

**Disorder effects in the quantum kagome antiferromagnet  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$** M. J. Rozenberg<sup>1</sup> and R. Chitra<sup>2</sup><sup>1</sup>*Laboratoire de Physique des Solides, CNRS-UMR8502, Université de Paris-Sud, Orsay 91405, France*  
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Motivated by the recent NMR experiments on  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ , we study the effect of nonmagnetic defects on the antiferromagnetic spin- $\frac{1}{2}$  kagome lattice. We use exact diagonalization methods to study the effect of two such defects on finite-size systems. Our results, obtained without adjustable parameters, are in good quantitative agreement with recent  $^{17}\text{O}$  NMR data. They provide support for the experimental interpretation of the presence of defects within the kagome layers due to Zn/Cu substitutions. Our results also show that disorder effects become relevant at lower temperatures, raising questions about the experimental evidence for the absence of an intrinsic spin gap in the kagome two-dimensional layers.

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The quest for spin liquids in frustrated quantum magnets remains one of the main challenges in condensed-matter physics. Spin liquids are quantum spin systems where quantum fluctuations thwart any kind of ordering of the spins even in the limit of  $T \rightarrow 0$ . Typical criteria for a candidate system include: a high degree of frustration, low dimensionality, and small spin. All three features are realized in the spin- $\frac{1}{2}$  Heisenberg antiferromagnet on a kagome lattice, which is a two-dimensional (2D) network of corner sharing triangles. In this context, the recent discovery of the compound herbertsmithite,  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ ,<sup>1,2</sup> presumed to be a perfect physical realization of such a model, has triggered a spate of experimental studies devoted to unveiling the intrinsic behavior of the kagome antiferromagnet. A host of experimental techniques, including neutron scattering,<sup>3</sup> NMR (Refs. 5 and 6), and  $\mu\text{SR}$  (Ref. 4) have already been used to study the magnetic behavior of this compound. However, comparisons of experimental and theoretical results are hampered by the fact that not much is known about the kagome system except that the ground state is a singlet, the spectrum is characterized by a macroscopic quasidegeneracy of low lying singlet states, a very short correlation length, and possibly a small gap to a macroscopic number of quasidegenerate triplet excitations.<sup>7,8</sup>

Surprisingly, the plethora of experimental data obtained shows that magnetic degrees of freedom remain active at low frequencies and temperatures and these do not conform to the naive picture of a gapped system. This has generated a debate as to whether the experimental systems are pure enough to reveal intrinsic kagome behavior, or, alternatively, whether additional interactions that go beyond simple nearest-neighbor antiferromagnetic coupling should be included. From a chemical perspective, the most delicate aspect is the control over the positions that the Cu and Zn atoms occupy. The former are magnetic and should be ideally confined to the two-dimensional (2D) kagome planes, while the latter, nonmagnetic, should occupy interlayer sites that effectively decouple the planes. For each exchange of these atoms, two defects are created: (i) the Cu that occupies

the Zn site at the interlayer remains rather weakly coupled and contributes an effective “free” spin- $\frac{1}{2}$  term to the bulk susceptibility, and (ii) the Zn that occupies a Cu site in a layer creates a nonmagnetic defect within the kagome plane which will likely modify the intrinsic kagome behavior.

On the theoretical front, different ideas were proposed to account for the unexpected observations; in Ref. 9 it was shown that the inclusion of Dyazolinshki-Moriya (DM) interactions may enhance the uniform susceptibility at intermediate temperatures. On the other hand, other studies have shown that magnetic defects may also account for several experimental observations including the uniform susceptibility, the specific heat,<sup>10</sup> and the dynamical susceptibility.<sup>11</sup>

