The antiferromagnetic order in an F-AF random alternating quantum spin chain: (CH$_3$)$_2$CHNH$_3$Cu(Cl$_x$ Br$_{1-x}$)$_3$

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A possibility of the uniform antiferromagnetic order is pointed out in an $S = 1/2$ ferromagnetic (F) - antiferromagnetic (AF) random alternating Heisenberg quantum spin chain compound: (CH$_3$)$_2$CHNH$_3$Cu(Cl$_x$ Br$_{1-x}$)$_3$. The system possesses the bond alternation of strong random bonds that take ±2J and weak uniform AF bonds of −$J$. In the pure concentration limits, the model reduces to the AF-AF alternation chain at $x = 0$ and to the F-AF alternation chain at $x = 1$. The nonequilibrium relaxation of large-scale quantum Monte Carlo simulations exhibits critical behaviors of the uniform AF order in the intermediate concentration region, which explains the experimental observation of the magnetic phase transition. The present results suggest that the uniform AF order may survive even in the presence of the randomly located ferromagnetic bonds.

Randomness often disorders the order, but sometimes it brings order to the disorderly. This phenomenon is referred to as order by disorder. In the studies of the low-dimensional quantum spin systems the appearance of magnetic order due to the impurity doping of a spin-disordered system has been attracting interest both in experimental and theoretical research. The systems commonly possess a good one-dimensionality and have a finite energy gap above the nonmagnetic ground state mostly caused by the singlet dimer state. The impurity doping may destroy the dimers, creating magnons, and cause the antiferromagnetic (AF) order. When the magnetic interactions are all antiferromagnetic, the appearance of uniform AF order becomes easily recognizable.

Recently, Manaka et al.[1] found another example of the order by disorder phenomenon. Two spin-gapped compounds with the nearly identical structure, but with different origins for their energy gap, were investigated. One compound is (CH$_3$)$_2$CHNH$_3$CuCl$_3$ (IPACuCl$_3$), which realizes the F-AF bond alternation Heisenberg chain for $J_{\text{strong}} \sim 54K (F)$ and $J_{\text{weak}} \sim -23K (AF)$. Because of the strong F bonds the ground state of this compound is considered the Haldane state. The other compound mixed is (CH$_3$)$_2$CHNH$_3$CuBr$_3$ (IPACuBr$_3$), which realizes the AF-AF bond alternation Heisenberg chain for $J_{\text{strong}} \sim -61K (AF)$ and $J_{\text{weak}} \sim -33K (AF)$. The ground state is the dimer state. In the region of intermediate concentration in the mixed compound, 0.44 < $x$ < 0.87 in IPACu(Cl$_x$ Br$_{1-x}$)$_3$, they observed a magnetic phase transition through the susceptibility measurement and the specific heat measurement. Dependences of the susceptibility on the direction of the external field suggested that the order is antiferromagnetic, but the magnetic structure has not been experimentally clarified yet.

In the mixed compound, a kind of the random-bond quantum spin chain is realized. The randomness is considered to destroy the energy gap, causing a magnetic order to appear in the gapless region with the assistance of the very weak but finite interchain interactions. From knowledge of the quantum random spin chain[2][3] one finds the uniform order to be totally destroyed when the F bonds are randomly located. However, in actuality these F bonds and the AF interchain interactions cause randomly-located frustration. Despite these adverse circumstances the uniform AF order may become critical in the one-dimensional model. Particularly, the uniform AF magnetization at the fully random point decays algebraically with an exponent that is almost same as the gapless $S = 1/2$ uniform antiferromagnetic Heisenberg (AFH) chain. This evidence suggests that the uniform AF order appears in a significant way when the interchain interactions exist. The gapless phase bounds have also been estimated, and they agree with the experimental observation of the magnetic phase. Singular randomness on the strong bonds, ±2J, and the alternate uniform bonds are clarified to cause a power-law effective bond distribution. This distribution is the origin of the critical behavior of the AF order.

