Experimental investigation of the low-temperature features of a random Heisenberg spin chain

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Abstract. Low-dimensional spin systems, consisting of arrays of spins arranged in chains or ladders, have been investigated intensively in recent years using both exactly solvable theoretical models as well as a variety of experimental techniques. In case of random variations of the exchange couplings the renormalization group theory predicts the existence of a random-singlet (RS) state, corresponding to spins coupled at all possible distances and energy scales. The scarce availability of suitable random systems, however, has so far prevented the experimental identification of this peculiar magnetic ground state. In a combined effort using nuclear magnetic resonance (NMR), dc magnetometry and numerical simulations, we now find compelling evidence for the formation of a random-singlet state in this class of materials. Randomness seems to generate a broad distribution of local magnetic fields, in turn reflected in stretched exponential NMR relaxations. This distribution exhibits a progressive broadening with decreasing temperature, caused by the growing inequivalence of magnetic sites, as expected from the RS theory. Our findings suggest that NMR is the tool of choice for probing the low-energy physics also in other disordered magnets, where extended-scale excitations are dominant.

1. Introduction

Quantum fluctuations (QFs) are known to dominate the physical properties of low-dimensional systems at low temperatures. For example, in 1D Heisenberg antiferromagnetic spin systems, QFs suppress ordinary long-range order (LRO) at $T = 0$, leading to unusual magnetic states, such as, e.g., spinon deconfinement with excitation continua [1, 2]. The same systems are particularly sensitive to disorder, which introduces the breaking of translational invariance through, e.g., a random coupling between individual spins. Such a situation may be caused by random exchange couplings between spin sites via bond randomness. A promising way to analyze its consequences is offered by the real-space renormalization group (RG) method [3, 4], which is well adapted to cope with the lack of translational invariance. By using this approach, Fisher showed that the behaviour of spin-$1/2$ random antiferromagnetic AFM chains is strongly dominated by randomness even in case of modest disorder [5]. Indeed, at low temperature these systems enter the so-called random-singlet (RS) phase [3, 4, 5], characterized by the random coupling of spins at arbitrary distances to form weakly bound singlets. Since spins far apart are more weakly bound than those lying closer together, a lowering of temperature
below the coupling strength $J$ of the latter renders the respective singlets inactive, leading to a broadening of the distribution of effective coupling strengths. Consequently, the low-temperature thermodynamic properties of these systems are universally dominated by the weakly bound pairs, because their ground state is controlled by an RG fixed point.

Due to the scarcity of appropriate physical realizations, only a few experimental tests of these theories have been reported to date. In a recent study we probed the compound BaCu$_2$(Si$_{1-x}$Ge$_x$)$_2$O$_7$, a prototype 1D random antiferromagnetic Heisenberg spin chain (RHC). In our case different Si and Ge covalent radii imply random variations of the exchange-coupling constant between spin sites [6]. To investigate the consequences of randomness we employed mainly $^{29}$Si nuclear magnetic resonance (NMR), a technique which is particularly well suited for probing energy transfers of the order of $\mu$eV and hence for providing access to the low-energy/long-time scales characteristic of the disordered systems. Our low-temperature data indicate a broad distribution of NMR relaxation rates, which is highly suggestive of the formation of random-singlet states in this class of materials, a cornerstone of the RHC theory presented in [5]. This conclusion is further supported by results of temperature- and field-dependent magnetization measurements, as well as by detailed numerical simulations.

2. Experimental details and results

The chain compounds BaCu$_2$Si$_2$O$_7$ and BaCu$_2$Ge$_2$O$_7$ are among the best realizations of spin-1/2 Heisenberg chain systems, characterized by low ordering temperatures ($T_N < 10$ K) and by large exchange couplings ($J_{\text{Si}} = 24.1$ meV and $J_{\text{Ge}} = 50$ meV) (for a global classification see, for instance, Tab. 1 in Ref. [7]). For a clear and unambiguous identification of the implications of randomness, we performed a comparative investigation of single-crystalline samples of the pure Si ($x = 0$) and the SiGe ($x = 0.5$) compound, corresponding to no and to full randomness, respectively. First we compare the results of the magnetic susceptibility measured via de SQUID magnetometry. Subsequently, magnetic-resonance line shapes and spin-lattice relaxation times $T_1$, measured using standard pulse techniques, provide a microscopic insight into the distribution of couplings typical of the random-singlet state.

