Impurity Effect on Spin Ladder System

Yukitoshi Motome, Nobuyuki Katoh, Nobuo Furukawa and Masatoshi Imada

Institute for Solid State Physics, University of Tokyo,
Roppongi 7-22-1, Minato-ku, Tokyo 106

(Received March 23, 2022)

Effects of nonmagnetic impurity doping in a spin ladder system with a spin gap are investigated by the exact diagonalization as well as by the variational Monte Carlo calculations. Substantial changes in macroscopic properties such as enhancements in spin correlations and magnetic susceptibilities are observed in the low impurity concentration region, which are caused by the increase of low-energy states. These results suggest that small but finite amount of nonmagnetic impurity doping relevantly causes the reduction or the vanishment of the spin gap. This qualitatively explains the experimental result of Zn-doped SrCu$_2$O$_3$ where small doping induces gapless nature. We propose a possible scenario for this drastic change as a quantum phase transition in a spin gapped ladder system due to spinon doping effects.

KEYWORDS: spin ladder model, spin gap, SrCu$_2$O$_3$, Zn doping, nonmagnetic impurity, spinon doping, long-range RVB

Quantum effects in low-dimensional antiferromagnetic spin systems have intensively attracted theoretical and experimental interests. One of such effects is observed as a formation of a spin gap, which competes with antiferromagnetic long-range order instabilities. The origin of the spin gap arising from the structural feature has been extensively studied in a unified way for various systems.\textsuperscript{1}

An example for such systems is the integer spin antiferromagnetic Heisenberg (AFH) chain which exhibits the Haldane gap.\textsuperscript{2} For a finite size $S = 1$ AFH chain with an open boundary condition, the existence of $S = 1/2$ states at the ends of the chain has been shown from the valence-bond solid (VBS) picture.\textsuperscript{3} This situation is realized if we dope impurities which disconnect the topological connection of the chain. Provided that the impurity concentration is low, nearly-free spin degrees of freedom localized around impurities are activated in the low-temperature region while the bulk spin gap structure remains almost unchanged. Experimentally, a typical $S = 1$ quasi one-dimensional antiferromagnet Ni(C$_2$H$_8$N$_2$)$_2$NO$_2$(ClO$_4$)
(NENP) exhibits a spin gap behavior. The spin degrees of freedom for edge states have been observed in Cu-doped NENP, which gives an experimental evidence to support the existence of the VBS state. In this material, impurity effect has played an important role as a probe to investigate the microscopic properties.

In contrast with the $S = 1$ chain, recent experiments on spin-gapped system CuGeO$_3$ with spin-Peierls distortion have shown that small amount of Zn doping induces the AF long-range order. Here, Zn$^{2+}$ ion plays a role of nonmagnetic impurity on the parent Cu$^{2+}$ ($S = 1/2$) lattice. To understand the origin of this contrast, it seems to be important to consider relatively large interchain coupling for CuGeO$_3$.

Another compound which shows the spin gap behavior is the 2-leg spin ladder system, SrCu$_2$O$_3$. The origin is understood from the short-range resonating valence bond (RVB) picture. Recently, experimental studies of Zn-doped compounds Sr(Cu$_{1-x}$Zn$_x$)$_2$O$_3$ has been performed. Experimental results suggest that, at $x \geq 0.01$, there exists the antiferromagnetic phase in the low temperature region. Above the critical temperature, thermodynamical properties are similar to those of a quasi one-dimensional gapless antiferromagnet. The phenomena observed in Sr(Cu$_{1-x}$Zn$_x$)$_2$O$_3$ suggest that, unlike the case for impurity doping in NENP, a substantial change has occurred in the bulk spin state by Zn doping of less than 1%.

In this paper, we investigate nonmagnetic impurity effects in a 2-leg spin ladder system at low concentration of impurities, which may correspond to the Zn doping effects in experiments. In the present results, the exact diagonalization (ED) of clusters as well as variational Monte Carlo (VMC) calculations show that even small concentration of nonmagnetic impurities reduces the spin gap and remarkably enhances the antiferromagnetic correlation.

