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Spin Liquid State in the Diluted Triangular Lattice $Sc_2Ga_2CuO_7$ Revealed by NMR

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We present microscopic magnetic properties of a two dimensional triangular lattice $Sc_2Ga_2CuO_7$, consisting of single and double triangular Cu planes. An antiferromagnetic (AFM) exchange interaction $J/k_B \approx 35$ K between Cu^{2+} ($S = 1/2$) spins in the triangular bi-plane is obtained from the analysis of intrinsic magnetic susceptibility data. The intrinsic magnetic susceptibility, extracted from ^{71}Ga NMR shift data, displays the presence of AFM short range spin correlations and remains finite down to 50 mK suggesting a non-singlet ground state. The nuclear spin-lattice relaxation rate ($1/T_1$) reveals a slowing down of Cu^{2+} spin fluctuations with decreasing T down to 100 mK. Magnetic specific heat (C_m) and $1/T_1$ exhibit a power law behavior at low temperatures implying gapless nature of the spin excitation spectrum. Absence of long range magnetic ordering down to $\sim J/700$, nonzero spin susceptibility at low T, and power law behavior of C_m and $1/T_1$ suggest a gapless quantum spin liquid state. Our results demonstrate that persistent spin dynamics induced by frustration maintain a quantum-disordered state at $T \to 0$ in this triangular lattice antiferromagnet.

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Collective excitations, frustration, and quantum fluctuations are key ingredients in driving novel ground state properties of correlated electron systems. Geometrically frustrated magnets harbor exotic physical phenomena such as spin glass, quantum spin liquid (QSL), spin ice, and superconductivity[1–5]. The incompatibility of magnetic exchange interactions in achieving minimum energy yields degenerate ground states and the associated strong quantum fluctuations prevent the spin system from undergoing a symmetry breaking phase transition[1,3–9]. The experimental realization of exotic states such as QSL in real materials is an exciting prospect in answering some of the key issues in condensed matter and set an enduring theme following Anderson's resonance valence bond theory[10,11]. The most prominent QSL candidates reported so far are $S = 1/2$ kagomé lattices $ZnCu_3(OH)_6Cl_2$, $Cu_3Zn(OH)_6Cl_2$, $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$, S =1/2 hyperkagomé $PbCuTe_2O_6$, $Na_3Ir_4O_8$, and organic $S = 1/2$ triangular lattice, $EtMe_3Sb[Pd(dmit)_2]_2$, κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, and κ-(ET)$_2$Cu[N(CN)$_2$]Cl. The spin excitation spectra in the QSL state can be gapped or gapless with exotic magnetic properties[4,12–29,32–37]. The frustrated novel quantum magnets are proposed to host emergent fractional excitations in the gapless QSL state, which is reflected as power law behavior in bulk and microscopic observables[1,38–44]. Recently, the observation of intriguing magnetic properties in $Ba_3TSb_2O_9$ (T=Cu, Co, Ni) and 5d iridates has rekindled enormous research activities in quantum materials in the context of novel quantum states[1,2,23,45–51]. Among the frustrated magnets, the edge-shared triangular lattice AFM with $S = 1/2$ offers the simplest archetype for QSL and to test theoretical models in other relatively complex lattices[13,26,28,29]. Furtheremore, the role of site dilution or disorder in stabilizing a QSL state in frustrated quantum magnets has recently been suggested[19,30,31,49].

In view of the vastly evolving field of frustrated magnetism, significant attention has recently been paid to the growth and design of new quantum magnets which could epitomize as model materials for hosting exotic excitations pertinent to novel states and to test theoretical conjectures[1,4,5,9]. In the quest for novel states in frustrated magnets with low spin where inherent quantum effects lead to emergent phenomena, we synthesize and investigate an inorganic $S = 1/2$ antiferromagnet $Sc_2Ga_2CuO_7$ (henceforth SGCO). Recent detailed synchrotron x-ray and neutron diffraction measurements revealed that the magnetic lattice comprises of triangular bi-planes of correlated Cu^{2+} spins diluted by 50 % Ga^{3+} ions and the single triangular plane is mainly occupied by non-magnetic Ga^{3+} ions and 15 % Cu^{2+} in the single triangular plane give rise to a paramagnetic behavior. The bulk magnetic susceptibility at low temperature is dominated by defect contributions and specific heat displays no signature of long range ordering down to 0.35 K, which invokes microscopic investigations[52]. Absence of significant anisotropy and no appreciable spin-orbit coupling suggest that SGCO might be a promising quantum magnet to address low lying excitations intrinsic to the triangular lattice.

