# Anomalous impurity effect on magnetization in frustrated one-dimensional ferro- and ferrimagnets

Masanori Kohno and Xiao Hu
*Computational Materials Science Center, National Institute for Materials Science, Tsukuba 305-0047, Japan*
(Received 13 September 2007; published 5 November 2007)

Significant decrease of spontaneous magnetization in frustrated one-dimensional ferro- and ferrimagnets due to nonmagnetic impurities is predicted. Using the density-matrix renormalization group method and the exact diagonalization method, we confirm that the total spin can vanish due to a single impurity in finite chains. Introducing the picture of magnetic domain inversion, we numerically investigate the impurity-density dependence of magnetization. In particular, we show that even with an infinitesimal density of impurities, the magnetization in the ground state is reduced by about 40% from that of the corresponding pure system. Conditions for the materials which may show this anomalous impurity effect are formulated.

DOI: 10.1103/PhysRevB.76.174409 PACS number(s): 75.10.Pq, 75.10.Nr, 75.30.Cr, 75.30.Hx

## I. INTRODUCTION

Frustrations in quantum spin systems have attracted much attention for their potential to exhibit new phenomena which have never been observed in unfrustrated systems. Various possibilities in frustrated systems have been suggested, such as exotic excitations near critical points,[1] incommensurate orders in magnetic fields,[2] chiral orderings,[3–6] and disordered ground states.[7,8] The property we will discuss in this paper is also one of the phenomena where frustrations play an essential role, and will never be observed in unfrustrated systems. The property is an impurity effect on frustrated one-dimensional ferro- and ferrimagnets.

Usually, a small amount of impurities has little influence on bulk magnetic quantities because the mean distance between impurities is so long that the correlation between them is very weak and usually they affect only local quantities. However, in some special situations, a small amount of impurities can cause a bulk effect. An example is the magnetic long-range order of moments induced by nonmagnetic impurities in quasi-one-dimensional spin-$1/2$ spin-gap systems, which was thoroughly investigated by theoretical,[9–11] numerical,[12,13] and experimental[14,15] approaches. The main feature of this effect is roughly explained as follows: Without an impurity, spins form dimers locally. By introducing nonmagnetic impurities, moments are induced around impurity sites. The moments couple to one another and exhibit long-range order. Hence, the long-range order and low-energy spin-wave excitation appear far below the original high-energy triplet excitation. For this effect, the spin gap and the correlations between induced moments play an essential role. In this paper, we present another example that a bulk quantity, magnetization, is substantially influenced by a small amount of impurities due to a different mechanism from that of the impurity-induced magnetic order. The impurity effect will be realized even with an infinitesimal density of impurities in frustrated ferro- and ferrimagnetic chains that satisfy the conditions we will present in this paper. Thus, in such systems, the magnetization in the ground state will be significantly reduced from that of the corresponding pure systems even with a usually negligible amount of impurities. We notice that without the knowledge developed in this work, reduction of magnetization from the expected values tends to be explained by assuming complex, higher order interactions such as the Dzyaloshinsky-Moriya interaction or interchain antiferromagnetic couplings.

## II. MODEL

In order to demonstrate the anomalous effect of nonmagnetic impurities on frustrated ferro- and ferrimagnets, we consider the minimal models defined by the following Hamiltonian:

$$\mathcal{H} = J_1 \sum_i \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1} + J_2 \sum_i \boldsymbol{S}_{2i-1} \cdot \boldsymbol{S}_{2i+1}, \tag{1}$$

