_2 vortices which are known to survive below the maximum of the specific heat [18] and which have been advocated to explain the spin liquid state observed in $NiGa_2S_4$ [19]. Clearly, neutron data are required to clarify the nature of the ground state and of these excitations which are revealed through our local probe μSR and NMR studies.

3. Cr^{3+} Kagome bilayers

Among the HFMs, the chromium-based $S = 3/2$ Kagome bilayer compounds $SrCr_{9p}Ga_{12-9p}O_{19}$ (SCGO(p)) and $Ba_2Sn_2ZnCr_{7p}Ga_{10-7p}O_{22}$ (BSZCGO(p)) appear as particularly good realizations of the Heisenberg Hamiltonian on a corner-sharing lattice and prove to retain the essence of a spin liquid ground state. In both SCGO and BSZCGO, Cr^{3+} ions are located at corners either of tetrahedra or triangles and the structure is essentially 2D (figure 5). Here again, the antiferromagnetic interaction between nearest neighbouring spins arises from a direct overlap exchange, resulting in a coupling of $J \sim 40$ K. This coupling is almost two orders of magnitude larger than the perturbation terms, like the single-ion anisotropy $\sim$0.08 K, dipolar interactions [13–15] $\sim$0.1 K, and next nearest neighbour interactions <1 K [20]. These compounds have Ga/Cr substitutional disorder, and a Cr coverage of the frustrated bilayer higher than $p = 0.95$ and 0.97 cannot be reached in SCGO(p) and in BSZCGO(p). This results in spin vacancies (Ga^{3+} is non-magnetic) in the magnetic structure, and the related magnetic defects that they produce turn out to be insufficient to destroy the spin liquid behaviour of the ground state.

At low T, the macroscopic susceptibility is dominated by the Curie-like contribution associated with defects which adds up to the intrinsic susceptibility of the Kagome bilayers. One of the unique advantages of a local technique such as NMR is that it allows one to separate these two contributions, and to reveal the intrinsic physics associated with geometric frustration. The contribution of defects is indeed reflected in the linewidth and that from the intrinsic susceptibility in the lineshift, which one can easily discriminate. The intrinsic susceptibility is marked by a maximum around $J/2$ (figure 6) which proves to have little dependence on the rate of substitution, indicating therefore an intrinsic and robust

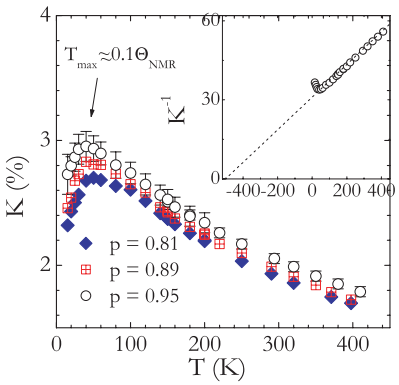

Figure 6. Variation with T of the NMR lineshift for various lattice coverings in SCGO. Inset: the inverse shift plotted versus T yields a Weiss temperature of -450 K.

character [13]. This maximum is the signature of a strengthening of magnetic correlations whereas the finite $T \to 0$ value of the susceptibility simply indicates that the correlation length remains finite at $T = 0$. Such findings are further confirmed by neutron scattering results [21].

A detailed study of the lineshape in SCGO shows that non-magnetic defects generate a staggered response which probably extends over the correlation length, a well established scenario in high T_c cuprates and spin chains, also supported by numerical simulations on the Kagome lattice. In SCGO, the linewidth extrapolates to zero when $p \to 1$, whereas in BSZCGO, it extrapolates to a finite value. This is the signature of the feature that in the latter compound, an additional kind of defect plays a role, which is probably associated with the existence of bond defects induced by the 50% random occupation by Zn^{2+} of the Ga^{3+} site inside the bilayer for charge balance purposes [14].