The microscopic details pertaining to the magnetic properties inherent to the magnetic lattice at very low temperature is a very crucial step forward for establishing the ground state convincingly and in exploring the nature of low lying excitations. Herein, we report the first nuclear magnetic resonance (NMR) studies on a new $S = 1/2$ inorganic triangular lattice SGCO. NMR being a powerful local probe sheds light on the intrinsic spin susceptibility and the dynamic spin susceptibility via spectra and spin-lattice relaxation rate ($1/T_1$) measurements, respectively, from a microscopic point of view. The intrinsic spin susceptibility suggests the presence of AFM spin correlations with $J/k_B \approx 35$ K between Cu^{2+} spins in the triangular bi-planes and non-singlet state without signature of long range magnetic ordering (LRO) down to 50 mK. The $1/T_1$ data suggest a slowing down of Cu^{2+} spin fluctuations with decreasing temperature down to 100 mK and power law behavior of magnetic specific heat (C_m) and $1/T_1$ imply gapless spin excitations. Our comprehensive results establish a gapless quantum spin liquid state in SGCO.

Polycrystalline sample of $Sc_2Ga_2CuO_7$ was prepared by a method described elsewhere[52]. SGCO crystallizes in a hexagonal structure with a space group $P6_3/mmc$ and lattice constants $a = b = 3.30479(4)$ Å and $c = 28.1298(4)$Å . The magnetic structure comprises of alternating single and double triangular planes. The interaction between the Cu^{2+} spins is confined to the 2D triangular bi-plane only, with negligible interlayer interactions[52].

Shown in Fig. 1(a) is the temperature dependence of bulk magnetic susceptibility $\chi_{\rm obs}$, which is found to be strongly enhanced at low temperatures without exhibiting any signature of long range magnetic ordering (LRO) down to 1.8 K. We did not observe ZFC and FC splitting in $\chi_{\rm obs}$ and no hysteresis was found in magnetization[52]. The green dotted line in Fig. 1(a) shows the magnetic susceptibility $\chi_{\rm sub}$ after subtracting from $\chi_{\rm obs}$ a contribution due to the presence of 15% Cu spins on the triangular plane assuming a simple Curie behavior of $S = 1/2$ for the Cu spins. The Curie-Weiss (CW) fit of $\chi_{\rm sub}$ at high temperatures above 100 K yields a CW temperature $\theta_{\rm CW} = -44$ K, an effective magnetic moment (μ_{eff}) of 1.83 $\mu_{\rm B,}$ and $g \approx 2$. The negative value of $\theta_{\rm CW}$ indicates the presence of AFM interaction between Cu^{2+} spins on the triangular bi-plane. The T-dependence of magnetic specific heat (as shown in Fig. 1(b)) in different magnetic fields don't display any sign of LRO. The magnetic specific heat (C_m) exhibits a power law ($\sim T^{1.9}$) behavior indicating a non-singlet state[1,23,39–45,52,53].

Figure 2(a) shows the typical temperature evolution of field swept ^{71}Ga NMR spectra of SGCO at a frequency $\nu = 69.5$ MHz. With decreasing T, although the ^{71}Ga NMR spectra broaden, NMR shift ^{71}K for the main line shows a broad maximum around 70 K, which is a characteristic feature of low dimensional AFM spin systems due to short range spin correlations. Below the broad maximum, ^{71}K decreases and levels off at low T and then remains nearly constant down to 50 mK. The frustration parameter (f) is considered to be a measure of the depth of the spin liquid regime and is defined as $f = \mid \theta_{CW} \mid /T_N$. In the present case we did not observe magnetic ordering down to 50 mK, so $f \;\; \geq\mid \theta_{CW} \mid/50$ mK ~ 900[1,55]. This suggests the presence of strong magnetic frustration inspite of the large site inversion. The frustration between Cu^{2+} spins residing in the 2D triangular bi-planes of SGCO might offer a route for the persistent spin dynamics of Cu^{2+} spins down to 50 mK and these fluctuating spins preclude LRO. In addtion to the main ^{71}Ga NMR line, we have observed a weak line (labeled as Ga(II) in Fig. 2(a)) whose NMR shift $K_{\rm II}$ shows a CW behavior as shown in Fig. 2(b). Since the estimated signal internsity of the Ga(II) line is 19 % of the total ^{71}Ga NMR intensity, which is in good agreement with an expected signal intensity of which 20 % Ga ions touching one Cu ion in the nearest neighbor of the single layer, the Ga(II) signal can be ascribed to Ga ions in single layers. The main Ga(I) line (Fig. 2(a)) is attributed to Ga ions in the triangular bi-plane. We were not able to detect Ga(II) line and hence $K_{\rm II}$ at temperatures below 100 K due to inhomogeneous broadening of the spectra perhaps because of Cu^{2+} spins in the single triangular planes.

