Neutron Spin-Echo Investigation of Slow Spin Dynamics in Kagomé-Bilayer Frustrated Magnets as Evidence for Phonon Assisted Relaxation in $SrCr_{9x}Ga_{12-9x}O_{19}$

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A neutron spin-echo investigation of the low temperature spin dynamics in two well-characterized kagomé bilayer compounds $SrCr_{9x}Ga_{12-9x}O_{19}$ ($x = 0.95$, SCGO) and $Ba_2Sn_2ZnCr_{7x}Ga_{10-7x}O_{22}$ ($x = 0.97$, BSZCGO) reveals two novel features. One is the slowing down of the relaxation rate without critical behavior at T_g, where a macroscopic spin-glass-like freezing occurs. The second is, in SCGO at 4 K ($\approx T_g$) $< T <$ 7 K, the relaxation rate activation energy $E_a = 7 \pm 0.4$ meV, equal to the energy of a phonon mode, pointing out the role of spin-lattice coupling.

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Magnetic systems with geometrical frustration provide an interesting field of investigation of complex dynamic behavior in apparently simple entities governed by local interactions [1–3]. The well-known manifestations are antiferromagnets on triangular or kagomé lattices, or on corner sharing tetrahedra such as in the pyrochlore lattice. A general feature of frustrated magnets is the existence of short-range correlations leading to clusters with local order and fluctuations [4,5] reminiscent of those observed in molecular nanomagnets consisting of truly individual units [6], with the additional ingredient of the macroscopic collective degeneracy characteristic of the frustrated magnets. At low temperatures the selection of a particular ground state is associated with the lifting of that degeneracy by system dependent interactions that cannot be treated perturbatively [3]. Instead of long-range ordered or liquid-like collective singlet, slow dynamics or freezing can result. The energy scales associated with these phenomena can fall orders of magnitude below that of the dominating magnetic interactions and one can expect that other than purely magnetic degrees of freedom can manifest themselves. The role of lattice distortions in the selection of an ordered ground state has been studied recently [7]; subsequently a link between a phonon and the magnetic correlations was observed [8]. However, the composite degrees of freedom related with spin-lattice coupling remain largely open questions in the dynamic aspects of frustrated magnets.

The compounds studied in the present work, $SrCr_{9x}Ga_{12-9x}O_{19}$ (SCGO) [9–12] and $Ba_2Sn_2ZnCr_{7x}Ga_{10-7x}O_{22}$ (BSZCGO) [13–15] are representative examples of frustrated magnets. Both have a magnetic sublattice built up of Cr atoms located on kagomé bilayers, also called pyrochlore slabs due to the connection of the kagomé layers with an intertwining triangular layer. Unavoidable dilution by nonmagnetic defects is present in the form of Ga substitution on the magnetic Cr sublattice, with concentrations $x = 0.97$ for the BSZCGO [14], and $x = 0.95$ for the SCGO [12] samples we studied. The two compounds are similar in the higher T range, where their properties are understandable in terms of $S = 3/2$ spins with antiferromagnetic nearest neighbor Heisenberg interactions characterized by a Curie-Weiss temperature of the order of $\theta_{CW} \approx -400$ K [12,16]. This is consistent with the full width of the spin dynamics extending up to 30 or 40 meV [17]. A considerably lower energy scale dominates the low-T phenomena. A partial ''freezing,'' observed at $T_g \approx 4$ K and $T_g \approx 1.5$ K for SCGO and BSZCGO, respectively, is indicated by a sudden increase of the resolution-limited, ''elastic'' response with neutrons [18]. This strongly slowed down response in the μeV range involves about 1/4 of the total possible ordered magnetic moment in the pyrochlore slabs, as has already been shown for SCGO [10,18], and also holds for BSZCGO as shown below. The Q dependence of the whole magnetic response, including the elastic part [17], follows a form characteristic of correlations on the length scale of the triangular or tetrahedral local units. Below T_g and down to the mK range a plateau in the T dependence of muon spin relaxation (μSR) rate has been associated with spinon dynamics in a collective singlet ground state [19]. The low-T properties do not comply with standard spin-glass behavior [10].