Consider the following $S = 1/2$ random alternating quantum Heisenberg chain,

$$
\mathcal{H} = - \sum_i^{N} J_{2i-1} S_{2i-1} \cdot S_{2i} + J_{2i} S_{2i} \cdot S_{2i+1},
$$

where $J_{2i} = \pm 2J$ indicating the strong random bonds and $J_{2i-1} = -J$ indicating the weak uniform bonds. From the crystal structure analyses of the pure compound[4] it is known that there are two Cl ions or two Br ions that bridge between the Cu ions: Cu$^{4+}$Cl$^{-}$Cu or Cu$^{4+}$Br$^{-}$Cu. They are linked stepwisely along the c-axis. The exchange interactions within a step are strong, whereas those between steps are weak. This has been explained by the overlap of the orbitals of Cu and (Cl, Br). The bridging angle may differ between Cl and Br because of a different ion radius, causing changes in the exchange interactions. In the mixed compound, the exchange interactions on the weak bonds may be insen-
sible to the bridging angles because the overlap of the orbitals is small. Thus, the difference in amplitude on the weak bonds is neglected (-23K for IPACuCl₃ and -33K for IPACuBr₃), and instead they are set to a uniform AF value: \( J_{2i-1} = -J \). On the other hand however, the sign of the exchange interaction may change by subtle differences in the bridging angles along the strong bonds due to the large overlap of the orbitals. Therefore, the magnitude is set as twice the weak bonds and the sign is random: \( J_{2i} = \pm 2J \). There are three types of bridging ion configurations: Cu\( <\text{Cl}_1\)Cu with probability \( x^2 \), Cu\( <\text{Br}_1\)Cu with \( (1-x)^2 \), and Cu\( <\text{Cl}_1\) Cu with \( 2x(1-x) \). It is considered that the Cu\( <\text{Cl}_1\) Cu configuration yields the AF interactions by the following reasoning suggested by Manaka. Let an F bond concentration (not the Cl ion concentration, \( x \)) build up in the random part denoted by \( p \). If one assumes that the Cu\( <\text{Br}_1\) Cu configuration yields the F interaction, then \( p = x(2-x) \). The magnetic phase appears for \( 0.44 \leq x \leq 0.87 \) in the experiment. This directly corresponds to the appearance of the dimer phase during \( 0 \leq p \leq 0.69 \), and the appearance of the Haldane phase only during \( 0.98 \leq p \leq 1 \). This assumption contradicts our sense that the Haldane phase is rather robust against randomness compared to the dimer phase. Therefore, the Cu\( <\text{Cl}_1\) Cu configuration and the Cu\( <\text{Br}_1\) Cu configurations correspond to the AF interactions, and only the Cu\( <\text{Cl}_1\) Cu configuration corresponds to the F interaction. Then, we get \( p = x^2 \).

Hyman and Yang investigated a very similar model wherein the alternate even bonds are randomly AF and the other bonds are randomly F or AF. In their model the random singlet phase appears where the spin correlation decays algebraically as \( r^{-2} \). However, numerical results presented subsequently show that the AF magnetization behaves qualitatively the same as the gapless \( S = 1/2 \) uniform AFH chain at the fully random point. Thus, a subtle difference in the bond distributions may produce different results. As for the connection with the real materials, the random bond distribution of our model can be realized by the intercalation in the spin-gapped compounds. Thus, the model may account for the various impurity-induced magnetic-order phenomena.

In our research the quantum Monte Carlo with the nonequilibrium relaxation analysis was used. Since the nonequilibrium relaxation method essentially handles the size-independent relaxation process, the obtained results can be considered as having an infinite Trotter number and infinite system size. In actuality, the nonequilibrium relaxation functions of different values of the ratio \( \beta/m \) (\( \beta \): the inverse temperature, \( m \): the Trotter number) ride on the same curve when we rescale the Monte Carlo time step by the correlation time \( \tau(m) \) dependent on the Trotter number. The \( m \)-dependence only appears due to the finite-size effect. The value of \( \beta/m \) is fixed to 1/2 in these results. The simulations start with spin configurations of either a quantum ground state of the pure system (the dimer state or the Haldane state) or the classical uniform AF state. In the case of the quantum state start-up, the uniform AF susceptibility is observed whether it diverges algebraically or converges to a finite value. When it shows the converging behavior the system is considered to be in a state of disorder or in the gapful state. Otherwise, when it shows an algebraic divergence, the AF order is critical and the system is in the gapless phase. The uniform AF magnetization is observed whether it decays exponentially or algebraically when starting from the classical AF state. The typical size of the system \( N = 161(322 \) spins), \( m = 1000 \) at \( \beta J = 500 \) and the numbers of the random bond configurations are more than 5000 in the simulations for the quantum states, and \( N = 1601, m = 400, \beta J = 200 \) with several hundreds configurations in the simulations for the classical state. These sizes of the simulations determine the resolution limit of the obtained physical quantities. The resolution of the susceptibility is on the order of \( 1/T \), which corresponds to the AF magnetization per spin \( \langle M_{AF} \rangle \sim 1/\sqrt{mN} \sim 3 \times 10^{-3} \). The resolution of the AF magnetization when starting from the classical state is on the order of \( 1/\sqrt{mN} \times \) (number of samples) \( \leq 10^{-4} \). Both simulations are consistent when within the resolution of \( \langle M_{AF} \rangle > 10^{-3} \). It is difficult to estimate the resolution of the experiment observing the magnetic phase transition, but if one assumes \( \langle M_{AF} \rangle \sim 10^{-3} \) then the numerical results presented in this paper quantitatively explains the experiment.
FIG. 1. Nonequilibrium relaxations of $\chi_{AF}(t)$. The F bond concentrations $p$ values, from top to bottom, correspond to the data from top to bottom. The behavior changes from converging to diverging at $p \sim 0.75$ ($x \sim 0.87$) in the Haldane side and at $p \sim 0.2$ ($x \sim 0.44$) in the dimer side.