The Hamiltonian is a conventional $S = 1/2$ AFH model with the nearest neighbor interaction written as $\mathcal{H} = J \sum_{<i,j>} \mathbf{S}_i \cdot \mathbf{S}_j$ on the 2-leg ladder structure with the periodic boundary condition, where $J$ represents the spin exchange coupling. In the present work, the nonmagnetic impurity effect is treated as the annihilation of impurity sites in the parent system. Since we are interested in impurity effects at low concentration of impurities, we focus on the case with two impurity sites which are apart from each other as far as possible, that is, two impurities are on the site 1 and $3L/2 + 1$ in the $L \times 2$ system. (We assign the site number from 1 to $L$ on the first leg and from $L + 1$ to $2L$ on the second leg. For example, in the $12 \times 2$ system, the two impurities are located at the site 1 and 19, as shown in the inset of Fig. 1.) The ground state becomes singlet when $L = 4n$, where $n$ is an integer.

We first show the spin correlations in the real space calculated by the ED method in Fig. 1. To investigate the impurity effect on the spin correlation around the impurity site, we measure the spin correlation $(-1)^{|i-j|} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ with $i$ fixed at the nearest-neighbor site to
the impurity. In the pure system, the spin correlation decays sharply since this system has a
spin gap in the thermodynamic limit. In the impurity doped system, the antiferromagnetic
correlation is enhanced.

Next, we show the ED results for the temperature dependence of the uniform magnetic
susceptibility $\chi$ per spin in Fig. 2. In the pure system, the susceptibility decays exponentially
as the decrease of temperature due to the finite spin gap. On the contrary, the behavior of $\chi$
for the impurity doped system is apparently different from that for the pure system. As
a reference, the $S = 1/2$ AFH chain with the periodic boundary condition is also shown in
Fig. 2, which is a typical spin gapless system in the thermodynamic limit. For $T/J \gtrsim 0.15$,
it is found that the temperature dependence of $\chi$ for the impurity doped system is rather
similar to that for the AFH chain than the ladder case. The sudden decay of $\chi$ appears at
temperature below $T/J \sim 0.15$ for both the impurity doped ladder system and the AFH
chain, which may be due to a finite size effect. The important point of these results is
that the ground state property may change qualitatively due to the impurity doping at low
concentration.

To understand the microscopic origin of above behaviors, we calculate the low energy
spectrum by the ED method, as shown in Fig. 3. In the pure ladder system, the low-lying
states are very sparse. However, when two impurities are injected to the pure system, the
number of low-lying excited states increases. The low energy excitation spectrum of the
impurity doped system is similar to that of the AFH chain rather than that of the ladder
system.

In order to study effects of impurities at low concentration region in a systematic way, we
treat larger size systems with the VMC technique. We show that variational wave functions
in our calculation have excellent properties in the small size systems compared with the
ED results. In the variational approaches, we can get physical intuitions from trial wave
functions.

We use the RVB type wave function, originally introduced for the $S = 1/2$ AFH model on
a square lattice, which is defined by,

$$|\Psi\rangle = \sum_{i_1, j_1, \ldots} h(R_{i_1j_1}) \cdots h(R_{i_nj_n}) \cdot (i_1j_1) \cdots (i_nj_n),$$

where $h(R_{ij})$ is a weight function for a singlet pair $(ij)$ lying between the different sublattice
$A$ and $B$, whose form is determined variationally. Here, $R_{ij}$ is the Manhattan distance
between the site $i$ and $j$. In the impurity doped case, we make the following ansatz; $R_{ij}$ is
defined as the length of the shortest path from the site $i$ to $j$ without passing over impurity
sites. In the present work, we take two types of $h(R)$ with two variational parameters for
each type. Both have one free parameter $h(3)$ (we set the normalization as $h(1) = 1$) because
the energy is sensitive to the functional form of $h(R)$ in the short distance. For $R \geq 5$, one type has an exponential tail; $h(R) = h(3) \exp [\kappa \cdot (3 - R)]$, and the other has an algebraic tail; $h(R) = h(3) (3/R)^p$. Here, $\kappa$ and $p$ are variational parameters controlling the tail of the weight function. Among these wave functions, the optimized state is chosen to give the lowest variational energy $\langle \Psi|\mathcal{H}|\Psi \rangle / \langle \Psi|\Psi \rangle$. We focus on the same configuration of two impurities as in the ED calculations. We also calculate for some other configurations of two impurities and have qualitatively same results.