The NMR shift consists of T dependent spin shift $K_{\rm spin}(T)$ and T independent orbital (chemical) shift $K_{\rm chem}$; $K(T) = K_{\rm spin}(T) + K_{\rm chem}$, where $K_{\rm spin}(T)$ is proportional to the spin part of magnetic susceptibility $\chi_{\rm spin}(T)$ via hyperfine coupling constant $A_{\rm hf}$, $K_{\rm spin}(T) = A_{\rm hf}\chi_{\rm spin}(T)/N_{\rm A}$. Here $N_{\rm A}$ is Avogadro's number. The hyperfine coupling constant is estimated to be $A_{\rm hf} = -3.8 \pm 0.2$ kOe/$\mu_{\rm B}$ for the main Ga(I) line from the slope of the so-called K-χ plots using $\chi_{\rm sub}$ data at $T \geq 150$ K. $K_{\rm chem}$ values are estimated to be 0.049 % for the main Ga(I) line. The T-dependence of the intrinsic magnetic susceptibility $\chi_{\rm int}$ obtained from $K_{\rm spin}$ data for the main line is shown by solid spheres in Fig. 1(a). The $\chi_{\rm int}$ shows a broad maximum around ~ 70 K and decreases at low temperatures, but does not approach zero. The nonzero value of $\chi_{\rm int}$ at low T (~ 40 % of the maximum value) is strong evidence of the absence of spin gap in SGCO. Similar behavior of $\chi_{\rm int}$ is reported in the well known spin liquid material $ZnCu_3(OH)_6Cl_2$[16,17].

The T dependence of $\chi_{\rm int}$ above ~ 30 K is reasonably reproduced by the high temperature series expansion (HTSE) of an $S = 1/2$ triangular lattice Heisenberg model[56,57] as shown in Fig. 1(a) by the red line where the (4,7) Padé approximant is adapted with an effective exchange coupling between Cu^{2+} spins with $J/k_{\rm B} = (35 \pm 3)$ K (see Supplemental Material[53]). The good fit indicates that, although more than 50% of Cu^{2+} ions in the triangular bi-planes are diluted, the intra-plane magnetic interaction is still maintained. It should be noted that $\chi_{\rm int}$ does not coincide with $\chi_{\rm sub}$ at low T. This indicates that the large enhancements of $\chi_{\rm obs}$ at low T cannot be explained only by the ~ 15 % Cu^{2+} spins due to the antisite effects. The exact origin for the difference between $\chi_{\rm obs}$ and χ_{int} is not clear at present but could be associated with the site inversion between Cu and Ga sites in the system[52]. As shown in Fig. 2(c), the full width at half maximum (FWHM = ΔH) of the NMR spectrum for the main line increases with decreasing T and saturates below 2 K. The T-independent ΔH below 2 K is found to be independent of the applied magnetic field indicating both H and T-independent internal field at ^{71}Ga sites. These results suggest that Cu^{2+} spins fluctuate slowly *i.e.*, at less than the NMR frequency (~ 50 MHz) at low

T. From the saturated ΔH value at low T, we estimated the Cu magnetic moments of magnitude 0.19 μ_B, which is quite small compared to the total magnetic moment expected for $S = 1/2$. The ^{45}Sc NMR spectra, shift and ΔH also exhibit a similar T-dependence with those of ^{71}Ga NMR results.

Figure 3 (a) depicts the T dependence of spin-lattice relaxation rates $1/T_1$ of ^{71}Ga, together with that of ^{45}Sc. $1/T_1$ is almost independent of T above 100 K and starts to decrease at low T and then levels off below $\sim$ 10 K down to 2 K. With further decreasing T, as shown in Fig. 3(a), independent of probing nuclei, $1/T_1$ decreases and displays a power law behavior *i.e.*, $1/T_1 \sim T^{3.2}$ down to 100 mK. $1/T_1$ is almost independent of magnetic field above 2 K, but is suppressed strongly with magnetic fields at low T as shown in the Fig. 3(a).