Figure 1 shows the nonequilibrium relaxation functions of the uniform AF susceptibility multiplied by the temperature in the simulations of the Haldane state (a) and of the dimer state (b). After the initial relaxation of 50 steps, the susceptibility begins to diverge algebraically in the intermediate region of $0.2 < p < 0.75$, which corresponds to $0.44 < x < 0.87$ by $p = x^2$. This displays the critical behavior of the uniform AF order in the one-dimensional level, and that the AF order may appear if there exist finite interchain interactions. The phase boundary coincides quantitatively with the experimental observation of the magnetic phase, and thus the order is speculated to be the uniform AF order. Of course there may be a possibility of other magnetic structures we do not mention here, such as the $\uparrow\downarrow\uparrow\downarrow$ state in the Haldane side or the generalized staggered state. Investigations on these ordered states are left for future study.

Starting the simulation from the classical AF-ordered state and observing the uniform AF magnetization can check the critical nature of the uniform AF state. Figure 2 shows the nonequilibrium relaxation. For comparison, the relaxation function of the pure base system at $p = 0$ (dimer chain) and $p = 1$ (Haldane chain) and the gapless $S = 1/2$ uniform AFH chain have been plotted. In the intermediate region the relaxation function exhibits the critical decay after an initial relaxation that rides on the relaxation of the pure gapful system. Note that the length of the initial relaxation, $t < 50$, agrees with that of the susceptibility simulations in Fig. 1. The numerical value of the AF magnetization at which the relaxation begins critical behavior is roughly considered as the magnitude of the order. At $p = 0.1$, an algebraic decay begins below the susceptibility resolution limit, $3 \times 10^{-3}$, and therefore critical behavior was not detected by the susceptibility simulation nor by the experiment. Within the present accuracy of the AF-magnetization simulation the phase boundary in the dimer side resides between $p = 0.04$ and $p = 0.1$: at $x = 0.2 \sim 0.3$, which is lower than the experimental observation $x = 0.44$. When the resolution of the experimental probe is much sharper, the magnetic phase can be observed in wider region. For $p > 0.75$, the relaxation shows a multi-exponential type decay, suggesting a discrete distribution of the energy gap. However, as the randomness increases the relaxation looks like an algebraic decay. At the fully random point $p = 0.5$ the magnetization takes a maximum value. The slope of the relaxation at this point is almost the same as that of the $S = 1/2$ uniform AFH spin chain, but the amplitude is reduced to 1/4. This behavior guarantees the observation of a weak antiferromagnetic phase transition assisted by the interchain interactions.

The algebraic decay in the intermediate region can be explained by the power-law distribution of the energy gap. In the Haldane side ($p > 0.5$), we may consider the strong AF bonds as the impurity that may be replaced by effective weak bonds (just like the real-space renormalization procedure). As long as the successive perturbation is good, the strength of the effective bond replacing $n$ aligned strong AF bonds is $\exp[-\lambda n]J$ with $\lambda = \log 4$. The probability of the realization is $(1 - p)^n$. Given these, the distribution of the effective bonds is

$$P(J) \sim \frac{1}{\lambda} J^{-1+\frac{1}{\lambda}} \propto \alpha J^{-1+\alpha},$$