To elucidate this situation, a rather powerful experimental technique is the NMR using oxygen isotopes. The oxygen atoms only occupy sites within the 2D planes and since the hyperfine coupling is very short ranged, oxygen NMR probes the physics of the plane and is insensitive to the spin- $\frac{1}{2}$  magnetic contributions from misplaced Cu that occupy interlayer sites. Moreover, NMR probes both static and dynamic behaviors. This decisive experiment was recently performed by Olariu *et al.*<sup>12</sup> The main results reported were (i) the existence of nonmagnetic defects within the 2D layers and (ii) the apparent absence of a spin gap. To comprehend the effect of defects, here we study a spin- $\frac{1}{2}$  antiferromagnetic kagome lattice model with nonmagnetic impurities and obtain the theoretical predictions for the temperature dependence of the NMR spectra and the nuclear spin-relaxation rate  $1/T_1$ . The quantitative agreement between our results and the experimental data unambiguously demonstrates the existence and importance of nonmagnetic defects within the kagome layers of the herbertsmithite. However, we also find that the disorder due to these defects produces a smearing of the NMR line that is most significant at low temperatures, raising questions about the experimental evidence for the absence of a spin gap in the *intrinsic* kagome lattice system.

The pure Hamiltonian is given by the Heisenberg model on the kagome lattice,

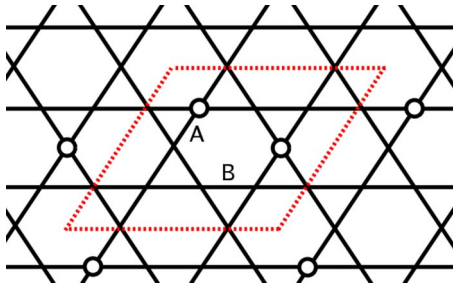


FIG. 1. (Color online) Schematic of the 12 site kagome lattice with two nonmagnetic defects. The bond A denotes a bond with a single spin and bond B denotes a bond with two spins. For a given configuration of defects, there are many inequivalent A and B bonds.

$$\mathcal{H} = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where  $\mathbf{S}$  represent the spin- $\frac{1}{2}$  operators and  $J$  the antiferromagnetic interactions between two nearest-neighbor spins. Nonmagnetic defects are introduced by eliminating a spin operator at a given site. This model is not very amenable to analytic studies and is usually studied using numerical methods.<sup>7</sup> Here, due to the defects, we cannot take advantage of the symmetries of the pure lattice and moreover, as we are interested in the full temperature dependence, we employ exact diagonalization. We therefore consider a finite-size system of 12 sites as the one schematically depicted in Fig. 1 with periodic boundary conditions. Note that the 12 site cluster (in the pure case) preserves all the original symmetries of the full lattice. In addition, since the magnetic correlation length in the pure system is extremely short, of the order of one lattice spacing,<sup>14</sup> we expect that the 12 site cluster calculation may be adequate for the specific issues addressed in the present study.<sup>15</sup>

We now study the effect of defects in the 12 site cluster. We do not consider the case of a single defect, since this would induce local moments which would then contribute a Curie-like term to the shift. No such contribution has been seen in the  $^{17}\text{O}$  NMR study of Ref. 12 which probes only the magnetic response in the kagome layers. In contrast, a free spin- $\frac{1}{2}$  contribution was in fact seen in a previous NMR study,<sup>6</sup> using Cu and Cl, which probed both in and out of the layer magnetic sites. Thus, the Curie-like contribution should be attributed to an interlayer Zn/Cu substitution. In what follows, we consider all possible configurations of two nonmagnetic defects. Figure 1 shows an example of one such configuration. Two impurities in the twelve site cluster correspond to a defect concentration of 16% which is larger than the experimental estimate of 6%–10%. However, due to the very short correlation length in the pure Kagome system, we expect our results to remain valid for a relatively large range of impurity concentrations, including the experimental estimate.

The specificity of the  $^{17}\text{O}$  NMR stems from the structure of  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ , where oxygen is confined to the kagome planes. In a perfectly pure structure, each oxygen atom would have two equivalent magnetic Cu(2+) neighbors that