First, we check the efficiency of VMC by comparing with the exact results for small size systems. Our variational wave function (1) is found to give good agreement with the exact ground state energy. For example, for the $12 \times 2$ system, variational energy per site are $-0.5777 \pm 0.0001 J$ for the pure case and $-0.4890 \pm 0.0002 J$ for the impurity doped case, while the exact results are $-0.5784 J$ and $-0.4912 J$ respectively. The spin correlations for the $12 \times 2$ system calculated with the optimized wave functions are shown in Fig. 1. The apparent difference between the pure and impurity doped case is well reproduced within this VMC calculation.

We calculate larger-size systems up to $96 \times 2$ sites. For all the sizes, the variational wave function changes drastically by the impurity doping in spite of very low concentration: For pure cases, the wave function with the exponential decay form of $h(R)$ gives lower energy than that with the algebraic decay form. However, if impurities are introduced, the latter has the lower energy. (In the pure case, the energy difference between these two types is small, for example, $\simeq 0.0003 J$ for the $48 \times 2$ case which is comparable to errorbars due to the strong decay of $h(R)$ and the finite size effects. On the other hand, in the impurity doped case, the difference is considerable, for example, $\simeq 0.0013 J$ for the $48 \times 2$ system.) The spin correlations calculated with the optimized wave functions are shown in Fig. 4. For all the sizes, the spin correlations decay exponentially in the pure case, which indicates the existence of the spin gap by the short-range RVB. Our results show that impurities cause the remarkable enhancement of the spin correlations.

All above results suggest that, in the ladder system, nonmagnetic impurities even at the low concentration cause drastic changes: As shown in the ED study, the susceptibility $\chi$ and the low energy spectrum in the impurity doped cases are apparently different from those of the pure ladder system and rather similar to those of the AFH chain which is a gapless system. The variational wave function for the impurity doped cases is optimized with the long-range RVB weights which directly result in the remarkable enhancement of the spin correlation. All these results indicate that the doped impurities intensively reduce or destroy the spin gap.

We now discuss the effect of nonmagnetic impurity doping on the ladder system. The
undoped state, that is, the pure ladder system has a finite spin gap \( \sim 0.5J \). This state can be qualitatively understood as the resonating state of dimer singlets \( \text{[1]} \) schematically depicted in Fig. 5(a). The special topological character of the 2-leg ladder favors this dimer gapped state, rather than the long-range RVB state which generally contains more singlet states resonating to each other in the summation of eq. \( \text{[1]} \). A doped impurity breaks a dimer singlet pair and leaves an unpaired spin, as shown in Fig. 5(b). In this sense, the nonmagnetic impurity doping can be considered as the doping of topological solitons with \( S = 1/2 \) or so-called spinons \( \text{[1]} \). So far as the impurity concentration is very low and randomly doped impurities are far apart from each other on average, induced spinons may be localized near the impurity sites: As depicted in Fig. 5(c), the motion of spinons rearranges the dimer configuration. Within this type of ‘staggered’ dimer configuration in the traces of moving spinons, dimer singlets cannot resonate to each other. Therefore, the system loses the resonance energy proportional to distances between spinons and impurity sites, which may cause the pinning of spinons. \( \text{[1]} \) In this phase, the spin correlation decays exponentially.