Motivated by the above considerations we have performed a neutron spin-echo (NSE) examination of the two pyrochlore slab compounds. Using NSE we achieve a direct observation of the spin dynamics in the time domain [20]. Compared to other high-resolution neutron methods [cold neutron time-of-flight (ToF), backscattering], the discrimination of the magnetic signal due to the use of a polarized beam and the extended dynamic range appear as decisive advantages of the spin-echo method. The intrinsic high energy resolution of NSE results in

sensitivity to slow fluctuations on the nanosecond time-scale and complements the work done with NMR and μSR. Using any of these three methods we expect to access the local, i.e. Q-averaged, dynamic susceptibility. The μSR method stands out due to its high sensitivity and the very slow time scales (up to μs) that are accessible. However, questions concerning the spatial averaging of the response of potentially heterogeneous systems [21] need to be addressed. In comparison NSE senses the average dynamics of the complete spin system and provides a quantitative signal with no sample-dependent coupling constants. Indeed, the NSE data obtained in the present work give a totally new vision of the low-T spin dynamics. The first remarkable observation is that in the temperature range encompassing the macroscopic freezing, the relaxation covers the full dynamic range of the instrument, almost 3 orders of magnitude in time, both in terms of its extent in time and its temperature dependence. Secondly, in the SCGO compound we observe a thermally activated relaxation regime in which the activation energy coincides with the energy of a phonon mode, indicating that coupled spin and lattice degrees of freedom play a role.

The NSE experiments were performed on the IN11C spin-echo spectrometer [22] at the Institut Laue-Langevin, operating at a neutron wavelength of 5.5 Å (bandwidth 15%) giving a dynamic range of 5 ps $\lesssim t \lesssim$ 1.5 ns. The sample [23] was cooled down to $T = 1.5$ K in the experiment on SCGO and down to 50 mK in the experiment on BSZCGO. We examined the momentum transfer range $0.7\,\text{Å}^{-1} \leq Q \leq 1.7\,\text{Å}^{-1}$, in order to cover the peak of the magnetic structure factor at $Q \approx 1.5$ Å^{-1} associated with the short-range magnetic correlations [14,24]. The phonon response was examined at $T = 300$ K at $Q > 3$ Å^{-1} where the magnetic signal is weaker and also with Raman spectroscopy in a backscattering geometry (microscope) using a $\lambda = 514.5$ nm beam from an Ar+ laser focused onto a 2 μm spot on the surface of a crystallite. The spectra were collected with a resolution of 2 cm^{-1}. The Rayleigh scattering was eliminated using a foremonochromator.

The NSE signal we observe is essentially the intermediate scattering function $I(Q, t)$, that gives, through a time-frequency Fourier transform, the usual scattering law, $S(Q, \omega)$. The amplitude scales of Fig. 1 are normalized to the powder averaged magnetic scattering without any time (energy) analysis, i.e. $s(0) = \int (k_f/k_i) \times S(Q, \omega) d\Omega_Q d\omega$ where the integration is over the (Q, ω) range accessed in the measurement. Therefore $s(0) \neq \int I(Q, 0) d\Omega_Q = \int S(Q, \omega) d\Omega_Q d\omega$ due to the (k_f/k_i) factor in the cross section and to the energy transfer range limited by the incident energy, $E_i \approx 3$ meV. We get a quantitative estimate for the initial amplitude using polarized neutron diffraction performed in essentially similar conditions with respect to the kinematic range [14,24]. This gives $s(0) \approx 6\ \mu_B^2$/Cr atom in the pyrochlore slab for both systems. This is about 1/3 of the full moment squared $g^2 S(S+1)\mu_B^2 = 15\ \mu_B^2$/Cr atom. In order to quantify the dynamic behavior we have fitted the data using a stretched exponential line-shape, $s(t) = s_i \exp -(t/\tau)^\beta$ which describes well the observed slow decay after an initial rapid decay that happens on the $t <$ ps time-scale. We have used these fits to extract the temperature dependence of the characteristic relaxation time τ, with fixed values of $s_i = 0.6$ and $\beta = 0.2$ for SCGO [25]. In SCGO the slowing down occurs over some 8 orders of magnitude in time, and over only a few degrees in temperature. Because of the small value of the stretching exponent β the major part of the time dependence extends to over 6 orders of magnitude in time. This is depicted in Fig. 2 which shows the scaled time dependence $s(t, T)$ *versus* $t/\tau(T)$. As a function of $t/\tau(T)$ the parts of relaxation observed at various temperatures fall on a unique curve. In the case of BSZCGO the spin-relaxation is visible even at $T = 50$ mK. Best fits were obtained using the stretched exponential with fixed values of $s_i = 0.5$ and $\beta = 0.5$. Here again, the plot using the scaled time, Fig. 2, supports the applicability of the fitting procedure used for quantifying the relaxation rate. The temperature dependence of the characteristic time is weaker than that observed in SCGO. Moreover, there is a clear saturation of the relaxation rate at the lowest temperatures. A continuous

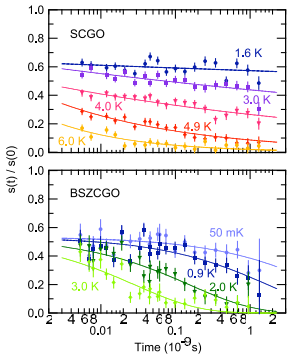

FIG. 1 (color online). The NSE signals for the SCGO and BSZCGO compounds at various temperatures, including the stretched exponential fits; for details see the text.