A simple scenario for the decrease in $1/T_1$ due to suppression of magnetic fluctuations of isolated paramagnetic spins at high field and low T cannot be attributed for the observed behavior. For the simple paramagnetic spin fluctuations of isolated spins, $1/T_1$ is known to be proportional to the first derivative of the Brillouin function, $dB_s(x)/dx$ (x=$g\mu_B SH/k_B T$) which gives an exponential behavior of $1/T_1$ in T following exp(-$g\mu_B H/k_B T$) function, in contrast to the power law behavior in the observed $1/T_1$. As shown in Fig. 3(a), the exponent of the power law in $1/T_1$ is almost independent of magnetic fields implying the intrinsic and robust nature of the ground state properties. It is worth mentioning here that the power law dependence of spin-lattice relaxation rate $1/T_1 \sim T^{\eta}$ has been discussed in the context of Dirac Fermion model in interpreting QSL[29,40,58]. $1/T_1 \sim T^{1.5}$ behavior in the $S = 1/2$ triangular lattice κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ has been reconciled in the framework of Z_2 spin liquid (SL) with quantum critical spin excitations[26,29,39,41,59–61]. Recently, another plausible theoretical conjecture in interpreting the role of randomness in driving a gapless SL state of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ is proposed[30,64]. However, a general consensus in interpreting the T dependence of $1/T_1$ in the SL materials is still lacking and little progress has been made in evolving a more generic and comprehensive framework. This is due to the unavailability of many model SL materials and experimental challenges in interpreting the implications of various subtle theoretical scenarios[1,26,30]. Furthermore, one would expect a T- independent behavior of $1/T_1T$ in the case of a spin liquid with a spinon Fermi surface and $1/T_1T$ should drop exponentially in the case of gapped SL[1,4,39,59–61,65]. Our results are not in accord with the above cited two scenarios but could be associated with the interpretation of not a fully gapless SL where at least some part of the q-space is gapped[28,64]. In view of the power law behavior of magnetic specific heat and $1/T_1$, a detailed theoretical investigation call for in interepreting these results in the context of emergent excitations in the gapless QSL, which is beyond the scope of the present study, but renders a direction for further explorations[38–44].

Finally, it is important to point out that our T_1 data indicate a slowing down of Cu^{2+} spin fluctuations at low temperature. $1/T_1$ is generally expressed by the Fourier transform of the time correlation function of the transverse component $\delta h_{\pm}$ of the fluctuating local field at nuclear sites with respect to the nuclear Larmor frequency ω_N as[66,67] $\frac{1}{T_1} = \frac{\gamma_N^2}{2}\int_{-\infty}^{+\infty}\langle\, h_{\pm}(t)h_{\pm}(0)\,\rangle e^{i\omega_N t}dt$, where γ_N is the gyromagnetic ratio of the nuclear spin. When the time correlation function is assumed to decay as $e^{-\Gamma t}$, one can write $\frac{1}{T_1T\chi} = A\frac{\Gamma}{\Gamma^2+\omega_N^2}$ (eq.1) where A is a parameter related to the hyperfine field at nuclear sites and χ is the magnetic susceptibility. In our case, Γ would correspond to the inverse of the correlation time of the fluctuating hyperfine fields at the Ga or Sc sites, due to the Cu^{2+} spins. When Γ is much higher than ω_N, one finds that the $\frac{1}{T_1T\chi}$ is proportional to $1/\Gamma$. On the other hand, if $\Gamma \ll \omega_N$, $\frac{1}{T_1T\chi}$ should depend on the magnetic field. When $\Gamma = \omega_N$, $\frac{1}{T_1T\chi}$ reaches a maximum value. Thus, the slowing down of the fluctuation frequency Γ of Cu^{2+} spins yields a peak in $\frac{1}{T_1T\chi}$. Figure 3(b) represents the temperature dependence of $\frac{1}{T_1T\chi}$, where the χ values are used for corresponding $K_{\rm spin}$ for each nucleus. When Γ is independent of T, $1/T_1TK_{\rm spin}$ should be constant, which is indeed observed above 50 K. This indicates $1/T_1$ above 50 K is explained by the paramagnetic fluctuations of the Cu^{2+} spins, whereby the Cu spins fluctuate almost independently. Below 50 K, the $1/T_1TK_{\rm spin}$ starts to increase and shows H dependent peaks at low T below 2 K. This can be explained by the slowing down in fluctuation frequency of spins at low T. These results indicate that the peak observed in $1/T_1TK_{\rm spin}$ originates from the slowing down (but not critical) of fluctuation frequency of Cu^{2+} spins, whereby the fluctuation frequency below the peak temperature is less than the NMR frequency range ($\sim$10 - 100 MHz). To derive the T dependence of the fluctuation frequency of Cu^{2+} spins in a wide temperature range, we extract the T-dependence of Γ from the T-dependence of $1/T_1TK_{\rm spin}$, assuming eq. (1) is valid for all temperature regimes. The estimated T dependences of Γ for the different magnetic fields are shown in Fig. 4, together with the data estimated from ^{45}Sc-T_1. Γ shows $T^{2.2}$ behavior at low T and is almost a constant with $\Gamma \sim 3\times10^9$ Hz at high T. At low T below $\sim$ 1 K, Cu^{2+} spins fluctuate with low frequency. Such a slow spin dynamics is consistent with the observed broadening of the NMR spectra below $\sim$2 K. The absence of critical slowing down and no loss of NMR signal intensity rule out the possibility of spin glass phase down to 50 mK in SGCO. This is further substantiated by the absence of critical divergence of $1/T_1$ or cusp structure in $1/T_1$ generally expected in spin frozen state[30].