Next, we consider what happens when the impurity concentration increases gradually. In the ladder system, the nonmagnetic impurity doping may not break the one-dimensional structure at low impurity concentration. \( \text{[1]} \) The increase of the number of spinons nearly equal to the number of impurities drives spinons to move more coherently in order to gain more kinetic energy. The motion of spinons might destruct the short-range dimer structure and totally reconstruct them to have longer bond lengths, as schematically depicted in Fig. 5(d). Consequently, the gains for both the spinon kinetic energy and the RVB resonance energy will be reconciled by the RVB with the weight given by the algebraic decay. Due to the power-law tail of RVB weights, the bulk spin gap may be intensively reduced or destroyed and the spin correlation may decay algebraically. In this state, spinons are also involved in the reconstructed long-range RVB, as shown in Fig. 5(d). Therefore, we cannot distinguish spinons from other RVB any more, which means that the particle picture of spinons should break down.

The above transition, characterized by the change of the spin correlation from exponential decay to algebraic decay, takes place when the impurity concentration increases beyond a critical value. Our results for the finite size systems suggest that the phase with reconstructed long-range RVB is realized even at a very small concentration of impurities \( \gtrsim 0.01 \) (as seen in \( 96 \times 2 \) case). It should be noted that the structural character of the ladder system may have an important role to the change of the bulk properties. These phenomena can be considered as a new type of the quantum phase transition induced by the spinon doping.

Our results may explain the experimental results on \( \text{Sr(Cu}_{1-x}\text{Zn}_x\text{)}_2\text{O}_3 \) mentioned before. The specific heat data above the critical temperature \( \text{[2][3]} \) can be understood as the gap-
less nature due to the long-range RVB at the low doping region of nonmagnetic impurities. Nevertheless, there still remain some problems which seem to be beyond the framework of our present study. For example, Sr(Cu$_{1-x}$Zn$_x$)$_2$O$_3$ shows the AF long-range order at low temperature and the $x$ dependence of the Curie constant slightly above the critical temperature.\[2,3]\] Some additional factors which exist in the real system, such as the interladder coupling, the frustration in the spin exchange or the random configurations of impurities, may be relevant to these problems. We leave them for further study.

To summarize, we have investigated the impurity effect on the spin gapped system. The nonmagnetic impurities are doped into the 2-leg ladder system and various physical properties are investigated by the exact diagonalization and the variational Monte Carlo method. Our results suggest that the doping of nonmagnetic impurities into the ladder system leads to drastic changes above very small critical concentration with a reduction or disappearance of the bulk spin gap and a remarkable enhancement of the spin correlation. We propose a possible scenario for this substantial change. These phenomena observed here can be considered as a new type of the quantum phase transition induced by the spinon doping. An experimental relevance of this spinon doping effects is also mentioned.

The authors thank M. Azuma and M. Nohara for stimulating discussions. We have used a part of codes provided by H. Nishimori in TITPACK Ver.2. This work is supported by a Grant-in-Aid for Scientific Research on the Priority Area ‘Anomalous Metallic State near the Mott transition’ from the Ministry of Education, Science and Culture, Japan. The computation in this work has been done using the facilities of the Supercomputer Center, Institute for Solid State Physics, University of Tokyo.