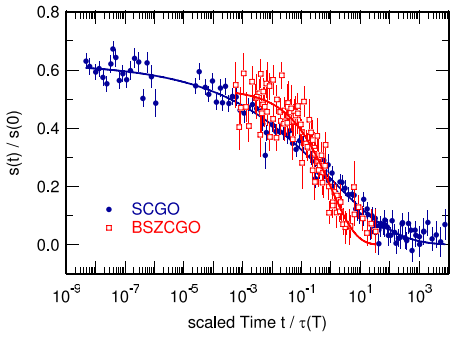

FIG. 2 (color online). The scaled NSE signal for SCGO and BSZCGO, showing the overall agreement with the stretched exponential time dependence over the full range of temperatures. Scaling is by the relaxation time $\tau(T)$ obtained for each temperature in individual fits to the stretched exponential function.

curvature of the log-log plot $\tau(T)$ is seen over the full range examined; see inset of Fig. 3. The main panel of Fig. 3 shows the plot of $T\log\tau$ *versus* T for SCGO and BSZCGO. For SCGO this reveals a well-defined range of thermally activated dependence $\tau = \tau_0 \exp[E_a/(k_B T)]$, $E_a/k_B = 80 \pm 5$ K. Meanwhile the BSZCGO data does not show any such behavior in the range observable by NSE (note that increasing T would push the signal out of the observation window). The activated dependence of the relaxation time suggests that there is a unique energy barrier controlling the relaxation in the SCGO system. We could not find such a signature in the magnetic response at low Q. However, the Raman shift and the higher Q neutron spectrum show a sharp phonon mode at an energy of ~7 meV, shown in Fig. 4, which corresponds to this activation temperature of ~80 K. Accordingly we conclude that the magnetic relaxation could occur via a phonon-assisted mechanism in the thermally activated regime.

Comparing SCGO and BSZCGO, the NSE data show a similar relaxation rate at the macroscopic freezing temperature, $1/\tau(T_g) \approx 10^{10}$ s^{-1}. Well above, $T \geq 3T_g$, the observed higher energy transfer responses of the two systems are very similar [17,18] but the exact details concerning the crossover to the higher-T regime are, due to the limited dynamic range, out of reach with NSE and also difficult to pinpoint with standard ToF techniques due to lower resolution and lack of magnetic selectivity. In spite of these shortcomings we conclude that in the vicinity of T_g ($T \leq 2T_g$) we observe major qualitative and quantitative differences concerning both time and temperature dependence—the most remarkable being this observation of a possible phonon-assisted relaxation in SCGO. A phonon mode at close to the same energy (~7 meV) has also been seen in BSZCGO with Raman spectroscopy but it is not apparent in the measured magnetic relaxation measured by NSE, which is, in any case, a lot faster than in SCGO. It is possible that phonon-assisted relaxation does occur in BSZCGO, but there must be a faster parallel relaxation channel that masks this process. The large difference in the phenomenological stretching parameter, β, also indicates that the relaxation in the two systems is different, but we must keep in mind that for the moment the physical reasons behind the stretching are not resolved. Overall, in spite of the different time scales probed with the two techniques, the NSE observations are somewhat unexpected in view of the μSR results [15] which show no qualitative difference between the two samples and only about 1 order of magnitude difference in the μSR relaxation rate. Here it is also worth pointing out that the quantitative relation between the relaxation as seen by NSE and that observed by μSR is not trivial and has not been worked out in detail for our case.