are also located within the 2D kagome layer, and with whom it interacts via the hyperfine coupling. In an NMR experiment, a strong magnetic field is applied producing a local magnetization of the Cu ions. This magnetization modifies the strength of the hyperfine coupling with the nuclear moment, producing a shift in the nuclear-magnetic-resonance line. Thus, the shift in the oxygen line is a direct measure of the individual magnetizations and hence of the spin susceptibility of the neighboring Cu sites (more precisely of the combined effect of the two neighbors). Knowledge of the local fields then gives us information about the existence of any underlying spin order. For example, if two neighboring spin sites were strongly antiferromagnetically correlated they would produce no net shift to the central oxygen line. In a pure system, since all oxygen sites are equivalent, the NMR spectra should have a single well defined peak with a temperature dependent shift. However, if nonmagnetic defects are present, then the oxygen ions may encounter two types of magnetic environments: one comprising two nearest-neighbor Cu, and the other with only one Cu. (The case of two nonmagnetic neighbors would produce no NMR shift.) This would then be directly reflected in the NMR spectra as a superposition of two peaks, each one related to the respective contribution arising from the two kinds of magnetic environments that an oxygen moment may see.

We now present our theoretical predictions for the NMR. The only parameter in our model is the magnitude of the antiferromagnetic coupling  $J$ , which we set to the experimentally estimated value  $\sim 170$  K. The longitudinal magnetic field in our work  $H=0.05$  J is of similar magnitude to the value of 7 T used in Ref. 12. To obtain the shifts, we first compute the finite temperature magnetization at every site  $m_i$ . The magnetic shifts  $K_{ij}$  at the “oxygen sites” (which in the physical structure are equidistant to two neighboring vertex of the kagome lattice) are then estimated as the sum of the two contributions  $m_i$  and  $m_j$  of the induced moments at the two sites  $i$  and  $j$  of each bond of the lattice. The defect free two-spin bonds, such as bond B, depicted in Fig. 1 have in fact two contributions; however, the one-spin bonds, such as bond A, have a contribution from a sole magnetic moment  $m_i$ . Note that for any given configuration of defects, since the translational symmetry is broken, there are many inequivalent one-spin bonds and two-spin bonds. The 24 shifts  $K_{ij}$  for each of the four nonequivalent two-defect configurations are computed, and the data at each temperature are condensed into a histogram for the distribution of the magnitudes of the  $K_{ij}$ s. These histograms can be directly compared to the NMR spectra obtained at different temperatures.<sup>16</sup>

Figure 2 summarizes our results for the predicted NMR spectra as a function of temperature. In a pure, defect free system, all sites would be equivalent and the histograms would simply show a single sharp peak, whose position depends on the temperature. Since the shift is proportional to the local magnetizations due to the external field, its magnitude is directly proportional to the uniform susceptibility. However, when defects are introduced, translational invariance is broken and a distribution of local magnetic moments is induced, which results in the histograms of Fig. 2. The main features that emerge from the data are the presence of two prominent “ridges” that can be inferred from the tem-

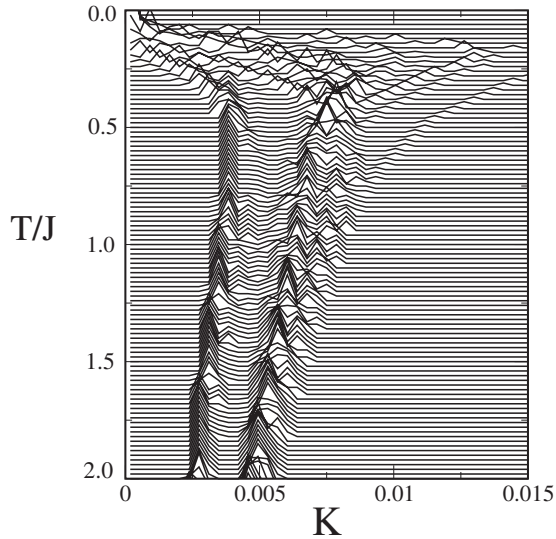


FIG. 2. Histograms for the values of the sum of the local magnetization of the spins on each lattice bond. The magnetizations are proportional to the shifts of NMR. The histograms correspond to the theoretical estimate for the NMR spectra.

perature dependence of the histograms. There is a clear manifestation of the presence of two types of magnetic environments: some bonds have two spins (i.e., no defect), while others have only one spin (and one defect). The position, or shift, of the rightmost ridge is larger by a factor of 2 compared to the other one. In fact, the former originates from contributions of bonds with two spins while the latter from that of bonds with one spin and one defect. At high temperatures, as the spins are effectively decoupled, this scaling feature is intuitively expected. However, the fact that this scaling remains valid well below  $T/J \sim 1$  is a nontrivial signature of strong frustration and an extremely short correlation length, which are to be expected in a spin fluid state. Significantly, this behavior is in very good agreement with the experimental  $^{17}\text{O}$  NMR data.<sup>12</sup>