Figure 1 shows the temperature-dependent magnetization, $M(T)$, for an $x = 0.5$ single crystal, whose key feature is the low-$T$ divergence of the magnetization. As predicted by the RS theory [5], this divergence is due to the low-energy states of the weakly bound singlets, which give rise to a susceptibility of the type $\chi(T) \sim T^{-1} \ln^{-2}(\Omega/T)$, with $\Omega$ a fitted cutoff energy. In our case $\Omega = 66.3(7)$ meV and, generally, it is a measure of the temperature above which the entire chain is in a paramagnetic regime, while below it an increasing fraction of “frozen” singlets coexists with a shrinking fraction of weakly-coupled unpaired spins. The observed magnetic response of the fully random compound ($x = 0.5$) is significantly different from that of the pure case ($x = 0$), where $\chi(T)$ is almost constant with temperature (not shown). Similarly to the disordered case, also the pure Ge ($x = 1$) compound shows a low-$T$ divergence of $\chi(T)$ [9]. However, upon closer inspection this turns out to be related to the critical behavior above a magnetic phase transition of ferromagnetic type, not encountered in the $x = 0.5$ case. Indeed, while the weak ferromagnetism of the pure Ge compound results in a strongly anisotropic magnetic response, the random SiGe compound exhibits a nearly isotropic behaviour.

The results of the magnetization measurements are fully reproduced by Quantum Monte Carlo (QMC) simulations of Heisenberg spin-1/2 chains. In our case, 6000 spin sites with randomly distributed but equally probable $J_{\text{Si}}$ and $J_{\text{Ge}}$ couplings were used. Magnetization data vs. temperature and vs. field obtained via a directed-loop algorithm [10] within the alps 2.0 QMC simulation package [11] were averaged over more than 40 different random configurations. At all the considered temperatures ($T > T_N$) the quantitative agreement with the experimental $M(T)$ data is very good, especially in view of the fact that no free parameters were used. A similarly good agreement was obtained also for the magnetic-field dependence $M(H)$ (not shown) [13].
A further refinement of this already satisfactory model was to consider the effects of interchain interactions in the $M(T)$ behaviour (see figure 1). For this purpose a mean-field (MF) type correction to the magnetization of the single chains was implemented by redefining

$$\chi = \frac{\chi_0}{1 + \alpha \chi_0}, \quad \text{with} \quad \alpha = \frac{4zJ'}{g\mu_B}. \quad (1)$$

Here $\chi_0$ represents the susceptibility of non-interacting chains (expressed in the same units as in figure 1), $\alpha$ is a parameter depending on the interchain coupling $J'$, while $z = 4$ is the number of the nearest-neighbour chains. A good agreement is obtained for $\alpha \simeq -90$, corresponding to a ferromagnetic value of $J' \simeq 7.5$ K (0.64 meV). We note that in comparison with the in-chain coupling $J = 280$ K (24 meV), the inter-chain interaction is indeed negligible. Moreover, although a simple mean-field approach was used to estimate $J'$, its numerical value is not much different from 0.41 meV, the mean-field value determined by neutron scattering measurements in the pure Si system [12]. To conclude, QMC numerical simulations provide not only reliable results but also a strong argument for claiming the formation of a random-singlet state, in particular when considering that no single $J$ value (not even the average, $J_{av} = 37$ meV) can reproduce the experimental data shown in figure 1.

The presence of a multitude of $J$ values in the fully random compound implies a rather wide distribution of internal fields. On the contrary, in the pure $x = 0$ case only a few well-defined local field values at Si sites are possible. This heuristic view is fully confirmed by $^{29}$Si NMR line shapes (see figure 2), which provide direct histograms of the local susceptibilities, as sensed by the Si nuclei via the relevant hyperfine interactions with the electronic spins $S_j$ at the Cu sites. Taking into account the $Pnma$ orthorhombic space group of BaCu$_2$Si$_2$O$_7$, crystal-symmetry arguments predict two different peaks below the AF transition and a single peak above it, as is indeed observed. Fitting the data below $T_N$ allows us to determine the components of the hyperfine coupling tensor. The case $x = 0.5$ is clearly much different, displaying a unique,
Figure 3. $^{29}$Si NMR spin-lattice relaxation data of BaCu$_2$(Si$_{1-x}$Ge$_x$)$_2$O$_7$ for $x = 0$ and $x = 0.5$ (no and maximum randomness, respectively) at selected temperatures. The simple exponential recovery of magnetization in the pure case becomes stretched in the random case, with a stretch parameter $\beta$ in the 0.5–1 range.

featureless and tenfold broader peak across the covered temperature range. Figure 2 compares the line shapes measured in single crystals oriented along the $a$ direction in both cases. The detailed analysis of the order parameter, angular dependence and anisotropy for the pure case is beyond the scope of the present article and will be reported elsewhere.

