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

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Significant decrease of spontaneous magnetization in frustrated one-dimensional ferro- and ferrimagnets due to non-magnetic 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.

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Frustrations in quantum spin systems have attracted much attention for its 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 [1,2], incommensurate orders in magnetic fields [2,3], chiral orderings [3,4,5,6] 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, since 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 impurity-induced antiferromagnetic long-range order (AFLRO) in quasi-one-dimensional spin-1/2 spin-gap systems, which was thoroughly investigated by theoretical [3,10,11], 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 non-magnetic impurities, moments are induced around impurity sites. The moments couple one to another and exhibit antiferromagnetic alignment. Hence, AFLRO and low-energy spin-wave excitation appear in the background of 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 AFLRO. 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.

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

\[ H = J_1 \sum_i S_{2i-1} \cdot S_{2i+1} + J_2 \sum_i S_i \cdot S_{i+1}, \]

where \( S_i \) 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 one half. The coupling constant \( J_1 \) is antiferromagnetic (\( J_1 < 0 \)), and \( J_2 \) is ferromagnetic (\( J_2 > 0 \)). Model 2, the spin lengths at even sites are one half, and those at odd sites are one; both coupling constants are antiferromagnetic (\( J_1 \) and \( J_2 \) > 0). Model 1 is nothing but the one proposed by Hamada and his coworkers in Ref. [16]. Model 2 can be reduced to well-known models by neglecting \( J_1 \) or \( J_2 \): At \( J_2 = 0 \) this model is equivalent to the \( S = 1 \) Heisenberg chain and free spins, and at \( J_1 = 0 \) it is nothing but the spin-alternating Heisenberg chain. The ground states of models 1 and 2 become ferro- and ferrimagnetic, respectively, when \( |J_2| \) is sufficiently larger than \( J_1 \). Hereafter, the number of unit cells and the number of sites are denoted by \( L \) and \( N_s \), respectively.
in the ground state. The numerical results on $S_L$ and $S_R$ shown in Fig. 2 (b), this anomalous impurity effect does not only on even sites but also on odd sites. Here, the cases we have investigated. There is no mathematical proof on this relation for quantum spin systems with frustrations, hence it is nontrivial. The physical 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 and the exact diagonalization method. The coupling constants are set to be $J_1=0.1$ and $J_2=1$. We calculated the total spin $S$ in the ground state by using the formula $S(S+1)=⟨(\sum_i S_i)^2⟩=(\sum_{i,j} S_i \cdot S_j)$, where $i$ and $j$ run over all sites, and $⟨⟩$ 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. There is no mathematical proof on this relation for quantum spin systems with frustrations, hence it is nontrivial. 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, since 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 with or without an impurity.

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

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

when impurities are doped at even sites. Taking this relation into account, we have calculated magnetization $M$ 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 $M=\sum_j S_j$. 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. 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; $M(x→0)\approx 0.577 \times M(x=0)$.

This feature is contrasted with that without frustrations: As an example, we consider the model 1 with all coupling constants ferromagnetic. In this model, the ground state is ferromagnetic with or without an impu-
The ground states with small \( S_z \) reflecting ferromagnetic fluctuations in domains. Quantum systems are almost degenerate, which would be a gap of the order of the Ising model where the lowest excitation has a finite singlet state \[20\]. This feature is contrasted with that of \( S_z \) within the subspaces of fixed \( S_z \) of the fully polarized state are denoted by \( S_{\text{max}} \) and \( S_{\text{max}} \), respectively.

We calculated magnetic field \( H \) by using a discretized form of the derivative of energy \( E \) with respect to \( S^z \): 
\[
H = \frac{\partial E}{\partial S^z} \approx \frac{E(S_{\nu+1}^z) - E(S_{\nu}^z)}{S_{\nu+1}^z - S_{\nu}^z},
\]
where \( S_{\nu}^z = n \) 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 \( J_1 \) as expected from the picture of domain inversion (Fig. 2 (a)).

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 such 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 (a-2)) and the diamond-like chain (Fig. 6 (b)) will be the models that exhibit this effect with all spins one half and all coupling constants antiferromagnetic. In the decorated triangle chains, when \( J_2 \) is sufficiently larger than \( J_1 \), the spins on decorating sites align parallel, resulting in a ferromagnetic 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 \( J_1 \), 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 $J_1=0.1$, $J_2=1.0$ and $J_3=0.5$.

In the case of the model in Fig. 6 (b), the ground state becomes ferrimagnetic, when $J_2$ is sufficiently larger than $J_1$. 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, $J_1$ has to be larger than the effective coupling by $J_2$’s 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, since 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.

In summary, we have investigated effects of non-magnetic 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 deserves careful experimental investigations.

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[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, since it behaves as a free spin.