In summary, the intrinsic spin susceptibility ($\chi_{\rm int}$) obtained from NMR does not vanish and remains finite at T = 50 mK, reflecting a non-singlet ground state in Sc$_2$Ga$_2$CuO$_7$. The T-dependence of $\chi_{\rm int}$ is well reproduced by the HTSE of the $S = 1/2$ Heisenberg model, indicating that the 2D magnetic interactions between Cu^{2+} spins in the bi-plane are still maintained although more than 50% spins are diluted. Quantum fluctuations enhanced by strong frustration between Cu^{2+} spins in the 2D triangular bi-plane suppress the LRO down to 50 mK despite an AFM exchange interaction $J/k_B \approx 35$ K. The spin-lattice relaxation rate exhibits a slowing down of Cu^{2+} spin fluctuations and short range spin correlations at low T. The power law behavior of C_m and $1/T_1$ with decreasing temperature down to 100 mK infer gapless excitations consistent with $\chi_{\rm int}$ and suggest a quantum spin liquid state. The effect of site dilution, defect, and disorder in frustrated quantum magnets have been discussed in the context of exotic magnetism such as spin liquids recently[19,30,31,64]. The absence of spin freezing and no spin gap down to 50 mK suggest that the low energy excitations might be mediated by deconfined spinons, which is generic to a gapless QSL state in frustrated quantum magnets. This point towards the generic nature of deconfined spinons in QSL state in case of the randomness induced by disorder due to Cu/Ga site inversion and frustration in achieving electron localization[68]. In this context SGCO offers a fertile ground for exploring the effect of dilution or disorder, and the role of control parameters in tuning novel states in frustrated quantum magnets.

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Figure Captions:

Fig. 1 (Color online) (a) Temperature dependence of the observed magnetic susceptibility $\chi_{\rm obs}$ (solid line) at 7 T and the subtracted magnetic susceptibility $\chi_{\rm sub}$ (dotted line) after subtraction of 15 % Cu spin contributions due to the site inversion as discussed in the text. The solid spheres depict the intrinsic magnetic susceptibility $\chi_{\rm int}$ estimated from ^{71}Ga-NMR shift. The red solid line is a fit as discussed in the text. (b) The inset shows the T-dependence of magnetic specific heat (C_m) in different magnetic fields and the solid line depicts the power law ($\sim T^{1.9}$) behavior.

Fig. 2 (Color online) (a) Temperature evolution of field swept ^{71}Ga NMR spectra at 69.5 MHz. The vertical broken line corresponds to zero-shift ($^{71}K = 0$) position. (b) T dependence of both ^{71}K for main and Ga(II) lines. (c) T dependence of NMR line width (ΔH) at 69.5 MHz and 24.25 MHz.

Fig. 3 (a) (Color online) Temperature dependence of ^{71}Ga and ^{45}Sc $1/T_1$ at different frequencies. The solid line represents $T^{3.2}$ behavior (b) T dependence of $1/T_1TK_{\rm spin}$ ($1/T_1$ divided by temperature and respective spin susceptibilities $|^{45}K|$ and $|^{71}K|$).

Fig. 4 (Color online) Temperature dependence of Γ estimated from ^{71}Ga and ^{45}Sc $1/T_1$ as explained in the text. The solid line is the $T^{2.2}$ behavior.

