Dynamics and Scaling in a Quantum Spin Chain Material with Bond Randomness

T. Masuda,[1] A. Zheludev,[1] K. Uchinokura,[2] J.-H. Chung,[3,4] and S. Park[3,4]

[1]*Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6393, USA*
[2]*The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-0198, Japan*
[3]*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*
[4]*Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA*

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Single crystal inelastic neutron scattering is used to study dynamic spin correlations in the quasi-one-dimensional quantum antiferromagnet $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$, where the exchange constant fluctuates due to a random distribution of Si and Ge atoms. The measured low-energy spectrum is dominated by localized excitations and can be understood in the framework of the random singlet model. The observed scaling relations for the frequency dependencies of the correlation length and structure factor are in excellent agreement with recent theoretical predictions for the renormalization group fixed point.

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The interplay between quenched disorder and quantum correlations is at the heart of many exciting and diverse phenomena in condensed matter. Among these are weak localization, quantum Hall effect [1], percolation in quantum magnets [2], Griffith phases [3], etc. Certain quantum systems that are *critical* in the absence of randomness are extremely susceptible to even weak disorder. At sufficiently large length and time scales they behave as if the magnitude of disorder was *infinite*. Such models exhibit *universal* behavior and scaling that can often be exactly predicted theoretically. Moreover, their realizations in real materials are very robust: the hard to characterize details of quenched disorder (e.g., defect size and distribution) conveniently become irrelevant. Experiments on real-world compounds can thus be directly interpreted in the framework of purely hypothetical and esoteric "infinitely disordered" models.

The best known example is the one-dimensional (1D) quantum $S = 1/2$ Heisenberg antiferromagnet (AF) with random-bond strengths. In the absence of disorder the model is a critical Luttinger spin liquid [4]. With disorder it rapidly flows to the so-called random singlet (RS) phase [5,6], where randomly selected pairs of distant spins are weakly bound into singlets. Renormalization group (RG) theory was very successful in predicting universal thermodynamic [5–8] and spin transport [9,10] properties, as well as universal scaling of the instantaneous [6] and dynamic [9,10] structure factors. Only a handful of experimental realizations of the random 1D Heisemberg AF have been found to date [11,12]. Spin correlations were extensively studied in $(CD_3)_4NMn_xCu_{1-x}Cl_3$ [11,13], which realizes the random *classical* model, due to the large value of spin involved ($S = 5/2$ for Mn^{2+}). However, recent theories for the dynamic scaling properties of the quantum RS phase [9,10] have not yet been put to the test. In the present work we address this issue in inelastic neutron scattering experiments on the random $S = 1/2$ quantum spin chain compound $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$.

Solid solutions with the general formula $BaCu_2(Si_{1-x}Ge_x)_2O_7$ seem to be an almost ideal realization of the $S = 1/2$ quantum random exchange model. The $x = 0$ system, $BaCu_2Si_2O_7$, is a prototypical $S = 1/2$ quasi-1D Heisenberg AF with an in-chain coupling constant $J = 24.1$ meV [14–16]. Weak interchain interactions result in long-range AF ordering at $T_N = 9.2$ K. Previous extensive neutron scattering studies focused on the interplay between continuum and single-particle spin excitations in this compound [17]. The material with $x = 1$ is very similar, but has a larger exchange constant $J = 50$ meV and orders at $T = 8.5$ K [14,16]. Neither Si nor Ge atoms are directly involved in the slightly zigzag $—Cu^{2+}—O^{2-}—Cu^{2+}—$AF spin chains that run along the c axis of the orthorhombic structure, with the Cu^{2+} sites carrying $S = 1/2$. The difference in J is due to the contrast in the covalent radii of Si and Ge that indirectly affect the in-chain bond angles. In materials with intermediate Ge content J may thus be expected to vary randomly due to random fluctuations in the local Si/Ge environment of each chain segment.