where $\boldsymbol{S}_i$ denotes the spin operator at site $i$. The lattice structure is shown in Fig. 1(a). In model 1, the spin lengths of all spins are $1/2$. The coupling constant $J_1$ is ferromagnetic ($J_1<0$), and $J_2$ is antiferromagnetic ($J_2>0$). In model 2, the spin lengths at even sites are $1/2$, and those at odd sites are 1; both coupling constants are antiferromagnetic ($J_1$ and $J_2>0$). Model 1 is nothing but the one proposed by Hamada *et al.* in Ref. 16. Model 2 can be reduced to well-known models by neglecting $J_1$ or $J_2$: At $J_1=0$, this model is equivalent to the $S=1$ Heisenberg chain and free spins, and at $J_2=0$, it is nothing but the spin-alternating Heisenberg chain. The ground states of models 1 and 2 become ferro- and ferrimagnetic, respectively, when $|J_1|$ is sufficiently larger than $J_2$. Hereafter, we take the unit $g\mu_B=1$, where $g$ is the $g$ factor and $\mu_B$ is the Bohr magneton. The number of unit cells, the number of sites, and the number of impurities are denoted by

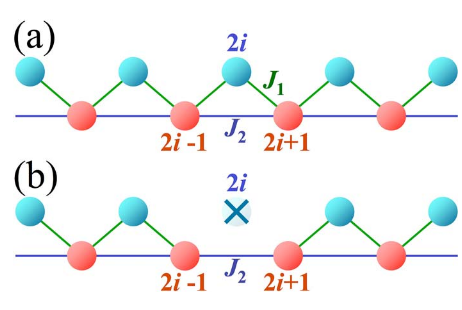


FIG. 1. (Color online) Lattice structure of models 1 and 2 (a) without an impurity and (b) with an impurity at site $2i$.

 

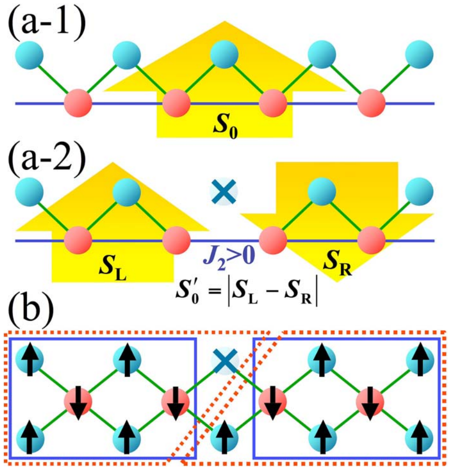


FIG. 2. (Color online) (a) Schematic picture of magnetic domains (a-1) without an impurity and (a-2) with an impurity. The total spins in (a-1) and (a-2) are denoted by $S_0$ and $S_0'$, respectively. The total spins of the blocks to the left and right of the impurity site are denoted by $S_L$ and $S_R$ in (a-2). (b) Ferrimagnetic chain on a bipartite lattice, where the spin lengths of all spins are 1/2 and all coupling constants are antiferromagnetic.

$L$, $N_s$, and $N_{\rm imp}$, respectively, and open boundary conditions are applied. In models 1 and 2, $L=N_s/2$.

### III. SINGLE IMPURITY

When a nonmagnetic impurity is doped at an odd site, the system is decomposed into two pure systems. Then, the situation is rather trivial. Thus, we first concentrate on the case where an impurity occupies an even site, as shown in Fig. 1(b). Because the interactions from the impurity site are removed, the remaining interaction between the spins adjacent to the impurity site is $J_2$, which is antiferromagnetic. Hence, we expect that the total spin $S$ in the ground state, which corresponds to the spontaneous magnetization, becomes $|S_L - S_R|$, where $S_L$ and $S_R$ are those of the blocks to the left and right of the impurity site, respectively. The expected picture of this inversion of magnetic domains is schematically shown in Fig. 2(a). As a special case where $S_L=S_R$, the total spin will vanish due to a single impurity.