with $\alpha = (1/\lambda) \log(1/(1-p))$. Because the VBS picture is valid in this region, the singlet dimers are located on the weak AF bonds between the strong F bonds. This bond distribution is directly interpreted by the gap distribution $P(\Delta)$, and it is equivalent to the distribution in the random singlet phase, $P(\Delta) = \alpha \Omega^{-\alpha} \Delta^{-\alpha-1}$, with a characteristic energy scale $\Omega$. Since each energy gap contributes to the exponential decay of the AF magnetization with a contribution $\exp[-\Delta^z t]$ ($z$: the dynamic exponent), the collection of these exponential decays by the distribution $P(\Delta)$ becomes the power-law decay as

$$\int \exp[-\Delta^z t] P(\Delta) d\Delta = \Gamma(\alpha/z + 1)(t/\tau)^{-\alpha/z},$$

with the characteristic time scale $\tau \sim \Omega^{-z}$. Therefore, the AF magnetization is expected to decay algebraically with the exponent $\alpha/z = (1/\alpha) \log(1/(1-p))$, which is dependent on the concentration $p$. The slope of the algebraic decay in Fig. 2 quantitatively agrees with this expression supposing $z = 2.2$ for $p > 0.6$, and $z = 2.0$ for $0.5 \leq p < 0.6$. In the dimer side ($p < 0.5$), the interpretation is not straightforward. It is not good to deplete the
strong AF bonds which are the majority. Depletion of the strong F bonds (the Haldane cluster) is possible, and weak effective bonds of the amplitude $\exp[-J' n]$ may replace them. This way we can obtain the same critical behavior. However, the estimated values of the exponent do not coincide with the numerical results of Fig. 2, regardless of its success on the Haldane side. For the quantitative agreements, we need further interpretation.

Theoretical speculations on the phase boundary are possible. It is pointed out by Hida$^{16}$ that the Haldane phase is stable as long as the gap distribution is not singular at $\Delta = 0$. In the present model, it corresponds to $p = 0.75$ by $\alpha = 1$. This value is consistent with the numerical results of both Fig. 1 and Fig. 2. It is also commented by Yang and Hyman$^{9}$ that the random singlet phase begins at $\alpha \sim 0.67$ for the algebraic bond distribution $P(J) \sim \alpha J^{-1+\alpha}$. This point corresponds to $p \sim 0.6$, and in actuality the dynamic exponent $\zeta$ seems to change the value at this point from $\zeta = 2.2$ to $\zeta = 2$. In the neighborhood of the fully random point, $0.4 < p < 0.6$, the exponent is weakly dependent on $p$ suggesting a universal phase. However, the critical behavior, like the uniform AFH chain, suggests that the spin correlation decays as $r^{-3}$ not as $r^{-2}$ in the random singlet phase. This point is still unclear, and further investigations are necessary. In our preliminary simulations the relaxation of the string order parameter suggests that the string order is more than critical (ordered or critical) for $0 < p < 0.1$. It is pointed out by Hida$^{16}$ that the Griffiths phase might exist in the region of $0 < p < 0.1$. Regardless, the uniform AF order becomes critical in the gapless region, $0.1 < p < 0.75$, as is observed in the experiment. A speculated phase diagram is shown in Fig. 3. This phenomenon is quite interesting because the uniform AF order survives despite the randomly located ferromagnetic bonds. This may mean the role of the ferromagnetic bonds in the quantum system should be reconsidered.

| Dimer | Gapless | Haldane |
|-------|---------|---------|
| 0.1   | 0.4     | 0.6     |
| (0.32)| (0.63)  | (0.77)  |
|       |         | (0.87)  |
|       | random singlet$^{(？)}$ | Griffiths$^{(？)}$ |
| $P$   |         |         |
|       |         | (x)     |

FIG. 3. A rough speculation of a phase diagram.

In this paper the magnetic ordered phase observed in the experiment of IPACu(Cl$_2$ Br$_{1-x}$)$_3$ is explained and the magnetic structure is speculated to be the uniform AF order. The phase boundaries estimated in the simulation quantitatively agree with the experimental results. Behaviors of the relaxation function in Fig. 2 suggest the following scenario for the appearance of the AF order. Short-range AF correlations are first destroyed by local dimer states or local Haldane states that appear during the initial relaxation of the exponential decay. Beyond these local states there exist very weak but finite effective interactions that have the power-law distribution. Collections of the exponential decay due to these effective interactions becomes the algebraic decay seen in Eq. (3). This is considered as the origin of the criticality of the uniform AF order, and with help of the interchain interaction the magnetic phase is observed in the experiment. The present mechanism may explain, and thus serve as a new interpretation for, general impurity-induced long-range order phenomena.

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