---

[1] N. Katoh and M. Imada: J. Phys. Soc. Jpn. 64 (1995) 1437.
[2] F.D.M. Haldane: Phys. Rev. Lett. 50 (1983) 1153.
[3] I. Affleck, T. Kennedy, E.H. Lieb and H. Tasaki: Phys. Rev. Lett. 59 (1987) 799; Commun. Math. Phys. 115 (1988) 477.
[4] See, e.g., J.P. Renard, V. Gadet, L.P. Regnault and M. Verdaguer: J. Mag. Mag. Mat. 90&91 (1990) 213, and references therein.
[5] M. Hagiwara, K. Katsumata, I. Affleck, B.I. Halperin and J.P. Renard: Phys. Rev. Lett. 65 (1990) 3181.
[6] S. B. Oseroff, S-W. Cheong, B. Aktas, M. F. Hundley, Z. Fisk and L. W. Rupp, Jr.: Phys, Rev, Lett. 74 (1995) 1450.
[7] M. Hase, K. Uchinokura, R. J. Birgeneau, K. Hirota and G. Shirane: to appear in J. Phys. Soc. Jpn.
[8] Z. Hiroi, M. Azuma, M. Takano and Y. Bando: J. Solid State Chem. 95 (1991) 230.
[9] M. Azuma, Z. Hiroi, M. Takano, K. Ishida and Y. Kitaoka: Phys. Rev. Lett. 73 (1994) 3463.
[10] E. Dagotto and T. M. Rice: Science 271 (1996) 618, and references therein.
[11] S. R. White, R. M. Noack and D. J. Scalapino: Phys. Rev. Lett. 73 (1994) 886.
[12] M. Nohara, H. Takagi, M. Azuma, Y. Fujishiro and M. Takano: preprint.
[13] M. Azuma, Y. Fujishiro, M. Takano, T. Ishida, K. Okuda, M. Nohara and H. Takagi: preprint.
[14] S. Liang, B. Doucot and P. W. Anderson: Phys. Rev. Lett. 61 (1988) 365.
[15] S. A. Kivelson, D. S. Rokhsar and J. P. Sethna: Phys. Rev. B. 35 (1987) 8865.
[16] This situation is related to the confinement of a local moment in the edge of the open ladder with an unpaired edge site investigated in ref. [11].
[17] In the low doping concentration region, impurities rarely disconnect the multi-leg ladder structure when they are doped randomly. The disconnection of the ladder is one of the randomness effects which we neglect in this paper. On the other hand, the $S = 1$ chain system is always disconnected by doped impurities. Therefore, induced $S = 1/2$ spins at the ends of each open chain cannot obtain quantum coherency so that the bulk gap structure is not destroyed upon impurity doping.
Figure Captions

Fig. 1. Spin correlations in the real space on the same leg for the $12 \times 2$ systems obtained by the ED calculation. Site index $i$ is fixed at site 2 and index $j$ takes site 3, 4, 5, 6, 7. (Inset shows the assignment of site number in these systems.) Open symbols represent the spin correlations of the pure ladder system, while filled symbols are for those of the ladder system with two impurities. Square symbols are for the ED results, while circles show the VMC results for comparison.

Fig. 2. Temperature dependence of the uniform magnetic susceptibility per spin calculated by the ED method. Broken, solid and dash-dotted line correspond to the susceptibilities of the pure ladder system of the $6 \times 2$ size, the ladder system with two impurities of the $8 \times 2$ size and the $S = 1/2$ AFH chain with 14 sites, respectively.

Fig. 3. Excitation spectrum in the low-energy region obtained by the ED method. Horizontal axis represents the excited energy scaled by the spin exchange $J$ which is measured from the ground state energy. Figures (a), (b) and (c) correspond to the low-energy spectrums of the pure ladder system of the $6 \times 2$ size, the ladder system with two impurities of the $8 \times 2$ size and the $S = 1/2$ AFH chain with 14 sites, respectively.

Fig. 4. Semi-log plot of spin correlations in the real space obtained by VMC. We take the similar assignment for sites $i$ and $j$ as the ED study in Fig. 1. For all sizes, open and filled symbols show the pure and impurity doped cases, respectively.
Fig. 5. Physical pictures for the pure and impurity doped ladder systems. (a) A typical configuration of short-range RVB in the pure case. The dotted RVB states show a resonance of singlet pairs. (b), (c) and (d) Three different pictures on the doped state. Gray ovals represent singlet pairs. Crosses and arrows show impurity sites and spinons, respectively. See text for details.
Fig. 1. Y. Motome, N. Katoh, N. Furukawa and M. Imada
Fig. 2. Y. Motome, N. Katoh, N. Furukawa and M. Imada
Fig. 3. Y. Motome, N. Katoh, N. Furukawa and M. Imada
Fig. 4. Y. Motome, N. Katoh, N. Furukawa and M. Imada
Fig. 5. Y. Motome, N. Katoh, N. Furukawa and M. Imada
\[ (-1)^{|i-j|} \langle S_i \cdot S_j \rangle \]
The diagram shows the dependence of the magnetic susceptibility $\chi$ on the temperature ratio $T/J$. The susceptibility is plotted in arbitrary units against $T/J$ for various temperatures, indicated by different lines on the graph.
\( \rho(\omega) \) (in arb. unit)

\( \omega / J \)