In order to confirm this substantial decrease in spontaneous magnetization, we calculated $S$ in the ground states of models 1 and 2 with a single impurity put at all possible even sites in up to 40-site chains with even $L$ by the density-matrix renormalization group (DMRG) method[17] and the exact diagonalization method. The coupling constants are set to be $|J_1|=1$ and $J_2=0.1$. We calculated the total spin $S$ in the ground state by using the formula $S(S+1)=\langle(\Sigma_i \boldsymbol{S}_i)^2\rangle$ $(=\langle\Sigma_{i,j}\boldsymbol{S}_i\cdot\boldsymbol{S}_j\rangle)$, where $i$ and $j$ run over all sites and $\langle\ \rangle$ denotes the expectation value in the ground state. The numerical results on the total spin $S$ satisfied the relation $S=|S_L-S_R|$ in all the cases we have investigated, although there is no mathematical proof on this relation for quantum spin systems with frustrations. The physical picture of the domain inversion can be intuitively understood by considering the corresponding Ising models, for which this relation holds with total spin $S$ replaced with total $z$ component of spins $S^z$.

It should be noted, on the other hand, that in unfrustrated ferrimagnetic chains on bipartite lattices such as shown in Fig. 2(b), this anomalous impurity effect does not occur because the sign of the effective coupling between domains does not change due to impurities: In both definitions of domains denoted by solid and dotted lines in Fig. 2(b), the sign of the effective coupling remains the same before or after impurity doping. Actually, in these systems, ferrimagnetic ground states are ensured by the Marshall-Lieb-Mattis theorem[18,19] with or without an impurity.

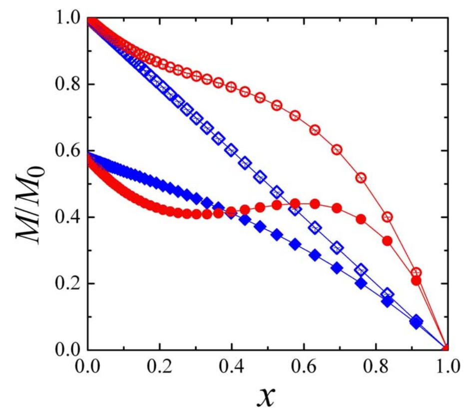


FIG. 3. (Color online) Dependence of magnetization $M$ on impurity density $x$. The magnetization without an impurity is denoted by $M_0$. Solid diamonds and circles denote the results on models 1 and 2, respectively. Open symbols denote those of the corresponding unfrustrated systems by setting $J_2$ to be ferromagnetic.

### IV. RANDOMLY DISTRIBUTED IMPURITIES

Based on the above numerical results for models 1 and 2 doped with an impurity, it is natural to expect that the total spin $S$ is expressed in terms of those in domains ($S_k$) as

$$S=\left|\sum_k(-1)^k S_k\right|, \tag{2}$$

when impurities are doped at even sites. Taking this relation into account, we have calculated magnetization in an infinitesimal magnetic field with impurities randomly distributed on a chain, where impurities can sit not only on even sites but also on odd sites. Here, the magnetization $M$ in an infinitesimal magnetic field is expressed in terms of the total spin $S_l$ in the $l$th isolated cluster as $M=\Sigma_l S_l$. To be concrete, we have calculated the average of $M$ over 10 000 chains. Each chain has $100/x$ sites and 100 randomly distributed impurities, where $x$ is the impurity density defined by $x\equiv N_{\rm imp}/N_s$. The numerical result on the impurity-density dependence of magnetization is shown in Fig. 3. Magnetizations of models 1 and 2 are drastically reduced due to impurities (solid diamonds and circles, respectively). In particular, in the limit of small impurity density, the magnetizations decrease down to about 57.7% of those of the corresponding pure systems; $M(x\to 0)\simeq 0.577\times M(x=0)$.

This feature is contrasted with that without frustrations: As an example, we consider model 1 with all coupling con-