The quantitative difference observed in the present spin-echo results between SCGO and BSZCGO could stem from bond disorder. This effect is due to the random distribution of Ga^{3+}/Zn^{2+} ions that occupy the nonmagnetic $2d$ sites in the structure of BSZCGO [13,14]. Such atomic disorder can induce static lattice distortions, thus influencing the exchange coupling as well as the lattice dynamics. The effect on the low-energy magnetic properties in BSZCGO is shown by the disorder contribution that persists at the undiluted limit in the static bulk susceptibility [16]. Additionally, the affirmed two-dimensional nature of BSZCGO, compared to the more 3D SCGO, could be the reason for the more dynamic ground-state properties. A common feature between the two compounds is the weaker T dependence of the relaxation below T_g. This we can associate with the quantum regime already evoked by the μSR work. For this regime, in spite of its apparent simplicity (Q dependence ignored) the quantum spin-glass picture [26] provides some interesting features and could be considered as an effective model treating the interactions between spin degrees of freedom generated in the

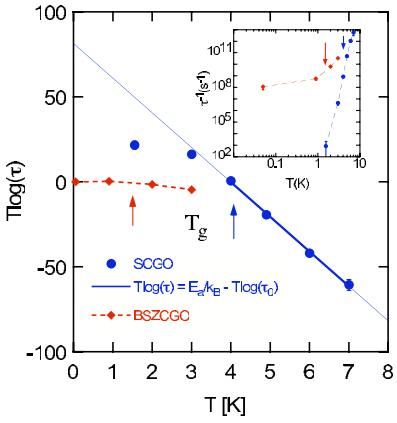

FIG. 3 (color online). The temperature dependence of the NSE determined relaxation rate shown as $T\log\tau$ *versus* T for SCGO and BSZCGO. The arrows indicate the macroscopic freezing temperatures. The solid line is a fit to the SCGO data (for $T \geq 4$ K) with $\tau = \tau_0 \exp[E_a/(kT)]$. The inset shows $1/\tau$ *versus* T on a log-log scale.

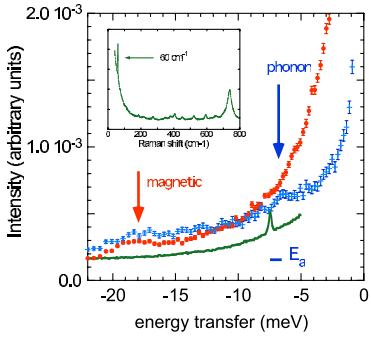

FIG. 4 (color online). Neutron and Raman spectroscopy at room temperature show in SCGO a phonon mode at $\hbar\omega \approx 7$ meV (60 cm^{-1}). The inset shows the full Raman spectrum and the low energy part has been converted and replotted for comparison below the neutron energy gain data (crosses with error bars). The position of the activation energy $E_a = 7 \pm 0.4$ meV is marked. The lower Q-range magnetic scattering data (dots with error bars) show the dimer level at $\hbar\omega \approx 18$ meV [11].

collective singlet by the nonmagnetic dilution. A main ingredient forthcoming from this theoretical treatment is the purely elastic component of the magnetic response, associated with the Edwards-Anderson spin-glass order parameter, identifiable as the long time limit $q_{EA} = s(t \rightarrow \infty)$ of the autocorrelation function we measure using NSE [27]. Assuming that the low-T dynamics are indeed due to the spinon excitations in coherent singlet state [19] fluctuations in the ground state are possible, resulting in a time dependence of the spin autocorrelation function, visible as a slow decay of the order parameter q_{EA}, as observed. Moreover the decrease of T_g and of the "frozen" moment as a function of the dilution x [28] would be due to the effect of dilution by perturbing the coherence of the singlet state [19]. Accordingly the balance of the two competing mechanisms, coherence and spinon generation, controls the stability of the frozen state. The stretching of the relaxation reflects the randomness of the effective interactions mediated by the spinons, providing the main ingredient of the SU(N) Heisenberg spin-glass model and a partial reason for its successful features.

To conclude, we have observed a thermally activated phonon-assisted relaxation regime highlighting the relevance of composite degrees of freedom in the particular case of SCGO. In the closely similar system BSZCGO the spin dynamics is faster and no thermally activated regime appears in the measured time and temperature range. These observations point out the importance of system specific details which become apparent in the lowest energy levels of these highly frustrated magnets. More work is needed to clarify the interplay of spin-lattice coupling and quantum phenomena in these and other frustrated magnets.