In order to visualize the results under a different light, we redisplay the temperature dependent histograms as an intensity plot in Fig. 3. For reference, we also show in the inset the calculated data for the uniform spin susceptibility  $\chi(T)$  for the pure system with no defects. At higher temperatures,  $\chi$  shows the Curie tail, while at low  $T$  it shows an exponentially activated behavior due to the presence of a gap in the energy spectrum. The main panel shows that the maximum intensity line shapes of the two ridges roughly follow the behavior of  $\chi(T)$ . However, in contrast to the  $\chi(T)$  of the pure system, the  $T$  dependence of both line shapes becomes flat between 70 and 100 K where they attain their respective maximum values. Significantly, a similar flattening in the same temperature regime around  $T \approx 0.5$  J was experimentally observed in Ref. 12.

Another interesting feature that our results of Figs. 2 and 3 show, is the dramatic smearing of the peaks in the histogram at low temperatures. Nevertheless, below  $T \approx 50$  K ( $\approx 0.3$  J) one observes that while the lower ridge remains relatively well defined, the upper one shows a substantial dispersion. This behavior can be qualitatively interpreted as

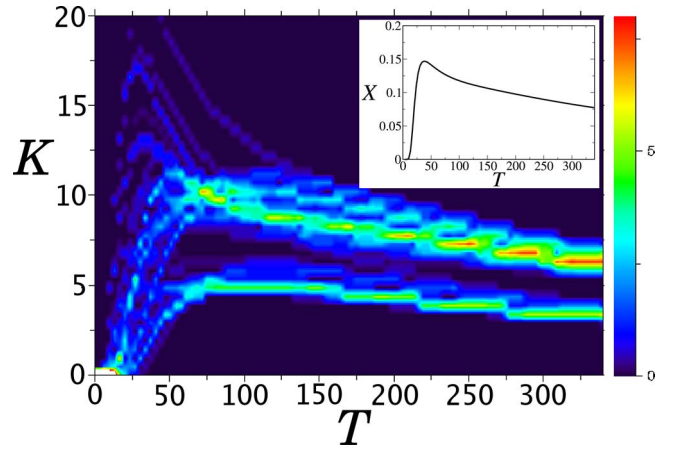


FIG. 3. (Color online) The results for the histograms of the NMR shifts  $K$  (in arbitrary units) as a function of temperature  $T$  of Fig. 2 recast as an intensity plot. The two lines of highest intensity can be directly compared to the experimental data of Fig. 2 in Ref. 12. For reference, the uniform magnetic susceptibility  $\chi(T)$  for the pure 12 site system is shown in the inset.

follows: the lower ridge arises from A bonds which all share the common feature that their spins are adjacent to a defect site. In contrast, the higher ridge receives contributions from B bonds whose spins may be located at different distances from the defects and hence results in a significant smearing of the histogram. This feature is also qualitatively observed in the experimental NMR data of Ref. 12. There, the peak of the lower shift (denoted D in Ref. 12) remains very sharp, while that of the higher shift (denoted M) becomes significantly rounded beneath 85 K. This defect induced smearing, which is most significant at lower temperatures, casts doubts on the experimental evidence for the closing of the *intrinsic* spin gap in the kagome system.<sup>12</sup> In fact, in the measured NMR spectra, the peaks can no longer be resolved beneath 10 K. Our results rather suggest a scenario where the apparent low lying magnetic excitations reported in the experiment should be attributed to disorder effects stemming from uncontrolled substitution of Zn and Cu atoms in the structure of the kagome planes.<sup>17</sup>