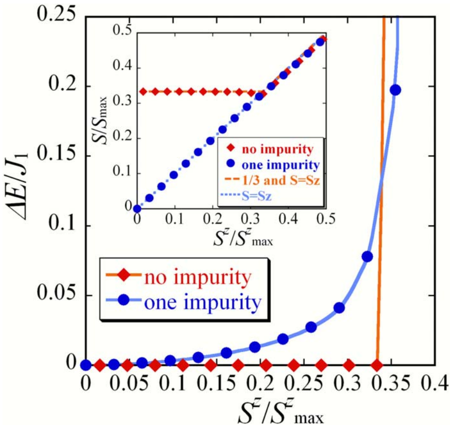


FIG. 4. (Color online) Ground-state energies as a function of $S^z$ measured from that of $S^z=0$ in a 42-site cluster of model 2 with $J_1=1$ and $J_2=0.1$ without an impurity (diamonds) and with an impurity at the 20th site (circles). Solid lines are a guide for the eyes. The inset shows the calculated $S$ in the ground state within the subspace of fixed $S^z$. Dashed and dotted lines indicate typical behaviors of ferrimagnets and spin liquids, respectively. The maximum values of $S$ and $S^z$ are denoted by $S_{\max}$ and $S^z_{\max}$, respectively.

stants ferromagnetic. In this model, the ground state is ferromagnetic with or without an impurity. Thus, the magnetization decreases by the amount of the spins at impurity sites. Namely, the magnetization linearly decreases as a function of the impurity density, i.e., $M/M_0=1-x$, as shown in Fig. 3 (open diamonds). Because the corresponding Ising models show the same impurity effect for the $z$ component of spins, it is expected that the effect shown here will also be realized in $XXZ$ models with Ising-like anisotropy.

## V. EXCITATIONS

Let us consider excitations in doped systems with nonmagnetic impurities. We calculated energies of a 42-site chain of model 2 with open boundary conditions, where an impurity is put at the 20th site. The coupling constants are set to be $J_1=1$ and $J_2=0.1$. The finite-size algorithm of the DMRG method[17] is applied with truncation number up to $m=150$. We performed ten sweeps and confirmed convergence by calculating $S(S+1)=\langle\Sigma_{i,j}\boldsymbol{S}_i\cdot\boldsymbol{S}_j\rangle$. In the inset of Fig. 4, we plot the calculated $S$ in the ground state within the subspace of fixed total $z$ component of spins $S^z(=\Sigma_i S_i^z)$. The calculated values of $S$ almost coincide with the typical behaviors of ferrimagnets and spin liquids (dashed and dotted lines, respectively), indicating that the wave functions with various $S^z$ are well converged. This figure also shows that the ground state changes from a ferrimagnetic state to a spin-singlet state due to a single impurity. The ground-state energies within the subspaces of fixed $S^z$ measured from that of $S^z=0$ are shown in Fig. 4. This figure suggests that there is a low-energy continuous excitation from a spin-singlet state.[20] This feature is contrasted with that of the Ising model where the lowest excitation has a finite gap of the order of $J_1$ or $J_2$ independent of the cluster size. The ground states with small

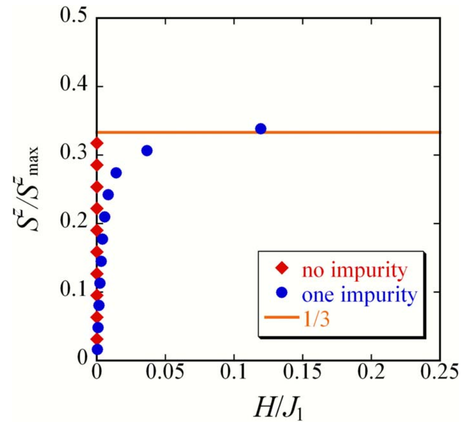


FIG. 5. (Color online) Magnetization curve of model 2. The parameters are the same as those in Fig. 4. We take the unit $g\mu_B=1$.

$S^z$ in doped quantum systems are almost degenerate, which would be reflecting ferromagnetic fluctuations in domains.

We calculated magnetic field $H$ by using a discretized form of the derivative of energy $E$ with respect to $S^z$: $H=\partial E/\partial S^z \simeq \{E(S^z_{n+1})-E(S^z_n)\}/\{S^z_{n+1}-S^z_n\}$, where $S^z_n=n$ or $n+0.5$ with or without an impurity $(n=0,1,\ldots)$. The result on the magnetization curve is shown in Fig. 5. The magnetic field required for the magnetization to recover up to the spontaneous magnetization of the pure system is about 0.1 which is the order of $J_2$ as expected from the picture of domain inversion [Fig. 2(a)].