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[1] A. Ramirez, in *Handbook of Magnetic Materials*, edited by K. Buschow (Elsevier, Amsterdam, 2001), Vol. 13, p. 423.
[2] *Proceedings of the Highly Frustrated Magnetism 2003 Conference*, edited by J. Stewart, [J. Phys. Condens. Matter 16 (2004)]; these proceedings contain an account of the recent developments.
[3] R. Moessner and A. Ramirez, Phys. Today **59**, No. 2, 24 (2006).
[4] W. Ratcliff II, S.-H. Lee, C. Broholm, S.-W. Cheong, and Q. Huang, Phys. Rev. B **65**, 220406 (2002).
[5] S.-H. Lee, C. Broholm, W. Ratcliff II, G. Gasparovic, Q. Huang, T. H. Kim, and S.-W. Cheong, Nature (London) **418**, 856 (2002).
[6] O. Waldmann, C. Dobe, H. Mutka, A. Furrer, and H.-U. Güdel, Phys. Rev. Lett. **95**, 057202 (2005).
[7] S. Lee, C. Broholm, T. Kim, W. Ratcliff II, and S. Cheong, Phys. Rev. Lett. **84**, 3718 (2000).
[8] A. B. Sushkov, O. Tchernyshyov, W. Ratcliff II, S. Cheong, and H. D. Drew, Phys. Rev. Lett. **94**, 137202 (2005).
[9] X. Obradors, A. Labarta, A. Isalgu, J. Tejada, J. Rodriguez, and M. Pernet, Solid State Commun. **65**, 189 (1988).
[10] S.-H. Lee, C. Broholm, G. Aeppli, A. Ramirez, T. Perring, C. Carlile, M. Adams, T. Jones, and B. Hessen, Europhys. Lett. **35**, 127 (1996).
[11] S.-H. Lee, C. Broholm, G. Aeppli, T. Perring, B. Hessen, and A. Taylor, Phys. Rev. Lett. **76**, 4424 (1996).
[12] L. Limot, P. Mendels, G. Collin, C. Mondelli, B. Ouladdiaf, H. Mutka, N. Blanchard, and M. Mekata, Phys. Rev. B **65**, 144447 (2002).
[13] I. Hagemann, Q. Huang, X. Gao, A. Ramirez, and R. Cava, Phys. Rev. Lett. **86**, 894 (2001).
[14] See P. Bonnet *et al.*, in [2], p. S835.
[15] See D. Bono *et al.*, in [2], p. S817.
[16] D. Bono, P. Mendels, G. Collin, and N. Blanchard, Phys. Rev. Lett. **92**, 217202 (2004).
[17] H. Mutka, P. Bonnet, C. Payen, C. Ritter, M. Danot, and P. Fabritchnyi, Physica B (Amsterdam) **350**, e289 (2004); also (unpublished), work both on SCGO and BSZCGO.
[18] C. Mondelli, H. Mutka, B. Frick, and C. Payen, Physica (Amsterdam) **266B**, 104 (1999).
[19] D. Bono, P. Mendels, G. Collin, N. Blanchard, F. Bert, A. Amato, C. Baines, and A. D. Hillier, Phys. Rev. Lett. **93**, 187201 (2004).
[20] G. Ehlers, J. Phys. Condens. Matter **18**, R231 (2006).
[21] D. MacLaughlin, R. Heffner, O. Bernal, K. Ishida, J. Sonier, M. Nieuwenhuys, G. J. ans Maple, and G. Stewart, J. Phys. Condens. Matter **16**, S4479 (2004).
[22] In an earlier attempt to investigate SCGO with NSE the wide angle version of IN11 was not yet available, and therefore the results were not conclusive; see Y. J. Uemura *et al.*, J. Magn. Magn. Mater. **177**, 701 (1998).
[23] The same samples were used in the NMR and μSR investigations reported earlier [12,16].
[24] C. Mondelli, K. Andersen, H. Mutka, C. Payen, and B. Frick, Physica (Amsterdam) **267–268B**, 139 (1999).
[25] We obtain s_i from the lowest temperature data by extrapolation to $t = 0$. We know from the higher energy range measurements that this quantity does not change in the temperature range examined and therefore we keep it fixed. Note that the initial value of the fit is less than the initial amplitude, $s_i < s(0)$, indicating a rapid initial decay associated with fast spin dynamics in the meV range. The higher temperature data ($T \leq 5$ K) consistently show the same value of β, and finally this is used at all temperatures for a final fit of the relaxation rate.
[26] A. Camjayi and M. J. Rozenberg, Phys. Rev. Lett. **90**, 217202 (2003); Phys. Rev. B **69**, 020404(R) (2004).
[27] A. P. Murani and A. Heidemann, Phys. Rev. Lett. **41**, 1402 (1978).
[28] C. Mondelli, H. Mutka, and C. Payen, Can. J. Phys. **79**, 1401 (2001).