The bulk magnetic properties of $BaCu_2(Si_{1-x}Ge_x)_2O_7$ were investigated in Refs. [16] and interpreted in the mean field spirit, ignoring any disorder effects. The $\chi(T)$ curves were described in terms of an "effective" exchange constant J_{eff} that was deduced from the position of the Bonner-Fischer maximum and found to vary linearly with x. This approach entirely fails to explain an important phenomenon observed in all $0 < x < 1$ materials and absent in the two pure systems, namely, the apparent divergence of susceptibility at low temperatures. The effect has nothing to do with three-dimensional ordering, as $\chi(T)$ starts to increase dramatically well above T_N. In Ref. [16] such behavior was attributed to

the Curie behavior of "chain moments," though no explanation was given.

A more careful look reveals that the anomalous divergence of $\chi(T)$ is most certainly *not* Curie-like. In Fig. 1 we plot the magnetic susceptibility measured in $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$ and $BaCu_2Si_2O_7$ powder samples using a commercial SQUID magnetometer. The $x = 0$ material is disorder-free and shows conventional quasi-1D behavior: a Bonner-Fischer maximum at $T \approx 163$ K is followed by 3D ordering at low temperature. In contrast, the random-bond $x = 0.5$ compound does not order magnetically in the studied temperature range. Instead, following a weak Bonner-Fischer maximum at $T \approx 230$ K, below $T \sim 50$ K the system shows a huge increase of susceptibility. From the log-log plot it is obvious that this feature does *not* correspond to the $1/T$ free-spin Curie scaling, and must be related to the randomness of exchange interactions. A key characteristic of a random-bond spin chain are abundant low-energy excitations. These correspond to transitions within the large-scale singlets of loosely coupled spin pairs in the RS ground state. The density of such excited states diverges as $1/|\omega \ln^3 \omega|$ at $\omega \to 0$ [5], giving rise to peculiar thermodynamic properties. In particular, $T\chi(T) \propto \ln^{-2}(T/\Omega_0)$ for $T \ll \Omega_0$, where Ω_0 is the microscopic cutoff that is roughly of the order of J. As shown by the solid line in Fig. 1, our susceptibility data for $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$ measured up to $T = 50$ K is reasonably well reproduced by this scaling relation. The fit yields $\Omega_0 = 43(2)$ meV, which is consistent with the effective exchange constant for $x = 0.5$, estimated as $J_{\text{eff}} = 37$ meV in Ref. [16].

The full impact of randomness on the spin correlations in $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$ becomes apparent in inelastic neutron scattering experiments. For these measurements we used two coaligned single crystal samples of total mass 0.5 g and mosaic spread 0.6°. The lattice parameters (space group *Pnma*) are $a = 6.92$ Å, $b = 13.28$ Å, and $c = 9.94$ Å. Neutron data were taken in the energy range 3–15 meV (note: $\hbar\omega \ll J_{\text{eff}}$) using the HB1 3-axis spectrometer installed at the High Flux Isotope Reactor at ORNL. Neutrons with a fixed final energy $E_f = 13.5$ meV were used in conjunction with a pyrolitic graphite (PG) monochromator and analyzer and a PG higher-order filter after the sample. Somewhat limited data were collected in the range $0.5 < \hbar\omega < 4$ meV using the SPINS cold 3-axis spectrometer at the NIST Center for Neutron Research. In this experiment we employed $E_f = 5$ meV fixed final energy neutrons with a PG monochromator, horizontally focusing the multiblade PG analyzer and Be filter.