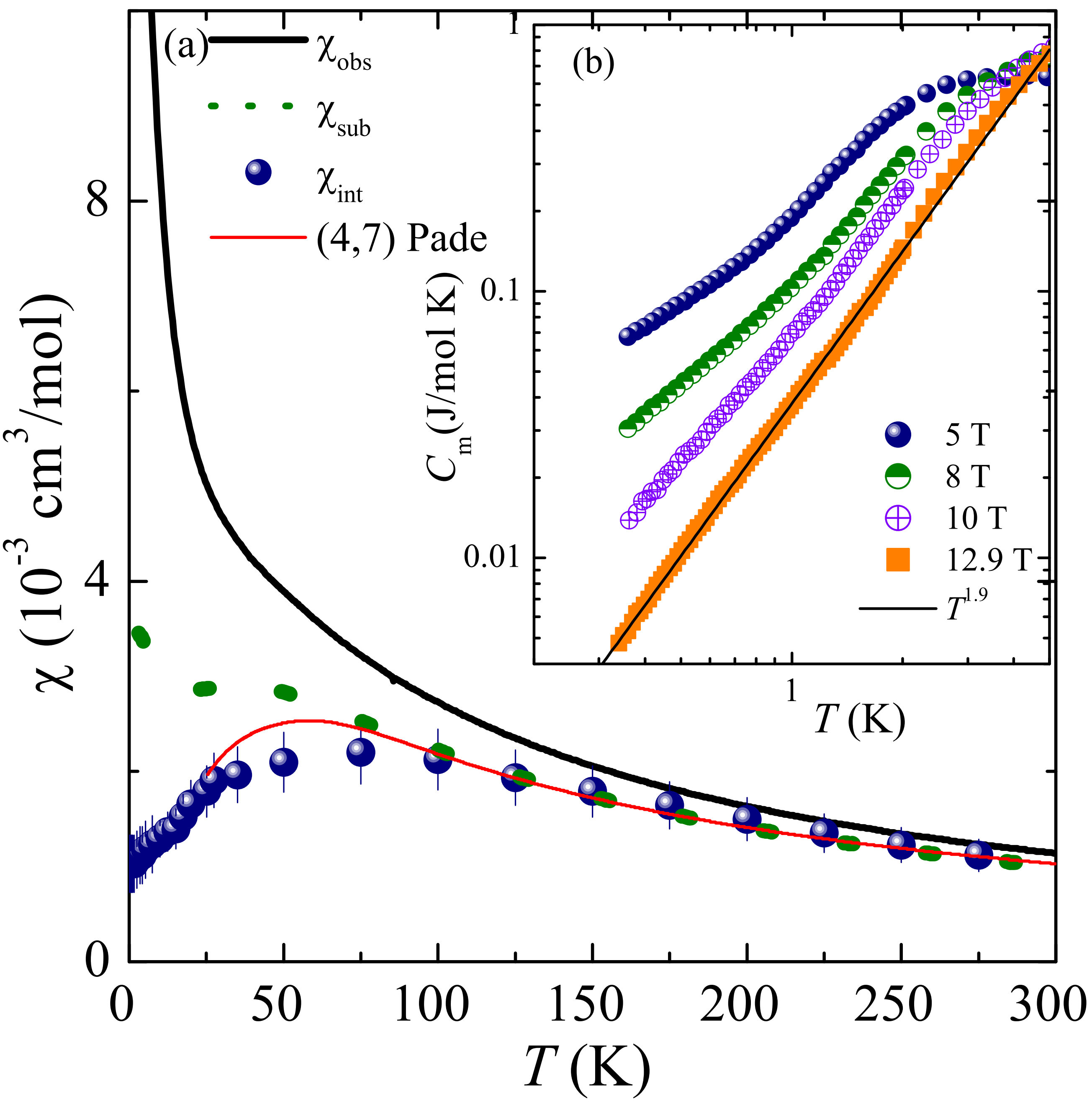

Figure 1 28Mar2016