Both magnetization and NMR line-shape data provide insight into the static magnetic properties of RHCs. $^{29}$Si NMR relaxation measurements, on the other hand, probe their dynamic properties [13]. The latter results complement the previous ones and again can be accounted for by assuming the presence of a random-singlet state, as summarized below. Figure 3 shows the recovery of the $^{29}$Si nuclear magnetization for $x = 0$ and $x = 0.5$ at temperatures above the AF transition. Because of the large $J$ values with respect to the applied field, the chains can safely be considered as noninteracting and effectively in zero field. Remarkable differences are observed between the pure and the random case. While the magnetization recovery is a simple exponential in the pure Si compound, it acquires a stretched-exponential character in the random SiGe case (see figure 3). By assuming that the stretched-exponential ansatz captures the essential physics of the relaxation process in the random case, the global relaxation arises from a distribution $\rho(\tau, T)$ of relaxation times $\tau$ [14, 15] such that

$$\int_0^\infty \rho(\tau, T) e^{-\frac{t}{\tau_s(T)}} d\tau = e^{-\left[\frac{t}{\tau_s(T)}\right]^{\beta(T)}}. \tag{2}$$

Although we have direct experimental access only to the global parameters $\beta(T)$ and $\tau_s(T)$ (via numerical fits, as shown in figure 3b), it is still possible to use a numerical inversion procedure to extract $\rho(\tau, T)$, the probability distribution of the relaxation times. At high temperatures we find that $\beta \rightarrow 1$, implying a distribution of relaxation times which tends to a delta function peaked at $\tau = \tau_s(T)$. At low temperatures, on the other hand, the stretch parameter $\beta$ decreases monotonously, reflecting a broader distribution of exchange couplings. Both these results are consistent with the random-singlet state theory, according to which as the temperature is lowered the spin dynamics becomes increasingly dominated by the frozen singlets.

3. Discussion

All the quoted experimental results as well as the QMC simulations of the BaCu$_2$(Si$_{1-x}$Ge$_x$)$_2$O$_7$ system, show qualitatively different features for the pure ($x = 0$) and the fully disordered ($x = 0.5$) system. The stretched-exponential magnetization recovery for $x = 0.5$ is consistent with the multitude of exchange couplings envisaged by the random-singlet state theory. It is the increasing fraction of paired spins which introduces the observed distribution of relaxations.
Except at very low temperatures (below 0.3 K), where interchain interactions give rise to a spin-glass state (observed as hysteretic effects in the $M(T)$ data), the SiGe compound represents an excellent realization of a random system. This is reflected in the ample temperature range described by a stretched-exponential relaxation regime, extending up to beyond 100 K. The good match between the NMR energy scales and those present in disordered systems, dominated by extended-scale, low-energy excitations, suggests that NMR represents a privileged technique for investigating RHC properties. Corresponding experiments require only small single-crystalline samples and, more importantly, they can explore low-energy regions inaccessible by standard neutron-scattering techniques.

In conclusion, the presented experimental facts and their consistency with the RG theory indicate that the long predicted random-singlet phase is indeed the low-temperature ground state adopted in disordered spin-chain systems. Nevertheless, open questions such as how to predict the characteristics of NMR relaxation in the presence of disorder, or that of defining a lower limit for the parameter $\beta$, ought to be addressed by theoretical work in the future.

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References

[1] Lake B, Tennant D A, Frost C D and Nagler S E 2005 Nature Mater. 4 329
[2] Zaliznyak I A 2005 Nature Mater. 4 273
[3] Ma S K, Dasgupta C and Hu C K 1979 Phys. Rev. Lett. 43 1434
[4] Dasgupta C and Ma S K 1980 Phys. Rev. B 22 1305
[5] Fisher D S 1994 Phys. Rev. B 50 3799
[6] Yamada Y, Hiroi Z and Takano M 2000 J. Solid State Chem. 156 101
[7] Broholm C et al 2002 High Magnetic Fields (Lecture Notes in Physics vol 595) ed C Berthier et al (Berlin: Springer) pp 211–234
[8] Johnston D C, Kremer R K, Troyer M, Wang X, Klümper A, Bud’ko S L, Panchula A and Canfield P C 2000 Phys. Rev. B 61 9558
[9] Tsukada I, Takeya J, Masuda T and Uchinokura K 2000 Phys. Rev. B 62 R6061
[10] Alet F, Wessel S and Troyer M 2005 Phys. Rev. E 71 036706
[11] Bauer B et al (ALPS collaboration) 2011 J. Stat. Mech. P05001
[12] Kenzelmann M, Zheludev A, Raymond S, Ressouche E, Masuda T, Böni P, Kakurai K, Tsukada I, Uchinokura K and Coldea R 2001 Phys. Rev. B 64 054422
[13] Shiroka T, Casola F, Glazkov V, Zheludev A, Prša K, Ott H and Mesot J 2011 Phys. Rev. Lett. 106 137202
[14] Lindsey C P and Patterson G D 1980 J. Chem. Phys. 73 3348
[15] Montroll E W and Bendler J T 1983 J. Stat. Phys. 34 129
[16] Johnston D C 2006 Phys. Rev. B 74 184430