Typical raw constant-E scans measured at $T = 12$ K near the 1D AF zone center $q_0 = \frac{3\pi}{d}$, $d = a/2$ [18], are shown in solid symbols in the insets of Fig. 2 . Subtracting a sloping background yields the scans plotted in open symbols in the main panels. As a clear indicator of dominant AF correlations, each scan shows a peak centered at the AF zone center. However, the shape of this

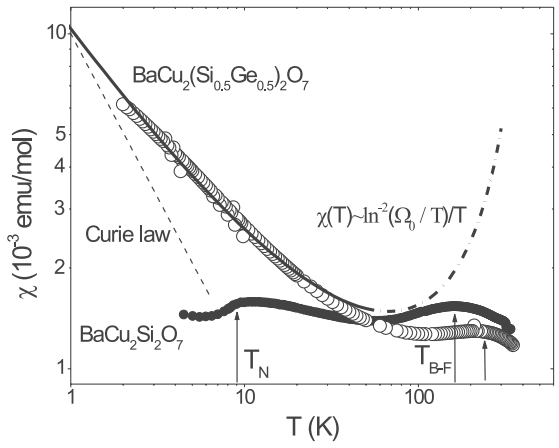

FIG. 1. Temperature dependence of magnetic susceptibility measured in $BaCu_2Si_2O_7$ (solid symbols) and $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$ (open symbols). The thin dashed line indicates free-spin Curie behavior. The heavy solid and dash-dotted lines are a fit to the data up to $T = 50$ K using the exact result for the RG fixed point. Arrows indicate the 3D ordering temperature and the positions of the Bonner-Fischer maxima.

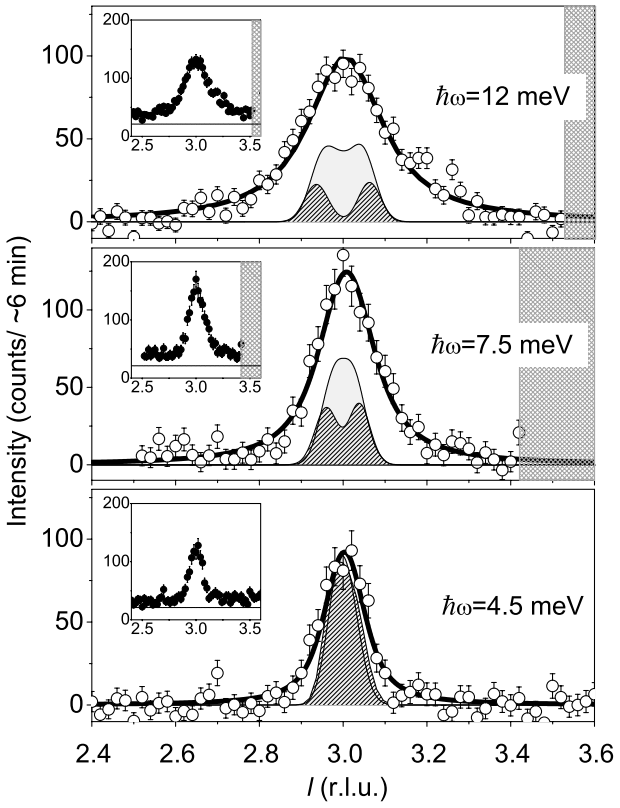

FIG. 2. Symbols: constant-E scans collected in $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$ at $T = 12$ K near the 1D AF zone center $l = 3$. Insets: raw data. Main panels: after subtracting a sloping background. The hatched areas in the right indicate strong spurious scattering from Al in the sample holder. Lines and shaded and hatched peaks are as described in the text.