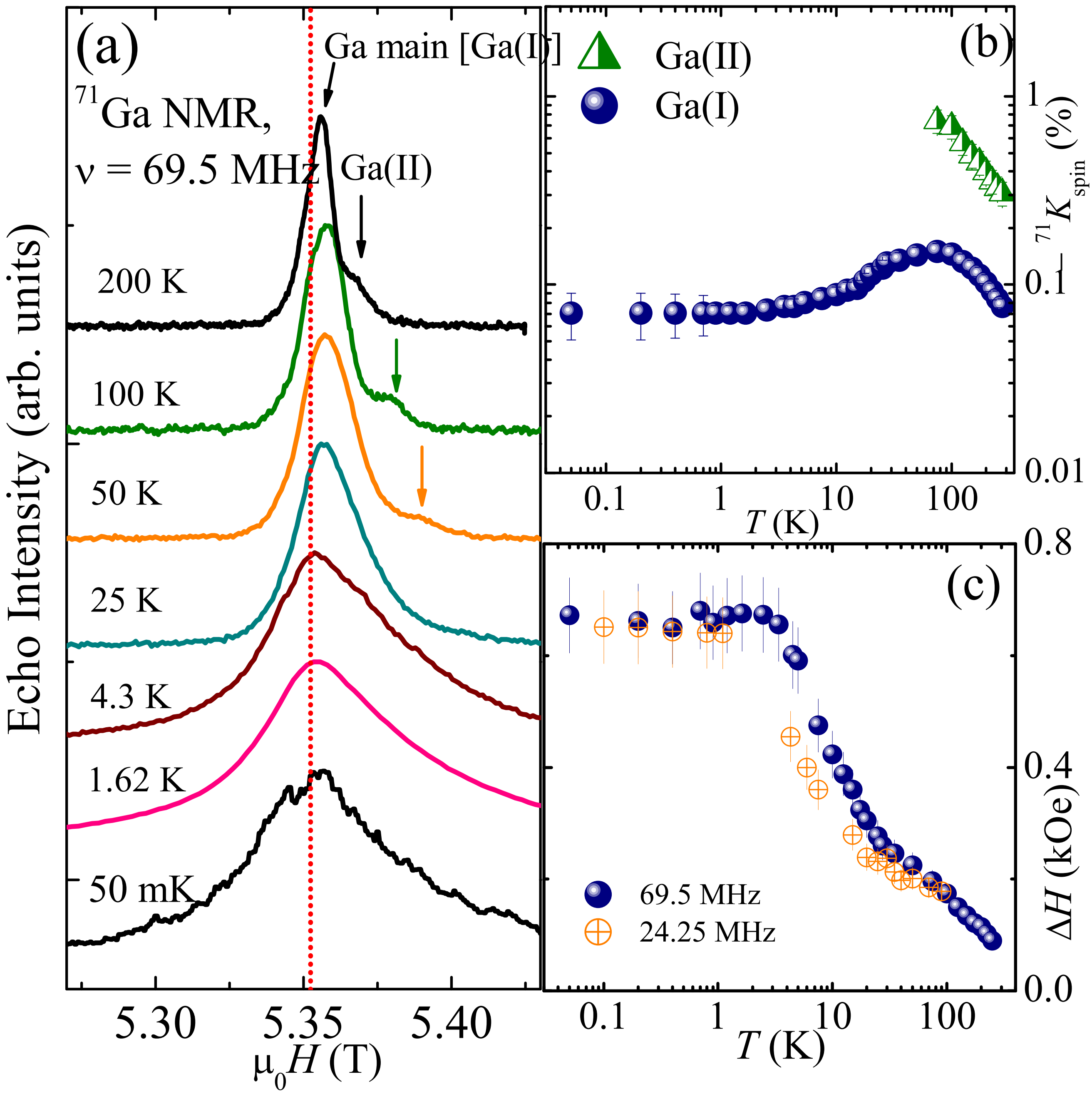

Figure 2 28Mar2016

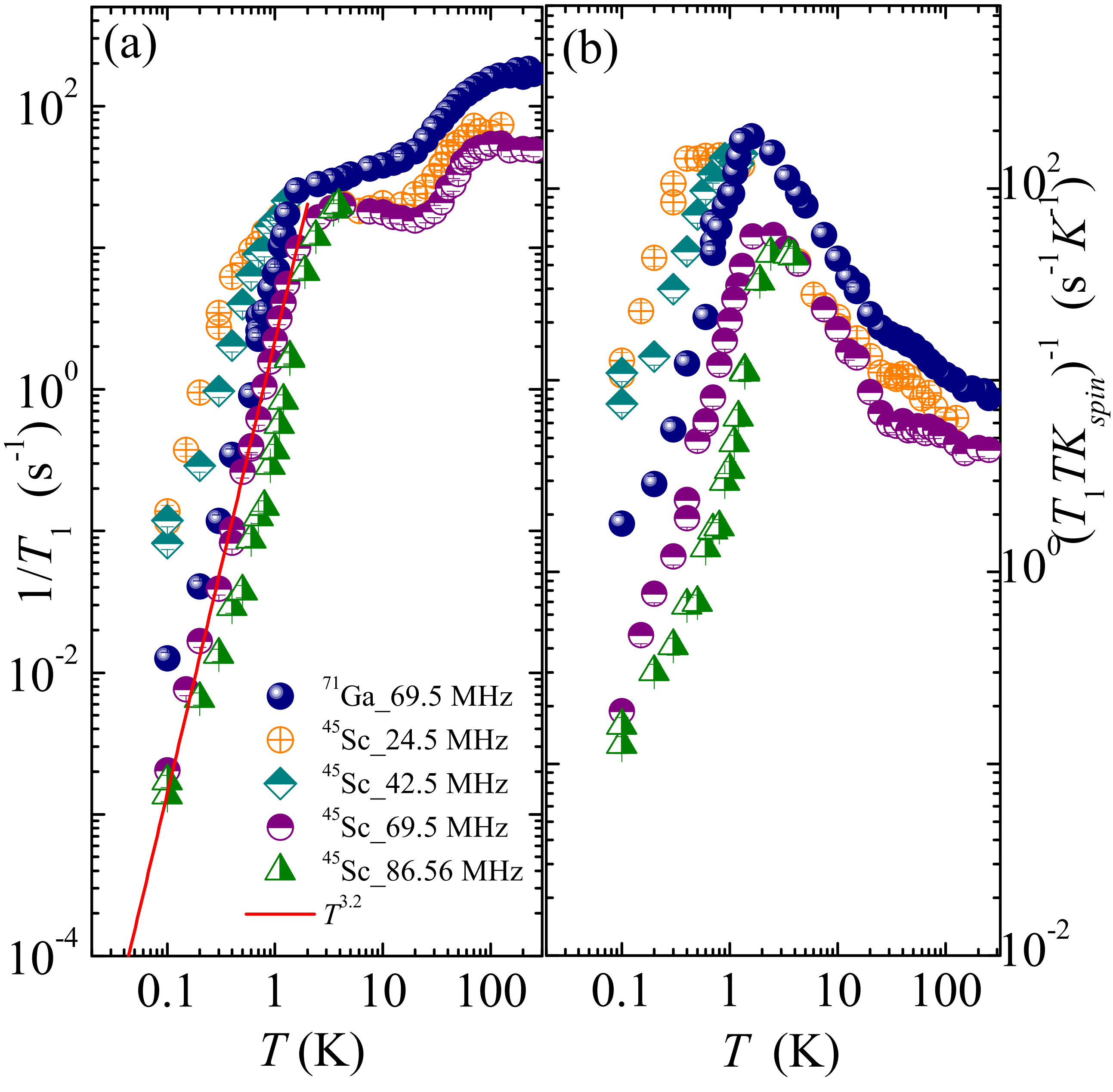