## VI. CONDITIONS FOR IMPURITY EFFECTS

Based on the above considerations, we list the conditions for the anomalous impurity effect. (1) The system should be one dimensional. Namely, interactions between chains should be much smaller than those in chains. (2) The ground state without an impurity should have spontaneous magnetization. (3) Local interactions near impurity sites should be set so that the effective interaction between magnetic domains changes from ferromagnetic to antiferromagnetic due to impurities. The third condition leads to frustration.

The models that satisfy the above conditions will exhibit the anomalous impurity effect. For example, the decorated triangle chains [Figs. 6(a-1) and 6(a-2)] and the diamondlike chain [Fig. 6(b)] will be the models that exhibit this effect with all spins 1/2 and all coupling constants antiferromagnetic. In the decorated triangle chains, when $J_1$ is sufficiently larger than $J_2$, the spins on decorating sites align parallel, resulting in a ferrimagnetic ground state. If an impurity is doped on the top site of a triangle, the remaining interaction between the spins adjacent to the impurity is $J_2$, which is antiferromagnetic. Thus, the domain inversion and substantial decrease in magnetization due to impurities are expected. Actually, we have confirmed by exact diagonalization that the total spin $S$ in the ground state behaves as $S=|S_L-S_R|$, when an impurity is doped on top sites of triangles in up to 24-site clusters with $J_1=1$, $J_2=0.1$, and $J_3=0.5$.[21]

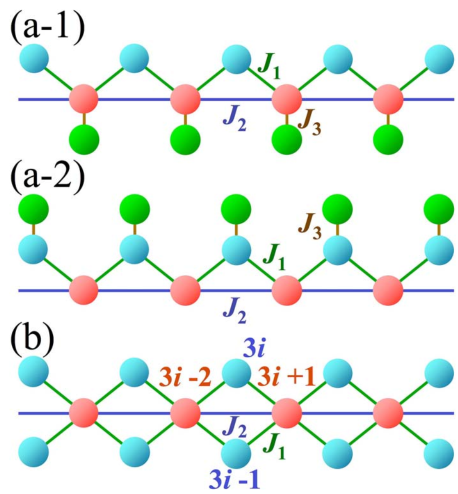


FIG. 6. (Color online) Possible models for the anomalous impurity effect with spins 1/2 and coupling constants antiferromagnetic. (a) Decorated triangle chains. (b) Diamondlike chain.

In the case of the model in Fig. 6(b), the ground state becomes ferrimagnetic, when $J_1$ is sufficiently larger than $J_2$. If an impurity is doped at site $3i$, the effective interaction between the spins at sites $3i-2$ and $3i+1$ is mainly determined by the three-site Hamiltonian of sites $3i-2$, $3i-1$, and $3i+1$. In order for the effective interaction to be antiferromagnetic, $J_2$ has to be larger than the effective coupling by $J_1$ through the spin at site $3i-1$. If such a parameter can be chosen, the magnetic domain inversion due to impurities will be realized. In this paper, we do not intend to determine the precise boundaries for this effect because in delicate systems, such as that of Fig. 6(b), the phase boundary will depend on the system size. Instead, we would like to emphasize that, as demonstrated in this paper, there actually exist systems that exhibit this impurity effect in some parameter regimes for frustrated ferro- and ferrimagnets in one dimension.

## VII. SUMMARY

In summary, we have investigated effects of nonmagnetic impurities on frustrated ferro- and ferrimagnets in one dimension by the DMRG method and the exact diagonalization method. Based on the numerical results, we pointed out that in these systems, a small amount of impurities can drastically decrease magnetization in the ground state. Introducing the picture of magnetic domain inversion, we have investigated impurity-density dependence of magnetization. In particular, we have shown that the magnetization with an infinitesimal density of impurities becomes as small as 57.7% of that without an impurity. The energy scale of this impurity effect is of the order of the remaining effective interaction between the spins adjacent to impurity sites. The low-energy excitations in doped systems are continuous from the lowest spin state (except the finite-size gap). We also listed the conditions for this impurity effect.