A spin glass phase has long been known to occur in this defect channel [22] which proves to have a low p dependent freezing temperature, at least in the low dilution limit (figure 7). This underlines its non-conventional character since one would rather expect naively that the transition temperature scales with the concentration of defects. The major limitation of NMR study is due to the wipe-out effect which is observed below 20 K [13]. This reveals a slowing down of the dynamics, better tracked through μSR, which has long proven to be a powerful tool in the field of HFM as first pointed out in the seminal work of Uemura and Keren [23]. Whereas one would expect a peak in the relaxation rate around T_g in a conventional spin glass transition, a plateau of the relaxation rate is found. The finite value of the relaxation rate at $T = 0$ is clearly associated with a dynamical ground state. Our contribution to this field through μSR has been to establish a phenomenological fit of the relaxation data, valid over a broad range of dilutions, fields and temperatures which allows two contributions: that from an RVB-like state where the sporadic dynamical unpairing of singlets explains the undecoupled Gaussian observed in many frustrated systems and a more conventional term associated with substitution defects which turns out to be important for explaining the p evolution of the relaxation rate [15]. One should note that if this picture is correct, the singlet–triplet gap should have a very small value in order to allow excitations at our base temperature of 30 mK to be compared with exact calculations performed on $S = 1/2$ small samples which predict a gap $\leqslant J/20$ [2]. In any case, the mere model independent analysis of the values of the relaxation rates at $T = 0$ indicates that fluctuations are not associated with single spins but rather correspond to localized modes; fully occupied triangles and hexagons are needed to explain the variation

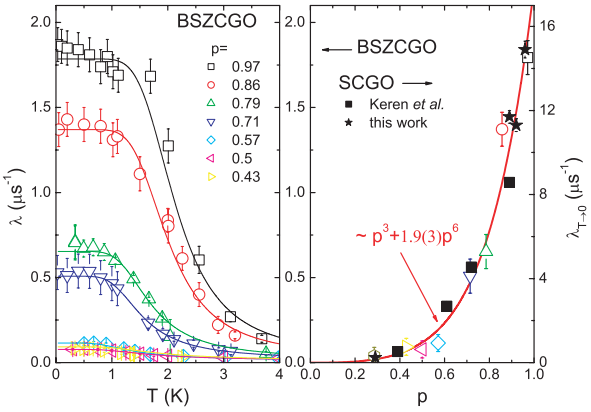

Figure 7. Left panel: T variation of the relaxation rate for varying p in BSZCGO. Right panel: the $T \to 0$ values are reported versus p. The solid line is a $p^3 + 1.9(3)p^6$ fit.

with p. This is in line with the observation that no spectacular effect is found at the percolation threshold [15, 24].

4. Possibly distorted $S = 1/2$ Kagome lattice: the case of volborthite

A few years ago, volborthite $Cu_3V_2O_7(OH)_2{\cdot}2H_2O$ was rediscovered by Hiroi *et al* and pointed out at as one of the first examples of a $S = 1/2$ Kagome lattice [7]. This compound consists of CuO layers well separated from each other by V_2O_7 pillars and water molecules. Cu^{2+} are the only magnetic atoms and form planes of corner-sharing triangles. Due to a monoclinic distortion, there might exist two sets of Cu–Cu exchange constants, i.e. the Kagome lattice is built on isosceles triangles rather than equilateral ones. This asymmetry of the exchange paths has hardly been investigated theoretically [25] to our knowledge. On experimental grounds, most of the properties found for volborthite resemble those of the Kagome bilayers. The susceptibility goes through a small maximum around 25 K without showing any sign of a gap [7]. A slowing down of spin fluctuations is observed below 5 K followed by nearly T independent fluctuations below 1.5 K and down to 50 mK, demonstrating the liquid nature of the ground state [26]. In the pure compound, from the comparison with the magnitudes of the Curie tails detected in Zn/Cu substituted samples, we estimate a high coverage, $p \simeq 0.99$. Here again, a spin glass-like transition is found with $T_g \sim 1.2$ K [16].