feature is highly unusual. In a classical magnet with no randomness the excitations are sharp spin waves with a linear dispersion relation $\hbar\omega_q = v|q - q_0|d$ at low energies. Additional multimagnon excitations occur at higher energies. In the more relevant model of a disorder-free $S = 1/2$ quantum spin chain, the spectrum is a multispinon continuum with a sharp lower bound that follows the same "dispersion relation" [19,20]. The crucial point is that in both cases the dynamic spin correlations are *confined* to a triangular "wedge" $\hbar\omega > \hbar\omega_q$, which is a signature of coherent quasiparticle propagation. This, indeed, is the case in $BaCu_2Si_2O_7$ [17]. In contrast, in $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$ there is clearly *no sharp lower bound* to the dynamic structure factor, and the observed peak has extended "tails" that stretch most of the Brillouin zone. To illustrate this fact, we have simulated scans for the classical and quantum $S = 1/2$ disorder-free-spin chains using the effective value $J = 37$ meV. The spinon continuum in the quantum model was approximated using the Müller ansatz function [20]. The simulation takes into account experimental resolution effects, and the results are plotted as hatched and shaded areas in Fig. 2. The measured peaks are considerably broader than the simulated ones. Unlike the simulations, they lack any internal structure and can be very well approximated by Lorentzian profiles convoluted with the calculated Gaussian q resolution. The corresponding Voigt fits are shown in heavy solid lines in Fig. 2. The obtained intrinsic Lorentzian half-width Γ is the inverse correlation length and is plotted as a function of energy in Fig. 3.

A comparison with expectations for disorder-free chains also reveals an anomalous behavior of the *intensity* of scattering measured in $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$: when integrated over q, it *increases* with energy. For comparison, q-integrated intensity $S(\omega)$ for classical spin waves decreases with energy transfer as $1/\omega$, and is practically energy independent for the spinon continuum in the quantum model. The area of the Lorentzian feature measured in $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$ is plotted against energy transfer in Fig. 4, where it has been scaled by ω for the benefit of the discussion below.

All the unusual scaling properties observed in $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$ are related to bond disorder and can be understood within the existing theories for the RG fixed point. Here the excitations are not coherently propagating quasiparticles as in the pure system. Instead, they are localized and diffusive in nature, and hence lack the characteristic dispersion wedge. Their size diverges as a power of $\ln\omega$ at $\omega \to 0$, as does the typical distance between them. The dynamic structure factor was predicted to have a universal scaling form that in our case can be written as [9,10]

$$S(q, \omega) \propto \frac{1}{\omega \ln^3(\Omega_0/\omega)} \mathcal{F}\left(|q - q_0|d\frac{J}{\delta J}\ln^2(\Omega_0/\omega)\right), \tag{1}$$

where δJ is the variance of the exchange constants in the chains, and $\mathcal{F}$ is a universal function. Equation (1) implies the following scaling laws:

$$\omega S(\omega) \propto \ln^{-5}(\Omega_0/\omega), \tag{2}$$

$$\Gamma \propto \ln^{-2}(\Omega_0/\omega). \tag{3}$$

These relations fit our experimental data on $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$ remarkably well, as shown by solid lines in Figs. 3 and 4. The energy scales obtained from these fits are $\Omega_0 = 164(25)$ meV and $\Omega_0 = 46(4)$ meV for Eqs. (2) and (3), respectively, reassuringly of the same order of magnitude as the average exchange constant in the chains. The fact that the two values differ by a factor of 3 is not necessarily a reason for concern: the two expressions contain different powers of the logarithmic energy variable, and therefore involve different effective cutoff frequencies.

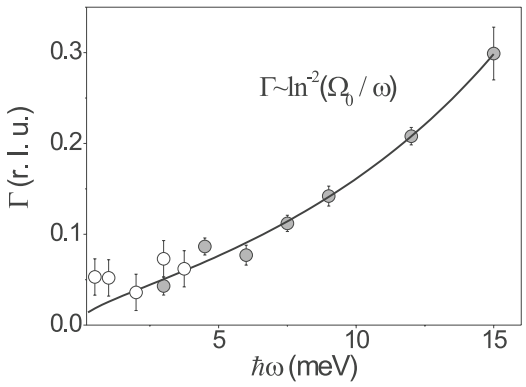

FIG. 3. Energy dependence of the reciprocal correlation length, as measured in $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$. Open and shaded symbols represent cold- and thermal-neutron data, respectively. The line is a fit using the universal scaling function of Ref. [9].