Finally, we study the NMR spin-relaxation rate estimated as

$$T_1^{-1} \propto T \frac{\text{Im} \chi(\omega_o)}{\omega_o}, \quad (2)$$

where  $\omega_o$  is the Larmor frequency of the applied external magnetic field and  $\chi(\omega)$  is the dynamical susceptibility. We compute the local  $\chi(\omega)$  for all sites and all defect configurations. The NMR rate  $1/T_1$  is estimated as the average over sites and configurations of the strengths of the pole occurring at  $\omega_o$ . We should note, however, that unlike the magnetization previously computed for the NMR shifts, the NMR rate probes the low-frequency behavior of the dynamic susceptibility and consequently more prone to finite-size effects. Nonetheless, we expect our results to provide useful qualitative insight. Our calculations for the finite temperature relaxation rate are shown in Fig. 4. We plot the data for four



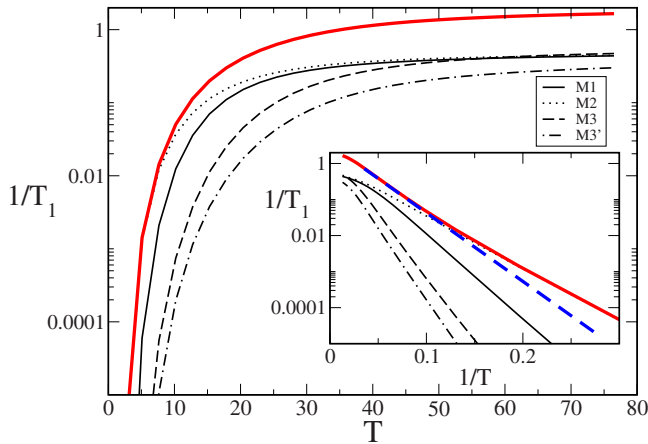


FIG. 4. (Color online) The relaxation rate  $1/T_1$  as a function of  $T$ . M1, M2, M3, and M3' denote configurations with the defects at distances 1, 2, and 3, respectively (there are two inequivalent realizations for distance 3). The solid line is the sum of the four contributions. The inset shows the same quantities on a semilogarithmic scale as a function of inverse temperature. Straight lines indicate simple activated behavior. The dashed (blue) straight line is drawn for reference.

particular defect configurations denoted by the Manhattan distance between the two defects (M1, M2, M3, and M3') and also the average of the four sets of data (multiplied by 4 for easier visualization). In the inset of the figure, we show the results as a function of inverse temperature  $1/T$  on a semilogarithmic scale. The data for M1, M2, M3, and M3'

are linear at low  $T$ , which is expected from simple activated behavior. In contrast, the average data (solid red line) clearly deviates from simple activated behavior, displaying a gentle upward curvature. These results are consistent with the experimental data of Ref. 12. The lack of linearity of the measured  $1/T_1$  and a putative power-law fit to the data was interpreted as a signature of the closing of the *intrinsic* spin singlet-triplet gap in the system. However, our results indicate that an alternative scenario is that the nonlinear behavior is associated with the existence of a multitude of small activation gaps resulting from the presence of defects.

To conclude, we have studied the effects of nonmagnetic impurity defects on a finite-size kagome lattice using exact diagonalization techniques. With no adjustable parameters our results show remarkable agreement with recent  $^{17}\text{O}$  NMR data and validate the experimental interpretation regarding the origin of two prominent lineshifts in the NMR spectra that were associated with Zn/Cu substitution in the 2D kagome planes. In particular, the model results reproduce the factor of 2 scaling between the lineshifts which persists down to low temperatures which is indicative of the spin liquid nature of the underlying system. It also captures the peculiar temperature dependence of the measured spin susceptibility and provides insight on the unequal smearing of the two lineshifts. On the other hand, our results also cast important doubts on the experimental evidence for the absence of a spin gap in the system, suggesting that disorder strongly affects the low-temperature behavior. This calls for renewed efforts to achieve a better chemical control on sample quality.

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<sup>15</sup>Note that similar small clusters were studied in Refs. 9 and 13.

<sup>16</sup>Note that while in our model the shifts are positive (as given directly by the local magnetizations), the experimental shifts happen to be negative due to the physical hyperfine coupling constant.

<sup>17</sup>Although the gap value should be affected by finite-size effects, extrapolations from larger systems data still predict a finite gap. Therefore one may expect our results to be qualitatively valid.