In the materials which are effectively described by frustrated spin models, other interactions such as the Dzyaloshinsky-Moriya interaction or biquadratic interactions are sometimes not negligible. Although their influence on the impurity effect requires further study, the prediction in this paper would deserve careful experimental investigations.

## ACKNOWLEDGMENTS

We thank M. Hase for valuable discussions and comments on related materials. M.K. was supported in part by Grant-in-Aid for Scientific Research (C) No. 10354143 from MEXT, Japan.

[1] T. Senthil, A. Vishwanath, L. Balents, S. Sachdev, and M. P. A. Fisher, Science **303**, 1490 (2004).
[2] N. Maeshima, K. Okunishi, K. Okamoto, and T. Sakai, Phys. Rev. Lett. **93**, 127203 (2004).
[3] D. Grohol, K. Matan, J.-H. Cho, S.-H. Lee, J. W. Lynn, D. G. Nocera, and Y. S. Lee, Nat. Mater. **4**, 323 (2005).
[4] S. Fujiki and D. D. Betts, Can. J. Phys. **65**, 76 (1987); Prog. Theor. Phys. Suppl. **87**, 268 (1986).
[5] H. Nishimori and H. Nakanishi, J. Phys. Soc. Jpn. **57**, 626 (1988).
[6] P. W. Leung and K. J. Runge, Phys. Rev. B **47**, 5861 (1993).
[7] P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).
[8] P. Fazekas and P. Anderson, Philos. Mag. **30**, 432 (1974).
[9] H. Fukuyama, T. Tanimoto, and M. Saito, J. Phys. Soc. Jpn. **65**, 1182 (1996); H. Fukuyama, N. Nagaosa, M. Saito, and T. Tanimoto, *ibid.* **65**, 2377 (1996).
[10] M. Sigrist and A. Furusaki, J. Phys. Soc. Jpn. **65**, 2385 (1996).
[11] N. Nagaosa, A. Furusaki, M. Sigrist, and H. Fukuyama, J. Phys. Soc. Jpn. **65**, 3724 (1996).
[12] Y. Motome, N. Katoh, N. Furukawa, and M. Imada, J. Phys. Soc. Jpn. **65**, 1949 (1996).
[13] Y. Iino and M. Imada, J. Phys. Soc. Jpn. **65**, 3728 (1996).
[14] M. Hase, K. Uchinokura, R. J. Birgeneau, K. Hirota, and G. Shirane, J. Phys. Soc. Jpn. **65**, 1392 (1996); M. C. Martin, M. Hase, K. Hirota, G. Shirane, Y. Sasago, N. Koide, and K. Uchinokura, Phys. Rev. B **56**, 3173 (1997).
[15] M. Azuma, Y. Fujishiro, M. Takano, M. Nohara, and H. Takagi, Phys. Rev. B **55**, R8658 (1997); M. Azuma, M. Takano, and R. S. Eccleston, J. Phys. Soc. Jpn. **67**, 740 (1998).
[16] T. Hamada, J. Kane, S. Nakagawa, and Y. Natsume, J. Phys. Soc. Jpn. **57**, 1891 (1988).
[17] S. R. White, Phys. Rev. Lett. **69**, 2863 (1992); Phys. Rev. B **48**, 10345 (1993).
[18] W. Marshall, Proc. R. Soc. London, Ser. A **232**, 48 (1955).
[19] E. H. Lieb and D. Mattis, J. Math. Phys. **3**, 749 (1962).
[20] In finite-size systems, there should be a gap due to the discreteness of energy levels. Here, we mean that an asymptotically continuous low-energy excitation exists, which reflects the quantum nature of the system.
[21] For the model in Fig. 6(a-2), the degrees of freedom of the spin on the decorating site connected to the impurity are neglected because it behaves as a free spin.