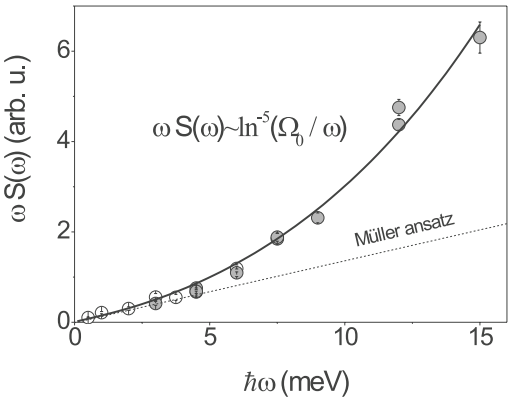

FIG. 4. Energy dependence of the q-integrated intensity of the peak seen in constant-E scans. Open and shaded symbols represent cold- and thermal-neutron data, respectively. The heavy solid line is a fit using the universal scaling function of Ref. [9].

The actual form of the universal function $\mathcal{F}$ should be considered separately from the scaling laws. Its analytical form was derived in Refs. [9,10] and is plotted in Fig. 3 of Ref. [10]. It can be described as a peaklike "feature" centered at the AF zone center q_0 resting on top of an "incoherent" flat component. The peak value is exactly twice the incoherent level. In practice, a flat magnetic signal is hard to separate from the background originating from the spectrometer, multiphonon scattering in the sample, etc. For this reason, our data analysis procedure (fits using Voigt profiles with a sloping background) is designed to measure *only* the properties of the feature. Knowing the "dark" background generated by the instrument (dashed line in the insets of Fig. 2), we can put an upper limit on the flat component of $\mathcal{F}$. In all measured scans it is considerably smaller than the amplitude of the peak. In this our data are at variance with the analytical predictions for the scaling function.

An additional discrepancy is in the actual shape of the peak feature. Theory predicts a weakly oscillatory form, so that the central peak in $\mathcal{F}$ is surrounded by a pair of shallow minima [9]. No hint of such minima are observed in our data, which instead follows a plain Lorenzian shape. A likely source for the discrepancies is that $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$ is, after all, *not* an infinitely disordered system. The authors of Ref. [10] have specifically cautioned that higher-order renormalizations of the spin operators, not included in their calculations, can affect the q dependence of the structure factor of a realistic system with finite disorder. In particular, they pointed out that the feature in $\mathcal{F}$ may actually become rescaled by a factor of the order of unity, and the relative strength of the incoherent contribution may change as well.

The characteristic width of the peak in $S(q, \omega)$ is not expected to be strongly affected by higher-order renormalizations of spin operators. Making only a small leap of faith, we can thus estimate $\delta J/J$ by comparing the coefficient obtained in fitting Eq. (3) to the data shown in Fig. 3 with the full width at half maximum of the universal scaling function of Ref. [9]. This comparison yields $\delta J/J \approx 0.03(1)$ for $BaCu_2(Si_{0.5}Ge_{0.5})_2O_7$. Unfortunately, this quantity is difficult to independently estimate based on structural considerations. It largely depends on the radius of effect ρ (number of Cu—O—Cu bonds influenced) that each Ge atom substituted on a Si site has on the nearby spin chains. The width of the distribution of exchange constants decreases very rapidly with increasing ρ, and the estimated $\delta J/J$ is compatible with ρ spanning of a couple of lattice repeats.

In summary, we have found an interesting experimental realization of the quantum $S = 1/2$ spin chain with random bonds. The new material allowed us to directly measure the universal scaling laws for the dynamic spin correlations in the random singlet spin chain. Future experiments will tackle two important issues: the effect of finite temperature and the evolution of dynamic properties with the continuously changing disorder strength x in $BaCu_2(Si_{1-x}Ge_x)_2O_7$ systems. For either problem, very little theoretical guidance is currently available.

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