Through V NMR, we were able to measure the relaxation rate which offers a complementary approach to that of μSR. Indeed, the V nucleus is a probe situated at a high symmetry site of the magnetic structure (the centre of Cu hexagons), whereas the muon probably binds to on oxygen or hydroxyl group in a non-symmetric position. The fact that we observe a peak of the NMR relaxation rate at the transition, at variance with μSR findings, indicates that fluctuations have a high symmetry and are filtered out at the V site (figure 8). Such a finding has been discussed at length in [16] and a sketch of a classical soft mode leading to such effects is displayed in figure 8.

Dilution effects have been studied by replacing Cu^{2+} ions by non-magnetic Zn^{2+}. Contrary to the case for SCGO, such a dilution has a quite drastic effect both on the value of the relaxation rate and on the spin freezing transition (figure 9). Whether this relates to the pure Kagome geometry, to $S = 1/2$ spins or to the asymmetry of interactions is not clear at the present stage.

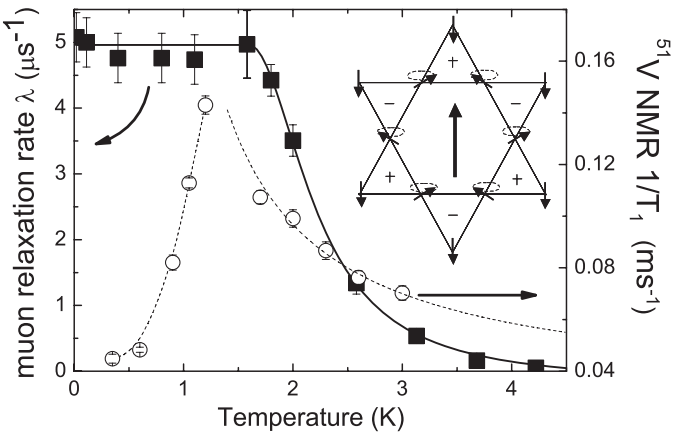

Figure 8. Left (right): μSR (V NMR) relaxation rate. The sketch shows a zero-energy mode which is filtered out at the V site and, hence, does not contribute to V NMR relaxation.

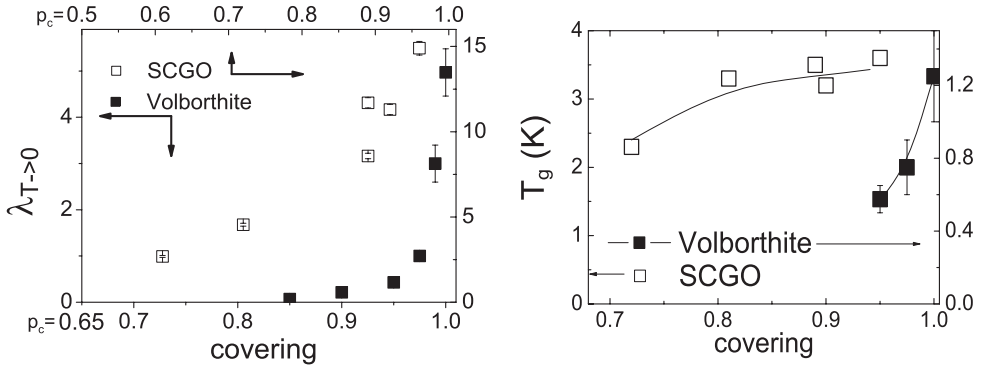

Figure 9. Comparison of the effect of dilution for SCGO and the volborthite: left, $T \to 0$ μ^+ relaxation rate; right, 'spin glass' temperature.

5. Concluding remarks

There are now numerous compounds which display original fluctuations and certainly more to come in the near future. Whereas in the edge-sharing geometry one observes either an extended dynamical crossover to an ordered state as for $NaCrO_2$ or even a spin liquid-like state as for $NiGa_2S_4$, the presence of order at $T = 0$ such as that featured in Kagome-based lattices appears quite marginal. For the latter, the high density of $T = 0$ excitations dominates the low T physics and appears as the main consequence of the corner-sharing geometry. Whether the RVB conjecture can be realized in such lattices remains one of the experimental challenges still to be addressed through materials more 'ideal' than the existing ones.

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