Figure 3 28Mar2016

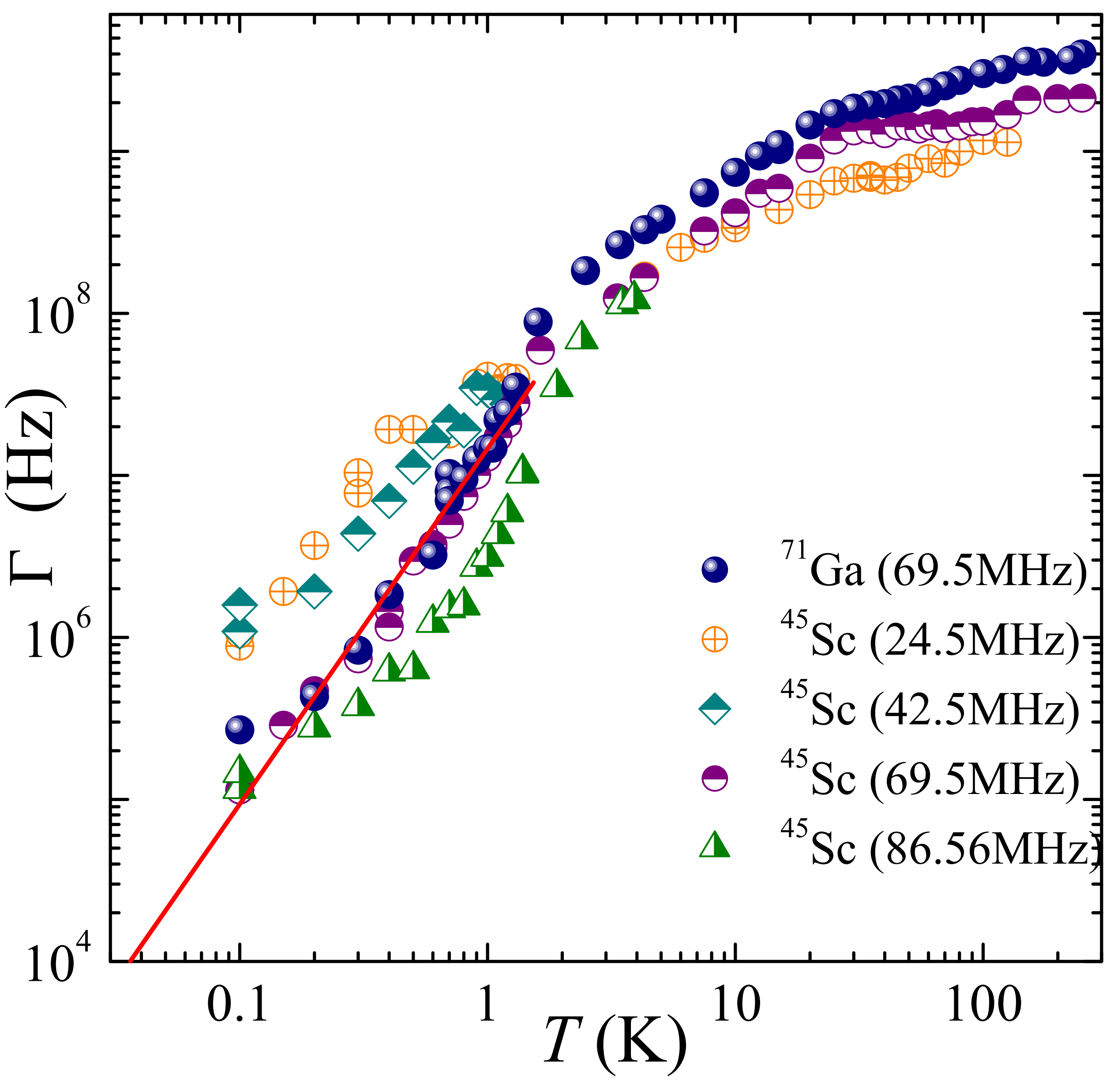

Figure 4 28Mar2016